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A QUARTZ CRYSTAL MICROBALANCE STUDY OF THIOL:ENE POLY(IONIC LIQUID) POLYMERIZATION AND GAS ABSORPTION

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A QUARTZ CRYSTAL MICROBALANCE STUDY OF THIOL:ENE POLY(IONIC LIQUID) POLYMERIZATION AND GAS ABSORPTION

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Master of Science

By

Yueming Wu

June 2017
A QUARTZ CRYSTAL MICROBALANCE STUDY OF THIOL:ENE
POLY(IONIC LIQUID) POLYMERIZATION AND GAS ABSORPTION

DATE APPROVED: _________________

_________________________________
Thesis Advisor

_________________________________
Member, Thesis Committee

_________________________________
Member, Thesis Committee

_________________________________
Member, Thesis Committee

_________________________________
Collegiate Graduate Coordinator

_________________________________
Dean of College

_________________________________
Graduate Studies Coordinator

_________________________________
Provost
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ABSTRACT

The polymerization process of, and gas absorption by, imidazolium-containing thiol:ene poly (ionic liquid)s (PILs), prepared from bisallylimidazolium bis(trifluoromethyl sulfonyl)imide [NTf₂⁻] and pentaerythritoltetrakis(3 mercaptopropionate), was studied. The thiol:ene PILs examined were recently reported by groups at Murray State University. The advantage of thiol:ene PILs over other reported PILs is that thiol:ene polymers are made rapidly by UV exposure and exhibit high mechanical and thermal stability due to high cross-linking. The properties of interest for the thiol:ene PILs were studied using a quartz crystal microbalance (QCM). QCM techniques are based on the piezoelectric effect, where certain crystals (e.g., quartz) will oscillate mechanically (vibrate) under an oscillating electrical potential. The frequency of crystal vibration has been shown to depend on the properties of the environment of the crystal surface, including adsorbed mass, and both the density and viscosity of the surrounding fluid. The frequency of vibration can be measured with such high sensitivity that QCM has picogram detection limits.

There are three major models which were applied to the data obtained in this project: Sauerbrey’s equation, Kanazawa’s equation, and an equation combining Henry’s Law and Sauerbrey’s equation. Sauerbrey’s equation is the simplest model used to evaluate mass changes in thin, rigid films. Many cases do not fulfill the requirement for Sauerbrey to be valid (e.g. thick, viscoelastic films). Therefore, other models have been employed. For example, in liquid contact measurements Kanazawa’s equation is used to measure density and viscosity changes. In some measurements of gas absorption by ionic
liquids, an equation derived from Sauerbrey and Henry’s Law has been used to determine gas solubilities.

The polymerization process for five thiol:ene ratios was studied. Bisallylimidazolium was mixed in various ratios pentaerythritol tetrakis(3-mercaptopropionate) (PTMP), along with ~1 wt% of the photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone (DMPA). The mixture was shaken until homogeneous and spin coated onto a QCM crystal. After the chip was loaded into the QCM, instrument frequency was monitored until an equilibrium response was obtained. The crystal then was exposed to UV light until re-equilibration. From the measured data, both the rate of frequency change/polymerization, and change in \( \rho_L \) (density) and \( \eta_L \) (viscosity) could be obtained.

Gas absorption by PILs was also studied. Monomers were prepared and spin coated onto the crystal as before. Then, before loading into the QCM instrument, photopolymerization was performed. In these experiments, the instrument was placed inside an airtight chamber that could be evacuated and filled with the desired gas. After crystal vibration achieved equilibrium the chamber was subjected to vacuum then filled with either \( \text{CO}_2 \) or \( \text{N}_2 \). Based on change of quartz oscillation frequency (\( \Delta f \)) between vacuum and \( \text{CO}_2/\text{N}_2 \) filled, the various models mentioned earlier could be applied. Then, the relative absorption/solubility of the gases by the various thiol:ene polymers could be determined.
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CHAPTER 1

INTRODUCTION

The first publication describing an ionic liquid (IL) occurred about 100 years ago, in 1914 by Paul Walden, who observed the special physical properties of ethylammonium nitrate (mp 13-14 °C) [1]. An ionic liquid (IL) is defined as a pure ionic substance with a melting point below 100 °C; however, some definitions of ILs state that the melting point should be lower than ambient temperature [2], also known as room temperature ionic liquids (RTILs). Due to the ionic nature of ILs, they have low flammability, low volatility, high thermal stabilities, large conductivities, and strong solvation properties [3]. As a result, ILs have been used in separations, as reaction solvents, and for electrochemical energy storage devices.

Studying the thermal, mechanical, and electrochemical properties of ionic liquids have made them very useful both for industrial and academic applications [4]. Since ILs can be constructed from a variety of both organic and inorganic ions, and the ILs can be custom-tailored, the application of ionic liquids can vary widely [5]. Most ILs are monovalent, and their liquid character is derived from a judicious choice of ionic structures that have weak tendencies to coordinate with oppositely charged ions [4]. Weak intermolecular interactions, low or sterically-hindered charge density, asymmetric chemical structures, and ionic bulk all cause ILs to form liquids at low temperature [5].
In the past decade, polymeric/polymerized ionic liquids or poly(ionic liquids) (PILs), based on at least one IL monomer, have been demonstrated, and have taken an enabling role in some fields of polymer chemistry and material science. PILs are a special kind of polyelectrolytes, which carry an IL species in each of the repeating units. PILs combine the unique physical and chemical properties of IL and enhanced thermomechanical properties of macromolecules. PILs provide novel properties and functions that have huge potential in a multitude of applications such as sensors, absorbents, functional membranes, and porous polymers [5]. Since PILs also have advantageous electrochemical, thermal, and mechanical properties, they have been widely used as catalysts, in chemical sensors, and in other electrochemical devices[6-7].

