## PROOF OF CONCEPT ANALYSIS OF USING PHOTO-CLICK CHEMISTRY ON IONIC LIQUID MONOMERS WITH PROPARGYL FUNCTIONALITY

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master in Chemical Engineering

Summer 2017

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#### ACKNOWLEDGMENTS

There are a number of people I would like to thank for their support and assistance through my Master's program. Firstly, I would like to thank my advisor Dr. Chris Kloxin for his endless support, insight and helping me make the most out of my time here in Delaware. I would next like to thank my research group from helping me adapt and learn. A special thank you to Dr. Andrew Tibbits, who mentored me in the beginning of my project and taught me the techniques I've used in my work, and Bassil El-Zaatari for his assistance and insight on the photo-CuAAC project in Chapter 2 and in helping me improve the framework of my thesis. I would also like to thank Stephen Ma, Dr. Srimoyee Dasgupta, Abhishek Shete, Dr. Melissa Gordan, Bryan Sutherland, Kaleigh Reno, Nicole Halaszynski, Benjamin Carberry, Justin Paloni, Jonathan Galarraga, Derek Bischoff, Shea Cole, and Grant Knappe, all of who have had positive impact on me and my work with their presence in the lab. I would also like to thank my supervisors at the English Language Institute, Maria Riera-Jose and Karen Asenavage, who constantly supported my endeavors in working at the ELI while being able to balance my academic work successfully. I would like to thank everybody else who I had the pleasure of meeting in Delaware and my friends who I met before Delaware, whose presence and friendship in my life I am impacted by and cherish. Finally, I would thank my parents and my brother for their unconditional support and encouragement at all stages of my life, without which I could not have made it this far.

| LIST | OF TABLES   | vi       |
|------|---|----------|
| LIST | OF FIGURES  | ⁄ii      |
| ABS  | ГКАСТ   | ix       |
| Chap | ter   |          |
| 1    | INTRODUCTION  | . 1      |
|      | Ionic Liquids   | . 2      |
|      | Ionic Liquid Synthesis  | . 3      |
|      | Materials   | .4       |
|      | Procedure: Bromide form of ionic liquid (Procedure adapted from Ref. $8$ ) <sup>8</sup> | 4        |
|      | Procedure: Anion metathesis to obtain TFSI form of ionic Liquid                         | .5       |
| 2    | COPPER (I) CATALYZED AZIDE ALKYNE CYCLOADDITION<br>USING IONIC LIQUID MONOMERS          | .6       |
|      | Introduction and motivation   | .6       |
|      | Experimental Methods and Synthesis  | . /      |
|      | Materials   | .7       |
|      |   | . 0      |
|      | Reactivity and Kinetics of Propargyl Ionic Liquids in photoinitiated<br>CuAAC system    | .9       |
|      | Effect of the anion present in the ionic liquid   | .9       |
|      | Effect of the cation structure  | 2        |
|      | Summary and Conclusion  | 4        |
| 3    | THIOL-YNE CLICK REACTION USING IONIC LIQUID<br>MONOMERS                                 | 15       |
|      |   |          |
|      | Introduction and Motivation   | 15<br>17 |
|      | Materials   | 17       |
|      | Sample Preparation for Spectroscopy Experiments   | 8        |
|      | Sample Preparation for Network Casting  | 8        |

## TABLE OF CONTENTS

|     | Reactivity and Kinetics of Propargyl Ionic Liquids in Photoinit | otoinitiated Thiol- |  |  |
|-----|---|---------------------|--|--|
|     | yne System  | 19                  |  |  |
|     | Kinetics of the Triethylammonium System                         | 19                  |  |  |
|     | Kinetics of the Methylimidazolium System                        |                     |  |  |
|     | Effect of the anion   |                     |  |  |
|     | Effect of the cation structure                                  |                     |  |  |
|     | Network Properties  | 27                  |  |  |
|     | Methods   | 27                  |  |  |
|     | Results   | 27                  |  |  |
|     | Summary and Conclusion  |                     |  |  |
|     | SUMMARY AND OVERARCHING CONCLUSIONS                             |                     |  |  |
| REF | ERENCES   |                     |  |  |
| App | endix   |                     |  |  |
|     | <sup>1</sup> H NMR ANALYSIS                                     | 35                  |  |  |
|     | Synthesis of 1-Propargyl-3-Methylimidazolium Bromide [PrM       | eIm][Br]35          |  |  |
|     | Synthesis of 1-Propargyl-3-Methylimidazolium TFSI [PrMeIm       | ][TFSI] 36          |  |  |
|     | Synthesis of 1-Propargyl-3-Methylpyrrolidine Bromide [PrMel     | Py][Br] 37          |  |  |
|     | Synthesis of 1-Propargyl-3-Methylpyrrolidine TFSI [PrMePy][     | TFSI]38             |  |  |
|     | Synthesis of N-propargyl-,N,N-triethylammonium bromide [Pr      | TEA][Br].39         |  |  |
|     | Synthesis of N-propargyl-,N,N-triethylammonium TFSI [PrTE.      | A][TFSI]40          |  |  |

