ALTERNATIVE SOLVENTS FOR CATALYSIS AND ORGANIC REACTIONS

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The Academic Faculty

By

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ALTERNATIVE SOLVENTS FOR CATALYSIS AND ORGANIC REACTIONS

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For my Mom and Dad-
Without them I would have never made it through
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<td>ACN</td>
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</tr>
<tr>
<td>AgTfa</td>
<td>Silver trifluoroacetate</td>
</tr>
<tr>
<td>amu</td>
<td>Atomic mass units</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
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<tr>
<td>[bmim][PF₆]</td>
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</tr>
<tr>
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<td>Benzylchloride</td>
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<tr>
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SUMMARY

The field of separations has long been explored by chemical engineers. Many researchers are looking to improve the efficiency of traditional separations, such as distillations. One way to optimize separations is through solvent manipulation. Ideally, a chemical process would be able to run in the absence of any solvents. In fact, many reactions have been carried out under solvent-free conditions. However, this option is not usually feasible when designing reactions and separations. The second best alternative is through a systems approach or using a single solvent for both the reaction and separation unit operations. At first consideration this seems like an impossible task as a solvent dissolves molecules and will therefore not be efficient for removing them. However; through molecular design, smart solvents can be created. Smart solvents undergo step or gradual changes in properties when activated by a stimulus. These property changes enable unique chemistry and separations.

This thesis explores the application of two different types of smart solvents: switchable and tunable solvents. First we show that a neutral liquid can react with carbon dioxide and be switched into an ionic liquid which can then be thermally reversed back to its molecular form. Each form that the solvent takes has unique properties that can be structurally tuned to span a large range. We also look at a tunable solvent system that is initially homogeneous, but induced to a heterogeneous system through carbon dioxide pressurization. Finally, we look at the advantage of using carbon dioxide as a co-solvent that is easily removed post-reaction for the grafting of functional molecules onto polyolefin backbones.
CHAPTER 1. INTRODUCTION

With a growth in environmental consciousness, there has been a plethora of research dedicated to the field of sustainable technology and engineering. One aspect of this field involves the creation of novel benign solvents [1]. These solvents alleviate several problems associated with the use of traditional volatile organic compounds, while generating new technologies along the way. Alternative solvents can also solve some of the problems associated with traditional separation techniques, such as high energy requirements and large waste generation. Examples of alternative solvents that have gained academic and industrial attention include: ionic liquids, water (including near-critical water), supercritical fluids, gas-expanded liquids, liquid polymers, and fluorous compounds [2]. This thesis centers on this key subject. Our research examines the properties and application of new “smart” solvents with either a built-in “switch” or “tune”. “Smart” solvents take advantage of the large in-situ change in properties that the solvent can experience when properly designed. The ability to change a solvent’s properties significantly is advantageous for chemical processes involving multiple steps (e.g. reactions, extractions, and/or separations) each of which may require different solvent environments. While creating these molecules, our goal is to combine many typically wasteful processing steps into a single unit. For example, coupling a reaction and separation step. We also enable reuse of the solvent systems and/or catalysts which is crucial to ameliorating hazardous waste production common in most industries. The overall goal is not only to improve the sustainability of processes, but to also make them
run more efficiently and increase economic gain. At this stage, industries are more likely to implement new technologies.

“Switchable” solvents are those solvents whose properties can turn “on” or “off” when activated by a stimulus. In Chapter 2, we explore the switch of a molecular solvent to an ionic solvent and vice versa upon reaction with carbon dioxide. This switch accompanies substantial solvent property changes, most notably conductivity, viscosity, and polarity. These one component solvents derived from silylated amines are thermally reversible and reusable. In addition, these solvents possess tunable properties upon simple structural modifications. We demonstrate how these reversible ionic liquids can be used as recyclable solvents for two energy applications: purification of contaminated crude oil and carbon capture from post-combustion flue gas streams.

“Tunable” solvents are those whose solvent properties can be gradually adjusted through use of a pressurized gas. Properties such as solvent power and transport properties can span a wide range between those of organic liquids and gases [3]. In Chapter 3, we look at systems based on low molecular weight liquid polyethylene glycol (PEG), common organic liquids, and CO₂. We apply these systems to the palladium catalyzed C-O coupling of aryl halides with bases to produce substituted phenols and aromatic ethers, harnessing the advantages of homogeneous catalysis and heterogeneous separation. An additional benefit of the tunable solvent system for this application is the use of carbonic acid, which is the reversible in-situ acid formed from the equilibrium of CO₂ with water. For this reason, CO₂ is utilized for two purposes in the process: separation and post-reaction neutralization. Reversible acids eliminate the waste and cost generated by traditional acids.
In Chapter 4, we investigate the peroxide initiated grafting of alkoxy silanes onto polyethylene backbones. Grafted polymers often possess advantageous properties such as increased electrical stability and thermal resistance. In this study, simple hydrocarbons are used as polymer model compounds to ease analysis. Supercritical carbon dioxide is used as a co-solvent to the hydrocarbon phase. During polymer extrusion, CO$_2$ can decrease the viscosity of the polymer phase and reduce mass transfer issues commonly associated with grafting reactions. By tuning CO$_2$ pressure, we can limit the extent of grafting on each model compound and thus control the resulting grafted product’s properties. With less silane grafts per polymer chain, moisture induced crosslinking is still enabled and the use of grafting material is improved. This efficiency increase positively impacts overall reaction economics. The overall project goal is to increase the theoretical understanding of radical grafting reactions due to a dearth amount of relevant literature.

The final chapter, Chapter 5, will include recommendations for future work in the areas covered throughout this thesis and how this research can extend to other applications. Amongst others, this includes the generation of reversible ionic liquids using SO$_2$, developing structure-property relationships to better design solvents for a specific need, and improving environmental impact of tunable solvents by recording phase behavior of PEG-alcohol-CO$_2$ systems.
1.1. References


CHAPTER 2. ONE-COMPONENT, SWITCHABLE IONIC LIQUIDS DERIVED FROM SILYLATED AMINES

2.1. Introduction

Switchable solvents are those which undergo large step changes in properties when exposed to a stimulus (e.g. light or heat). The ability to change a solvent’s properties significantly is advantageous for chemical processes involving multiple steps (e.g. reactions, extractions, and/or separations) each of which may require different solvent environments. For this reason, the design of switchable smart solvents is valuable. There are a few switchable solvents that have been reported [1-4]. This chapter will focus on the creation of a new class of switchable ionic liquids. Ionic liquids are salts with melting points below 100°C. They have been considered “green” alternative solvents to volatile organics due to their negligible volatility/vapor pressure. The properties of ionic liquids can be tuned by varying the combination of cation and anion. Therefore, their use spans a range of applications. For the aforementioned reasons, many articles highlight the use of ionic liquids as catalysts and as green reaction media; however, few address the issue of separation. The low volatility of ionic liquids make them difficult to remove from high boiling point products. Switchable ionic liquids can increase the utility of conventional ionic liquids by including a facile, built-in separation. Recently, we described two-component, reversible ionic liquid systems based on amidines or guanidines with alcohols [4]. Here we present a new class of one-component, thermally reversible...
ionic liquids derived from silylated amines and carbon dioxide (CO₂) (See Scheme 2.1) [5]. While other groups have investigated the capture of carbon dioxide by reaction with amine groups tethered onto ionic liquids, their systems greatly differ from ours [6-8]. In all of these cases, task specific ionic liquids were converted to different ionic species. In contrast, we examine a switch from a neutral solvent to an ionic liquid. Other groups have looked at preparing organic-inorganic hybrid materials based on siloxylated amine structures; however, their focus is not on the creation of liquid reversible solvents [9]. When compared with their two-component counterparts, our one-component systems are simple from a processing standpoint. Maintaining a 1:1 molar stoichiometry is not required when using a single component. Also, our one-component ionic liquids incorporate a silicon center into their structure which introduces weak Lewis acid functionality and subsequently alters the solvent’s physical properties, most notably viscosity. In addition, we show how one-component, reversible, ionic liquid solvents could be used in two energy applications: extracting hydrocarbons from tar sands/oil shale and post-combustion flue gas stream carbon capture [10].

Scheme 2.1. Reversible reaction of silylamine precursors with carbon dioxide where R= methoxy, ethoxy, ethyl, or propyl.
2.2. **Materials**

The following chemicals were stored in a nitrogen filled glovebox until use: (3-aminopropyl)-trimethoxysilane (Fluka, 97%), (3-aminopropyl)-triethoxysilane (Sigma-Aldrich, 98%), allylamine (Sigma-Aldrich, 99%+%), triethylsilane (Sigma-Aldrich, 99%), tripropylsilane (Sigma-Aldrich, 99%), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Sigma-Aldrich, ~2% solution in xylene). Anhydrous toluene (Sigma-Aldrich, 99.8%) and high performance liquid chromatography (HPLC) methanol (Sigma-Aldrich, 99%+) were used as received. Carbon dioxide was supercritical fluid chromatography (SFC) grade (Air Gas, 99.999%) and further purified via a Matheson gas purifier and filter cartridge (Model 450B, Type 451 filter). Crude oil was supplied from Professor Phillip Jessop’s laboratory at Queen’s University in Ontario Canada, which was originally obtained from Shell Oil Company. The crude oil sample was analyzed by Chevron (Briarpark, Texas) for sulfur content and hydrocarbon fractions. The sample contained 1.17 wt% sulfur, which is relatively low but still a sour crude oil. The largest hydrocarbon cut boiled at 235°C (See Figure 2.1), which is similar to the boiling point for the straight chain C13 hydrocarbon, tridecane (234°C). $^1$H NMR of the crude oil showed only two aliphatic peaks with shifts corresponding to CH$_2$ and CH$_3$ groups. The oil was medium grade: its density was 0.88 g/mL as determined using a 2.0 mL pycnometer (API density of 28.7 (See equation 1)). Bitumen was provided by ConocoPhillips and used as received having a density of 1.03 g/mL (API density of 5.9) also determined by the pycnometer described above.
Figure 2.1. Simulated distillation of crude oil sample: percentage of oil removed vs. temperature

\[ API\_\text{density} = \frac{141.5}{Specific\_Gravity} - 131.5 \] (1)

2.3. Experimental Methods

2.3.1 Ionic Liquid Formation

Molecular precursors (silylated amines) were reacted with CO₂ by bubbling through these liquids at room temperature until completion of the exothermic reaction. This reaction proceeds within minutes. NMR of the reactants and products was run at room temperature using a Varian-Mercury VX400 MHz spectrometer. Neat NMRs were run using a capillary tube (containing the lock solvent) placed inside a standard size NMR tube. Infrared (IR) experiments were performed on a
Nicolet 4700 fourier transfer infrared (FT-IR). Samples were sent for elemental analysis to Atlantic Microlab, Atlanta GA.

2.3.2 Hydrosilylation Reactions

Hydrosilylations were run according to literature procedure [11]. Silane (1 equivalent), platinum (0) catalyst (100 ppm), and toluene (30 mL) were added to a round bottom flask in the glove box. Allylamine (3 equivalents) was then added dropwise via an addition funnel to the mixture. The reaction was stirred with a magnetic stir bar and run at 110°C for 5-24 hours. Any vapor generated was condensed by a cooling water condenser. Following reaction, the mixture was rotovaped at room temperature to remove toluene and unreacted silane or allylamine. To remove trace quantities of catalyst the sample was distillation purified. The product was then analyzed by $^1$H and $^{13}$C NMR using CDCl$_3$ (NMRs were run at room temperature using a Varian-Mercury VX400 MHz spectrometer), elemental analysis (Atlantic Microlab Inc., Atlanta GA), and electron spray ionization mass spectrometry (ESI-MS) (Georgia Institute of Technology Mass Spec Laboratory).

2.3.3 Viscosity Experiments

Viscosity measurements were made on a Anton Paar MCR 300 rheometer using a 0.97 mL coquette geometry sample holder with Peltier temperature control. Shear rates increased from 0-100 sec$^{-1}$ and then decreased from 100-0 sec$^{-1}$, with the reported values being the average of all data points from 10-100 sec$^{-1}$.
2.3.4 Nile Red Polarity Tests

Ultraviolet-visible (UV-Vis) spectra were collected using a HP 8453 UV-Vis Spectrophotometer and a quartz cuvette. Nile red was added to the liquids at a concentration that kept the UV-Vis absorbance lower than a value of one and a half, thereby ensuring that there was no saturation of the detector. The wavelength of maximum absorption was then determined and the average of three repeats was taken as the Nile red $\lambda_{\text{max}}$. For the viscous ionic liquid samples, Nile red was added to the molecular liquids which were then converted to the ionic liquids by bubbling CO$_2$ through the cuvette. This procedure eased the dissolution of Nile red into the liquids.