One of the chemical applications for PILs is the capture of carbon dioxide and its separation from gas mixtures [2]. Carbon dioxide is known as a “greenhouse” gas, causing global warming dramatically in the past few decades. Based on U.S. Environment Protection Agency (EPA) data, in 2014 U.S. carbon dioxide emissions totaled 6870 million metric tons (15.1 trillion pounds) [21]. In 2013, coal and natural power plants accounted for roughly 31% of U.S. CO₂ emissions [6], and vehicles’ exhaust gas also contribute a great amount to CO₂ emission. Recycling or sequestering CO₂ would reduce U.S. emissions by ca. 1800 million metric tons [6]. Based on the U.S. Department of Energy (DOE) data lists for 2013 CO₂ separation cost targets are $40/ton captured by 2020-2025 and $10/ton captured by 2030-2035, with commercial deployments in 2025 and 2035, respectively [7].

Recently, using ILs and RTILs for CO₂ applications is attracting interest due to their unique characteristics such as high CO₂ solubility and permeability [8-10]. According to
many studies, imidazolium-containing ILs and PILs are one of the most popularly investigated targets due to the special properties of the imidazolium-containing material [11].

Many studies have focused on solubility of gases by RTIL membranes. For example, Baltus et al. studied solubility of CO₂ in a series of imidazolium-based RTILs measured with a quartz crystal microbalance (QCM) [20]. The results from their study indicate that CO₂ solubility increases as the length of the alkyl side chain on the imidazolium ring increased, but was lower in ionic liquids with phenyl groups when compared to alkyl groups on the imidazolium ring. Cardiano et al. have demonstrated fast and reversible CO₂ response of vinylimidazolium-based PILs. A series of 1-vinyl-3-hexylimidazolium based PILs were synthesized and CO₂ absorption response has been tested through QCM investigation [22]. The results showed that vinylimidazolium-based PILs have a high potential as CO₂ sensing materials. Those PILs also have selectivity towards CO₂. Mineo et al. research group also investigated tetraalkylammonium based IL CO₂ response [23]. According to their results, the CO₂ sensing behaviors of the PILs were very remarkable with extremely rapid and completely reversible response without any memory-effect. It has also been found that ammonium-based PILs have better CO₂ sorption capacity than imidazolium-based PILs.

Other studies have also focused on permeation of gases across poly(RTIL) membranes. For example, Tome et al. investigated difunctionalized ILs, containing a triethylene glycol monomethyl ether chain and a nitrile group on a pyrrolidinium or imidazolium unit. These membranes exhibited CO₂/CH₄ and CO₂/N₂ permselectivities (the rate of CO₂
transport normalized to the material thickness) of up to 30, which are higher than monofunctionalized ILs [24-25].

Carlisle, et al. synthesized and evaluated six vinyl-based poly(RTIL) membrane gels for their CO$_2$/N$_2$ and CO$_2$/CH$_4$ separation performance. Their primary focus was on RTIL design, specifically maximizing CO$_2$ selectivity by changing RTIL backbone [e.g., poly(ethylene), poly(styrene), and poly(acrylate)] and functional cationic substituent [e.g., alkyl, fluoroalkyl, oligo(ethylene glycol), and disiloxane] [10]. The results showed that increasing free IL content led to improvements in gas transport properties compared to neat PIL materials. A number of other permeation studies have been performed using imidazolium composites, iongels, and with solid additions, as well [6].

In this study, a series of thiol-ene PILs were prepared by combining bisallylimidazolium bis(trifluoromethylsulfonyl) imide [NTf$_2^-$] with pentaerythritol tetrakis(3 mercaptopropionate) (PTMP) through a photopolymerization method. The structures of these compounds are shown in Figure 1.

**Figure 1:** Chemical Structure of (a) Bisallylimidazolium [NTf$_2^-$] (b) Pentaerythritol tetrakis(3-mercaptopropionate) (PTMP)
Different molar ratios of PTMP ("thiol") to IL ("ene") were studied in order to determine the impact of IL content and cross-linking on observed properties. The specific thiol:ene ratios studied in this research were 1.0:1.0, 1.0:1.5, 1.0:2.0, 1.0:2.5, and 1:3.0. Polymerization of these thiol:ene mixtures resulted in homogeneous crosslinked networks. Thermal, mechanical and conductive properties of these thiol:ene PILs have been previously published [12]. These polymers are of interest in CO2 applications because they contain the imidazolium cation, have demonstrated great versatility in terms of synthesis, and are easy to prepare rapidly [12, 13-16].

