**INTRODUCTION**

Poly(ionic liquid)s (PILs) remain a fascinating and important class of polyelectrolytes, combining the unique properties of ionic liquids (ILs) (high thermal and electrochemical stability, variable solubility, viscosity, and ionic conductivity) with the tunable functionality and mechanical stability of various macromolecular architectures.1–4 The thermal, mechanical, and conductive properties of PILs are primarily varied by changing the chemical structure of the cation (ammonium, phosphonium, and imidazolium polycations (with counteranion (Br\(_{-}\), NO\(_{3}^{-}\), BF\(_{4}^{-}\), OTf\(_{-}\), and NTf\(_{2}^{-}\))), and crosslink density (acrylate/acetoacetate ratio) affected thermal, mechanical, and conductive properties. TPIL networks were found to exhibit ionic conductivities in the range of 10\(^{-6}\)–10\(^{-9}\) S/cm (30 °C, 30% relative humidity), as determined from dielectric relaxation spectroscopy, despite their highly crosslinked nature. Temperature-dependent conductivities demonstrate a dependence on polymer glass transition, with free-ion concentrations impacted by various ions’ Lewis acidity/basicity and ionic mobilities impacted by freely mobile anion size.

Poly(ionic liquid)s (PILs) have become more prominent due to the development of the copper(I)-catalyzed azide–alkyne “click” cycloaddition reaction.20,21 Drockenmuller et al. have pioneered efforts in the synthesis of a variety of TPILs, several approaches of which have been recently reviewed.22 Such TPIL synthetic efforts have ranged from the direct step-growth polyaddition of azides and alkynes to the chain-growth polymerization of 1,2,3-triazolium-containing (meth)acrylic monomers. Within their library of TPILs, several covalently crosslinked networks were prepared and evaluated for various applications. For example, an epoxy-functionalized IL monomer was reacted with a poly(propylene glycol)-based diamine, containing two acidic protons, an additional Michael addition will occur in the presence of excess diacrylate, resulting in covalent crosslinking. The degree of crosslinking (and thus the thermal and mechanical properties of the network) can be easily controlled through the manipulation of the acrylate/acetoacetate ratio.16 Previous work from our research group has demonstrated the versatility of the Michael addition polymerization as a method for the preparation of imidazolium17,18 and 1,2,4-triazolium PIL networks.19 Variations in network architecture (crosslink density, counteranion, cation) have led to a library of PILs that display a wide range of thermal and mechanical properties.

Although the majority of the PIL literature has focused on ammonium, phosphonium, and imidazolium polycations (with mobile counteranions), 1,2,3-triazolium-based poly(ionic liquid)s (TPILs) have become more prominent due to the development of the copper(I)-catalyzed azide–alkyne “click” cycloaddition reaction.20,21 Drockenmuller et al. have pioneered efforts in the synthesis of a variety of TPILs, several approaches of which have been recently reviewed.22 Such TPIL synthetic efforts have ranged from the direct step-growth polyaddition of azides and alkynes to the chain-growth polymerization of 1,2,3-triazolium-containing (meth)acrylic monomers. Within their library of TPILs, several covalently crosslinked networks were prepared and evaluated for various applications. For example, an epoxy-functionalized IL monomer was reacted with a poly(propylene glycol)-based diamine,
under anhydrous conditions and CO₂ permeability values of 59
membranes with conductivities of up to 10⁻⁸ S/cm at 30 °C under anhydrous conditions and CO₂ permeability values of 59–110 barrer with CO₂/N₂ selectivities of 25–48 were also synthesized.²³ TPIL vitrimer networks utilizing thermally reversible C–N bond transalkylation exchanges have also been reported and were found to exhibit ionic conductivities up to 10⁻⁸ S/cm (30 °C, anhydrous) as well as reshaping and recycling behavior.²⁵,²⁶

TPIL polyester networks, which contained an asymmetrically substituted 1,2,3-triazolium group with a limited set of counteranions, were recently communicated by our laboratory.⁷ Electrochemical impedance spectroscopy, utilizing a four-electrode cell, showed that the resulting TPIL networks exhibited good conductivities between 10⁻⁶ and 10⁻⁸ S/cm (25 °C, 30% relative humidity (RH)), indicating the promising nature of this class of PILs. Most notable was the appearance of a common “crossover” temperature (~85 °C) in the ionic conductivity curves, given the same monomer ratio. At temperatures below the crossover point, T₁/₂, chain dynamics were found to correlate well to ionic conductivity. Above the crossover temperature, however, ionic conductivities correlated inversely to the size of the counteranion on the order of [Br] > [NO₃] > [BF₄] > [OTf] > [NTf₂]. All of the 1,2,3-triazolium acetoacetate monomers were clear, room-temperature ionic liquids with varying degrees of yellow to orange color.¹H and ¹³C NMR spectroscopies, as well as elemental analysis, were used to identify the products and determine purity, respectively, and residual [Br] for PILs 6–9 was found to be <0.1% w/w by ion chromatography.²⁷

Analysis of the thermal properties of acetoacetate monomers 5–9 was conducted prior to polymerization. Differential scanning calorimetry (DSC) T₁/₂ values (Table 1) correlated inversely to the size of the counteranion on the order of [Br] > [NO₃] > [BF₄] > [OTf] > [NTf₂]. Here, assessment of the relative anion sizes is based upon molar masses and thermochemical radii.²⁸ The ability of ionic liquids to exhibit glass-forming behavior has been previously described using techniques such as DSC, X-ray diffraction, and Raman

**RESULTS AND DISCUSSION**

Synthesis of the 1,2,3-triazolium acetoacetate monomers began by first converting commercially available ethyl-6-bromohexanoate to the azide with sodium azide (Scheme 1). Reaction with trimethylsilylacetylene under Cu-catalyzed click cyclization conditions resulted in the tetramethylsilane-substituted triazole ring (not isolated), which was subsequently treated with a fluoride source (tetrabutylammonium fluoride, TBAF) to provide the desired 1,2,3-triazole ester 1.²¹ Reduction of the ester was then accomplished with diisobutylaluminum hydride (DIBAL-H), resulting in 1-(6'-hydroxyhexyl)-1,2,3-triazole 2. Transesterification with tert-butylacetate, followed by coupling with 6-bromohexylacetate 4, resulted in the targeted acetoacetate [Br] monomer 5. Various anion metathesis reactions (AgNO₃, AgBF₄, AgOTf, LiNTf₂) were then employed to gain access to other counteranions of interest (monomers 6–9). All of the 1,2,3-triazolium acetoacetate monomers were clear, room-temperature ionic liquids with varying degrees of yellow to orange color.