2.3.5 Differential Scanning Calorimetry (DSC)/Thermal Gravimetric Analysis (TGA)

DSC was run from 20ºC to 300ºC or 400ºC (for higher boiling point precursors) at 20ºC/min or 30ºC/min on a Q20 TA Instruments machine. Nitrogen flow was set at 50 mL/min. The reversal temperature, or first endotherm from the thermogram, was taken as the average of three repeats. TGA on the ionic liquids was run from 20ºC to 500ºC at 20ºC/min on a Q50 TA Instruments machine. Nitrogen flow was set to 40 mL/min.

2.3.6 Crude Oil Purification Proof of Principle Recycles

Crude oil was added at 50 wt% to triethoxysilylpropyl amine producing a single-phase system. At this stage filtration may be needed to remove inorganic salts, sand, or other non-soluble contaminants, but for the crude oil sample investigated, this was not necessary. After bubbling CO$_2$ until completion of the exothermic reaction, the single
phase became more viscous indicating ionic liquid formation. This solution was centrifuged to speed the separation between the non-polar hydrocarbon phase and the polar ionic liquid phase. The need to centrifuge is attributed to the high viscosity of the system. Each phase was sampled to determine impurity via $^1$H NMR integration. The top phase was decanted and the bottom phase was heated at 120°C for two hours to reverse the ionic liquid. The cycle was then repeated three times by reintroducing oil. Each recycle experiment was repeated three times and the average of the three runs was reported as the separation efficiency. Bitumen tests were run using a mixture of 20 wt% bitumen to molecular liquid precursor. This mixture was then filtered under aspirator vacuum before bubbling CO$_2$.

2.3.7 Carbon Capture Capacity

A Specac, Ltd. heated “Golden Gate” attenuated total reflectance (ATR) accessory with diamond crystal and ZnSe focusing lenses was used in combination with a custom-made high pressure reactor. The Fourier transform infrared (FT-IR) absorbance measurements were collected with a Shimadzu IRPrestige21 using a DLATGS detector, with 32 scans and a resolution of 1 cm$^{-1}$. The ionic liquids were prepared ex-situ and transferred to the reaction chamber, which was heated to 35°C. CO$_2$ was then introduced via an ISCO syringe pump at a pressure of 61.5 bar, and the ATR FT-IR spectra were recorded after the system had reached equilibrium. The CO$_2$ sorption and swelling were calculated following procedures outlined by Kazarian [12-13], with two small changes in technique:
(1) a CO$_2$/methanol system was used to determine the relationship between absorbance of the $\nu_3$ band of CO$_2$ (ca. 2335 cm$^{-1}$) and CO$_2$ concentration by comparing our ATR FT-IR results to experimental values reported in literature [14] (thereby assuming a negligible change in penetration depth of the evanescent wave in methanol and ionic liquid samples)

(2) the C-H stretching vibrations (located <3000 cm$^{-1}$) were used to determine swelling as we observed many peaks overlapping with the $\delta$(CH$_3$) band in our samples.

The ionic liquid sample densities were measured using a 2.0 mL pycnometer and a total of three samples were averaged. This information was used to calculate the CO$_2$ absorption capacity from the ATR FT-IR experimental data on a CO$_2$-free basis of amine solvent. The CO$_2$ reaction capacities were calculated from the stoichiometric ratio of 1:2 (mole CO$_2$:mole amine), again reported on a CO$_2$-free basis.

2.3.8 Stability Tests

Liquids were set under various atmospheres (argon or standard) and/or concentrations of H$_2$O (either 0 vol% or 10 vol%). Samples were drawn weekly and analyzed via $^1$H NMR to determine degradation, if any. This was continued over a period of approximately two months.

2.3.9 Scale-up Simulations

A simulation for the removal of hydrocarbons from tar sands was created using Aspen HYSYS version 2006.5 and the extended NRTL fluid package. Tar sand was
mixed with the molecular liquid, TESA, at 25°C and entered a 100% efficient filter. The composition of tar sand was assumed to be 80 wt% sand and the remainder oil. The TESA to oil mixture entering the first conversion reactor was in a 50:50 mass ratio. Carbon dioxide was added stoichiometrically to the mixture to initiate the forward reaction. The forward reaction is exothermic and the stream exiting the first conversion reactor leaves at 42°C. Emulating experimental results, the forward conversion was set to 100%. Four mol % (value from experiments) of the ionic liquid was taken off in a decantation step along with the hydrocarbon product; the remaining ionic liquid was sent to a second reactor. Here, the reverse reaction took place at 110°C, which was the reversal temperature as determined from experiments. Carbon dioxide leaves in this step and TESA was recycled back to the tar sand/precursor mixer after cooling to 25°C and reused. For comparison, a simulation was made for processing the same quantity of tar sands by steam explosion. Tar sands and water (50:50 mass ratio) were preheated to 100°C and mixed in a tank. The exiting vapor stream, comprised of oil and water, was cooled to room temperature and oil was decanted from water.

2.4. Results

2.4.1 Siloxylated Amines

Trimethoxy and triethoxysilylpropylamine have been shown to react with carbon dioxide (CO₂) at room temperature and atmospheric pressure to form the corresponding ionic liquids: 3-(trimethoxysilyl)-propylammonium 3-(trimethoxysilyl)-propyl carbamate (TMSAC) and 3-(triethoxysilyl)-propylammonium 3-(triethoxysilyl)-propyl carbamate (TESAC). Ionic liquid
formation was evidenced by a viscosity increase and reaction exotherm. The products, TMSAC and TESAC, were characterized by \(^1\)H NMR, \(^{13}\)C NMR, IR, and elemental analysis. While these one-component ionic liquids would not operate well in high water environments, due to reactive alkoxy groups, modest structural variations could ameliorate this limitation (See Section 2.4.4). Characterization of TMSAC and TESAC follows.

- **TMSAC**

  Ammonium carbamate formation was confirmed by the appearance of the characteristic carbamate carbon peak in the \(^{13}\)C NMR spectra (162.6 ppm referenced to CDCl\(_3\)). All other carbon peaks were shifted from trimethoxysilylpropylamine (TMSA).

\(^{13}\)C NMR for TMSAC \(\delta_{ppm}\): 50.0 (OCH\(_3\)), 43.9 (CH\(_2\)N), 42.8 (CH\(_2\)N), 23.8 (CH\(_2\)), 23.2 (CH\(_2\)), 5.8 (CH\(_2\)Si); for TMSA \(\delta_{ppm}\): 49.7 (OCH\(_3\)), 45.0 (CH\(_2\)N), 27.1 (CH\(_2\)), 6.1 (CH\(_2\)Si).

\(^1\)H NMR peaks were also shifted from TMSA along with the appearance of hydrogen peaks for the hydrogens attached to nitrogen. \(^1\)H NMR for TMSAC \(\delta_{ppm}\): 6.0 (3H, br, NH\(_3\)), 4.5 (1H, br, NH), 3.5 (18H, br, OCH\(_3\)), 3.0 (2H, br, CH\(_2\)N), 2.6 (2H, br, CH\(_2\)N), 1.6 (2H, br, CH\(_2\)), 1.5 (2H, br, CH\(_2\)), 0.6 (4H, br, CH\(_2\)Si); for TMSA \(\delta_{ppm}\): 3.9 (9H, s, OCH\(_3\)), 2.9 (2H, t, CH\(_2\)N), 1.8 (2H, m, CH\(_2\)), 0.9 (2H, t, CH\(_2\)Si). In addition, elemental analysis verified the complete conversion to products (Found: C, 38.34; H, 8.57; N, 6.95. Calc. for C\(_{13}\)H\(_{34}\)N\(_2\)O\(_8\)Si\(_2\) : C, 38.78; H, 8.51; N, 6.96 %). IR also validated product formation (\(\nu_{max}/\text{cm}^{-1}\) 3400-2400 br (-NH\(_3^+\) stretch) 1570 and 1471(-CO\(_2^-\) asymmetric and symmetric stretch), 1071 (Si-OR stretch), and 2940 and 2839 (C-H stretch)). Figure 2.2 and Figure 2.3 show the IR spectra for both TMSA and TMSAC, respectively.
Figure 2.2. IR spectrum of TMSA
Ammonium carbamate formation was confirmed by the appearance of the carbamate carbon peak in the neat $^{13}$C NMR spectra (162.5 ppm referenced externally to a CDCl$_3$ capillary). Each of the other carbon peaks were shifted upfield from the precursor triethoxysilylpropylamine (TESA). $^{13}$C NMR for TESAC $\delta_{\text{ppm}}$: 57.7 (OCH$_2$), 44.1 (CH$_2$NH), 41.5 (CH$_2$NH), 23.7 (CH$_2$), 21.3 (CH$_2$), 17.9 (CH$_3$), 7.6 (CH$_2$Si), 7.4 (CH$_2$Si); for TESA $\delta_{\text{ppm}}$: 58.1 (OCH$_2$), 45.3 (CH$_2$NH$_2$), 27.6 (CH$_2$), 18.3 (CH$_3$), 7.8 (CH$_2$Si). Neat $^1$H NMR peaks were also shifted from TESA. Hydrogen peaks appeared for the hydrogen atoms attached to the nitrogen atoms. $^1$H NMR for
TESAC $\delta_{ppm}$: 9.6 (3H, br, NH$_3$), 6.0 (1H, br, NH), 4.0 (12H, br, OCH$_2$), 3.2 (2H, br, CH$_2$NH), 3.0 (2H, br, CH$_2$NH), 1.9 (2H, br, CH$_2$), 1.7 (2H, br, CH$_2$), 1.4 (18H, br, CH$_3$), 0.8 (4H, br, CH$_2$Si); for TESA $\delta_{ppm}$: 4.1 (6H, m, OCH$_2$), 2.9 (2H, t, CH$_2$NH$_2$), 1.8 (2H, m, CH$_2$), 1.5 (9H, t, CH$_3$), 0.9 (2H, t, CH$_2$Si). In addition, elemental analysis verified the complete conversion to products (Found: C, 46.66; H, 9.49; N, 5.77. Calc. for C$_{19}$H$_{46}$N$_2$O$_8$Si$_2$: C, 46.88; H, 9.53; N, 5.76%). IR also validated product formation ($\nu_{max}/cm^{-1}$ 3400-2400 br (-NH$_3^+$ stretch) 1570 and 1481(-CO$_2^-$ asymmetric and symmetric stretch), 1070 (Si-OR stretch), and 2972 and 2882 (C-H stretch)). Figure 2.4 and Figure 2.5 show the IR spectra for both TESA and TESAC, respectively.
Figure 2.4. IR spectrum of TESA
Figure 2.5. IR spectrum of TESAC
These ionic liquids can be thermally reversed at moderate temperatures to their molecular precursors. Reversibility of the siloxylated ionic liquids was demonstrated by TGA, DSC, and NMR. TGA indicated a mass loss of 13% by 88°C and 9% by 125°C corresponding to CO₂, in TMSAC and TESAC respectively (See Figure 2.6). Both TESAC and TMSAC show two endotherms in their DSC thermograms. For TESAC, the DSC plot showed loss of CO₂ starting at 50°C and finishing at 150°C, which is then followed by decomposition of the amine precursor at 237°C (See Figure 2.7). For TMSAC, the DSC showed the loss of CO₂ starting at 75°C and ending by 175°C followed by precursor decomposition starting at 260°C. The separation in endotherms/events (greater than 50°C) is important for ensuring minimal solvent loss, capability for solvent recycle, and a clean CO₂ stream. The separation between the precursor molecules and CO₂ was not seen for our two-component ionic liquids based on short chain alcohols and guanidine. For example, the DSC thermogram for the two-component ionic liquid formed between tetramethylbutylguanidine (TMBG) and methanol is shown in Figure 2.8. Two endotherms are seen overlapping at 75°C and 125°C. Methanol is concurrently removed with CO₂ which will increase downstream processing costs. A ¹³C NMR study of the formation and reversal of TESAC is shown in Figure 2.9 as an example. Figure 2.9 presents the ¹³C NMR for the precursor, TESA, (spectrum A), the ionic liquid, TESAC, (spectrum B), and TESAC after heating at 120°C for 2 hours to reverse it back to TESA (spectrum C). The carbamate peak appears upon ionic liquid formation (spectrum B) and then disappears after reversal (spectrum C). Therefore, these one-component systems offer simple processing opportunities for industrial applications upon addition and removal of CO₂ alone. It appears that these compounds are oxygen stable
up to the temperatures required for ionic liquid reversal as the DSC does not show an additional decomposition event, the $^{13}$C NMR experiment shows a clean spectrum upon ionic liquid reversal, and stability tests show no reaction with oxygen (See Section 2.4.4, where reaction was only seen with water).