## LIST OF TABLES

| Table 1 | Material properties of Network of Ionic Liquid monomer | and ETTMP |
|---------|--|-----------|
|         | 1300 thiol at 25°C                                     |           |

## **LIST OF FIGURES**

| Figure 1  | Commonly used ionic liquid systems (Adapted from Ref. 7) <sup>7</sup> 2   |
|-----------|---|
| Figure 2  | All ionic liquids synthesized and used in this work   |
| Figure 3  | Chemicals used in ionic liquid synthesis4   |
| Figure 4  | Mechanism of photo-CuAAC reaction in an ionic liquid7   |
| Figure 5  | Chemicals used in conjugation with ionic liquids for the CuAAC reaction   |
| Figure 6  | Effect of the anion on Propargyl Triethylammonium system10  |
| Figure 7  | Effect of the anion on Propargyl Triethylammonium system11  |
| Figure 8  | Effect of the anion on Propargyl Triethylammonium system12  |
| Figure 9  | Effects of the cation structure on CuAAC reaction13   |
| Figure 10 | Intermediate steps of CuAAC for the formation of triazole linkage<br>using an ionic liquid. [Cu] here represents ligated Cu(I) ion,<br>responsible for catalyzing this reaction |
| Figure 11 | Trend in the kinetics of the CuAAC reaction as explained by the degree of unsaturation (DoU) of each cationic molecule  |
| Figure 12 | Radical initiated thiol-ene mechanism   |
| Figure 13 | Radical initiated thiol-yne mechanism16   |
| Figure 14 | Chemicals used during kinetic experiments of thiol-yne reactions 17   |
| Figure 15 | Thiol-yne reaction between [PrTEA][TFSI] and PETMP20  |
| Figure 16 | Thiol-yne reaction between [PrTEA][TFSI] and ETTMP 130021   |
| Figure 17 | Conversion of Thiols in [PrMeIm][TFSI] system   |
| Figure 18 | Conversion of Thiols in [PrMeIm][TFSI] system23   |
| Figure 19 | Conversion of Thiols in [PrMeIm][Br] system24   |
| Figure 20 | Conversion of Alkynes in [PrMeIm][Br]25   |

| Figure 21 | Effect of Cation structure on thiol-yne   | .26  |
|-----------|---|------|
| Figure 22 | On the left is a network cast by [PrMeIm][Br] and on the right, is a network cast by [PrMeIm][TFSI] | .27  |
| Figure 23 | Storage modulus of [PrMeIm] system  | .28  |
| Figure 24 | Tan delta of the [PrMeIm] system.   | .29  |
| Figure 25 | Synthetic route and <sup>1</sup> H NMR Analysis spectrum confirming the structure of [PrMeIm][Br]   | .35  |
| Figure 26 | Synthetic route and <sup>1</sup> H NMR Analysis spectrum confirming the structure of [PrMeIm][TFSI] | .36  |
| Figure 27 | Synthetic route and <sup>1</sup> H NMR Analysis spectrum confirming the structure of [PrMePy][Br]   | .37  |
| Figure 28 | Synthetic route and <sup>1</sup> H NMR Analysis spectrum confirming the structure of [PrMePy][TFSI] | .38  |
| Figure 29 | Synthetic route and <sup>1</sup> H NMR Analysis spectrum confirming the structure of [PrTEA][Br]    | . 39 |
| Figure 30 | Synthetic route and <sup>1</sup> H NMR Analysis spectrum confirming the structure of [PrTEA][TFSI]  | .40  |

#### ABSTRACT

Click chemistry refers to a specific set of organic chemistry reactions that proceed under mild conditions, are high yielding, and are extremely selective. Due to their orthogonality, these types of reactions have opened doors for the fabrication of materials of many kinds. This work explores the applicability of click chemistry used in conjunction with ionic liquids.

The kinetics of light initiated click chemistry reactions of CuAAC and thiol-yne on ionic liquids functionalized with alkyne are examined, setting up the foundation for many applications including but not limited to ion-containing membranes, adhesives, and organic catalysts. Photo-click chemistry is a recent discovery and all its facets have not been explored yet. While it is evident that photo-click reactions have made the already friendly click reactions even more amicable, there is a vast gap in the literature on the fundamentals of this reaction.