**Table 1. Thermal Properties of 1,2,3-Triazolium-Containing Acetoacetate Monomers**

| compound | anion  | DSC T₁/₂ (°C) | TGA Tₘ%/Tg (°C) |
|----------|-------|---------------|-----------------|
| 5        | Br    | −46.3         | 188             |
| 6        | NO₃   | −54.9         | 194             |
| 7        | BF₄   | −55.4         | 223             |
| 8        | OTf   | −60.5         | 239             |
| 9        | NTf₂  | −67.9         | 260             |
It is also worth noting that the observed relationship between anion size and \(T_g\) has been observed previously with imidazolium- and 1,2,4-triazolium-containing acetoacetate monomers.\(^{17-19}\)

Thermal stability, as defined by \(T_{d5\%}\) (the temperature at which 5\% of the material has decomposed), correlates inversely to the Lewis basicity of the counteranion on the order of \([\text{NTf}_2]^+ > [\text{OTf}]^- > [\text{BF}_4]^- > [\text{NO}_3]^- > [\text{Br}]^-\) (Table 1 and Figure S19).\(^{32}\) All of the acetoacetate monomers exhibited a one-step degradation except for [BF\(_4\)]\(^-\) where a two-step process was observed. Recent work by Clarke et al. using direct insertion mass spectrometry investigated the decomposition products of 1-alkyl-3-methylimidazolium [BF\(_4\)] ILs and found fluoride to be a thermally induced product of the reaction between tetrafluoroborate and the imidazolium cation.\(^{33}\) We hypothesize here that as IL monomer [BF\(_4\)] is being heated, fluoride is generated. As fluoride is a stronger Lewis base (compared to tetrafluoroborate), the first step results from decomposition of the monomer from [F] (the exact nature of the decomposition was not determined as part of this study). The second step would represent decomposition as a result of [BF\(_4\)]. To support this hypothesis, the production of fluoride from [BF\(_4\)] acetoacetate monomer 7 was observed as a function of time using isothermal thermogravimetric analysis (TGA) (at 200 °C) followed by analysis of the residue by ion chromatography. Fluoride content of monomer 7 (determined from the [F]/[BF\(_4\)] ratio) was found to be negligible, however, a 20-fold increase in fluoride concentration was observed during the first hour at 200 °C. Additional time found the amount of [F] and [BF\(_4\)] to decrease, presumably because both anions are being consumed as part of monomer decomposition. The results from this study clearly show that fluoride is thermally generated during the decomposition of [BF\(_4\)] monomer 7 and thus could influence the observed decomposition temperature.

1,2,3-Triazolium-containing acetoacetates 5–9 were polymerized following a standard Michael addition polymerization protocol developed by our laboratory. The appropriate amount of acetoacetate was allowed to react with commercially available 1,4-butanediol diacrylate in the presence of catalytic 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2 mol %) in a solution of dichloromethane (50 wt %) (Scheme 2).\(^{17-19}\) Each solution was placed into a poly(tetrafluoroethylene) (PTFE) mold and cured under ambient conditions for 48 h, followed by 48 h in a 60 °C. The films were then dried in a vacuum oven at 60 °C for an additional 48 h to ensure removal of trace solvent residue and moisture. Since conductive properties of the analogous imidazolium and 1,2,4-triazolium PIL Michael

**Table 2. Gel Fraction and Thermal Properties for TPIL Networks**

| polymer | anion (cation) | Acr/AcAc ratio | gel fraction (%) | % swelling | DSC \(T_g\) (°C) | TGA \(T_{d5\%}\) (°C) |
|---------|---------------|----------------|-----------------|-----------|----------------|------------------|
| 12      | Br            | 1.5:1.0        | 97.6 ± 0.4      | 129.0 ± 0.9 | 7.7            | 195              |
| 13      | NO\(_3\)      | 1.5:1.0        | 95.6 ± 0.1      | 131.6 ± 1.0 | 3.9            | 203              |
| 14      | BF\(_4\)      | 1.5:1.0        | 97.4 ± 0.2      | 130.4 ± 3.3 | 2.9            | 256              |
| 15      | OTf           | 1.5:1.0        | 95.2 ± 0.3      | 139.8 ± 0.8 | −5.2           | 302              |
| 16      | NTf\(_2\)     | 1.5:1.0        | 92.2 ± 0.3      | 155.1 ± 2.2 | −15.6          | 318              |
| 17      | NTf\(_2\)     | 1.2:1.0        | 93.1 ± 0.3      | 151.4 ± 2.5 | −22.0          | 312              |
| 18      | NTf\(_2\)     | 1.8:1.0        | 93.8 ± 0.8      | 140.2 ± 3.2 | −2.9           | 318              |
| 19      | (IM)          | 1.5:1.0        | 93.8 ± 0.1      | 151.5 ± 0.3 | −14.4          | 321              |
| 20      | (124TRI)      | 1.5:1.0        | 95.1 ± 0.4      | 155.7 ± 0.5 | −9.2           | 315              |
networks had not been previously measured, comparison networks were prepared fresh, which utilized previously reported imidazolium and 1,2,4-triazolium [NTf2] acetoacetate monomers (10 and 11, respectively). For PILs where a variation in cation or anion was of interest, the acrylate/acetoacetate ratio was held constant at 1.5:1.0. For PILs in which the cation or monomer ratio was varied, the anion was held constant at [NTf2].