Membrane separation technology is particularly attractive for CO2 applications because of low energy operating cost, smaller equipment required, and relatively facile retrofit integration with existing power plant design [10]. As noted previously, the critical properties in developing an ionic liquid membrane for CO2 separation are CO2 absorption and permeation selectivity. Membranes separate gas mixtures by sieving and/or sorption mechanisms, depending on whether the membrane is porous or non-porous, which allow for one or more components to pass through the membrane [5]. For the work described herein, the primary property measured was CO2 absorption using a QCM.

**Quartz Crystal Microbalance**

In order to monitor the change on the ILs and PILs during polymerization and gas absorption process, a quartz crystal microbalance (QCM) system was used. QCM techniques are based on the piezoelectric effect, where certain crystals (e.g., quartz) will oscillate mechanically (vibrate) under an oscillating electrical potential [17]. For example, when a potential is applied to the piezoelectric material, it will cause deformation of the material via elongation and compression. When an alternating potential is applied to the
material, then, the deformation also will alternate and lead to a phonon vibration. The frequency of crystal vibration has been shown to depend on the environment properties of the crystal surface, including adsorbed mass, and both density and viscosity of the surrounding fluid. The frequency of crystal vibration can be measured with extremely high sensitivity; for example, when using frequency change to measure mass on a crystal surface QCM has picogram detection limits. The quartz crystal shown in Figure 2. The exposed contact surface of the crystal is coated with gold to provide adhesive capability for modification.

![Figure 2: Picture of Quartz Crystal Chip: (a) Contact Surface and (b) Connection Surface](image)

The system is open to the environment, therefore it can measure the change of contact materials such as gas or liquid. The connection surface connects to the QCM electrode, where a potential is applied. The “C” shape area on the connection surface is also coated with gold to contact with the QCM electrodes. More details of the QCM system operation will be discussed in Chapter 2.
Models for QCM Data

There are three major models, which were applied to the data obtained in this project, Sauerbrey’s equation, Kanazawa’s equation, and an equation combining Henry’s Law and Sauerbrey’s equation. The simplest model describing the relationship between oscillation frequency and mass change at the crystal surface is the Sauerbrey equation:

$$\Delta f = -C_f \times \Delta m \quad (1)$$

where $\Delta f$ is frequency change in Hz, $\Delta m$ is change in mass per unit area ($\mu g/cm^2$), and $C_f$ is a crystal dependent sensitivity factor for quartz (56.6 Hz $\mu g^{-1} cm^2$ at room temperature).

In general, Sauerbrey’s sensitivity factor $C_f$ is a function of crystal properties:

$$C_f = \frac{2n f_0^2}{(\rho_q \mu_q)^{1/2}} \quad (2)$$

where $n$ is the number of the harmonic at which the crystal is driven ($n=1$ in this situation), $f_0$ is the resonant frequency of the fundamental mode of the crystal in Hz, $\rho_q$ is density of quartz (2.648 g cm$^{-3}$), and $\mu_q$ is the shear modulus of quartz ($2.947 \times 10^{11}$ g cm$^{-1}s^{-2}$). The Sauerbrey equation is applicable to uniform, rigid, thin-film deposits originating from a low pressure gas environment [19].

Many cases do not fulfill the requirement for Sauerbrey to be valid (e.g. thick, viscoelastic films and liquid immersions). Therefore, other models have been developed.

For example, in liquid contact measurements, Kanazawa’s equation is used:

$$\Delta f = -f_u^3 \left( \frac{\rho_L \eta_L}{\pi \rho_q \mu_q} \right)^{1/2} \quad (3)$$
where $f_u$ is the frequency of oscillation of an unloaded crystal, $\rho_q$ is the density of quartz, $\mu_q$ is the shear modulus of quartz, $\rho_L$ is the density of the liquid in contact with the electrode, and $\eta_L$ is the viscosity of the liquid in contact with the electrode [19].

In some measurements of gas absorption by neat, non-polymerized ILs [20], an equation derived from Sauerbrey and Henry’s Law has been used:

$$X_{CO_2} = \frac{(\Delta f_{CO_2} - \Delta f_{cc})/ (44 \text{ g/mol})}{\frac{\Delta f_{IL}}{MW_{IL}} + \left(\frac{\Delta f_{CO_2} - \Delta f_{cc}}{44 \text{ g/mol}}\right)}$$

(4)

where $X_{CO_2}$ is the mole fraction of CO$_2$ in the IL. The difference in frequency between the IL coated quartz and the frequency of the clean quartz is $\Delta f_{IL}$, both measured in a dry nitrogen environment. The difference between the frequency of the clean quartz in a dry nitrogen environment and the frequency of the clean quartz exposed to CO$_2$ is $\Delta f_{cc}$. The difference between the frequency of the IL coated quartz in a dry nitrogen environment and the frequency of the IL coated quartz exposed to CO$_2$ is $\Delta f_{CO_2}$. The solubility of CO$_2$ in the IL can be characterized using a Henry’s law constant

$$H_{CO_2} = \frac{y_{CO_2}}{X_{CO_2}}$$

(5)

where $y_{CO_2}$ is the CO$_2$ partial pressure, and $X_{CO_2}$ is the mole fraction of CO$_2$ in the IL.
CHAPTER 2

EXPERIMENTAL

Reagents
All chemicals used in this research project were purchased directly from Sigma-Aldrich and Acros, including 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, 99%), pentaerythritol tetrakis(3-mercaptopropionate) (PTMP, >95%), sulfuric acid (98%), and hydrogen peroxide (30%). The IL monomer 1,3-diallylimidazolium bis(trifluoromethylsulfonyl) imide (NTf₂⁻) were obtained from the research group of Dr. Kevin Miller at Murray State University. The preparation of 1,3-diallylimidazolium bis(trifluoromethylsulfonyl) imide has been previously reported [3]. All water used was 18 MΩ-cm ultrapure water from an ELGA Purelab Ultrafiltration system.