It was observed that the cationic structure of the ionic liquid monomer and the presence of the anion significantly affect the kinetics of the click reactions. For the CuAAC reaction, the fastest kinetics were produced by a weakly coordinating anion and aromatic structure cation combination and it was deduced that anions which strongly interact with Cu(I) inhibit the reaction. Additionally, it was discovered that the polarity of the thiol monomer has an effect on the thiol-yne click reaction. A more polar thiol in thiol-yne reactions with ionic liquids appears to facilitate the reaction to proceed to full conversion.

ix

#### Chapter 1

#### INTRODUCTION

Click chemistry is an umbrella term used for reactions that are selective, provide little to no byproducts, and if needed can be purified easily. They usually comprise of carbon – heteroatom bond forming reactions. Several click chemistry reactions have been defined in literature, including but not limited to the copper(I)-catalyzed azidealkyne cycloaddition (CuAAC), thiol-ene, thiol-yne, Diels-Alder addition, 1,3 dipolar cycloaddition, and tetrazole cycloaddition<sup>1</sup>. CuAAC is one of the most commonly used reactions with applications in organic synthesis, dendrimers, surface modifications, bioconjugations and polymers<sup>2</sup>. Thiol-yne chemistry has been used more recently than the CuAAC in polymer and material synthesis<sup>3</sup>. It has been demonstrated recently by Adzima et. al. and Fairbanks et. al. that the CuAAC reaction and the thiol-yne reaction can be initiated by light<sup>4,5</sup>. The advantage of using light-initiated click reactions is the spatial-temporal control that is achieved at convenience with the low cost of light and the ability to conduct reactions at room-temperature. It has also expanded the applications of this reaction in photolithography and 3D printing<sup>6</sup>.

While ionic liquids have been used within the click chemistry paradigm, literature on the understanding of photo-click reactions via the CuAAC or thiol-yne reactions on ionic liquids is largely absent. This thesis is divided into two major segments: (1) understanding the kinetics of using photo-initiated copper(I) catalyzed azide alkyne cycloaddition (CuAAC) with ionic liquid monomers; (2) understanding the kinetics of using thiol-yne click chemistry with ionic liquid monomers.

#### **Ionic Liquids**

Ionic liquids are molten organic salts with low melting points. There are myriad possibilities of what an ionic liquid constitutes. Depending on the application, the cation and anion of the ionic liquid can be modified and optimized, making them a highly tunable and versatile family of molecules. Figure 1 shows some of the commonly used system of ionic liquids.



| Some possible | Water-immiscible                |                                    | Water-miscible  |
|---------------|---------------------------------|------------------------------------|---|
| anions:       | [PF <sub>6</sub> ] <sup>-</sup> | [BF <sub>4</sub> ] <sup>-</sup>    | $[CH_3CO_2]^-$  |
|               | $[NTf_2]^-$                     | [OTf] <sup>-</sup>                 | [CF <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup> , [NO <sub>3</sub> ] <sup>-</sup> |
|               | $[BR_1R_2R_3R_4]^-$             | [N(CN) <sub>2</sub> ] <sup>-</sup> | Br⁻, Cl⁻, I⁻  |
|               |                                 |                                    | $[Al_2Cl_7]^-$ , $[AlCl_4]^-$ (decomp.)   |

Figure 1 Commonly used ionic liquid systems (Adapted from Ref. 7)<sup>7</sup>

Since this work explores the use of two click reactions involving alkynes, the ionic liquids are designed to incorporate the alkyne functionality. The cation of the ionic

liquid is functionalized with a propargyl (Pr) group. Two types of anions have been used. Figure 2 shows the system of ionic liquids used in this work



[PrMeIm][Br]:Propargyl Methyl Imidazolium Bromide



[PrTEA][Br]:Propargyl Triethylammonium Bromide



[PrMeIm][TFSI]:Propargyl Methyl Imidazolium Bistriflimide



[PrTEA][TFSI]:Propargyl Triethylammonium Bistriflimide



[PrMePy][Br]:Propargyl Methyl Pyrrolidinium Bromide

Figure 2

All ionic liquids synthesized and used in this work.

#### Ionic Liquid Synthesis

All the ionic liquid monomers used in this work were synthesized using procedures that are well documented in literature<sup>8</sup>. Figure 2 shows all ionic liquids that were synthesized in this work along with their structures and abbreviations. The formation of ionic liquids was confirmed by <sup>1</sup>H NMR analysis of the compound. NMR Spectrum and analysis of all the ionic liquids synthesized is attached in the Appendix.

#### Materials

1-Methylimidazole was obtained from Sigma -Aldrich, 1-methylpyrrolidine obtained from Fluke Analytical and triethylamine was obtained from TCI America. Propargyl bromide was obtained from TCI America and lithium bis(trifluoromethane)sulfonamide (LiTFSI) was procured from Alfa Aesar. Ethyl acetate and diethyl ether were obtained from Fisher Scientific. All the chemicals are shown in Figure 3.