Gel fraction and % swelling of the PIL networks were determined from Soxhlet extraction experiments using dichloromethane (Table 2). High gel fraction values (>92%) were observed for all of the networks studied here. Higher swelling values were observed with increasing anion size, presumably due to an increase in free volume within the network as a result of anion plasticization, although it is possible that the use of a more hydrophobic anion ([OTf] and [NTf2]) could result in stronger polymer–solvent interactions. As expected, an increase in the acrylate concentration (polymers 16–18) decreased the % swelling due to the increase in covalent crosslinking and a decrease in free volume within the network. Gel fraction and % swelling values were similar across the series in which the cation was varied (networks 16, 19, and 20).

PIL networks were initially analyzed by DSC to evaluate \( T_g \) and to correlate to changes in network structure (Table 2 and Figures S20–S22). An increase in the size of the counteranion led to a decrease in \( T_g \) on the order of [Br] > [NO3] ≈ [BF4] > [OTf] > [NTf2], likely due to a plasticizing effect that is often observed in PILs with larger, more hydrophobic anions. As expected, upon increasing the acrylate concentration and thus the crosslink density, the \( T_g \) increased, given the same counteranion [NTf2]), with the 1.8:1.0 acrylate/acetoacetate ratio PIL exhibiting the highest value of \(-2.9^\circ C\). Changing the cation led to little difference in \( T_g \) between the imidazolium and 1,2,3-triazolium PIL networks, however, the 1,2,4-triazolium [NTf2] PIL was observed to have a higher \( T_g \) value of \(-9.2^\circ C\), presumably due to the higher Lewis acidity of the cationic heterocycle, thereby creating stronger ionic interactions within the network.

TGA was utilized to investigate changes in thermal stabilities (\( T_{d50} \)) as a function of structural changes (Table 2 and Figures S23–S25). Analysis of the TPILs with variable counteranion indicated once again reflected the correlation between Lewis basicity and relative thermal stability in ILs and PILs. Overall, [Br] PIL 12 was observed to have the lowest \( T_{d50} \) value (195 \(^\circ C\)) than any of the other counteranion systems due to its relatively high Lewis basicity. In fact, \( T_{d50} \) values were found to be inversely related to Lewis basicity on the order of [NTf2] > [OTf] > [BF4] > [NO3] > [Br]. This trend is analogous to the previously discussed acetoacetate monomers, however, it is worth noting that the PIL networks exhibit higher thermal stabilities overall. Neither a change in crosslink density (acrylate/acetoacetate ratio) nor in cation structure appeared to adversely affect thermal stability, with all of the [NTf2] PIL networks exhibiting \( T_{d50} \) values in excess of 310 \(^\circ C\).

The mechanical properties of the 1,2,3-triazolium-containing polyester networks were analyzed using dynamic mechanical analysis (DMA). Networks which employed different anions were compared initially (Figure 1a) and it was observed that in general all of the TPILs exhibited similar rubbery plateau moduli \( E' \) above the \( T_g \) (Table 3). Such a finding was further supported by apparent crosslink density \( (\rho_x) \) values, which were calculated from rubbery elasticity theory according to the following equation

\[
\rho_x = E'/3RT
\]
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). All $T_g$ values were found to be in the range of $(5.30 \pm 6.76) \times 10^{-4}$ mol/cm$^3$ with no discernible correlation with anion size or Lewis basicity (Table 3). In line with the DSC $T_g$ data, the DMA $T_g$ values, as determined from the maximum of the corresponding tan $\delta$ curves (Figure S26), showed a correlation with anion size, with PILs employing the largest anions [NTf$_2$] 16 and [OTf] 15 resulting in the lowest DMA $T_g$ values (−2.40 and 13.8 °C, respectively) and the network with the smallest anion, [Br] 12, exhibited the highest DMA $T_g$ (37.5 °C).

Variation in acrylate/acetoacetate ratio gave a predictable response in the corresponding mechanical properties, where an increase in acrylate concentration led to an increase in crosslink density, an increase in $E$’ rubbery plateau modulus (Figure 1b), and an increase in DMA $T_g$ (Figure S27). Interestingly, a reduction in crosslink density led to an increase in the glassy plateau modulus. Although additional structural characterization is necessary, it is speculated that lower crosslinking may increase anion aggregation resulting from improved ion mobility, leading to a higher glassy plateau modulus. Variation in cation led to minimal change in crosslink density or $E$’ rubbery plateau modulus (Figure 1c); however, the 1,2,4-triazolium PIL network 20 was found to have a higher DMA $T_g$ (Figure S28). As with the previously described DSC $T_g$ data, this trend is presumably due to the higher Lewis acidity/coordination ability of the 1,2,4-triazolium cation.

To evaluate the ionic conductivity of the networks, frequency-dependent dielectric spectra were collected on each TPIL over a range of temperatures. Direct current conductivities ($\sigma$) were determined by first converting dielectric loss spectra ($\varepsilon''$) to the real conductivity ($\sigma'$) domain via the equation $\sigma' = \varepsilon'' \varepsilon_0 \omega$, where $\varepsilon_0$ is vacuum permittivity and $\omega$ is angular frequency in rad/s. The real conductivity spectra are characterized by a frequency-independent plateau region, and values of $\sigma$ were taken to be the plateau value. Exemplar real dielectric ($\varepsilon''$, $\varepsilon''$, and $\sigma'$ spectra for TPIL 14 at 80 °C are provided (Figure S29).