![Figure 2.6. TGA of TESAC](image)

Figure 2.6. TGA of TESAC
Figure 2.7. DSC thermogram of TESAC

Figure 2.8. DSC thermogram of ionic liquid formed from TMBG and methanol with carbon dioxide
Figure 2.9. $^{13}$C NMR of A) TESA B) TESAC C) TESAC heated for 2 hours at 120°C
In order to understand better, and thus to tune, the chemical and physical properties of these switchable solvents, polarity and viscosity measurements were carried out. The solvatochromic dye Nile red (Figure 2.10) was used as a measure of polarity to estimate the solvent’s polarity change upon formation of the ionic species. The Nile red wavelength of maximum absorbance, λ<sub>max</sub>, directly correlates with solvent polarity and has previously been used as a polarity probe for common organic solvents and ionic liquids [15-16]. The UV-Vis spectra for TESA and TESAC with Nile red is shown in Figure 2.11. TMSA showed a 9.8 nm λ<sub>max</sub> increase (from 528.5 nm to 538.3 nm) when reacting to form TMSAC, where TESA showed a 8.5 nm increase (from 524.0 nm to 532.5 nm) when forming TESAC. TESA(C) is less polar than TMSA(C) due to the increased organic and therefore non-polar nature of its side chain groups. In general, these solvents change from a polarity similar to benzene (525.4 nm) to one similar to chloroform (537.6 nm) [16]. These results also illustrate that by applying structure-property relationships one can tune the properties of the solvent for a desired application. Viscosity was also shown to vary with structure: TMSAC has a viscosity of 2,160 cP whereas TESAC has a viscosity of 930 cP. These values match visual observations that TMSAC is gel-like whereas TESAC is a viscous liquid. The viscosity of these materials decreases as the side chain unit is increased due to a disrupted packing efficiency. Specifically, the addition of a single methylene group to each silicon sidechain cut the ionic liquid’s viscosity in half. These solvents are both Newtonian fluids and no shear thinning is evident (See Figure 2.12).
Figure 2.10. Nile Red

Figure 2.11. Example UV-Vis spectra of TESA and TESAC with Nile red (dashed lines represent $\lambda_{\text{max}}$)
Figure 2.12. Viscosity vs. shear rate for TMSAC and TESAC while both increasing and decreasing shear rates
2.4.2 Application to Hydrocarbon Extraction from Crude Oil

Depletion of conventional oil reserves, increasing focus on energy independence, and rising oil prices may lead to the increased use of tar sands and oil shale as alternate fossil fuel resources. The United States has the world’s largest oil shale deposits located in the Green River Formation which contains an estimated 800 billion barrels of recoverable oil [17]. Currently, the isolation of hydrocarbons from tar sands and oil shale is difficult mainly due to the physical properties of these materials, such as high viscosity and density [18-19]. Steam has been used to extract oil from these unconventional sources, but the process is energy-intensive and produces large quantities of contaminated waste water. Although oil-miscible organic solvents can cut the viscosity of these oils enabling facile filtration, the process is cumbersome and wasteful. The common method for organic solvent recovery, distillation, is energy-intensive and the oil’s low-end carbon fractions will be distilled along with the volatile solvent. Our reversible solvents solve this problem by utilizing a built-in, energy-efficient and environmentally benign solvent separation technique. The polarity jump upon formation of the ionic liquid from the molecular liquid enables a phase change from a homogeneous mixture of precursor and hydrocarbon to a heterogeneous system (See Figure 2.13). In the same way, this separation occurred with crude oil. A proof of principle experiment was run using crude oil and TESA to quantify the separation efficiency and recyclability of the proposed process. TESA has shown to be the better choice for this application due to its lower viscosity and reversal temperature when compared with TMSA. Tar sands or oil shale were not used for preliminary experiments; however, the results from our model study
should directly transfer since the main difference in processing these feedstocks is a filtration step prior to entering the extraction cycle.

![Figure 2.13. Homogeneous to heterogeneous system of TMSA(C) and octane](image)

As a proof of principle for tar sand purification using smart solvents, we carried out three process recycles (See Figure 2.14) with crude oil and TESA. Table 2.1 shows the TESAC in the product phase as determined by $^1$H NMR peak integration over the course of the three recycles. The integration of the O-CH$_2$ peak (twelve hydrogens) from the ionic liquid was compared with the integration of the methyl peak (six hydrogens when assuming linear alkanes) from the hydrocarbon chains. The hydrocarbon phase has less than 4 mol% dissolved ionic liquid. These results also demonstrate that the separation has not considerably changed over the course of three recycles. The TESAC phase has a substantial amount of dissolved hydrocarbon, but this phase will be saturated after cycle one and recycled. The main drawback to hydrocarbon solubility in the ionic liquid phase lies in the increased precursor regeneration energy, as the dissolved oil will be heated along with the ionic liquid during the solvent reversal step. The TESAC phase is also expected to contain
other impurities such as sulfur, water, and heavy metals like arsenic which are common to crude oil. This secondary extraction provides an additional benefit to our main goal of extracting sand. We expect the separation to improve on a larger scale because the surface area to volume ratio will decrease.

![Figure 2.14. Process diagram for recyclable hydrocarbon extraction from crude oil with TESAC](image)

Table 2.1. mol% TESAC impurity in the hydrocarbon product phase after three recycles

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Hydrocarbon Phase (mol% TESAC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.6</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Bitumen was used as a more contaminated crude oil feedstock to verify separation potential. Bitumen and molecular precursor were filtered before the cycle was started to remove solid impurities. Again after converting the molecular liquid to the ionic liquid a phase separation was observed. The three fractions collected (two liquid phases and one solid phase) are currently under investigation.

A scale-up simulation for the extraction of hydrocarbons from tar sands was
run using HYSYS software. The simulation was set to produce 58 million barrels of crude oil per year for refining (See Figure 2.15). This capacity is typical for large refineries [20]. It was assumed that the process runs 80% of the year in order to account for maintenance downtime. The ideal, most profitable simulation assumed a perfect filtration of sand from oil/molecular liquid and perfect separation between the oil and the ionic liquid phases. The main processing cost arises from the energy requirements of the ionic liquid reversal step. Presently, electricity costs 6.93¢/kWh (industrial scale price averaged over the USA) [21]. Therefore, the total cost to run the idealized process, 42 M$/yr or 70 cents/barrel, is currently much less than the sale of the oil at $58.73/barrel thereby generating an annual profit of $3.4 billion [22]. For comparison, the current steam explosion technology was simulated using the same tar sand feedstock quantity (153 million barrels/yr) and composition as used for the reversible solvent process (See Figure 2.16). While still profitable, steam explosion costs an estimated $25 per barrel produced and generates less refined oil per year (40 Mbarrels per year). Therefore, our solvent technology can be nearly 35 times less costly than the steam explosion route.
Figure 2.15. HYSYS simulation of recyclable tar sand purification using reversible ionic liquids
2.4.3 Silylated Amine Synthesis and Characterization

Alkoxy side chains were replaced with alkyl groups to increase the chemical stability of these siloxylated precursor molecules (See subsequent section on amine stability). Because silylated precursor molecules are not commercially available, they were synthesized by the hydrosilylation reaction shown in Scheme 2.2. This synthetic route was chosen with scale-up in mind as only a single step is involved in the synthetic pathway. Both triethylsilylpropylamine (TEtSA) and tripropylsilylpropylamine (TPSA) were prepared and characterized.

![Diagram of HYSYS simulation of steam explosion for tar sand purification](image)

Figure 2.16. HYSYS simulation of steam explosion for tar sand purification

![Scheme 2.2. Reaction of alkysilanes with allylamine where R=ethyl or propyl](image)

Scheme 2.2. Reaction of alkysilanes with allylamine where R=ethyl or propyl

- TEtSA

$^1$H NMR on TEtSA (See Figure 2.17) confirms pure product formation. $^1$H NMR for TEtSA $\delta_{ppm}$: 2.6 (2H, t, CH$_2$N), 1.4 (2H, m, CH$_2$), 1.2 (2H, s, NH$_2$), 0.9 (9H, t, CH$_3$), 0.5 (8H, br, CH$_2$Si). ESI-MS was also performed on TEtSA and confirmed the formation of pure product with a molecular weight of 173 amu. Also, elemental analysis showed a product purity of 99.9% (Found: C, 62.41; H, 13.42; N,
7.94. Calc. for C\textsubscript{9}H\textsubscript{23}NSi : C, 62.35; H, 13.37; N, 8.08%). The ionic liquid, 3-(triethylsilyl)-propyl ammonium 3-(triethylsilyl)-propyl carbamate (TEtSAC), was then formed by bubbling CO\textsubscript{2} through TEtSA. Formation was evidenced by NMR, elemental analysis, and IR. The $^{13}$C NMR spectra for TEtSAC shows 9 peaks which include the carbamate peak $\delta$ ppm: 163.1 (O-C=O), 45.2 (CH\textsubscript{2}N), 43.0 (CH\textsubscript{2}N), 24.8 (CH\textsubscript{2}), 23.6 (CH\textsubscript{2}), 8.6 (CH\textsubscript{2}Si), 8.4 (CH\textsubscript{2}Si), 7.3 (CH\textsubscript{3}), 3.0 (CH\textsubscript{2}Si). $^1$H NMR for TEtSAC (See Figure 2.18) was consistent with product formation $\delta$ ppm: 7.9 (3H, s, NH\textsubscript{3}), 2.9 (2H, t, CH\textsubscript{2}N), 2.6 (2H, t, CH\textsubscript{2}N), 1.5 (2H, m, CH\textsubscript{2}), 1.3 (2H, m, CH\textsubscript{2}), 0.8 (18H, -CH\textsubscript{3}), 0.4 (16H, -CH\textsubscript{2}Si). Elemental analysis showed an ionic liquid purity of 99.8% (carrying over a 0.1% impurity from TEtSA) (Found: C, 58.60; H, 12.01; N, 7.06. Calc. for C\textsubscript{19}H\textsubscript{46}N\textsubscript{2}O\textsubscript{2}Si\textsubscript{2} : C, 58.40; H, 11.87; N, 7.17%). The IR was consistent with product formation ($\nu$ max/cm\textsuperscript{-1} 3500-2300 br (-NH\textsubscript{3}+ stretch) 1574 and 1312 (-CO\textsubscript{2} asymmetric and symmetric stretch), and 2972 and 2882 (C-H stretch)). Figure 2.19 and Figure 2.20 show the IR spectra for TEtSA and TEtSAC, respectively.

Reversal of TEtSAC was proven by DSC. The DSC thermogram shown in Figure 2.21 confirms the removal of CO\textsubscript{2} at 143°C followed by decomposition of TEtSA at 285°C. The endotherm at 37°C may represent the release of physically absorbed CO\textsubscript{2}. When compared to the siloxylated amine reversible ionic liquids, TEtSAC reverses at a higher temperature than TESAC (143°C vs. 108°C), but at a similar temperature to TMSAC (145°C). This might suggest that it is the number of atoms attached to the side group of the silicon center that is important for controlling regeneration temperature. Accordingly, the longer the side-chain the lower the reversal temperature is. This may
also be correlated with viscosity (longer side-chains have a lower viscosity) as the release of CO₂ may be mass transfer limited.