Figure 3 Chemicals used in ionic liquid synthesis

#### Procedure: Bromide form of ionic liquid (Procedure adapted from Ref. 8)<sup>8</sup>

The desired amine (1-Methylimidazole, 1-Methylpyrrolidine, or Triethylamine) was weighed and added to a round bottom flask containing ethyl acetate. The flask was

placed in an ice bath and maintained at 0°C. Propargyl bromide was added dropwise to the solution while stirring. The mixture was brought to room temperature and allowed to react for 48 hours. Subsequently, the product, which precipitated out, was extracted by washing with water and dried under vacuum.

#### Procedure: Anion metathesis to obtain TFSI form of ionic Liquid

Anion metathesis reaction was conducted to synthesize the ionic liquid with TFSI anion. The bromide form of ionic liquid was dissolved in water in a round bottom flask. Equivalent amount of Lithium TFSI, obtained from TCI America, was weighted and added to the flask. The mixture is stirred and allowed to react overnight. The product which precipitated out is extracted by washing with diethyl ether and dried under vacuum.

#### Chapter 2

#### COPPER (I) CATALYZED AZIDE ALKYNE CYCLOADDITION USING IONIC LIQUID MONOMERS

#### Introduction and motivation

The copper(I) catalyzed azide alkyne cycloaddition (CuAAC) reaction is one of the most prominent click reactions with diverse applications in pharmaceuticals<sup>9</sup>, bioconjugation chemistry<sup>10</sup> and material science<sup>11,12</sup>. As the name suggests, an azide and an alkyne react in presence of copper (I) to form triazole linkages. For the reaction to proceed, a copper (I) source is either directly incorporated in catalytic amounts or formed due to the reduction of copper (II) by a reducing agent such as sodium ascorbate<sup>13</sup>. However, Adzima et al. recently demonstrated that the CuAAC reaction can be initiated by photoreduction of Cu(II) to Cu(I) using a photoinitiator<sup>4</sup>.

A former student in the Kloxin lab, Andrew Tibbits, utilized the photoinitated CuAAC reactions for designing hydroxide exchange membranes (HEM)<sup>14</sup>. The use of the CuAAC reaction for HEM provides alternative chemistries to fabricate membranes which enhance ionic conductivity, flexibility and chemical stability<sup>15, 16, 17</sup>. The triazole linkage which is the product of the CuAAC reaction increases the rigidity of the network and has been reported to be alkaline stable<sup>18</sup>. Initiating this reaction with light provides spatial and temporal control, which is particularly useful when casting a membrane. Membranes can then be fabricated at room temperature simply by shining light of a particular wavelength and intensity as opposed to going through a phase inversion process, which is the most common way of casting membranes<sup>19</sup>. Ion-containing polymer networks have been made previously by quarternizing the CuAAC triazole-based product<sup>20-24</sup>. The CuAAC reaction has also been used between propargyl ionic liquid and azide functionalized polymer<sup>25-37</sup>, however it was done using sodium

ascorbate as a reducing agent via the in-situ reduction of copper (II) to copper (I) or by the direct incorporation of copper (I) complex. Figure 4 shows the mechanism of photo-CuAAC reaction on an ionic liquid.



Figure 4 Mechanism of photo-CuAAC reaction in an ionic liquid

This work aims to gain a better understanding of the kinetics of CuAAC reaction when reacting a monofunctional alkynyl ionic liquid and monofunctional azide. Using model systems, we explore the structural and anionic effects on the kinetics of the photo-CuAAC reaction.

#### **Experimental Methods and Synthesis**

#### Materials

All materials were pure ( $\geq$ 97%) and were used as-received without further purification. Methyl 2-azidoacetate, and copper(II) sulfate pentahydrate (CuSO4.5H2O) were obtained from Sigma Aldrich. Propargyl bromide (80% in THF) was purchased from TCI America. Irgacure 819 was obtained from BASF (Ciba). Dimethylformaide (DMF) was obtained from Fisher Scientific. The ionic liquids used were synthesized as described in Chapter 1. Figure 2 shows the ionic liquids that were used and Figure 5 shows the chemicals that were used in this chapter.



Figure 5 Chemicals used in conjugation with ionic liquids for the CuAAC reaction

#### Sample preparation

The experimental conditions used and monitored were as presented by El-Zaatari et al.<sup>38</sup>. Reaction system contained 5 mL DMF with 50 mM methyl-2azidoacetate, 50 mM of ionic liquid monomer, 10 mM CuSO4.5H2O, which was the copper(II) source used and 10 mM of Irgacure 819 which was the photoinitiator used. The reaction system was injected into a SL-2 sealed liquid cell equipped with calcium fluoride windows provided by International Crystal Laboratories. The liquid cell was then mounted onto a Nicolet iS50 Series Fourier transform infrared (FTIR) spectrometer. After about 30 seconds, the liquid cell is irradiated using OmniCure Series 2000 lamp that was filtered using a 405 nm band pass interference filter, equipped with a 200 Watt mercury arc bulb by Lumen Dynamics.