Once values were extracted from all spectra, conductivities were plotted for each TPIL as a function of temperature. These temperature-dependent conductivities are shown in Figure 2. Much to our surprise, the TPIL networks exhibited promising conductivity curves (log $\sigma$ vs 1000/T) for TPIL networks with (a) variable counteranion; (b) variable acrylate/acetoacetate ratio; (c) variable cation. The dashed curves represent Vogel–Fulcher–Tamman (VFT) fitting curves.

Figure 2. Ionic conductivity curves (log $\sigma$ vs 1000/T) for TPIL networks with (a) variable counteranion; (b) variable acrylate/acetoacetate ratio; (c) variable cation. The dashed curves represent Vogel–Fulcher–Tamman (VFT) fitting curves.
and displays the largest conductivity, whereas the 1.8:1.0 ratio contains the least ionic monomer and concomitantly the smallest conductivity. Therefore, the overall ion content of these three PILs may also be contributing to observed behavior.

Similarly, Figure 2c depicts the temperature-dependent conductivities of PILs where the anion and ratio are held constant and the nature of the cation is changed. As with the previous data, the three PIL’s conductivities follow the inverse relationship to \( T_g \) across the entire temperature range. The conductivity curve for the imidazolium PIL does rise more steeply with temperature than either of the triazolium PILs indicating there may be additional factors that govern ion transport. For instance, the conductivity trend for cations also follows a pattern associated to Lewis acidity of the cations (increasing conductivity with decreasing acidity), which can influence strengths of ionic interactions and thereby numbers of freely mobile anions in the PIL. All conductivity curves were fitted to the Vogel–Fulcher–Tamman (VFT) equation

\[
\sigma(T) = \sigma_\infty \times \exp \left( -\frac{DT_o}{T - T_o} \right)
\]

where \( \sigma_\infty \) is the infinite conductivity limit, \( T_o \) is Vogel temperature where ion motion stops, \( T \) is experimental temperature, and \( D \) is the strength parameter, which is inversely related to the fragility of polymer dynamics.\(^\text{14}\) The results from this fitting are shown in Table 4, and each dashed curve in Figure 2 depicts the VFT fit.

To elucidate the relative contributions of \( T_g \) versus other factors to PIL conductivity, each graph from Figure 2 was re-plotted using an x-axis of \( T_g/T \); these plots are shown in Figure 3. Such scaling of conductivity and other transport data has been used to de-emphasize differences in polymer segmental motion, to more clearly identify the extent to which other factors impact results. The more strongly that chain dynamics impact conductivity, the more that the individual conductivity plots will converge into something akin to a master curve. This convergence is most apparent with the data presented herein with PILs in which acrylate/acetoacetate ratio is varied, Figure 3b. So, although those PILs vary in percentage of ionic sub-units within the polymer, their conductivities appear to depend primarily on polymer dynamics within the range of temperatures studied. On the other hand, the conductivity profiles for anion variation and cation variation, Figure 3a,c, do not converge well indicating that other factors beyond polymer motion are contributing to observed behaviors.

Models of electrode polarization have been developed that can be applied to dielectric spectra (both \( \varepsilon' \) and \( \varepsilon'' \)) that allow the relative contributions of free-ion concentration (\( p \)) and free-ion mobility (\( \mu \)) toward conductivity to be determined.

### Table 4. Ionic Conductivity Data and VFT Fitting Parameters for TPIL Networks

| PIL network | anion (cation) | Acrylate/Acetoacetate ratio | \( \sigma \) at 30 \(^\circ\)C (S/cm) | \( \sigma_\infty \) (S/cm) | \( D \) | \( T_o \) (K) |
|-------------|----------------|-----------------------------|---------------------------------|--------------------------|------|--------------|
| 12          | Br             | 1.5:1.0                     | \( 6.5 \times 10^{-9} \)        | 9.0                      | 8.4  | 217          |
| 13          | NO\(_3\)       | 1.5:1.0                     | \( 1.3 \times 10^{-7} \)        | 1.2                      | 7.5  | 207          |
| 14          | BF\(_4\)       | 1.5:1.0                     | \( 6.2 \times 10^{-8} \)        | 10.7                     | 8.1  | 213          |
| 15          | OTf            | 1.5:1.0                     | \( 2.5 \times 10^{-7} \)        | 2.8                      | 8.2  | 202          |
| 16          | NTf\(_2\)      | 1.5:1.0                     | \( 9.3 \times 10^{-7} \)        | 0.8                      | 6.8  | 203          |
| 17          | NTf\(_2\)      | 1.2:1.0                     | \( 1.7 \times 10^{-6} \)        | 10.7                     | 11.5 | 175          |
| 18          | NTf\(_2\)      | 1.8:1.0                     | \( 2.2 \times 10^{-7} \)        | 1.5                      | 8.8  | 195          |
| 19          | (IM)           | 1.5:1.0                     | \( 4.1 \times 10^{-7} \)        | 5.6                      | 10.8 | 183          |
| 20          | (124TRI)       | 1.5:1.0                     | \( 2.5 \times 10^{-7} \)        | 0.6                      | 7.0  | 206          |

\( T_g \)-normalized ionic conductivity curves (log \( \sigma \) vs \( T_g/T \)) given (a) variable counteranion; (b) variable acrylate/acetoacetate ratio; (c) variable cation. The dashed curves represent VFT fitting parameters.
Electrode polarization results from an accumulation of mobile ions at the electrodes and is most clearly manifested via the rapid rise then plateau of ε’ when moving toward the lower frequency end of that spectrum. The region of the spectra where polarization dominates, then, can be described by modified MacDonald’s theory using a Debye-type relaxation function

$$\varepsilon_{EP}^*(\omega) = \frac{\Delta \varepsilon_{EP}}{(i\omega \tau_{EP})^{1-n} + i\omega \tau_{EP}}$$

where $\varepsilon_{EP}^*$ is the complex dielectric function, $\Delta \varepsilon_{EP}$ is the relaxation strength, $\tau_{EP}$ is the relaxation time (or time scale for full polarization), and $n$ is an exponent dependent upon electrode roughness.\(^{41-43}\) The relaxation time, then, can be correlated to $\mu$ and $p$ through the following relationship