Figure 2.17. ′H NMR of TEtSA
Figure 2.18. $^1$H NMR of TEtSAC
Figure 2.19. IR spectrum of TEtSA
Figure 2.20. IR spectrum of TEtSAC
Figure 2.21. DSC thermogram of TEtSAC
• TPSA

$^1$H NMR on TPSA (See Figure 2.22) confirms pure product formation, $\delta_{ppm}$: 2.6 (2H, t, CH$_2$N), 1.4 (2H, m, CH$_2$), 1.3 (2H, m, CH$_2$), 1.1 (2H, s, NH$_2$), 0.9 (9H, br, CH$_3$), 0.5 (8H, br, CH$_2$Si). ESI-MS was also performed on TPSA and confirmed the formation of pure product with a molecular weight of 215 amu. Also, elemental analysis showed a product purity of 99.8% (Found: C, 66.74; H, 13.64; N, 6.35. Calc. for C$_{12}$H$_{29}$NSi : C, 66.90; H, 13.57; N, 6.50%). The ionic liquid, 3-(tripropylsilyl)-propylammonium 3-(tripropylsilyl)-propyl carbamate (TPSAC), was then formed by bubbling CO$_2$ through TPSA. Formation was evidenced by NMR, elemental analysis, and IR. The $^{13}$C NMR spectra for TPSAC shows 11 peaks which include the carbamate peak $\delta_{ppm}$: 163.0 (O-C=O), 45.3 (CH$_2$N), 43.6 (CH$_2$N), 25.0 (CH$_2$CH$_2$CH$_2$N), 24.7 (CH$_2$CH$_2$CH$_2$N), 18.5 (CH$_2$CH$_2$CH$_3$), 17.3 (CH$_3$), 15.2 (CH$_2$Si), 15.1 (CH$_2$Si), 9.9 (CH$_2$Si), 9.7 (CH$_2$Si). $^1$H NMR for TPSAC was consistent with product formation $\delta_{ppm}$: 6.8 (3H, s, NH$_3$), 4.3(1H, s, NH), 3.0 (2H, t, CH$_2$N), 2.6 (2H, t, CH$_2$N ), 1.5 (2H, m, CH$_2$), 1.3 (18H, br, CH$_2$), 0.9 (26H, br, CH$_3$), 0.5 (24H, CH$_2$Si). Elemental analysis shows a purity of 99.6% (carrying over a 0.2% impurity from TPSA) (Found: C, 62.96; H, 12.33; N, 5.64. Calc. for C$_{25}$H$_{58}$N$_2$O$_2$Si$_2$: C, 63.23; H, 12.31; N, 5.90%). The overlay IR spectra of TPSA and TPSAC are shown in Figure 2.23 (taken using a Shimadzu IRPrestige21 described in Section 2.3.7). Reversal of TPSAC was proven by DSC. The DSC thermogram confirms the removal of CO$_2$ at 150ºC followed by decomposition of TPSA at 316ºC.
Figure 2.22. $^1$H NMR of TPSA
Figure 2.23. Overlay IR spectra of TPSA and TPSAC
The polarity and viscosity of the silylated amine molecular and ionic liquid solvents were investigated. Nile red measurements show a relative polarity, or $\lambda_{\text{max}}$, increase of 10.0 nm upon formation of TEtSAC from TEtSA (from 523.5 to 533.5 nm) and an increase of 8.4 nm upon formation of TPSAC from TPSA (from 522.3 to 530.7 nm). The polarity comparison of both siloxylated and silylated amines can be seen in Figure 2.24. The longer alkyl side groups show less of a polarity switch when going from molecular to ionic liquids due to their overall more organic and therefore nonpolar nature. Using the same reasoning, the compounds with longer alkyl chains are less polar in both molecular and ionic forms. Siloxylated liquids are more polar than silylated liquids due to the increased electrophilicity of oxygen when compared to carbon. Viscosity was also compared between the four ionic liquids, TMSAC/TESAC/TEtSAC/TPSAC, with the results shown in Table 2.2. The viscosity of TEtSAC was determined at 35°C due to the difficulty of obtaining an accurate measurement at 25°C. The viscosity of these materials decreases as the side chain unit is increased due to a disrupted packing efficiency. In addition, the siloxylated ionic liquids are less viscous than the silylated ionic liquids of the same chain length (e.g. TESAC vs. TPSAC). This viscosity decrease is due to oxygen drawing electron density from silicon and allowing for electronic interactions between molecules. The viscosity of all of the molecular liquid precursor molecules was less than 5 cP.
2.4.4 Amine Stability

TESA and TEtSA were chosen as model precursors to examine their comparative stabilities in either an argon atmosphere, a standard atmosphere, and in the presence of water. Over the course of the experiments, both liquids were stable under dry and inert conditions. In fact, TEtSA was stable under all conditions for the duration of the examination. Therefore, it can be inferred that alkylsilyl amines are

Table 2.2. Viscosity of reversible ionic liquids at 25°C

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>TMSAC</th>
<th>TESAC</th>
<th>TEtSAC</th>
<th>TPSAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity (cP)</td>
<td>2160</td>
<td>930</td>
<td>1690(^a)</td>
<td>4210</td>
</tr>
</tbody>
</table>

\(^a\) - Temperature was 35°C
stable molecules when exposed to common atmospheres. As hypothesized, the alkoxy groups on TESA reacted immediately with the added water. In addition, the TESA sample which was put under a standard atmosphere showed small signs of reaction with atmospheric moisture by week three. This reaction increased throughout the following weeks so that by the end of the tests there was a considerable amount of precursor degradation (See peak at 3.6 ppm in Figure 2.25). These results indicate that when applying these solvents to applications which contain water (including the applications presented here), alkylsilyl amines will remain stable whereas the alkoxy silyl amines are susceptible to degradation.
Figure 2.25. $^1$H NMR spectra for TESA under a standard atmosphere after top) 5 weeks, center) 3 weeks, and bottom) 1 week
We have explored the use of one-component, reversible ionic liquids in post-combustion scrubbing of CO$_2$ from fossil fuel fired power plants. We see benefit in focusing on this sector of carbon capture because one third of the emitted CO$_2$ arises from electricity production. The United States Department of Energy has set the target that by the year 2020 90% of the emitted CO$_2$ must be captured at only a 35% cost increase [23]. This goal is complicated by the fact that CO$_2$ comprises approximately only 13% of the released gas stream, with the major component being nitrogen. Therefore, a CO$_2$ selective solvent must be used. Another dilemma is the large quantity of CO$_2$ generated. Just one 350 MW power plant produces about 6000 tons of CO$_2$/day. While many technologies are currently under investigation for carbon capture, including membranes and solid sorbents, we have focused on novel liquid absorbents. Liquid absorbents provide short time frame solutions as this technology can be easily retrofitted to existing facilities.

There are two classes of liquid absorbents that are used for gas scrubbing: physical and chemical. Physical absorption relies on specific molecular interactions, such as van der Waals forces, to afford separation. The benefit of physical absorbents is the low energy required to regenerate the gas. Traditional, non-reactive ionic liquids, such as imidazolium salts, operate under this extraction class and have been shown to have high selectivities for CO$_2$ and low heats for CO$_2$ regeneration [24-26]. On the other hand, chemical absorption is extremely selective because it relies on a chemical reaction for separation. Therefore, inert gases will not be removed from the
Gas stream. However, there is usually a higher heat penalty for gas regeneration because chemical bonds must be broken.

Chemical absorbents have been implemented in the power industry for carbon capture. The current technology uses alcohol based amines like monoethanolamine to react with CO$_2$ through the same mechanism as our molecular precursors. However, several problems exist with this current process. Alkanolamines are dissolved in water to ease process handling difficulties. The cost for CO$_2$ regeneration is increased due to the surplus energy required to heat the solvent, water. Also, the maximum volumetric and gravimetric capacity for recovery are reduced. In addition, the volatile nature of these solvents causes them to contaminate the released CO$_2$ stream. This is a problem because transportation costs will be unnecessarily increased and solvent make-up streams will be required.

Our reversible ionic liquids can act as both chemical and physical absorbents for reactive gas molecules without addition of a solvent. This is because they are liquids at processing temperatures. As we have shown, our one-component ionic liquids produce a pure CO$_2$ stream upon reversal. By using structure-property relationships developed for a few of our ionic liquids, we can optimize the recovery of CO$_2$. Our collaborator from Queen's University, Professor Jessop, has calculated the CO$_2$ capacity of our two-component reversible amidine based ionic liquids [26]. He determined that the gravimetric capacity reached 19 wt% and the volumetric capacity reached 147 g/L liquid. These values show promise for our one-component systems.

The measured ionic liquid densities, swelling, and CO$_2$ capture capacities for
both physical absorption and chemical reaction at 35°C and 62.5 bar are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density (g/cm³)</th>
<th>Swelling (%)</th>
<th>CO₂ Absorption Capacity (mol CO₂/kg amine)</th>
<th>CO₂ Reaction Capacity (mol CO₂/kg amine)</th>
<th>Total CO₂ Capacity (mol CO₂/kg amine)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMSA</td>
<td>1.151</td>
<td>17%</td>
<td>10.9</td>
<td>2.79</td>
<td>13.69</td>
</tr>
<tr>
<td>TESA</td>
<td>1.060</td>
<td>23%</td>
<td>12.5</td>
<td>2.26</td>
<td>14.76</td>
</tr>
<tr>
<td>TEtSA</td>
<td>0.945</td>
<td>16%</td>
<td>12.3</td>
<td>2.88</td>
<td>15.15</td>
</tr>
<tr>
<td>TPSA</td>
<td>0.907</td>
<td>31%</td>
<td>17.9</td>
<td>2.32</td>
<td>20.2</td>
</tr>
</tbody>
</table>

Since the stoichiometric ratio of 1:2 (mole CO₂:mole amine) was used to determine reaction capacities, the capacity decreases with increasing solvent molecular weight. However, the data indicate that the trends in ionic liquid density, swelling, and CO₂ physically absorbed follow the viscosity trend. Specifically, as the alkyl side groups become longer, it is expected that the steric effects between the ionic pairs is also increased. Subsequently, the ordering of the ionic pairs in 3-D space is disrupted, which results in a decrease in density. This, in turn, results in more void volume between ionic species which allows for higher concentrations of CO₂ to be absorbed, which is directly related to the swelling percentages reported. The last column in Table 2.3 shows the total CO₂ capacity in terms of both reaction and absorption, highlighting the dual-capture mechanism of the reversible ionic liquids.
Although reversible ionic liquids exhibit high CO₂ absorption capacities through physical absorption and selective capture of CO₂ through reaction, the real benefit of their application to CO₂ capture can be visualized when considering their use for the treatment of dilute feed streams. Conventional amine scrubbing processes use a reactant, like diethanolamine (DEA), and require a solvent to ease processing (typically water), as the product formed from the reaction between alkanolamines with CO₂ is a solid. With reversible ionic liquids the reactant is the solvent. Although TEtSA does have a higher molecular weight than DEA, for DEA in solution with 70 wt% water the capacity in terms of mass of solvent required is twice that for TEtSA without even considering the physical absorption of CO₂ in the reversible ionic liquid. The result is a substantial energy savings in terms of solvent regeneration, which dominates the operating cost of amine scrubbing processes. The future of this project will investigate the thermodynamics of reversible ionic liquids to aid in process and solvent optimization. Also, the capture capacity of our solvents will be determined using flue gas stream characteristics (mixed gas streams and low partial pressures of CO₂).

2.4.6 Intramolecular Interaction: Siloxylated Amine Precursors

The alkoxysilylamine precursors exhibit intramolecular interactions between their nitrogen and silicon atoms. This five-membered ring interaction is sterically favorable and stabilized in hydrogen bond accepting solvents (Figure 2.26). The interaction was proven by peak doubling in the ′H and ′3C NMR spectra when deuterated dimethylsulfoxide (DMSO) was used as the NMR lock solvent (Figure 2.27). The largest
A chemical split was seen for the carbon adjacent to nitrogen because this carbon is most affected by the interaction, followed by the carbon nearest to silicon (Table 2.4). The interaction was not seen when spectra were taken neat or when d-chloroform or d-benzene were used as the NMR solvents (Figure 2.28). The peak doubling was concentration dependent and increased in intensity as the sample became more dilute in alkoxy silylamine and therefore further from neat conditions. Subsequently, a concentration NMR experiment was run to determine the concentration range where the doubling appeared. Peak splitting was seen with up to 30 mol% TMSA in d-DMSO. Increasing experiment temperature did not affect the split values (Table 2.4) or relative peak intensities. These finding are consistent with an intramolecular interaction over an intermolecular interaction. An intermolecular interaction would cause the relative intensity of the primary peak to the doubled peak to increase with increasing temperature.