# Reactivity and Kinetics of Propargyl Ionic Liquids in photoinitiated CuAAC system

Kinetics of the reaction were characterized via FTIR by monitoring the area of the azide peak which was calculated using a beer's law type analysis. The azide peak of the methyl-2-azidoacetate occurs between 2090 cm<sup>-1</sup> and 2140 cm<sup>-1</sup> and exhibits a maximum at 2109 cm<sup>-1</sup>. Using the six ionic liquid monomers, two aspects of the reaction were tested: the effect of the anion present in the ionic liquid and the effect of the structure of cation in the ionic liquid.

#### Effect of the anion present in the ionic liquid

It was observed that the ionic liquids with bromide anion reacted very little in the case of [PrTEA][Br] and did not react at all in case of the other two ionic liquids as shown in Figures 6,7 and 8. Having high concentrations of Br<sup>-</sup> ion when compared to that of copper(I) can be detrimental to this reaction since Cu(I) has a strong affinity for the ion<sup>39</sup>. It is hypothesized that this affinity affects the ability of copper(I) to form an acetylide capable of ligating to a second copper(I) ion, an extremely important step in the CuAAC mechanism<sup>13</sup>. Thus, copper is unable to catalyze the reaction effectively. However, it is observed that replacing the bromide anion with TFSI changes the kinetics drastically and allows for a very rapid reaction. This switch of anion not only eliminates the interactions between Cu(I) and the anion, but perhaps also enhances the kinetics since TFSI is a weakly coordinating ion. All the three ionic liquids reached almost complete conversion under 7 minutes.



Figure 6 Effect of the anion on Propargyl Triethylammonium system



Figure 7 Effect of the anion on Propargyl Triethylammonium system.



Figure 8 Effect of the anion on Propargyl Triethylammonium system.

#### Effect of the cation structure

Not all the ionic liquids have the same conversion rates. Methyl imidazolium cation reacts the fastest and triethylammonium reacts the slowest as shown in Figure 9. The difference in the kinetics due to the cation structure can be explained by taking a closer look at the intermediate steps of triazole formation shown in Figure 10<sup>40</sup>. Following Step 2, a carbon radical intermediate is formed. It is hypothesized that Step 2 is the rate limiting step and in the presence of an ionic liquid, this carbon radical

intermediate is stabilized by resonance, lowering the activation energy barrier to proceed to fast Step 3. Therefore, the carbon radical intermediate is better stabilized when the ionic liquid structure itself is more stable. The stability of the molecule is enhanced by the presence of resonance structures. As the degree of unsaturation increases, the number of resonance structures increase, leading to greater delocalization of electrons. This is supported by the kinetics obtained as the degree of unsaturation highest for the methyl imidazolium, followed by methyl pyrrolidine and triethylammonium. Figure 11 shows the trend in kinetics along with the degree of unsaturation (DoU) of each of the ionic monomers used.



Figure 9 Effects of the cation structure on CuAAC reaction



Figure 10 Intermediate steps of CuAAC for the formation of triazole linkage using an ionic liquid. [Cu] here represents ligated Cu(I) ion, responsible for catalyzing this reaction



Figure 11 Trend in the kinetics of the CuAAC reaction as explained by the degree of unsaturation (DoU) of each cationic molecule.

#### **Summary and Conclusion**

The work described here is a preliminary study that demonstrates the kinetics of a photo-initiated CuAAC reaction with an ionic liquid for the first time. Although it is difficult to assert since only three ionic liquid structures were evaluated, an aromatic structure with a weakly coordinated anion is the most favorable if fast reaction kinetics are desirable.

#### Chapter 3

#### THIOL-YNE CLICK REACTION USING IONIC LIQUID MONOMERS

#### **Introduction and Motivation**

As the name suggests, the thiol-yne click reaction is a reaction between an alkyne and two thiols producing two alkyl sulfides. The reaction occurs through anti-Markovnikov addition, where there is no carbon-cation intermediate. Rather it proceeds through a radical pathway. Therefore, thiol-yne reaction is typically facilitated by a radical initiator. Fairbanks et al. recently showed that this click reaction can occur via photoinitiation<sup>5</sup>.

The product and pathway of the thiol-yne click reaction is similar to that of a radical mediated thiol-ene reaction click reaction. In a thiol-ene reaction, thiol a forms thiyl radical upon initiation, which reacts with the alkene to form a carbon-centered radical. This carbon-centred radical abstracts a hydrogen from another thiol, regenerating the thiyl radicals and forming an alkyl sulfide (see Figure 12<sup>41</sup>). In case of the thiol-yne reaction, the thiyl radicals react with the alkyne forming an alkene and an alkyl sulfide. Following that, the alkene undergoes another reaction as if it were a thiol-ene system. Therefore, a single alkyne reacts as if it were two alkenes and produces a product that branches into two alkyl sulfides (see Figure 13<sup>41</sup>). Therefore, a single alkyne in this system is difunctional and a single thiol in this system is monofunctional.