Preparation and Spin Coating of Pre-Polymer
The UV polymerization of different thiol:ene molar ratio polymers (1:1,1:1.5,1:2,1:2.5,1:3) was investigated. For example, the 1:2 thiol:ene molar ratio monomer solution was prepared by mixing 1.147 g (2.67×10⁻³ mol) of bisallylimidazolium [NTf₂] with 0.653 g (1.34×10⁻³ mol) of PTMP and 10 mg of the photoinitiator DMPA. Then, the mixture was heated gently with a heat gun and shaken by hand until homogeneous; the pre-polymer was kept in dark until use to prevent stray light polymerization.
In order to coat a thin layer of IL pre-polymer on the QCM chip, a spin coater was employed; more specifically, a single wafer spin processor system (Laurell WS-400BZ-6NPP/LITE) was used. Spin coating was used because it is the most common and reliable way to apply uniform thin films to a substrate [18].

The substrate was held on a spinner chuck by vacuum, rotated at a high angular frequency (RPM) in order to spread the coated material by centrifugal force as shown Figure 3.

Figure 3: Spin Coating Process
When rotating the substrate at high speed, centripetal force combined with the surface tension of the coating material pulled the material into an even covering. The thickness of the coating material can be estimated by Equation 6 [26].

\[ t \propto \frac{K \times \eta^\alpha}{\omega^\beta} \]  

where \( t \) is the thickness of the coating material, \( K \) is an overall calibration constant, \( \eta \) is the viscosity of the IL, \( \omega \) is angular velocity, and \( \alpha, \beta \) are empirically-determined scaling factors.

A clean crystal chip was placed on the center of the spinner head and vacuum was applied to hold the chip in place. The spin coater used was programmable across all three stages used for spin coating: acceleration, maximum angular velocity, and deceleration. In order to have a uniform layer on the crystal chip surface, the acceleration and deceleration cannot be very fast. Therefore, in this work the first stage accelerated from 0 RPM to 3500 RPM over 15 seconds, then the spin rate was held at 3500 RPM for 90 seconds, and then deceleration occurred from 3500 RPM to 0 RPM over 15 seconds. Details of the programming process can be found in the manufacturer’s manual [18]. For each experiment, 100 µL of pre-polymer was dispensed onto the gold coated center of the chip and some pre-polymer spreading occurred on the surface. Then, spin coating was initiated as described above.
Analysis of Polymerization by QCM

Once coating was complete, the chip was loaded into the QCM holder shown in Figure 4 [19]. The details of steps to load the chip into the QCM hold can be found in manufacturer’s manual [19]. During all transfer and assembly processes, the coated chip was handled using soft tip forceps.

![Figure 4: Crystal Holder Components and Accessories](image)

As noted before, all pre-polymers were made fresh before each experiment to minimize self polymerization and exposure to stray light. After the pre-polymer coated chip was loaded into the QCM instrument, the frequency was monitored until an equilibrium response was obtained. This step was performed in a dark chamber and darkened room to prevent stray light polymerization. During the QCM pre-equilibration period, the UV lamp (UVP Blak-Ray B-100AP) was warmed up in a closed chamber. Then, the UV lamp was placed above the crystal, and the crystal was exposed to UV for 7-8 minutes. Then, the UV lamp was removed, and data collection continued for a few more minutes.
An example of data collected is shown in Figure 5. From the measured data, both the rate of frequency change/polymerization and change in IL density ($\rho_L$), and IL viscosity ($\eta_L$) were determined.

**Figure 5:** Example Frequencygram Taken During Thiol:ene Photopolymerization

In order to make accurate measurements, the QCM system needed to be “NULLED” prior to every experiment using the knob located on the QCM200 controller front panel to adjust until only the middle two lights are on. Then the switch is flipped to the “hold” position to hold the vibration frequency. More details of this capacitance cancellation can be found on page 19 of the QCM Manual [19]. Another important detail is that the UV lamp was turned on and warmed 10 minutes prior to use in order to provide consistent results [27].
After each experiment, the polymerized chip was cleaned with “Piranha” solution (3 parts concentrated sulfuric acid (trace metal grade) and 1 part 30% hydrogen peroxide) then rinsed with DI water three times before the next experiment [19]. The “Piranha” solution removed the polymerized IL coated on the surface of the crystal chip as well as any organic residue left on the chip. When handling the “Piranha” solution, extreme caution was required, as well as when mixing concentrated sulfuric acid and hydrogen peroxide since it releases significant heat.