This intramolecular interaction has also been proposed by Alauzun et al. [9] and is significant because silicon-oxygen-carbon bonds grow longer and become more reactive. Furthermore, the interaction is stabilized in DMSO because nitrogen’s hydrogen atoms are involved in hydrogen bonding with DMSO’s oxygen and therefore allow nitrogen’s lone electron pair to interact with silicon. This is also why the interaction is not seen in d-chloroform or d-benzene, where one solvent is a hydrogen bond acceptor and the other does not participate in hydrogen bonding. Interestingly, when a 12 mol% NMR sample of the alkylsilylamine precursors in d-DMSO was made, we observed no peak doubling. We suspect that the oxygen atoms attached to silicon draw electron density from the silicon center making it electron deficient and more available to interact with nitrogen’s electrons.
Figure 2.26. TMSA intramolecular interaction

Table 2.4. TMSA $^{13}$C NMR splits vs. temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C-Si</th>
<th>C-CH$_2$</th>
<th>C-NH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>1.423</td>
<td>0.070</td>
<td>3.917</td>
</tr>
<tr>
<td>30°C</td>
<td>1.418</td>
<td>0.076</td>
<td>3.953</td>
</tr>
<tr>
<td>50°C</td>
<td>1.411</td>
<td>0.069</td>
<td>4.021</td>
</tr>
</tbody>
</table>
Figure 2.27. TMSA $^{13}$C NMR at room temperature in DMSO
Figure 2.28. TMSA $^{13}$C NMR at room temperature in CDCl$_3$. 
2.5. Conclusions

We have developed a new class of one-component, reversible, ionic liquid solvents. These solvents have advantageous properties which can be tuned by varying their chemical structure. As presented here, TESAC has been successfully used in a recyclable process to remove hydrocarbons from contaminated crude oil with a built-in separation technique. Additionally, we show that these solvents can act as both chemical and physical extraction agents for the removal of CO₂ from post-combustion power plant flue gas streams affording high CO₂ capacities. We have also created silylated amine analogues to siloxylated amines as generation two, less reactive, ionic liquid precursors. NMR studies showed that these molecules have stable intramolecular interactions between their nitrogen and silicon atoms when surrounded by hydrogen bond accepting solvents. These studies allow postulation about how structure will affect the corresponding solvent’s properties thereby enabling molecular optimization through design (See CHAPTER 5: RECOMMENDATIONS).
2.6. References


CHAPTER 3.  HOMOGENEOUS CATALYSIS COUPLED WITH BENIGN SEPARATION IN POLYETHYLENE GLYCOL-ORGANIC-TUNABLE SOLVENT SYSTEMS

3.1.  Introduction

We couple the benefits of both homogeneous and heterogeneous catalysis by using Polyethylene glycol (PEG)-Organic-Tunable Solvent systems (POTS). Both homogenous and heterogeneous catalysis have associated benefits and drawbacks [1]. In homogenous catalysis, high reactivity and product selectivity is obtained at moderate reaction conditions; however, product/catalyst separation is often difficult. Separation is more facile in heterogeneous catalysis, but reactivity suffers and mass transfer may dominate. Ideally, the catalytic reaction would run homogeneously followed by a heterogeneous separation. Tunable solvent systems enable this model scenario by coupling reaction with separation. In POTS, carbon dioxide (CO$_2$) is added to induce a phase split between the polar protic PEG-rich phase and the non-polar aprotic organic-rich phase. Operationally, this phase split is easily reversed upon gas depressurization thereby allowing a solvent switch between homogeneous to heterogeneous and vice versa. Figure 3.1 depicts these phase transitions. Figure 3.2 shows how POTS can be used to couple reaction with separation.
Our group reported on the use of Organic-Aqueous Tunable Solvent systems (OATS) to couple reaction and separation for enzyme recycle in the hydrolysis of rac-1-phenylethyl acetate and for catalyst recycle in the hydroformylation of both 1-octene and $p$-methylstyrene [2-5]. For example, the hydroformylation of 1-octene in OATS showed reaction rates which were enhanced by two orders of magnitude over the same reaction run heterogeneously. This rate was consistent over the course of three process recycles and a 99.9 % product separation and catalyst recovery were achieved. However, PEG based tunable solvents offer advantages over using water as the polar phase, as in the
OATS process. These benefits include expanding the list of soluble organic co-solvents and expanding application to those reactions and/or catalysts that are water sensitive or have a water-unfavorable equilibrium. Tunable solvents based on fluorinated organics and ionic liquids have also been reported [6-7].

Tunable solvent separations are based on extractions. Extractions are useful for systems where distillation is not an option. For example, removing high boiling point products from non-volatile solvents requires a distillation alternative. Traditionally, this product separation would be performed by extraction into a volatile organic solvent. However, extractions usually generate large quantities of organic solvent waste. Gas-expanded organics, including tunable solvent systems, offer high solvent power, but generally entail the use of a smaller liquid quantity. For the application presented in this chapter, because PEG is a non-volatile solvent and our product molecules have high boiling points, tunable solvent systems provide an efficient and low waste separation tool.

PEG and carbon dioxide offer many benefits as tunable solvent components. Carbon dioxide is the most commonly used anti-solvent for tunable systems. Anti-solvents dissolve into the liquid phase and change the solvent properties of each component thereby forcing them to no longer be a single phase. CO$_2$ is benign, inexpensive, has well-characterized properties, and has accessible critical points. PEG is especially attractive as a solvent due to its ready availability, low cost, thermal stability, negligible vapor pressure, biodegradability, and nontoxicity [8] (See Figure 3.3). PEG has also been shown to increase reaction rates in cases involving inorganic salts as reactants. This is due to PEG’s ability to activate anions for reaction by binding them less tightly than the cation would [9]. For example, PEG 400 complexes with sodium
hydroxide with a log equilibrium constant, or stability constant, equal to 2.26 [9]. Sasson and co-workers determined that potassium salts complex more easily to PEG than sodium salts and that anions capable of hydrogen bonding, such as hydroxide, are transferred into the glycol more easily [9]. A study by Slaoui showed that PEGs significantly activated hydroxide anions in homogeneous saponification reactions [9]. According to these findings, the salt used throughout this chapter, potassium hydroxide, will be activated for reaction by the solvent used, PEG 400.

![Figure 3.3. Structure of PEG](image)

In designing tunable solvent systems, the applicability of the system to real processes depends strongly on phase equilibria. There is generally a limited region in pressure-temperature-composition space where two liquid phases exist. That region is most useful if it occurs at readily attainable conditions, and if it is large. Further, one seeks an area of relatively wide disparity in the compositions of the two liquid phases, so that solvent waste is minimized and the solute distribution is as skewed as possible, to yield efficient separation. Fluids are selected where specific interactions (hydrogen bonds, Lewis acid/base interactions, etc.) give preferential distributions. Finally, we need to choose fluids that do not interfere with the chemistry of the reaction. Then such
systems may be applied to couple homogeneous reaction with heterogeneous separation for enhanced reaction rates and minimal environmental impact.

The POTS system examined in this chapter is PEG 400, 1,4-dioxane, and carbon dioxide. PEG 400 is a liquid at room temperature and is therefore more easily handled than higher molecular weight PEGs, which are solids. In addition, the phase behavior of this system and therefore operating parameters has been well characterized [10]. Figure 3.4 shows the ternary phase diagram of PEG 400/1,4-dioxane/CO₂ at 25ºC and pressures ranging from 5.2-6.0 MPa (which envelopes the three phase region). Long tie lines prove that there is an efficient separation between the two liquid phases at moderate temperatures and pressures. At room temperature and 6 MPa less than 1 wt% PEG 400 was found in the dioxane-rich phase. At both 25ºC and 40ºC, a two liquid-phase operating region exists over a pressure range of approximately 0.8 MPa. This operating region is smaller than that seen with OATS systems. For example, acetonitrile/water/CO₂ systems have a 3.3 MPa two liquid phase region [5]. On the other hand, POTS generally show increased purity of the gas-expanded organic phase when compared with OATS.
Here we report the first application of PEG based tunable solvents. In this chapter, we specifically exploit POTS for the catalytic production of phenols and aromatic ethers. These functional groups are important synthetic intermediates and components for pharmaceutical and chemical compounds. For example in 1996, the world production of synthetic phenol was $4.9 \times 10^6$ tons/yr [11]. Commercially, the majority of synthetic phenols are produced from the cumene (or Hock) method. This three step synthesis includes the oxidation of cumene to an unstable hydroperoxide intermediate. The concentration of hydroperoxide must be maintained at a low level for safety and to minimize byproduct formation. Also, this reaction is wasteful from an atom economy standpoint because equal moles of acetone and phenol are produced. If the demand for acetone meets the demand for phenol, then the reaction would be optimal. Several other oxidative routes to phenols have been explored to improve upon the
cumene synthesis [12-16], but the focus of this chapter will be on non-oxidative synthesis.

Non-oxidative routes to phenols include the Dow and Bayer process which couples arylhalides with bases under severe conditions (T=360-390°C and P=280-300 bar) [11]. Coupling reactions are atom efficient and thereby generate little waste (although salts are produced as byproducts). However, the main drawbacks to this method are high energy consumption, need for an acidic neutralization workup step, and a costly initial investment on equipment that is capable of handling severe conditions. Recently, Buchwald et al. developed a palladium catalyzed route to phenols and aromatic ethers via carbon-oxygen coupling of aryl halides with hydroxide salts using mild reaction conditions [17]. Catalyst addition drastically reduces reaction conditions from 390°C and 300 bar to lower than 100°C and atmospheric pressure. The proposed catalytic mechanism, shown in Figure 3.5, combines an oxidative addition, displacement of halide with hydroxide, and reductive elimination to produce either phenols (black path) or aromatic ethers (red path). A biphasic water/organic solvent system was used for reactions, where the inorganic salt remained in the water phase and the aryl halide partitioned into the organic phase. A few solvents were examined and reaction selectivity to either phenol or ether was highest when 1,4-dioxane was used as the organic solvent component (other organic solvents tested were isopropylalcohol and t-amylalcohol). This result is promising as 1,4-dioxane is a component of the POTS system explored herein. The authors do not mention whether mass transfer, due to heterogeneous reaction conditions, is limiting. Also, no method for catalyst recycle was addressed. The ability for recycle would enhance the process’ economic feasibility and industrial use.
Therefore, we have implemented POTS to advance the application of palladium based catalysts for C-O coupling reactions to produce phenols and aromatic ethers. OATS is not an option for the reaction of interest because at low concentrations the reactant molecules disrupt the system’s phase behavior and induce heterogeneity between the organic and aqueous phase (system that Buchwald used) and therefore a homogeneous reaction phase is never obtained.

PEG has been used as an environmentally friendly recyclable media for palladium catalyzed Suzuki C-C coupling reactions, ruthenium catalyzed hydrogenations, and diacetate deprotections [18-20]. In a related case, Jessop et al. developed a PEG/scCO₂ solvent system for a rhodium catalyzed hydrogenation reaction and recycled the catalyst five times without loss of catalytic activity by extracting products into sweeping scCO₂ [21]. A review of reactions run in PEG was published in 2005 by Rogers et al [22].

![Figure 3.5. Catalytic mechanism for C-O coupling of aryl halides with hydroxide salts](image)

Figure 3.5. Catalytic mechanism for C-O coupling of aryl halides with hydroxide salts
In phenol synthesis, workup of phenoxide to phenol involves a post-reaction neutralization. Neutralization is needed because the pKa of the substituted phenols is lower than the reaction medium pH. For example, the pKa of phenol is 10 which is a similar value to most other phenols. Not only does this workup produce additional acidic waste, but strong acids can deactivate the catalyst and prevent its reuse. The use of POTS for catalyst recycle necessitates the removal of harsh acids from the process. We solve this problem by utilizing the water (a reaction byproduct/co-solvent)-carbon dioxide (separation anti-solvent) equilibrium with carbonic acid. This equilibrium is well-known and has been used in acid catalysis [23]. Here we utilize carbonic acid for post-reaction workup. The need for harsh workup conditions is eliminated and our catalyst remains active. In addition, any residual acid is easily and benignly reversed upon venting carbon dioxide. CO$_2$ serves a dual purpose in our system by generating a benign in-situ reversible acid and inducing a biphasic liquid-liquid system for facile product/catalyst separation.

3.2. Materials

The following materials were degassed by bubbling either nitrogen or argon through the liquids for 30 minutes: PEG 400 (Sigma-Aldrich), methyl capped PEG 400 (Fluka), 1,4-dioxane (Fischer Scientific, 99.9%), water (J.T. Baker, HPLC grade), 1-bromo-3,5-di-methylbenzene (Acros Organics, 98%), and 2-chloro-p-xylene (Sigma-Aldrich, 99.0+%). Carbon dioxide was SFC grade (Airgas, 99.999%) and further purified via a Matheson gas purifier and filter cartridge (Model 450B, Type 451 filter). The following materials were used as received from the suppliers:
tris(dibenzylideneacetone) dipalladium (Pd$_2$dba$_3$) (Strem, 21% Pd), 2-di-tert-butylphosphino-2’,4’,6’-triisopropylbiphenyl (L1) (Sigma-Aldrich, 97%), 1-bromo-3,5-di-tert-butylbenzene (Alfa Aesar, 99%), 2’-dicyclohexylphosphino-2,6-dimethoxy-3-sulfonato-1,1’-biphenyl hydrate sodium salt (L3) (Strem, >98%), [2-(dicyclohexylphosphino)ethyl]trimethylammonium chloride (L2) (Sigma-Aldrich), 2-(diphenylphosphino)ethylamine (L4) (Sigma-Aldrich, >95%), 2,5-di-methylphenol (Sigma-Aldrich, >99%), potassium chloride (J.T. Baker), 2,4-di-tert-butylphenol (Alfa Aesar, 97%), phenol redistilled (Sigma-Aldrich, >99%), o-tolyl-3,5-xylyl ether (TCI America, >97%), o-cresol (Sigma-Aldrich, >99%), cesium carbonate, sodium phosphate, nitrogen (Airgas, Ultra high purity >99.999%), argon (Airgas, Ultra high purity >99.999%), and hydrogen chloride technical purity (Matheson Tri-gas, 99%). Potassium hydroxide pellets (KOH, EMD Chemicals) were ground into fine particles before use.