Figure 12 Radical initiated thiol-ene mechanism



Figure 13 Radical initiated thiol-yne mechanism

In this work, the kinetics of the thiol-yne reactions are explored in the context of ion-containing network fabrication. Typically, fabrication of a polymer network involves the introduction of crosslinkers. Since, in a thiol-yne an alkyne reacts with two thiols producing two branched alkyl sulfides, the alkyne itself behaves as a crosslinker. A single alkyne can therefore be used with thiols having a functionality of three or above, without any other crosslinkers to form the network. This work utilizes propargyl ionic liquid monomers with commercially available multifunctional thiols to understand the kinetics of the photoiniated thiol-yne click reaction and is the first-time thiol-yne photochemistry has been used with ionic liquids.

#### **Experimental Methods and Syntheses**

#### Materials

All materials were highly pure ( $\geq 97\%$ ) and were used as-received without further purification. PETMP was obtained from Evans chemicals and ETTMP 1300 were obtained from Bruno Bock. Irgacure 184 was obtained from BASF (Ciba). Methanol was obtained from Fisher Scientific. Imidazolium based and Trialkylated ionic liquids used were synthesized as mentioned in the Chapter 1. Figure 2 shows the ionic liquids that were used and Figure 12 shows the chemicals that were used in this chapter.



ETTMP 1300: Ethoxilated-Trimethylolpropan Tri(3-Mercaptopropionate)

#### Figure 14 Chemicals used during kinetic experiments of thiol-yne reactions

#### Sample Preparation for Spectroscopy Experiments

The experimental conditions were used and monitored as presented by Fairbanks<sup>5</sup>. The reaction system contained 1 alkyne to 2 thiol equivalents of the ionic monomer and thiol monomers respectively. 3 wt.% of Irgacure I-184, the photoinitiator, was used. The sample was injected between KBr salt plates whose distance was controlled by spacers of 0.01 inches' thickness. The KBr plate system was then mounted into a Nicolet iS50 Series Fourier transform infrared (FTIR) spectrometer. After about 30-60 seconds, the sample was irradiated using OmniCure Series 2000 lamp that was filtered using a 365 nm band pass interference filter, equipped with a 200 Watt mercury arc bulb by Lumen Dynamics. Upon irradiation, the decrease in alkyne peak of the ionic liquid and the thiol peak, occurring between 2100-2260 cm<sup>-1</sup> and 2500-2600 cm<sup>-1</sup>, respectively, were monitored by the FTIR. Upon the successful formation of the network, a solid thin film was obtained upon separating the KBr salt plates. Failure to form a network resulted in a viscous liquid.

#### Sample Preparation for Network Casting

Networks were prepared using the same reaction conditions as above. The sample was injected between glass slides treated with Rain-X, separated by spacers of thickness of 0.02 inches. The sample was irradiated using OmniCure Series 2000 lamp that was filtered using a 365 nm band pass interference filter, equipped with a 200 Watt mercury arc bulb by Lumen Dynamics. Upon the successful formation of the network, a solid thin film can be obtained upon separating the glass slides.

# Reactivity and Kinetics of Propargyl Ionic Liquids in Photoinitiated Thiol-yne System

The reaction scheme of the thiol-yne reaction follows two steps (shown in Figure 13<sup>40</sup>). Step one is the conversion of alkyne to alkene sulfide. Step two is the conversion of the alkene sulfide into the alkyl disulfide. Eight combinations of networks: four ionic liquids with two types of thiols, were characterized. The ionic liquids varied by structure of the cations, one aromatic and other non-aromatic, each of which were paired with two types of anions, bromide, which is a strongly coordinating anion and TFSI which is a weakly coordinating anion. The thiols varied in functionality and structure. PETMP is a tetrafunctional thiol and ETTMP 1300 is a trifunctional thiol containing ethylene glycol groups. (See Figure 2 for ionic liquids used and Figure 14 for the thiols used)

#### Kinetics of the Triethylammonium System

The bromide for [PrTEA] was not soluble in either thiol monomer. Therefore, the kinetics of only TFSI form of [PrTEA] was tested with both PETMP and ETTMP 1300.