$$\tau_{EP} = \frac{L}{2L_D} \frac{\epsilon \epsilon_0}{\mu p}$$

and relaxation strength is equivalent to the following

$$\Delta \varepsilon_{EP} = \left(\frac{L}{2L_D} - 1\right) \epsilon'_s$$

where $L_D$, the Debye length, is defined as

$$L_D = \frac{1}{\epsilon} \left(\frac{\epsilon \epsilon_0 kT}{p}\right)^{1/2}$$

$L$ is sample thickness/electrode spacing, $\epsilon_s$ is the static dielectric constant, $\epsilon$ is elementary charge, and $k$ is Boltzmann’s constant. Therefore, simultaneous fitting of temperature-dependent $\epsilon'$ and $\epsilon''$ spectra with eq 3 allows for $\mu$ and $p$ to be calculated as a function of temperature from fitting parameters.\(^{45}\)

All of the obtained dielectric spectra were well fit by the modified MacDonald model except in the case of bromide-containing PIL 12. Example fits are shown in Figure S29 and a plot illustrating $\tau_{EP}$ as a function of temperature for the variable cation and variable anion PILs is shown in Figure S30; values of $n$ for fitting ranged from 0.67 to 0.82. Applying multiplicative shift factors to $\epsilon'$ spectra for each PIL resulted in well-converged master curves except in the case of [Br] 12 (Figure S31), and it appears that its polarization region should be modeled by a modified or additional relaxation functions. Attempts to include an interfacial polarization function in the fitting for [Br] 12 proved unsuccessful in fully describing its behavior.\(^{46,45}\) It should also be noted that fitting dielectric spectra with Havriliak–Negami functions at frequencies higher than the onset of electrode polarization were also attempted to explore polymer segmental relaxations. However, high-frequency features were subtle/weak (substantially dominated by electrode polarization) to nonexistent in the studied frequency range. The inability to observe such relaxations was confirmed via the use of derivative spectra ($\epsilon_{\infty,\omega}$), which is supposed to aid in such evaluation by eliminating contributions to the spectra from ion conduction.\(^{44}\)

Plots of temperature-dependent free-ion concentration and ion mobilities obtained from dielectric fitting are shown in Figure 4. The temperature dependence of free-ion concentration, or number density of conducting ions, is described by an Arrhenius function

$$p = p_\infty \times \exp \left(\frac{-E_a}{RT}\right)$$

where $p_\infty$ is the high-temperature limiting concentration and $E_a$ is the activation energy for conducting ions, which can be thought of as a binding energy for an ion pair. Therefore, the fitted line in Figure 4a was used to determine log $p_\infty$ from the y-intercept and $E_a$ from the slope. These values are shown in Table 5. The determined values of log $p_\infty$ are generally within the 21–22 cm$^{-3}$ range, which is sensible based on a calculated value for total possible free ions of approximately 21.1 cm$^{-3}$ obtained from monomer stoichiometries and molar masses. Furthermore, the activation energies of PILs 13–16 follow a pattern defined by the Lewis basicity of the anion, with the most weakly basic [NTf$_2$] forming the weakest ion pairs and thereby having the lowest $E_a$, whereas the most strongly basic [NO$_3$] forms the strongest ion pairs and requires the largest $E_a$.\(^{32}\) Similarly, variations in monomer cation (PILs 16, 19, and 20) result in $E_a$ values that trend with the cations’ Lewis acidities, again corresponding to strength of ion pairing interactions.

Temperature-dependent ion mobilities, like conductivities, are described by a VFT fitting

$$\mu(T) = \mu_\infty \times \exp \left(-\frac{DT_0}{T - T_0}\right)$$

where the parameters are defined similarly to eq 2. The data and VFT fit are shown graphically in Figure 4b, whereas...
obtained fitting parameters are listed in Table 5. With PILs that vary by anion, limiting mobilities increase with decreasing anion size, except with [BF4] behaving as an outlier. Mobilities of [BF4]-containing PILs that are 2 orders of magnitude greater than [NTf2] PILs have been reported in the past, though no other counteranions were included in that study. Furthermore, the [BF4] anion has demonstrated limited stability in ILs, particularly at elevated temperature and in the presence of water.47 Since high temperatures were employed in this study, and measurements were not made under anhydrous conditions, it is possible that [BF4] decomposition/hydrolysis may contribute to the behavior of TPIL 14, however, such analyses were beyond the scope of this work. With the PILs where anion is constant, but cation is varied, the limiting mobilities with [123TRI] and [124TRI] cations are very similar, but [IM] is nearly an order of magnitude greater. It is likely that this observed difference is due to crosslink density for [IM] being lower than with the two triazolium PILs (see Table 3). With higher crosslink density, it is expected that free ions would be required to take more tortuous paths during conduction, thereby lowering their apparent mobilities.

Figure 5 shows the ionic conductivity of TPIL [Br] 12 as a function of temperature at three different relative humidity values (RH 30, 60, and 90%), whereas Table 6 summarizes the water uptake (wt %) of TPIL [Br] 12 at each of these RH conditions after an overnight (16 h) soak (samples tested in triplicate). The bromide conductivity increases approximately 4 orders of magnitude when the RH was increased from 30 to 60%. A further increase of another order of magnitude was observed when the RH was held at 90%. These increases can be attributed to a water-assisted ion-transport mechanism, commonly seen in PILs, which contain hydrophilic ions, such as halides. Such a transport phenomenon has been likened to water–Nafion systems and has been observed with other bromide-containing PIL co-polymers, prepared from acrylic-functionalized imidazolium monomers.48 The strong likelihood of water-assisted bromide transport is further supported by their noticeably large water uptake (0.64–27.2 wt %) over the humidity range of interest (Table 6). Such a large increase in ionic conductivity, as expected, was not observed for the highly hydrophobic TPIL [NTf2] 16. For the more hydrophobic PIL [NTf2] 16, ion transport would be more strongly dictated by segmental motion and polymer dynamics. Although their conductivities at higher % RH were not examined, it must be noted that both the [NO3] and [BF4] TPIL networks did exhibit some water absorption at 30% RH (Table S1), though not nearly to the extent that TPIL [Br] 12 did. Regardless, this small amount of water absorbed could result in a slight enhancement of ionic conductivity that otherwise might not be observed under anhydrous conditions.