3.3. Experimental Methods

3.3.1 Reaction of 2-chloro-p-xylene and potassium hydroxide to produce 2,5-di-methylphenol in POTS

Solid components including potassium hydroxide (3 equiv., 160 mg, 3M concentration), Pd$_2$dba$_3$ (0.02 equiv., 18.3 mg), and monophosphine ligand (L1: 0.08 equiv., 34.0 mg; L2: 0.08 equiv., 25.6 mg; L3: 0.08 equiv., 41.0 mg; L4: 0.08 equiv., 18.4 mg) were added to glass Slenck line tubes equipped with magnetic stir bars and degassed. The metal to ligand molar ratio was maintained at 1:2 for all experiments. PEG 400 (1.0 mL), either alcohol or methyl capped, was then introduced via an air-tight degassed syringe. The reaction tubes were then temperature controlled at 100°C in an oil bath which was heated and stirred using a hot plate. The top of the tubes were water-
cooled to condense any vapor generated during the reaction. After an hour at 100ºC, 2-chloro-p-xylene (1 equiv., 0.13 mL, 1M concentration) was added to begin the reaction. Post-reaction, the glass tubes were cooled to room temperature and the mixture was neutralized by one of the following techniques: adding 1M hydrochloric acid until a neutral pH, bubbling hydrogen chloride for a few minutes, or bubbling carbon dioxide for 30 minutes. The products were then extracted into diethyl ether and analyzed using gas chromatography-mass spectroscopy (GCMS) (GC-2010 Shimadzu with a GCMS-QP2010S detector and SHR5XLB column or Agilent GC-HP 6890 with a GCMS-HP 5973 detector and HP-5MS column).

For reaction recycles, following decantation of the ethyl ether phase, KOH was reintroduced (3 equiv., 160 mg) into the reaction tubes which were reset into the oil bath, at 100ºC. 2-chloro-p-xylene (1 equiv., 0.13 mL) was immediately added to restart the reaction.

3.3.2 Reaction of 1-bromo-3,5-di-tert-butylbenzene with potassium hydroxide to produce 3,5-di-tert-butylphenol in POTS

Solid components including potassium hydroxide (3 equiv., 660 mg, 3M concentration), Pd₂dba₃ (0.02 equiv., 77 mg), L1 (0.08 equiv., 136 mg), and 1-bromo-3,5-di-tert-butylbenzene (1 equiv., 1.04 g, 1M concentration) were added to glass carousel reaction tubes (radleys carousel 12 plus reaction station as pictured in Figure 3.6) equipped with magnetic stir bars and degassed. PEG 400 (4.0 mL/100 wt%, 2.8 mL/72 wt%, or 2.3 mL/60 wt%), 1,4-dioxane (0.0 mL/0 wt%, 1.2 mL/28 wt%, or 1.0 mL/24 wt%), and HPLC water (0.0 mL/0 wt%, 0.0 mL/0 wt%, or 0.7 mL/16 wt%) were then introduced via an air-tight degassed syringe to keep the total solvent volume at 4 mL.
The carousel was temperature controlled at 80ºC for the overnight reaction. Work-up was performed by either adding 8 mL of 1M hydrochloric acid or bubbling carbon dioxide for 30 minutes. The products were extracted into 8 mL of diethyl ether and analyzed using the GCMS previously described. All reactions were run in triplicate.

Figure 3.6. radleys’ carousel 12 plus reaction station

3.3.3 Reaction of 2-chloro-p-xylene with basic salts to produce 1,1’-oxybis[2,5-dimethyl]benzene

Solid components including salts (3 equiv., CsCO₃ 1.0 g or Na₂HPO₄ 430 mg, 3M concentration), Pd₂dba₃ (0.02 equiv., 18.3 mg), and L1 ligand (0.08 equiv., 34 mg) were added to glass Slenck line tubes (as previously described) and degassed. PEG 400 (1.0 mL) and water (0.5 mL) were then introduced via an air-tight degassed syringe. After an hour at 100ºC, 2-chloro-p-xylene (1 equiv., 0.13 mL, 1M concentration) was added to begin the reaction. Post-reaction, the glass tubes were cooled to room temperature and the mixture was neutralized by adding 1M hydrochloric acid until a neutral pH was
reached. The products were then extracted into diethyl ether and analyzed using GCMS (as described above).

3.3.4 Reaction of 2-chloro-p-xylene with phenol and basic salts to produce 2,5-dimethyl-1-phenoxybenzene

Solid components including inorganic salts (1 equiv., KOH 52 mg, CsCO₃ 365 mg, or Na₂HPO₄ 157 mg, 1M concentration), phenol (1 equiv., 96 mg, 1M concentration), Pd₂dba₃ (0.02 equiv., 18.3 mg), and L₁ ligand (0.08 equiv., 34 mg) were added to glass Slenck line tubes (as previously described) and degassed. PEG 400 (1.0 mL) was then introduced via an air-tight degassed syringe. After an hour at 100ºC, 2-chloro-p-xylene (1 equiv., 0.13 mL, 1M concentration) was added to begin the reaction. Post-reaction, the glass tubes were cooled to room temperature and the mixture was neutralized by adding 1M hydrochloric acid until a neutral pH was reached. The products were then extracted into diethyl ether and analyzed using GCMS (as described above).

3.3.5 Reaction of 1-bromo-3,5-di-methylbenzene and o-cresol with potassium hydroxide to produce o-tolyl-3,5-xylyl ether in POTS

Solid components including potassium hydroxide (1 equiv., 220 mg, 1M concentration), o-cresol (1 equiv., 420 mg, 1 M concentration), Pd₂dba₃ (0.02 equiv., 77 mg), and L₁ ligand (0.08 equiv., 136 mg) were added to glass carousel reaction tubes (as previously described) and degassed. PEG 400 (4.0 mL/100 wt%, 2.8 mL/72 wt%, or 2.3 mL/60 wt%), 1,4-dioxane (0.0 mL/0 wt%, 1.2 mL/28 wt%, or 1.0 mL/24 wt%), and HPLC water (0.0 mL/0 wt%, 0.0 mL/0 wt%, or 0.7 mL/16 wt%) were then introduced via an air-tight degassed syringe to keep the total solvent volume at 4 mL. The carousel was
then temperature controlled at 80ºC. The top of the tubes were water-cooled to condense any vapor generated during the reaction. After an hour at 80ºC, 1-bromo-3,5-di-methylbenzene (1 equiv., 0.5 mL, 1M concentration) was added to begin the overnight reaction. Work-up of the products was performed according to the procedure outlined for 3,5-di-<i>tert</i>-butylphenol production.

3.3.6 Separation of 3,5-di-<i>tert</i>-butylphenol using POTS

The partitioning of 2,4-di-<i>tert</i>-butylphenol, a structural isomer of 3,5-di-<i>tert</i>-butylphenol, between the dioxane-rich and PEG-rich liquid phases was run in a 60 mL high pressure Jerguson® cell (apparatus shown in Figure 3.7). The cell was first evacuated. 1,4-Dioxane (4 mL/26 wt%), PEG 400 (9 mL/60 wt%), HPLC water (2 mL/14 wt%), and 2,4-di-<i>tert</i>-butylphenol (0.5 M concentration, 650 mg) were pre-mixed and added to the cell via an air-tight syringe. The cell temperature was monitored <i>in-situ</i> with a thermocouple (Omega type K) calibrated against a platinum RTD (Omega PRP-4) with DP251 Precision RTD Benchtop Thermometer (DP251 Omega), providing an accuracy of ±0.2 K. CO₂ was added to the cell by an ISCO syringe pump (Model 500D) to the desired separation pressure. Pressure in the cell was measured using a Druck pressure transducer (PDCR 910) and read-out box (DPI 260) calibrated against a hydraulic piston pressure gauge (Ruska, GE Infrastructure Sensing) with an uncertainty of ±0.1 bar. After equilibrium was ascertained, three 0.5 mL samples were taken from each liquid phase using a sample loop. The samples were rinsed and diluted in methanol and then analyzed by GCMS (as previously described). The average value of the three samples is reported.
3.3.7 Separation of \textit{o}-tolyl-3,5-xylyl ether using POTS

The partitioning of \textit{o}-tolyl-3,5-xylyl ether (0.5 M concentration, 1.2 mL) between the PEG-rich and dioxane-rich phases was determined using the experimental procedure and apparatus previously outlined for the separation of 2,4-di-\textit{tert}-butylphenol using POTS. The average value for the three samples is reported.

3.3.8 Separation of PdL\textsubscript{12} using POTS

The partitioning of the catalyst, PdL\textsubscript{12}, between the PEG-rich and dioxane-rich phases was determined using the experimental procedure and apparatus as previously outlined. L1 (20 mM, 110 mg) and Pd\textsubscript{2}dba\textsubscript{3} (5 mM, 66 mg) were mixed and heated to 80°C for 30 minutes in PEG 400, 1,4-dioxane, and HPLC water prior to addition into the cell. Sample concentrations were determined by ICP-MS and ICP-OES analyses (Columbia Analytical Services- lower detection limits 2 ppm and 20 ppm, respectively).
Figure 3.7. Jerguson® cell apparatus where dotted lines represent the temperature-controlled region.
3.3.9 Sweeping Carbon Dioxide Extraction of 2,4-di-methylphenol and \( o - \) tolyl-3,5-xylyl ether from PEG 400

Experiments were performed according to the method outlined by Brennecke et al. in a 100 mL Parr autoclave equipped with overhead stirring [24]. The Parr was loaded with 10 mL of PEG 400, 0.1 M potassium salt byproduct (exceeds the solubility limit in PEG 400), 0.5 M solute molecule and 5.8 MPa CO\(_2\). The Parr was then temperature controlled at 30ºC with a heating mantle. 1.4 bar samples of the vapor phase were extracted via a six-way, 0.5 mL sample loop every 20 minutes and bubbled through and rinsed with methanol to extract solute molecules. After each sample was collected, the Parr was reloaded to its original pressure, 5.8 MPa, with and ISCO syringe pump. The final sample was then analyzed by UV-Vis (2,4-di-methylphenol) or GCMS (\( o - \) tolyl-3,5-xylyl ether) and concentration was established by comparison with calibration curves (See Appendix C). The moles of CO\(_2\) passed through the system were calculated using the Span-Wagner equation of state [25]. The volume of the vapor phase was determined from subtracting the total cell volume from the liquid phase volume which was calculated from phase behavior data on the volume expansion of PEG 400 at the temperature (30ºC) and pressure (5.8 MPa) of the experiment (approximately 58 vol\% expansion).

3.4. Results

3.4.1 C-O coupling to produce phenols

The reaction between 2-chloro-\( p - \)xylene and potassium hydroxide, shown in Scheme 3.1, was run in PEG 400 using \( \text{Pd}_2\text{dba}_3 \) and L1 (structure shown in Figure 3.8) as the catalyst. This reaction was selected from Buchwald’s set due to a high product yield,
use of a commercially available ligand, and non-polar, CO₂-philic, side groups on the
desired product, 2,5-dimethylphenol. In addition, ortho-substitutions on the aryl halide
increase the rate of the reductive elimination step in the mechanistic pathway [17].
Initially, 1,4-dioxane and/or water were not added as co-solvents to PEG 400 in order to
independently assess the solvent power of PEG 400 for this reaction.

Scheme 3.1. Model reaction 1: Reaction of 2-chloro-p-xylene with potassium hydroxide to 2,5-
dimethylphenol

Figure 3.8. L1: 2-di-tert-butylphosphino-2’,4’,6’-triisopropylbiphenyl

When run overnight and neutralized with dilute hydrochloric acid, model reaction
1 reached 100% conversion with 100% selectivity to 2,5-dimethylphenol. The rate of this
reaction is extremely fast: the 15 minute reaction sample reached 100% conversion with
92% selectivity to 2,5-dimethylphenol (the byproduct detected was p-xylene: which is
formed from the reduction of the aryl halide by the solvent [26-27]). With methyl-capped PEG 400 as the solvent, the overnight reaction also reached 100% conversion with 100% selectivity to 2,5-dimethylphenol. The benefit of using methyl-capped PEG is that it is less reactive. For example, end-capped PEG would prohibit the formation of the side product, \( p \)-xylene, as was verified by experiments. However, an economic optimization may prove that the unprotected PEG is the preferred solvent.

Workup using dilute hydrochloric acid prohibits PEG recycle due to the accumulation of water in the PEG phase over time. Gaseous hydrogen chloride (HCl) was examined as a replacement neutralization material to overcome this dilemma. Table 3.1 shows the results for three recycles after a two hour per run reaction period using HCl\(_{\text{g}}\) to protonate the phenoxide to 2,5-dimethylphenol. These results show that gaseous protonation produces the desired phenol (cycle 1), but prevents catalyst recycle (cycle 2 and 3). Conversion decreased from 92% to 37% by only the third cycle. Additionally, HCl\(_{\text{g}}\) is extremely toxic and requires careful handling and specialized corrosive-resistant equipment.