To ensure 100% conversion of both alkynes and thiols, a reaction sample which used PETMP as the thiol, contained 3 mol of PETMP for every 6 mol of alkyne. Likewise, a reaction sample using ETTMP 1300 as the thiol contained 2 mol of ETTMP for every 6 mol of propargyl ionic liquid (PrIL) as shown by equation [1] and [2] [1] 6 mol PrIL  $\times \frac{1 \text{ alkyne}}{1 \text{ mol PrIL}} \times \frac{2 \text{ thiols}}{1 \text{ alkyne}} \times \frac{1 \text{ mol PETMP}}{4 \text{ thiols}} = 3 \text{ mol PETMP}$ [2] 6 mol PrIL  $\times \frac{1 \text{ alkyne}}{1 \text{ mol PrIL}} \times \frac{2 \text{ thiols}}{1 \text{ alkyne}} \times \frac{1 \text{ mol ETTMP 1300}}{3 \text{ thiols}} = 2 \text{ mol ETTMP 1300}$ 

Upon separating the salt plates of reaction system of [PrTEA][TFSI] with ETTMP 1300 and that of [PrTEA][TFSI] with ETTMP 1300 revealed no solid thin film and rather produced a viscous liquid, which is a preliminary indicator that the reaction did not go to completion. Consequently, it was observed from Figure 15 and 16 that only stoichiometric ratios of 50% and 67% for PETMP and ETTMP 1300, respectively, were converted. However, 100% conversions of alkynes indicate that all the alkynes were converted into alkene sulfides but second step of the thiol-yne mechanism did not proceed. Although further experiments are needed to verify this event, it can be concluded from this data that the second step of the thiol-yne reaction with [PrTEA][TFSI], is rate limiting.



Figure 15 Thiol-yne reaction between [PrTEA][TFSI] and PETMP



Figure 16 Thiol-yne reaction between [PrTEA][TFSI] and ETTMP 1300

#### Kinetics of the Methylimidazolium System

In the propargyl methyl imidazolium systems, both bromide and TFSI form produced thin films upon reaction with ETTMP 1300. From figures 17 through 20 it is evident that the reaction of the TFSI form was twice as fast as that of the bromide form. The reactions with PETMP were sluggish for both forms of ionic liquids, presumably because ETTMP 1300 reacts with the charged monomer better than PETMP. ETTMP 1300 has ethylene glycol groups present which makes the thiol, more polar and help in dissolving the charged monomers.

Reaction of [PrMeIm][TFSI] with PETMP and with ETTMP 1300 was performed with a slight excess of alkyne in the system. Figure 17 and 18 show the first fifteen minutes of the reaction comparing the thiol and the alkyne conversions, respectively. The reaction with PETMP was almost six times slower than that of ETTMP 1300.



Figure 17 Conversion of Thiols in [PrMeIm][TFSI] system



Figure 18 Conversion of Thiols in [PrMeIm][TFSI] system



Figure 19 Conversion of Thiols in [PrMeIm][Br] system



Figure 20 Conversion of Alkynes in [PrMeIm][Br]

### Effect of the anion

It is observed from figures 17, 18, 19 and 20 that the conversion is 5 times faster using the TFSI anion. Furthermore, only the TFSI form of [PrTEA] was able to dissolve and even undergo a reaction as shows in figures 15 and 16. This is an indication that a weakly coordinated anion provides faster kinetics. It has been a common observation through this work. However, the reason for this is unknown and paves way for further experiments.

#### Effect of the cation structure

Figure 21 shows the effect of cation on the kinetics of the thiol-yne system. Only the conversion of alkyne in the TFSI systems using ETTMP 1300 thiol was studied. Lowe et al. had observed that the kinetics were slower when the alkyne attached to an aromatic structure because of steric hindrance<sup>3</sup>. Using ionic alkynes does not seem to change this aspect. From figure 21 it is evident that the aromatic cation of [PrIm] results in a longer time to reach full conversion when compared with the branched alkylated cation of [PrTEA]. However, [PrTEA][TFSI] does not lead to the completion of the reaction with alkynes. Therefore, more experiments need to be conducted to understand the reaction.



Figure 21 Effect of Cation structure on thiol-yne

#### **Network Properties**

As mentioned above, it was possible to fabricate a network for both [PrMeIm][Br] and [PrMeIm][TFSI] as shown in Figure 22.





Figure 22 On the left is a network cast by [PrMeIm][Br] and on the right, is a network cast by [PrMeIm][TFSI]

#### Methods

The glass transition temperature and storage modulus were then characterized of the thin films using TA Instruments dynamic mechanical analyzer (DMA) Q800 in tensile mode. The strain rate was set to 0.1% at a frequency of 1.00 Hz and temperature was ramped from -70°C to 40°C at 3°C/min to measure the storage modulus and  $T_g$  of the materials.