Table 5. Free-Ion Concentrations and Ion Mobilities for TPILs

| PIL network | anion (cation) | log p∞ (cm⁻³) | Ea (kJ/mol) | log μ∞ (cm²/(V s)) | D | T∞ (K) |
|-------------|---------------|---------------|-------------|------------------|---|--------|
| 13          | NO₃          | 21.59         | 25.28       | -0.13            | 7.62 | 190.4 |
| 14          | BF₄           | 21.62         | 19.83       | 1.23             | 10.88 | 189.3 |
| 15          | OTf           | 21.51         | 18.92       | -1.54            | 2.98 | 237.1 |
| 16          | NTf₂         | 21.66         | 16.07       | -2.57            | 2.09 | 242.8 |
| 19          | (IM)          | 20.95         | 17.06       | -1.74            | 2.14 | 247.4 |
| 20          | (124TRI)      | 22.65         | 29.53       | -2.54            | 1.26 | 254.0 |

Obtained fitting parameters are listed in Table 5. With PILs that vary by anion, limiting mobilities increase with decreasing anion size, except with [BF₄] behaving as an outlier. Mobilities of [BF₄]-containing PILs that are 2 orders of magnitude greater than [NTf₂] PILs have been reported in the past, though no other counteranions were included in that study. Furthermore, the [BF₄] anion has demonstrated limited stability in ILs, particularly at elevated temperature and in the presence of water.47 Since high temperatures were employed in this study, and measurements were not made under anhydrous conditions, it is possible that [BF₄] decomposition/hydrolysis may contribute to the behavior of TPIL 14, however, such analyses were beyond the scope of this work. With the PILs where anion is constant, but cation is varied, the limiting mobilities with [123TRI] and [124TRI] cations are very similar, but [IM] is nearly an order of magnitude greater. It is likely that this observed difference is due to crosslink density for [IM] being lower than with the two triazolium PILs (see Table 3). With higher crosslink density, it is expected that free ions would be required to take more tortuous paths during conduction, thereby lowering their apparent mobilities.

Figure 5 shows the ionic conductivity of TPIL [Br] 12 as a function of temperature at three different relative humidity

<Figure 5. Ionic conductivity curves for TPIL [Br] 12, reflecting the effect of variable relative humidity.>

values (RH 30, 60, and 90%), whereas Table 6 summarizes the water uptake (wt %) of TPIL [Br] 12 at each of these RH

Table 6. Effect of Relative Humidity on Ionic Conductivity and Water Uptake of the [Br] and [NTf₂] TPIL Networks

| anion | 30% RH σ (S/cm) | 30% RH water uptake (%) | 60% RH σ (S/cm) | 60% RH water uptake (%) | 90% RH σ (S/cm) | 90% RH water uptake (%) |
|-------|----------------|------------------------|----------------|------------------------|----------------|------------------------|
| Br    | 6.46 × 10⁻⁹   | 0.64 ± 0.05            | 3.16 × 10⁻⁹   | 7.90 ± 0.10            | 2.45 × 10⁻⁹   | 27.2 ± 0.4             |
| NTf₂  | 9.33 × 10⁻⁷   | <0.01                  | 9.98 × 10⁻⁷   | 0.05 ± 0.02            | 1.23 × 10⁻⁷   | 0.67 ± 0.13            |

Data were obtained after a 16 h soak at 30 °C at the specified RH.

"Data were obtained after a 16 h soak at 30 °C at the specified RH."
CONCLUSIONS

A series of 1,2,3-triazolium-based bisacetoacetate monomers were synthesized using an azide–alkyne click cyclization strategy and subsequently polymerized using base-catalyzed Michael addition. The resulting TPIL networks were analyzed for their thermal (DSC, TGA), mechanical (DMA), and electrochemical (DRS) properties. The counteranion, crosslink density (acetoacetate/acrylate ratio), and cation were varied to observe changes in these properties.

DSC thermal analysis of the TPILs indicated an inverse correlation between $T_g$ and counteranion size, with $[\text{NTf}_2]^-$ TPIL exhibiting the lowest $T_g$. An increase in the $T_g$ was observed when the acrylate concentration was increased due to an increase in covalent crosslinking. An increase in thermal stability ($T_{d5\%}$) was observed with decreasing Lewis basicity of the anion on the order $[\text{NTf}_2]^->[\text{OTf}]^->[\text{BF}_4]^->[\text{NO}_3]^->[\text{Br}]$. Changes in crosslink density brought about by varying the acrylate/acetoacetate ratio did not appear to affect thermal stability. Dynamic mechanical analysis indicated that changes in counteranion did not influence the rubbery plateau storage modulus ($E'$) or the apparent crosslink density ($\rho_c$) in any discernable way, whereas DMA $T_g$ (tan $\delta$ max) was observed to be inversely related to counteranion size (supporting DSC $T_g$ results). An increase in acrylate concentration did result in an increase in $E'$ and crosslink density. Despite the network nature of the TPILs, obtained conductivities of $10^{-8}$–$10^{-9}$ S/cm at 30 °C were comparable to a number of previously reported PILs. Ion conduction demonstrated a reliance on cations/anions and on free anion size via those properties influence on free-ion concentration and ion mobility, respectively.