**Analysis of Gas Solubility by QCM**

An electronic washdown enclosure was purchased from McMaster-Carr Supply Company (part number 1037N6), and modified as shown in Figure 6. The approximate internal dimensions were 8.5” × 4” × 1.6”. Two holes were drilled into the chamber, one to connect a two-way valve and another for a BNC feedthrough. All of the connection joints were sealed with rubber o-rings and Torr-Seal (epoxy resin material) to prevent gas leaks. The BNC connector directly attached the external QCM25 oscillator to the crystal holder inside the chamber. The entire apparatus was placed on an vibration isolation plate since the QCM is very sensitive to vibrations in the environment.
Gas absorption by PILs of different thiol:ene ratios was studied. The two types of gas used in these experiments were carbon dioxide and nitrogen, both purchased from Airgas Company. Before each experiment started, the delivery pressure for both gases was adjusted close to atmospheric pressure via a pressure gauge (Ace Glass Digital Strain Vacuum Gauge #14034-38). Due to the inaccuracy of the gas regulators used, the delivery pressure varied by a small amount (~10 Torr) for each test.

Next, monomer solutions were prepared and spin coated onto the crystal as mentioned previously. Before loading the spin coated crystal into the QCM instrument, photopolymerization was performed. Then, the instrument was placed inside the designed chamber and the chamber was sealed with a gasket and screws. Data was recorded until crystal vibration achieved equilibrium, then a vacuum was applied to the chamber. The
chamber was maintained under vacuum until vibration again reached equilibrium, and then the chamber was filled with the desired gas. Subsequently, data was recorded until re-equilibration was obtained. An example of the results of these experiments is shown in Figure 7. After the experiment, the coated chip was cleaned with “Piranha” solution, and washed with DI water three times, and stored in a vacuum desiccator.

**Figure 7**: Example 1:2 Ratio IL CO₂ Absorption Data

Based on $\Delta f$ between vacuum and CO₂/N₂ filled, the various models mentioned earlier were applied. Then, the relative absorption/solubility of the gases by the various thiol:ene polymers were determined.
CHAPTER 3

EVALUATION OF POLYMERIZATION AND GAS ABSORPTION

Observation of Polymerization Process
The polymerization process of four thiol:ene ratios (1.0:1.5, 1.0:2.0, 1.0:2.5, and 1.0:3.0) was studied using QCM. Crude kinetic properties of different ratios of IL were evaluated. First, a blank test was conducted to show how much the UV lamp impacts a bare chip as well as the rest of the QCM system during an experiment. According to the example data shown in Figure 8, the impact of the UV lamp on a blank chip is very small (i.e., ~ ± 40 Hz) and is negligible compared to the frequency change observed with a loaded chip (see below). Since the UV light acts as a heating source, when the lamp is turn on/off the temperature around the chip changes slightly. In addition, some mechanical vibration from initiating/removing the lamp may contribute to the observed result.

Figure 8. Blank Frequencygram Following Photopolymerization Procedures
After the lamp blank, the polymerization process of a loaded or pre-polymer chip was studied. Figure 9 shows an example of the data collected during the photopolymerization of a 1:2 thiol:ene sample.

Figure 9. Frequencygram Collected During Photopolymerization of 1:2 Ratio

The large initial drop of frequency over a short period of time occurs due to the viscosity and density changes of the PIL according to Kanazawa. After the UV light is removed only a very small change was observed on the frequencygram due to the impact of temperature on the viscosity and the density of the PIL, indicating that polymerization was complete. Figure 10 shows the overlay of frequencygrams for all four thiol:ene ratios, while Figure 11 focuses on the frequency drop occurring when photopolymerization is initiated. Using the data collected, Kanazawa’s model, introduced previously, was applied under the assumption that the material is viscoelastic. The frequencygrams
plotted were the average of two or more independent experiments. More details and calculations will be discussed in the next section.

**Figure 10.** Overlaid Polymerization Frequencygrams; • - 1.0:1.5 Thiol:ene, • - 1.0:2.0 Thiol:ene, • - 1.0:2.5 Thiol:ene, • - 1.0:3.0 Thiol:ene

**Figure 11.** Frequencygrams During the First 65 Seconds of Polymerization; • - 1.0:1.5 Thiol:ene, • - 1.0:2.0 Thiol:ene, • - 1.0:2.5 Thiol:ene, • - 1.0:3.0 Thiol:ene
QCM not only measures the frequency change of the chip vibration but also measures the resistance changes at the chip surface as shown in Figure 12. This resistance comes from circuit modeling of the QCM and is considered a motional resistance of the crystal at series resonance [19]. The resistance drop will be discussed in the next section.

![Figure 12. Average Chip Resistance Change Occurring During Photopolymerization of 1.0:2.0 Thiol:ene](image)

**Models for Polymerization**

If the IL film coated on the chip were sufficiently thick that the film behaved as a viscous liquid, Kanazawa’s equation could be applied. Furthermore, since there was no substantial change in mass during this study, and since the IL density and viscosity changes during the polymerization process, Kanazawa’s equation (Eqn. 3) could be used to predict a frequency shift as the density and the viscosity of IL changes (Eqn. 3). There are two other kinetically-related parameters that describe the polymerization process: the slope of the initial polymerization curve and $t_{95\%}$ (time to reach 95% complete
polymerization; the average frequency of the low plateau on the frequencygram). These two parameters should be proportional to the reaction rate, but do not provide an exact description of the rate law. In order to determine the rate constant for the polymerization process, further investigation is needed. For each situation, all the Kanazawa parameters are constant except the density and the viscosity of the IL or PIL; therefore the density × viscosity \((\rho \times \eta)\) for each can be calculated by rewriting Kanazawa’s equation, as follows:

\[
\Delta f = -C(\rho \times \eta)^{\frac{1}{2}}
\]  

(6)

where \(C (-7173.13 \text{ cm}^2\text{g}^{-1}\text{s}^\frac{1}{2})\) represents all of the constants in the original Kanazawa’s equation, \(\rho\) is the density of the liquid in contact with the electrode and \(\eta\) is the viscosity of the liquid in contact with the electrode. The results for applying Kanazawa’s equation to the collected thiol:ene data are shown in Tables 1 and 2.