<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>97</td>
</tr>
</tbody>
</table>

We utilized the *in-situ* reversible acid formed upon reaction of CO\(_2\) with water, carbonic acid, to replace the costly traditional acidic neutralization step and maintain an active catalyst. Water was added as a co-solvent (concentration of 5M, 0.1 mL) to PEG 400 to increase the concentration of carbonic acid formed. After a two hour reaction of
2-chloro-\textit{p}-xylene with two equivalents of KOH, CO\textsubscript{2} was bubbled through the reaction mixture for 30 minutes and a conversion of 98\% was obtained. Even with three equivalents of KOH, CO\textsubscript{2} neutralization was successful: two hour conversion of 100\% and a 2,5-dimethylphenol selectivity of 95\%. Subsequently, a two hour per run recycle experiment using carbonic acid neutralization was carried out (See Table 3.2). Only two cycles were needed as it was apparent that our conversion was remaining high, unlike the case with hydrogen chloride gas.

\begin{table}[h]
\begin{center}
\begin{tabular}{|c|c|}
\hline
Cycle Number & Conversion (\%) \\
\hline
1 & 99 \\
2 & 98 \\
\hline
\end{tabular}
\end{center}
\caption{Model reaction 1 recycles using carbonic acid for acidification}
\end{table}

For recycle and reuse, the catalyst must remain in the polar, PEG-rich, solvent phase (See Figure 3.2). Structurally modifying L1 with polar side groups will increase the probability that the catalyst, PdL\textsubscript{12}, will partition into the PEG-rich phase. Three polar monophosphine L1 variations, L2-L4, were explored. Two of these ligands are salts (Figure 3.9a and Figure 3.9b) and one forms a salt upon reaction with CO\textsubscript{2} (Figure 3.9c and Scheme 3.2). The reaction of L4 with CO\textsubscript{2} was evidenced by \textsuperscript{13}C NMR as shown in Figure 3.10. Unfortunately, with these ligands, 2,5-dimethylphenol was not formed in the two hour reaction time frame.
Figure 3.9. Monophosphine ligands: 
6a) [2-(dicyclohexylphosphino)ethyl]trimethylammonium chloride 
6b) 2'-dicyclohexylphosphino-2,6-dimethoxy-3-sulfonato-1,1'-biphenyl hydrate sodium salt 
and 6c) 2-(diphenylphosphino)ethylamine
Scheme 3.2. Reversible reaction of 2-(diphenylphosphino)ethylamine with carbon dioxide

Figure 3.10. $^{13}$C NMR spectra of 2-(diphenylphosphino)ethylammonium 2-(diphenylphosphino)ethyl carbamate
The reaction between 1-bromo-3,5-di-tert-butylbenzene and KOH, shown in Scheme 3.3, was examined as a second model reaction. In this reaction, 2-chloro-p-xylene’s methyl groups are substituted with tertiary butyl groups. Overnight reactions were run at 80ºC in three different solvent environments: PEG 400, PEG 400 (72 wt%)/1,4-dioxane (28 wt%), or PEG 400 (60 wt%)/1,4-dioxane (24 wt%)/water (16 wt%). Conversion and selectivity (after aqueous HCl workup) for these experiments are shown in Table 3.3 and Figure 3.11. The side products detected were 3,5-di-tert-butylbenzene and 3,3’-5,5’-tetra-tert-butylphenylether. Higher conversions were reached in the solvent systems without water; however, as conversion increased, selectivity suffered. The substrate, 3,5-di-tert-butyl benzene, does not have any ortho-substituted side groups, which are known to increase the rate of reductive elimination (step three in the catalytic mechanism) [17]. The lack of an ortho-group may contribute to the increased side product production and subsequent lower specificity of this reaction for phenol when compared with the reaction between 2,5-di-methylbenzene and KOH. Also, bromides are more reactive than chlorides. Reactivity differences may affect the rate of oxidative addition and hydroxide displacement of the halide (steps one and two in the catalytic mechanism). The symmetrical ether is seen as a byproduct to the second model reaction whereas this product was not detected for the ortho,meta-di-methyl substituted reactions (model reaction 1).
Scheme 3.3. Model reaction 2: Reaction of 1-bromo-3,5-di-tert-butylbenzene with potassium hydroxide to form 3,5-di-tert-butylphenol

Table 3.3. Conversion and selectivity of model reaction 2 in various solvent environments after an overnight reaction at 80°C

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG 400</td>
<td>100±0</td>
<td>60±6</td>
</tr>
<tr>
<td>PEG 400/1,4-Dioxane</td>
<td>100±0</td>
<td>44±4</td>
</tr>
<tr>
<td>PEG 400/1,4-Dioxane/Water</td>
<td>80±7</td>
<td>68±2</td>
</tr>
</tbody>
</table>

Figure 3.11. Conversion and selectivity of model reaction 2 in various solvent environments after an overnight reaction at 80°C
The use of CO₂ to generate *in-situ* carbonic acid for product protonation was tested using the ternary solvent system consisting of PEG 400/1,4-dioxane/water. This novel workup method proved efficient as the overnight reaction showed 76% conversion and 71% selectivity to 3,5-di-tert-butylphenol (standard deviation of 1% and 4%, respectively). These values are consistent with those obtained when using the traditional neutralization (80% conversion and 68% selectivity).

3.4.2 C-O coupling to produce aromatic ethers

We extend the toolbox of C-O coupling reactions in POTS to include reactions of aryl halides with hydroxide salts to produce aromatic ethers. This product is kinetically unfavorable for the reactions previously discussed due to the slower attack of *in-situ* generated KOAr vs. KOH in the catalytic cycle (red vs. black path in Figure 3.5). However, Buchwald reported on the coupling of aryl halides with other bases, such as cesium and potassium carbonate, to exclusively form symmetric aromatic ethers [17]. The competing β-hydrogen elimination pathway (as seen with aryl aromatic ether formation), is eradicated due to the lack of a β-hydrogen on the hydroxide anion; however, an aryl halide reduction to a substituted benzene remains a possible side reaction. Consequently, the reaction of 2-chloro-\textit{p}-xylene to 1,1’-oxybis[2,5-dimethyl]benzene in PEG 400 was run for five hours using the same conditions and concentrations as previously described for the reaction of 2-chloro-\textit{p}-xylene to 2,5-dimethylphenol with the difference being the basic salts used (See Scheme 3.4). While no reaction to 1,1’-oxybis[2,5-dimethyl]benzene was seen upon reaction with Na₂HPO₄, reaction with CsCO₃ achieved 81% conversion of starting material with only a 7% selectivity to the desired ether product, 1,1’-oxybis[2,5-dimethyl]benzene. The reaction
between arylhalides and KOH to form ethers was revisited. When the molar ratio of 2-chloro-\textit{p}-xylene to KOH was 1:0.5 (standard reaction conditions call for 1:3), 1,1’-oxybis[2,5-dimethyl]benzene was formed. For this five hour reaction, the conversion obtained was 51% and the selectivity to 1,1’-oxybis[2,5-dimethyl]benzene was 42%. Therefore, as the ratio of aryl halide to KOH is increased, the selectivity to ether is increased. The opposite trend is seen for the selectivity to phenol. One can tailor this ratio in order to obtain the preferred product, either phenol or ether.

![Image of reaction scheme](image)

\textbf{Scheme 3.4. Reaction of 2-chloro-\textit{p}-xylene with basic salts to produce 1,1’-oxybis[2,5-dimethyl]benzene}

Due to the limited yield of desired product, the synthetic route was altered. A phenol was added to the solvent mixture containing the basic salts prior to addition of the aryl halide reagent (Scheme 3.5). The phenol reacts with the base to produce the corresponding phenoxide, which then reacts readily with the aryl halide. This synthetic method follows the steps of Williamson ether synthesis. The Williamson technique allows for the selective production of either asymmetric or symmetric aromatic ethers. Three bases, KOH, CsCO\textsubscript{3}, and Na\textsubscript{2}HPO\textsubscript{4}, were examined to determine which was most effective for the reaction of 2-chloro-\textit{p}-xylene and phenol to 2,5-dimethyl-1-phenoxybenzene (example reaction with KOH shown in Scheme 3.5). After three hours at 100°C, Table 3.4 shows that KOH resulted in both the highest conversion and ether
selectivity (side product was 2,5-di-methylphenol). Conversion was based on the disappearance of 2-chloro-\(p\)-xylene rather than the disappearance of phenol. In order to improve 2,5-dimethyl-1-phenoxybenzene specificity, the equivalents of KOH were varied between 0.1 and 0.9. Figure 3.12 shows that as the relative amounts of KOH increases, the selectivity decreases whereas the conversion increases. Both trends are linear and follow what is expected for base or acid catalyzed reactions. Again, the dependence of selectivity on the ratio of aryl halide to hydroxide is highlighted.

![Scheme 3.5. Reaction of 2-chloro-\(p\)-xylene with phenol and potassium hydroxide](image)

<table>
<thead>
<tr>
<th>Base (1 equiv.)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>69</td>
<td>75</td>
</tr>
<tr>
<td>CsCO(_3)</td>
<td>15</td>
<td>38</td>
</tr>
<tr>
<td>Na(_2)HPO(_4)</td>
<td>No product</td>
<td>No product</td>
</tr>
</tbody>
</table>
A third model reaction, between \( o \)-cresol, 3,5-dimethylbromobenzene, and KOH, was explored (See Scheme 3.6). After running overnight in three different solvent environments- PEG 400/1,4-dioxane/water (60, 24, 16 wt% respectively), PEG 400/1,4-dioxane (72, 28 wt% respectively), and PEG 400- the products were neutralized with 1M HCl (needed to quantify phenol produced as a side-product) and extracted into ethyl ether. The results are shown in Table 3.5 and Figure 3.13. Both conversion and selectivity were highest in the ternary solvent system. The side products detected were \( m \)-xylene, 3,5-di-methylphenol, 3,5,3’,5’-tetra-methylbiphenyl, and 1,1’-oxybis[3,5-dimethyl]benzene.
Scheme 3.6. Model reaction 3 of \( o \)-cresol with 1-bromo-3,5-di-methylbenzene and potassium hydroxide

Table 3.5. Selectivity and conversion of model reaction 3 after reaction overnight at 80°C in different solvent environments

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG 400</td>
<td>60±6</td>
<td>64±2</td>
</tr>
<tr>
<td>PEG 400/1,4-Dioxane</td>
<td>64±10</td>
<td>62±1</td>
</tr>
<tr>
<td>PEG 400/1,4-Dioxane/Water</td>
<td>81±9</td>
<td>66±6</td>
</tr>
</tbody>
</table>

Figure 3.13. Selectivity and conversion of model reaction 3 after reaction overnight at 80°C in different solvent environments
3.4.3 Sweeping CO₂

CO₂, in the absence of a co-solvent, was tested to determine its ability to extract substituted phenols or aromatic ethers from PEG 400. Experiments were performed by sweeping CO₂ over the liquid phase containing PEG 400 and solute. The solubility of various phenols in CO₂ has previously been examined. For example, at 308 K and 12 MPa the mol fraction solubility of 2,5-di-methylphenol (product of model reaction 1) in CO₂ is 7.7*10⁻³ [28].