EXPERIMENTAL SECTION

Materials. All commercial reagents and solvents were purchased from either Acros Organics or Sigma-Aldrich and used as received. Tetrahydrofuran (THF) (99.9%) and N,N-dimethylformamide (DMF) (99.9%) were purchased as anhydrous from Acros Organics and used as received. Ultrapure water having a resistivity of 18 MΩ was used as received. Tetrahydrofuran (99.9%) and anhydrous from Acros Organics was used as received. Polymeric fluidity, especially at lower measured temperatures. Analysis of dielectric data highlighted a further dependence of the nature of the TPILs, obtained conductivities of $10^{-8}$–$10^{-9}$ S/cm at 30 °C. The reaction was then slowly quenched with 3.0 M HCl (30 mL), followed by the transfer of the reaction mixture into a separatory funnel where the organic layer was separated. The aqueous layer was extracted once with dichloromethane, and the organic layers were combined, dried over Na$_2$SO$_4$/MgSO$_4$, and the solvent removed under reduced pressure to afford 4.45 g of a light yellow oil (84%).

Synthesis of 1-(6′-Hydroxyhexyl)-1,2,3-triazole 2. In a 500 mL, three-necked round-bottom flask was dissolved the 1,2,3-triazole ester 1 (6.60 g, 31.2 mmol) in dichloromethane (60 mL). The magnetically stirred solution was cooled to 0 °C under N$_2$ whereupon Dibal-H (93.7 mL of a 1.0 M solution in hexanes, 93.7 mmol) was added dropwise over a 45 min period, followed by warming to room temperature where stirring continued for 24 h. The reaction was then slowly quenched with 3.0 M HCl (30 mL), followed by the transfer of the reaction mixture into a separatory funnel where the organic layer was separated. The aqueous layer was extracted once with dichloromethane, and the organic layers were combined, dried over Na$_2$SO$_4$/MgSO$_4$, and the solvent removed under reduced pressure to afford 4.45 g of a light yellow oil (84%).

Synthesis of 1-(6′-Acetoacetoxyhexyl)-1,2,3-triazole 3. 1-(6′-Hydroxyhexyl)-1,2,3-triazole 2 (4.29 g, 25.4 mmol) was dissolved in acetonitrile (100 mL) in a 250 mL round-bottom flask. tert-Butylacetoacetate (12.03 g, 76.1 mmol) was then added, and the resulting magnetically stirred solution was warmed to reflux and held for 2 h. Volatiles were then removed under reduced pressure to afford 5.97 g (93%) of a light orange oil. 1H NMR (400 MHz, DMF-$d_6$): $\delta$ 1.21 (m, 2H), 1.27 (m, 2H), 1.36 (m, 2H), 1.80 (m, 2H), 3.35 (t, 2H), 4.33 (t, 2H), 4.70 (s, 1H), 7.70 (s, 1H), 8.11 (s, 1H). 13C NMR (100 MHz, DMF-$d_6$): $\delta$ 24.86, 24.99, 29.79, 32.28, 49.06, 60.51, 124.53, 133.14. Anal. calcd for C$_7$H$_7$N$_2$O$_2$: C 56.85, H 8.11, N 19.89. Found: C 56.78, H 8.29, N 19.86.

Synthesis of 1-(6′-Acetoacetoxyhexyl)-1,2,3-triazole 4. 1,2,3-triazole 2 (4.29 g, 25.4 mmol) was dissolved in acetonitrile (100 mL) and 1-acetoacetoxy-6-bromohexane (7.26 g, 25.4 mmol) were added. The reaction was stirred at room temperature for 2 h, then warmed to 50 °C, and held for 24 h. The mixture was then cooled to room temperature and poured onto ethyl ether (300 mL). The organic phase was separated and washed with 150 mL portions of a 3:1 mixture of saturated NH$_4$Cl/NH$_4$OH until the aqueous wash layer was colorless (i.e., no blue color). The organic phase was then further washed with brine, dried over a mixture of Na$_2$SO$_4$/MgSO$_4$, and the solvent removed under reduced pressure to afford an orange oil, which was immediately dissolved in anhydrous THF (50 mL). A 1.0 M solution of TBAF in THF (53.8 mL, 53.8 mmol of TBAF) was added, and the resulting solution was stirred at room temperature overnight. The residuals were removed under reduced pressure, and the crude oil was dissolved in ethyl acetate and washed sequentially with 5% NaCl solution twice and brine. The organic phase was separated, dried over Na$_2$SO$_4$/MgSO$_4$, and the solvent removed to give a brown oil, which was purified by column chromatography on silica gel with a gradient elution of 0–50% ethyl acetate in hexanes. Purification resulted in 5.77 g of a light yellow oil (61%). 1H NMR (400 MHz, CDCl$_3$): $\delta$ 1.17 (t, 3H), 1.29 (m, 2H), 1.58 (m, 2H), 1.86 (m, 2H), 2.21 (t, 2H), 4.03 (t, 2H), 4.32 (q, 2H). 13C NMR (100 MHz, CDCl$_3$): $\delta$ 14.29, 24.30, 25.96, 30.10, 33.98, 49.99, 60.39, 123.36, 133.81, 173.48. Anal. calcd for C$_{10}$H$_{17}$N$_3$O$_2$: C 56.78, H 8.29, N 19.86.
flask and stirred at 60 °C for 48 h under an atmosphere of nitrogen. The mixture was then cooled to room temperature and washed with ethyl ether (4 × 20 mL). The product was dried under reduced pressure, resulting in 4.30 g of an orange oil (91%). 1H NMR (400 MHz, DMSP-δ3): δ 1.31 (m, 8H), 1.56 (m, 4H), 1.92 (m, 4H), 2.17 (s, 6H, CH3 on AcAc group), 3.59 (s, 4H, CH3 on AcAc group), 4.04 (t, 2H, J = 6.6 Hz), 4.64 (t, 2H, J = 7.1 Hz), 8.99 (s, 2H). 13C NMR (100 MHz, DMSP-δ3): δ 24.50, 24.92, 27.70, 28.47, 30.00, 49.59, 52.95, 64.19, 130.87, 167.15, 201.49. Anal. calcld for C22H36BF4N3O6: C 50.30, H 6.91, N 8.00. Found: C 50.12, 53.02, 61.17, 130.87, 167.15, 201.49. Anal. calcld for C23H36F3N3O9S: C 47.01, H 6.18, N 7.15. Found: C 46.98, H 6.14, N 7.25.