<table>
<thead>
<tr>
<th>Thiol:ene Ratios</th>
<th>Change of Frequency (Hz)</th>
<th>(\Delta(\rho \times \eta) \text{ (g}^2\text{cm}^{-4}\text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:1.5</td>
<td>-9530</td>
<td>1.765</td>
</tr>
<tr>
<td>1.0:2.0</td>
<td>-14466</td>
<td>4.066</td>
</tr>
<tr>
<td>1.0:2.5</td>
<td>-8775</td>
<td>1.496</td>
</tr>
<tr>
<td>1.0:3.0</td>
<td>-8321</td>
<td>1.345</td>
</tr>
</tbody>
</table>

Table 1. Kanazawa’s Model For Pre-polymer with Various Monomer Ratios
Table 2. Kanazawa’s Model Comparing IL and PIL

<table>
<thead>
<tr>
<th>Thiol:ene Ratios</th>
<th>Change of Frequency (Hz)</th>
<th>PIL (ρ×η) (g²cm⁻⁴s⁻¹)</th>
<th>Δ(ρ×η) (g²cm⁻⁴s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1.5</td>
<td>-14575</td>
<td>4.128</td>
<td>2.363</td>
</tr>
<tr>
<td>1:2</td>
<td>-18553</td>
<td>6.689</td>
<td>2.622</td>
</tr>
<tr>
<td>1:2.5</td>
<td>-12760</td>
<td>3.164</td>
<td>1.667</td>
</tr>
<tr>
<td>1:3</td>
<td>-12066</td>
<td>2.829</td>
<td>1.483</td>
</tr>
</tbody>
</table>

Based on the results shown in the tables 1 and 2, all Δ(ρ×η) values, defined as the ρ×η for PIL minus ρ×η for IL, both relative to a bare chip, increase upon polymerization. This observation was expected since the PILs should have higher density and viscosity due to bond formation during polymerization. The order of the Δ(ρ×η) difference between IL and PIL is 1.0:2.0 > 1.0:1.5 > 1.0:2.5 > 1.0:3.0; this order follows the same trend as a study reported earlier for apparent crosslink density (νc) and the storage shear modulus (E’) [12]. Again, this observation was expected since νc increases as a more dense and viscous network is obtained. In the future, if the density and viscosity of IL pre-polymer and the density of PIL are measured separately, the viscosity of the PIL should be obtainable from QCM data based on Eqn. 3. Tables 3 and 4 show the t₉₅% and slopes of the polymerization curves, which as noted before should correlate to reaction rate.
Table 3. $t_{95\%}$ for Polymerization Curves

<table>
<thead>
<tr>
<th>Thiol:ene Ratios</th>
<th>$t_{95%}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1.5</td>
<td>34.17</td>
</tr>
<tr>
<td>1:2</td>
<td>41.65</td>
</tr>
<tr>
<td>1:2.5</td>
<td>41.98</td>
</tr>
<tr>
<td>1:3</td>
<td>42.23</td>
</tr>
</tbody>
</table>

Table 4. Slope of “Step” Region of Polymerization Curves

<table>
<thead>
<tr>
<th>Thiol:ene Ratios</th>
<th>Slope (Hz/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1.5</td>
<td>-1230.50</td>
</tr>
<tr>
<td>1:2</td>
<td>-509.31</td>
</tr>
<tr>
<td>1:2.5</td>
<td>-380.06</td>
</tr>
<tr>
<td>1:3</td>
<td>-357.92</td>
</tr>
</tbody>
</table>

From Tables 3 and 4, a pattern is observed; that $t_{95\%}$ increases and slope decreases when “ene” ratio is increased. The “thiol” is a tetrafunctional material, and “ene” is a bifunctional material. Therefore the functional group ratio between “thiol” and “ene” of 1:2 is the stoichiometric ratio. Any ratio less than 1:2 has excess “thiol” and any ratio more than 1:2 has excess “ene”. For the 1:1.5 ratio, $t_{95\%}$ is much smaller and slope is
much greater than others, which points to “thiol” dominating the reaction rate. For the 1.0:2.0, 1.0:2.5, and 1.0:3.0 ratios, $t_{95\%}$ increases and slope decreases, although slowly. To obtain a truer sense of relative thiol vs. ene importance, various other functionalities (mono, bi, tri) should be tested at a fixed ratio.