#### <u>Results</u>

Upon formation of the network, some preliminary mechanical properties analysis was performed using a DMA. The storage modulus (E') of the networks was obtained as shown in Figure 23. The tan  $\delta$  of the networks, which is the ratio between

the storage and the loss moduli, is shown in Figure 24. The value at which tan delta peaks is given as the glass transition temperature  $(T_g)$ . The crosslink density of is estimated from the rubbery modulus using the theory of rubber elasticity as given in the equation below<sup>42</sup>.

$$\rho_x = \frac{E}{2(1+v)RT}$$

where v is Poisson's ratio given as  $\frac{1}{2}$  assuming the material is incompressible, R is the gas constant, T is the temperature, and E is the elastic modulus, which is assumed to be interchangeable with E' for this material at 25°C at a strain of 0.1%. Table 2 gives the value of E', T<sub>g</sub> and  $\rho_x$ 



Figure 23 Storage modulus of [PrMeIm] system



Figure 24 Tan delta of the [PrMeIm] system.

Table 1Material properties of Network of Ionic Liquid monomer and ETTMP<br/>1300 thiol at 25°C

| Network                   | E' (MPa) | $T_{g}(^{o}C)$ | $\tan \delta @ T_g$ | $\rho_{x}(M)$ |
|---------------------------|----------|----------------|---------------------|---------------|
| [PrMeIm][TFSI]/ETTMP 1300 | 1.179    | -29.28         | 1.937               | 0.159         |
| [PrMeIm][Br]/ETTMP 1300   | 1.483    | -25.32         | 1.087               | 0.199         |

These values for  $T_g$ , E' and  $\rho_x$  are very small when compared to other thiol-yne networks in literature<sup>5</sup>. The crosslink density of a network of both the networks are

smaller than 1, this can be attributed to the size of the bulky ETTMP 1300 thiol. The crosslink density of [PrMeIm][Br]/ETTMP 1300 being slightly larger than that of [PrMeIm][TFSI]/ETTMP is presumably due to the size of the anion. However, both materials are rubbery. The tan delta curve of [PrMeIm][TFSI]/ETTMP is narrower than [PrMeIm][Br]/ETTMP indicates a more uniform network.

#### **Summary and Conclusion**

It was hypothesized that since this polymerization occurs in a neat environment, i.e., in the absence of solvents or crosslinkers, the kinetics of the network formation would reflect on the thiol-yne reaction kinetics. However, the amount of the variation in the behavior of the networks suggests the need to understand the kinetics of the model charged system. It is evident that the charge automatically changes the kinetics of the reaction. The kinetics of thiol-yne reaction using an ionic liquid remain at large since there are many variables yet to be optimized. However, it is an extremely feasible to cast an ion-containing network using thiol-yne photo-click chemistry and must be explored further.

#### Chapter 4

#### SUMMARY AND OVERARCHING CONCLUSIONS

As per the theme of this thesis, the kinetics of propargyl ionic liquids in photoclick reactions of the CuAAC and thiol-yne chemistry were mapped.

Chapter 2 presented model studies of a monofunctional azide and a monofunctional alkyne and demonstrated that an ionic liquid alkyne with an aromatic cation paired with a weakly coordinating is best suited for applications where fast kinetics are required. It paves the way for the formation of hydroxide exchange membranes using the photo-CuAAC reaction. Recommended future work would involve exploring the kinetics of the reaction by varying the anion to other anions which could not be as weakly coordinating as the TFSI and testing other cations which would contain other heteroatoms. It is also important to test if these trends in kinetics hold true for a polymeric ionic liquid. Literature has also suggested use of Cu-ligands rather than a Cu salt as a source of Cu(II), which could be taken up as a future endeavor as well.

Chapter 3 presented thiol-yne photo-click reactions which had never been performed using ionic-liquids. The results indicated that the experiments are at a very preliminary stage and it is necessary to perform NMR experiments and model studies of monofunctional thiols and alkynes to be able to understand the kinetics of the thiolyne network better. It was observed that the charge plays a significant role in how the reaction behaves and is almost the opposite of how a non-charged alkyne may behave. Therefore, the first step would be to acquire alkynes which have similar structure and test the contrast between the charged and the non-charged version.

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### Appendix

## <sup>1</sup>H NMR ANALYSIS

## Synthesis of 1-Propargyl-3-Methylimidazolium Bromide [PrMeIm][Br]



Figure 25 Synthetic route and <sup>1</sup>H NMR Analysis spectrum confirming the structure of [PrMeIm][Br]



Synthesis of 1-Propargyl-3-Methylimidazolium TFSI [PrMeIm][TFSI]

Figure 26 Synthetic route and <sup>1</sup>H NMR Analysis spectrum confirming the structure of [PrMeIm][TFSI]



Figure 27 Synthetic route and <sup>1</sup>H NMR Analysis spectrum confirming the structure of [PrMePy][Br]



Figure 28 Synthetic route and <sup>1</sup>H NMR Analysis spectrum confirming the structure of [PrMePy][TFSI]



Figure 29 Synthetic route and <sup>1</sup>H NMR Analysis spectrum confirming the structure of [PrTEA][Br]





Figure 30 Synthetic route and <sup>1</sup>H NMR Analysis spectrum confirming the structure of [PrTEA][TFSI]