**Synthesis of 1,3-Bis(6′-acetoacetoxyhexyl)-1,2,3-triazolium Nitrate 6.** A solution of silver nitrate (5 mL) was added, and the reaction stirred overnight, in the dark, at room temperature. The mixture was then cooled to room temperature and washed with ethyl ether (4 mL). A solution of lithium bis(trifluoromethylsulfonyl)imide (0.87 g, 3.04 mmol), dissolved in DI water (5 mL), was added to the reaction, and the resulting mixture was stirred at room temperature overnight. Dichloromethane (25 mL) was then added and the organic phase was separated, washed with DI water (3 × 10 mL), and then the solvent was removed under reduced pressure to afford 2.00 g (96%) of a light yellow oil. 1H NMR (400 MHz, DMSP-δ3): δ 1.32 (m, 8H), 1.56 (m, 4H), 1.91 (m, 4H), 2.17 (s, 6H, CH3 on AcAc group), 3.59 (s, 4H, CH3 on AcAc group), 4.04 (t, 2H, J = 6.6 Hz), 4.62 (t, 2H, J = 7.1 Hz), 8.92 (s, 2H). 13C NMR (100 MHz, DMSP-δ3): δ 24.48, 24.94, 27.71, 28.45, 30.08, 49.57, 53.00, 64.17, 119.43 (q, J = 319 Hz, −CF3), 130.84, 167.25, 201.55. Anal. calcld for C22H36F3N3O9S: C 50.97, H 7.00, N 8.11. Found: C 50.85, H 7.03, N 8.02.

**Procedure for Michael Addition Polymerizations.** All of the polymerizations were completed in dichloromethane (50 wt %). In a typical procedure, 1,3-bis(6′-acetoacetoxyethyl)-imidazolium bis(trifluoromethylsulfonylimide 9 (0.90 g, 1.25 mmol) and 1,4-butanediol diacrylate (0.37 g, 1.88 mmol, 1.5 M equiv) were dissolved in dichloromethane (1.25 g). DBU catalyst (9.5 mg, 2 mol %) was then added, and the resulting solution was mixed for 2 min. The solution was poured into a PTFE mold and cured for 48 h at ambient temperature, followed by curing in a 60 °C oven for 48 h. Complete solvent removal and sufficient dryness prior to analysis were ensured by placing the sample in a vacuum oven (<0.1 mmHg) for 24 h at 50 °C.

**Polymer Analysis.** All acetoacetate monomers and PIL network films were stored in a vacuum oven at 40 °C for 48 h prior to any analytical testing. Differential scanning calorimetry (DSC) was performed using a TA Instrument Q200 Differential Scanning Calorimeter with a heating rate of 5 °C/min on 4–8 mg samples. Glass transition temperatures (Tg) were determined from the second heating by the inflection point of the curve observed. A TA Instrument Q500 Thermogravimetric Analyzer was used to determine Tg (dry) the temperature at which 5% weight loss was observed, at a heating rate of 10 °C/min under an inert nitrogen atmosphere. The mechanical properties of the TPIL networks were analyzed using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) in film tension mode (single film). The in-plane sample was weighed (m0) and then placed in a vacuum oven (60 °C, 24 h) to obtain the dry weight (m0). Gel fraction was determined as follows: gel fraction = (m0−m0)/m0 × 100 where m0 is the original mass of the sample. Percent swelling was calculated as follows: % swelling = (msw/m0) × 100. The influence of water absorption was determined for each TPIL network (in triplicate) by conditioning the sample in the humidity chamber (Espnc BTL-433 benchtop temperature/humidity oven at 30, 60, 90% RH) for 16 h, followed by conductivity testing. Water absorption was determined using the following equation: water absorbed = ((msw−m0)/m0) × 100.

**Dielectric Relaxation Spectroscopy.** DRS was performed with a Metr烘FRA32M frequency response analyzer.
coupled to an ECI10M impedance interface and a custom-built (in-house) two-electrode cell (Figure S17). The cell was placed inside the aforementioned Espec BTU-433 controlled-temperature/humidity chamber to maintain constant conditions (between 30 and 150 °C and 30% RH) during each measurement. Sample membranes of ~12 mm diameter and 1 mm thickness were sandwiched between 304L stainless steel electrodes separated by a 1 mm thick PTFE spacer. Electrodes were polished to a mirror finish with 8000-, 14,000-, and 60 000-mesh diamond paste (Sandvik Hyperion; Worthington, OH) prior to use. For each sample, dielectric/impedance spectra were collected at various temperatures using a frequency range of 1–10\(^7\) Hz and alternating current amplitude of ±0.01 V. The stray admittance and residual impedance of the test cell were evaluated by open cell (no sample) and shorted cell measurements, respectively, using the same experimental conditions outlined above; shorted measurements were performed using a 12 mm dia by 1 mm thick disk of 99.99% pure Cu as the sample. Compensations for stray admittance and residual impedance were applied to all data via Excel, as outlined elsewhere. Additionally, all measured values of real dielectric (\(\epsilon'\)) were corrected for contribution from the spacer according to the method described by Johari.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01949.

1H and 13C NMR spectra for compounds 1–3 and 5–9 are provided along with representative DSC and TGA data for each of the diaacetate monomers 5–9; DSC thermograms; TGA traces and DMA tan \(\delta\) curves for TPIL networks 12–20; two-electrode cell used in DRS measurements (PDF)

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Notes

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