**Observation of Gas Absorption**

The gas absorption for three thiol:ene PILs (1.0:2.0, 1.0:2.5, 1.0:3.0) was also studied. As mentioned in previous sections, the polymerizations of monomer solutions were performed before mounting the quartz crystal in the QCM, and then gas absorption was investigated. The gas absorbed by the PILs can be calculated by using all three models introduced before. First, a blank test was conducted. The purpose of doing a blank test was to show how much the $N_2$ and $CO_2$ impacted a bare chip. Figure 13 shows the $N_2$ blank test, and Figure 14 shows the $CO_2$ blank test.

![Figure 13. Frequencygram Example Taken During $N_2$ Blank Test](image-url)
Based on these blank tests, both N₂ and CO₂ had a very small impact on the bare chip due possibly to a buoyancy or pressure effect. However, the result was very insignificant compared to the loaded PILs test, introduced next. After the blank, the gas absorption of PIL loaded chips was studied. Figure 15 shows an example of a frequencygram for a gas absorption experiment.
In Figure 15, recording data was initiated at time 0, and then vacuum was applied to the system. A drop of frequency was observed on the frequencygram, followed by frequency slowly reaching a new equilibrium. The reason a frequency drop was observed before coming back to a higher frequency equilibrium is likely due to an abrupt change in the chip environment occurring, as well as possible mechanical effects. After the chip became stable in the vacuum environment, the vibration frequency of the chip also equilibrated. Then, gas was introduced to the system with another big drop of frequency observed; again the vibration frequency stabilized at a new equilibrium. Since multiple ratios of thiol:ene PILs were studied for both N₂ and CO₂, in Figure 16 and Figure 17 shows the overlaid frequencygrams.

**Figure 16:** N₂ Gas Absorption Frequencygrams; • - 1.0:2.0 Thiol:ene, • - 1.0:2.5 Thiol:ene, • - 1.0:3.0 Thiol:ene
The same patterns were observed for both N$_2$ and CO$_2$ absorption frequencygrams. The frequencygrams plotted were the average of two or more independent experiments. Using the data obtained, Sauerbrey’s model, Kanazawa’s model and Henry’s model were applied.

**Models for Gas Absorption**

Sauerbrey’s model (Eqn. 1) predicts a linear response between mass uptake and frequency shift of a rigid film [20]. When a vacuum was applied, the equilibrated frequency of the resonating chip increased because of the decreased mass of absorbed atmosphere gas in the PIL chip coating. When gases were introduced to the system, the frequency of the resonating chip decreased, due to increased mass uptake. Therefore, $\Delta f$ used for Sauerbrey’s equation is the frequency difference between equilibrated frequency under vacuum and equilibrated frequency in a gas environment. The results of the Sauerbrey calculations are shown in Table 5.
**Table 5: Gas Uptake from Sauerbrey’s Model**

<table>
<thead>
<tr>
<th>Thiol:ene Ratios</th>
<th>$\Delta f$ in N$_2$ (Hz)</th>
<th>$\Delta m$ in N$_2$ (µg)</th>
<th>$\Delta f$ in CO$_2$ (Hz)</th>
<th>$\Delta m$ in CO$_2$ (µg)</th>
<th>CO$_2$/N$_2$ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:2.0</td>
<td>186.4</td>
<td>3.29</td>
<td>210.1</td>
<td>3.71</td>
<td>1.13</td>
</tr>
<tr>
<td>1.0:2.5</td>
<td>166.6</td>
<td>2.94</td>
<td>188.5</td>
<td>3.33</td>
<td>1.13</td>
</tr>
<tr>
<td>1.0:3.0</td>
<td>127.3</td>
<td>2.25</td>
<td>156.4</td>
<td>2.76</td>
<td>1.22</td>
</tr>
</tbody>
</table>

From the results shown above, there is a clear frequency difference between N$_2$ environment and CO$_2$ environment for all PILs. Based on Sauerbrey’s equation $\Delta m$ (mass change) on the membrane can be calculated. For all ratios, $\Delta f$ in N$_2$ is smaller than $\Delta f$ in CO$_2$, accordingly $\Delta m$ for N$_2$ is less than $\Delta m$ for CO$_2$. This pattern indicates that the PIL membranes have higher selectivity to CO$_2$ than N$_2$. Upon calculating a selectivity factor of $\Delta m_{CO_2}/\Delta m_{N_2}$ it can be seen that the 1.0:3.0 thio:lene PIL has the highest preference for CO$_2$ vs. N$_2$ among the PILs tested. Furthermore, if the mass uptake is scaled to the mass of PIL membrane used, the differences in CO$_2$ vs. N$_2$ mass uptake are 237.9, 487.8, and 571.0 µg/g membrane for 1.0:2.0, 1.0:2.5, and 1.0:3.0, respectively. These results indicated the 1.0:3.0 thiol:ene membrane to have the best combination of CO$_2$ solubility and selectivity. From Prakash’s study, it has been shown that CO$_2$ has quadrupolar and induced dipolar interactions that allows interaction with imidazole rings; such interactions are absent with N$_2$ [28].
Table 6: Gas Uptake from Kanazawa’s Model

<table>
<thead>
<tr>
<th>Thiol:ene Ratios</th>
<th>$\Delta (\rho \times \eta)$ (g$^2$cm$^{-4}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:2.0</td>
<td>$3.77 \times 10^{-3}$</td>
</tr>
<tr>
<td>1.0:2.5</td>
<td>$7.32 \times 10^{-3}$</td>
</tr>
<tr>
<td>1.0:3.0</td>
<td>$9.20 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

If the PIL membranes are considered as high viscosity liquids and sufficiently thin, Kanazawa’s model could be applied to these data. Results of such calculation are shown is Table 6. In the table, $\Delta (\rho \times \eta)$ is the difference between PIL $\rho \times \eta$ in the presence of CO$_2$ and in the presence of N$_2$. Based on the results, all three ratios absorb more CO$_2$ than N$_2$. Some reports show the viscosity of ILs decreases as CO$_2$ absorbs into the liquid because the CO$_2$ can disrupt the ionic bonds between cation and anion [29-30]. In this case, it appears the density and/or the viscosity of the PILs increases with CO$_2$ absorption, most likely due to increased intermolecular forces between CO$_2$ and imidazolium.

The two models discussed above both show that PILs have a higher selectivity for CO$_2$ than N$_2$, but there is a very critical experimental factor those two models do not include – pressure. The solubility of CO$_2$ in the PILs can be characterized using a Henry’s Law constant (Eqn. 5), which factors in pressure. Results for these calculations are shown in Table 7. It is helpful to remember that increased CO$_2$ solubility is indicated by lower $H_{CO2}$ values. It is only valid for small $\chi_{CO2}$ (i.e. 1 atm or below) [20].


According to the results, CO$_2$ solubility increases as ene/IL ratio increases, as well. From eqn. 5, this model evaluates CO$_2$ solubility relative to a dry N$_2$ environment. Therefore, Henry’s Law constant is only calculated for CO$_2$. Especially when the ene ratio is greater than stoichiometric ratio, which means there is excess “ene” in PILs, the excess “ene” material increases the solubility of CO$_2$. One possible assumption based on the result is that excess “ene” material weakens the polymer chain packing during polymerization, and increase free volume between polymer chains. The larger cavities may allow more CO$_2$ to permeate into the membrane. At the same time, having a greater amount of imidazolium in the PIL increases the number of sites where CO$_2$ can bind via intermolecular forces.

**Table 7. Henry’s Law Model Results**

<table>
<thead>
<tr>
<th>Thiol:ene Ratios</th>
<th>CO$_2$ Pressure (bar)</th>
<th>$\chi_{CO2}$</th>
<th>H$_{CO2}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:2.0</td>
<td>1.0053</td>
<td>0.00278</td>
<td>361.620</td>
</tr>
<tr>
<td>1.0:2.5</td>
<td>1.0196</td>
<td>0.01456</td>
<td>70.027</td>
</tr>
<tr>
<td>1.0:3.0</td>
<td>1.0184</td>
<td>0.01693</td>
<td>60.153</td>
</tr>
</tbody>
</table>
CHAPTER 4

CONCLUSION AND FUTURE PROSPECTS

The thesis is focused on the polymerization process and gas absorption by thiol-ene PILs. Design and integration of a polymerization apparatus and gas chamber system was completed successfully. Both polymerization and gas absorption were studied using a QCM system and the data was evaluated by three different QCM models, Sauerbrey’s model, Kanazawa’s model and Henry’s Law.

First, the study of the polymerization was completed successfully by monitoring the frequency change before, during, and after application of UV light. Based on the data collected, Kanazawa’s model demonstrated a pattern for change in density × viscosity consistent with earlier reports of modulus and crosslinking data. In addition, the slope of the polymerization curves and t_{95%} were also determined. Both results illustrated that higher thiol ratios reacted more rapidly than lower thiol ratios, highlighting the potential impact of PTMP on controlling reaction rate.

Second, gas absorption by the PILs was studied by comparing a loaded chip at equilibrium frequency in a vacuum environment in a N\textsubscript{2} or CO\textsubscript{2} environment. The basic Sauerbrey’s model, Kanazawa’s model, and Henry’s law-based model were applied to these data. All three models indicated that the PIL membranes absorbed more CO\textsubscript{2} than N\textsubscript{2}, with higher ene ratios having better selectivity and mass uptake, overall. The
imidazolium-based PILs have the tendency to interact with CO₂ better than N₂ because of CO₂ having quadrupolar and induced dipolar interactions, which N₂ does not form.

In the future, the investigation of polymerization process needs to be repeated in an enhanced way. By measuring the density and the viscosity of the IL pre-polymer mixture, and the density of resulting PIL in separate experiments, the viscosity of the PIL could be determined from QCM data according to eqn 3. By measuring the viscosity of the IL pre-polymer mixture, the spin coating process can be adjusted to better ensure uniform PIL layers across ratios. Finally, in order to have a clearer picture of the kinetics/rate law results, the same PIL ratio can be prepared and studied using different combinations of thiol (mono-, bi-, tri-, tetrafunctional) and ene functionality (mono-, bifunctional).

In gas absorption measurements, there are number of aspects that need to be improved, modified or repeated. First, the sealing of the gas chamber and gas delivery system needs to be improved (i.e., a new chamber needs to be designed and built). Second, dosed additions of CO₂ needs to be studied, both by gradually increasing CO₂ percentage in a mixed N₂/CO₂ system, and by examining various pure CO₂ pressures (0.1 atm, 0.2 atm, etc.). Third, the PILs themselves could be modified by changing the carbon chain length in the imidazolium monomer or by combining different anions with the imidazolium cation.
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