2,4-Di-tert-butylphenol and o-tolyl-3,5-xylyl ether were used as model phenol and ether substrates, respectively. 2,4-Di-tert-butylphenol required 26.5 mol of CO₂ per mol of solute in solution to recover 0.04 wt% of the phenol from PEG 400 at 30ºC and 5.8 MPa. Assuming a linear trend [24], it would require 4.9*10⁴ mol of CO₂/mol solute to eradicate 80 wt% of 2,4-di-tert-butylphenol into the vapor stream. Likewise, o-tolyl-3,5-xylyl ether used 50.8 mol of CO₂ per mol of solute in solution to remove 0.01 wt% from PEG 400 at 30ºC and 5.8 MPa. Assuming a linear trend, o-tolyl-3,5-xylyl ether requires 3.8*10⁵ mol of CO₂ per mol of solute to extract 80 wt % of its original loading into the CO₂ stream. An enormous amount of CO₂ is required to recover a reasonable amount of phenol or ether. These results are of the same order of magnitude as those found by Brennecke et al. when extracting solutes from imidazolium based ionic liquids with sweeping CO₂ [24]. Therefore, it was concluded that for the applications presented in this chapter, the sweeping CO₂ method is not practical and a co-solvent is needed.
3.4.4 Partitioning

- 2,4-Di-tert-butylphenol

The direct sampling method was used to probe each liquid phase and determine the partition coefficient of the solute between these phases. The direct sampling method has been verified against the synthetic method, which does not require system disruption [29-30]. The partition coefficient provides a guide as to the separation efficiency of the process. The ternary solvent system of PEG 400 (60 wt%) / 1,4-dioxane (26 wt%) / water (14 wt%) was used to provide improved partitioning. The partitioning of 2,4-di-tert-butylphenol, a structural isomer of the product from model reaction 2, between product (gas-expanded 1,4-dioxane) and catalyst phases (PEG 400/water) was determined at room temperature as a function of pressure ranging from 4.2 to 4.7 MPa (See Figure 3.14). Partition coefficient, \( K \), was defined as the concentration of solute in the organic phase divided by the concentration of solute in the PEG phase. 2,4-Di-tert-butylphenol’s partitioning into the dioxane-rich phase is highest at pressures of CO\(_2\) near the phase split, 4.2 MPa (See Figure 3.15). This is due to a dilution effect, where adding more CO\(_2\) preferentially expands the organic phase thereby decreasing the concentration of phenol in this phase. The purity of each liquid phase is not extremely pressure dependent and therefore the trend cannot be explained by this reasoning (See Figure 3.4). However, the partition coefficient reached a maximum of unity. Visually, the partition coefficient appears to be much higher than one (based on Figure 3.15). The discrepancy may be due to the larger volume of the PEG-rich phase when compared to the dioxane-rich phase which makes the partition coefficient low. Correcting for the volume of each phase, by
measuring the volume expansion as a function of CO₂ pressure, may confirm this hypothesis.

Figure 3.14. Partition coefficient for 2,4-di-tert-butylphenol between gas expanded 1,4-dioxane and PEG400/water (error bars represent root mean square deviations) at 20°C

Figure 3.15. High pressure view of homogeneous system of PEG400/1,4-dioxane/water and 2,4-di-tert-butylphenol (left) and heterogeneous separation (right)
The partitioning of o-tolyl-3,5-xylyl ether, between the dioxane-rich and PEG-rich liquid phases was determined by direct sampling at 20°C and 40°C as a function of pressure (after the phase split) and water concentration. Figure 3.16 displays these results for pressures ranging from 4 to 8 MPa. In the ternary solvent system (PEG 400 (60 wt%)/1,4-dioxane (26 wt%)/water (14 wt%)), the same pressure trend was detected as with 2,4-di-tert-butylphenol, where an increased CO₂ pressure decreased the partition coefficient. In this solvent system and slightly above the phase split pressure, the product is four times more concentrated in the organic-rich phase than in the PEG-rich phase. The addition of water as a co-solvent increased the partitioning of the product into the organic-rich phase by a factor of four. We attribute this to: 1) an increased polarity of the polar phase 2) hydrogen bonding between PEG and water which disrupts the interactions between PEG and the solute molecule and/or 3) 2 mL increased volume of the PEG phase by water (dilution effect). The pressure trend reverses when minimal water is present because both PEG and dioxane expand with CO₂. However, when water is present in co-solvent amounts, the PEG-rich phase expands modestly when compared with the dioxane-rich phase because of the limited solubility of CO₂ in water. Figure 3.16 also indicates that the partition coefficient increases at lower temperatures. This may be due to a larger volume expansion disparity between the dioxane-rich and PEG-rich phases at higher temperatures or to an improved phase separation at lower temperatures [10]. The phase behavior of PEG 400/1,4-dioxane/CO₂ at 25°C vs. 40°C shows that although the organic-rich phase’s purity is not temperature dependent, the PEG-rich phase has an increasing organic content with temperature (5 wt% at 25°C and 6
The PEG-rich phase also has an increasing CO₂ content with increasing temperature, which jumped from 28 wt% at 25°C and 6 MPa to 41 wt% at 40°C and 8 MPa. Therefore, the increased organic nature of the PEG-rich phase may be responsible for the decreased partition coefficient as temperature is increased. Again, the importance of phase behavior towards understanding the properties of the system is highlighted.

Figure 3.16. Partition coefficient of o-tolyl-3,5-xylyl ether between gas expanded 1,4-dioxane and PEG 400 (error bars represent root mean square deviations)
The separation of the catalyst, PdL1₂, from the organic-rich phase was determined at room temperature as a function of CO₂ pressures from 4.5 MPa to 4.8 MPa. The catalyst was premixed in the ternary solvent solution at 80°C for half an hour before injection into the pressure cell in order to mimic reaction conditions. The phase split observed is pictured in Figure 3.17. Figure 3.18 shows the results of these experiments in the solvent system consisting of PEG 400 (60 wt%)/1,4-dioxane (26 wt%)/water (14 wt%). At 4.7 MPa the catalyst is 27 times more concentrated in the solvent phase than in the product phase (calculated from 1/K). The limited solubility of the catalyst in the gas-expanded dioxane phase is most likely due to the non-polar, bulky side groups of L1 (See Chapter 5: RECOMMENDATIONS). The opposite partitioning trend of the products, 2,4-di-tert-butylphenol and o-tolyl-3,5-xylyl ether, and the catalyst, PdL1₂, with CO₂ pressure requires an overall process optimization to determine the most effective operating conditions.
Figure 3.17. High pressure view of PdL12 separation in POTS: top phase is 1,4-dioxane-rich and bottom phase is PEG-rich

Figure 3.18. Partition coefficient of PdL12 between gas-expanded 1,4-dioxane and PEG 400/water (error bars represent root mean square deviations)
3.5. Conclusions

We have shown the application of a novel tunable solvent system consisting of PEG 400, 1,4-dioxane, and carbon dioxide for coupling homogeneous catalysis with facile heterogeneous separation. The phase behavior for this system verifies an efficient phase split. We have specifically looked at applying this tunable system to the palladium catalyzed C-O coupling to produce phenols and aromatic ethers. This is the first report of the application of PEG-based tunable solvent systems. Reaction conversion and product specificity were high in our model systems. We were able to utilize CO$_2$ for two purposes: separation of the product phase from the catalyst phase, and generation of an *in-situ* acid for post-reaction workup to final product. While enhanced partitioning of the tested phenols into our product phase may not have been achieved, the model aromatic ether showed excellent results. In addition, POTS shows minimal catalyst leaching into our CO$_2$–expanded dioxane phase.
3.6. References


CHAPTER 4.  FUNCTIONALIZATION OF ETHYLENIC POLYMERS WITH SILANES

4.1. Introduction

Chemically functionalizing conventional polymers with alkoxy silanes enables facile crosslinking of these materials by simple exposure to water. Crosslinking enhances polymer properties including thermal stability and electrical resistance, and is therefore used to improve performance for applications such as coating wire cables and pipes. Towards this goal, we have investigated grafting alkoxy silanes onto polyethylene. From an industrial viewpoint, silane molecules are an inexpensive grafting selection. In addition, unlike maleic anhydride and acrylates, alkoxy silanes undergo almost no homopolymerization (an undesired side reaction). This was proven by 1) no reaction of vinylalkoxysilanes in the presence of radical initiators and 2) $^1$H NMR integration of the silane-grafted product (ratio of the hydrogens on the carbon adjacent to silicon vs. the alkoxy hydrogens) [1]. Due to the ubiquitous application of functionalized polymers, many researchers have explored grafting functional molecules, such as vinylsilanes [1-11], maleic anhydride [12-16] and acrylates [17-19], onto polyolefins. Still, a theoretical understanding of the mechanism and kinetics behind grafting reactions is lacking. This chapter focuses on elucidating the theory behind polymer grafting.

Three methods can be used to graft silanes onto polyethylene: peroxide initiation, UV initiation, or plasma initiation. Of these three, peroxide-initiated radical reactions are the most practical for large-scale use and therefore are of high industrial importance. The peroxide method’s main disadvantage lies in a wide distribution of grafted products.
Therefore, controlling the grafting distribution is difficult, but desired. Specifically, a minimal number of grafts per polymer chain is preferred. Fewer grafts per chain allows polymer crosslinking with efficient use of grafting material. The crosslinked, functionalized polymer possesses the desired physical properties with only a minimal amount of silane graft.

The radical reaction can take several pathways. These are pictured in Figure 4.1 and include an intramolecular hydrogen atom abstraction, an intermolecular hydrogen atom abstraction, or polymeric grafting. Literature points to intramolecular hydrogen atom abstraction as the major pathway. This suggests that as the radical is formed on one molecule, it propagates down the backbone of that molecule, rather than pulling a hydrogen of an adjacent molecule. Once on a given molecule, the radical can take several pathways. It can proceed by either a 1,3-shift, a 1,4-shift, or a 1,5-shift. The minimized configuration of the radical arbitrarily placed at position two is shown in Figure 4.2. The energy associated with this configuration is -1178.91009 au. Energetically a 1,3-shift is unfavorable, but both a 1,4 and 1,5-shift are possible (See Table 4.1). Literature precedent suggests a 1,5-shift as the predominant pathway.
Figure 4.1. Possible radical grafting mechanisms

Figure 4.2. On the top is the VTMS-g-dodecane radical in 2-position. The orbitals shown correspond to the SOMO (Single Occupied Molecular Orbital). On the bottom is the same VTMS-g-dodecane radical in 2-position.
Table 4.1. Minimized lower energy versus structure of the reaction intermediates

<table>
<thead>
<tr>
<th>Intermediate</th>
<th>Minimum energy (au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-VTMS-grafted dodecane</td>
<td>-1178.91009</td>
</tr>
<tr>
<td>1,3-shift radical</td>
<td>-1178.9017</td>
</tr>
<tr>
<td>1,4-shift radical</td>
<td>-1178.90334</td>
</tr>
<tr>
<td>1,5-shift radical</td>
<td>-1178.90478</td>
</tr>
</tbody>
</table>

Due to the analytical complexities associated with polymers containing a low grafterd content, many researchers have investigated model compounds to study grafting. We looked at heptane and dodecane as polyethylene model compounds. We chose tert-
butyl peroxide as the initiator due to its relatively long half-life: one hour at 150ºC (in solution with dodecane). For comparison, the half-life of dibenzoylperoxide, another commonly used initiator, is 1 hour at 92ºC (in solution with benzene). Long reaction times are amenable to facile kinetic studies. Also, tert-butyl peroxide can be safely handled. Vinyltrimethoxysilane (VTMS) was used as the grafting agent for all reactions.

The results presented in this chapter were obtained in collaboration with Dow Chemical Company. Their interests lie in using CO₂ to improve the processing and efficiency of polymer functionalization with silanes. Specifically, we hypothesize that CO₂ will contribute in three areas:

1) increase the solubility of the grafting material (VTMS) into the model compound,
2) lower the viscosity of the liquid phase, which may ameliorate mass transfer issues and ease extrusion processing, and
3) to change and/or control grafted product distribution.

Silanes have a limited solubility in polyethylene, and mass transfer may limit grafting reactions. Dense CO₂ is a polymer swelling agent and has been shown to carry molecules into a polymer matrix [20-22]. Further, silanes have a high affinity for CO₂,
and therefore their polymer solubilities should increase upon CO\textsubscript{2} addition. Because VTMS is miscible with the model alkanes explored, this aspect of CO\textsubscript{2} process improvement for polymer functionalization was not investigated, but will be crucial when extending the study to polymer systems. Also, because the viscosity of the model hydrocarbons is low when compared to typical polymer viscosities, viscosity as a function of CO\textsubscript{2} pressure was not directly explored, as this effect will be minimal. In addition, the decrease in polymer viscosity with CO\textsubscript{2} is well established in literature and therefore further verification may not be of central importance [23-24].

The efficiency of silane grafting as a function of CO\textsubscript{2} pressure has not been recorded. By tuning CO\textsubscript{2} pressure, we hoped to selectively decrease the degree of grafting per hydrocarbon chain. CO\textsubscript{2} is soluble in our model compound dodecane as well as in low density polyethylene (LDPE). The solubility of CO\textsubscript{2} at 200\textdegree C (radical reaction temperature) in LDPE is 5 wt\% [25]. The solubility of CO\textsubscript{2} in dodecane at 45\textdegree C is 0.3 wt\% [26]. The phase equilibria for dodecane/CO\textsubscript{2} shows that the dodecane phase is 38 wt\% CO\textsubscript{2} and the vapor phase is 99 wt\% CO\textsubscript{2} at 70\textdegree C and 100 bar [27]. The solubility of CO\textsubscript{2} in long chain alkanes at high temperatures has not been determined. Therefore, the future of this project will include using a McHugh cell apparatus to gather high temperature solubility information [28].

4.2. Experimental Methods

4.2.1 Materials

The following chemicals were stored in a nitrogen-filled glovebox until use: VTMS (Sigma Aldrich, 98%) and dodecane (Acros, 99%). Dodecane was further purified by washing with a concentrated mixture of sulfuric and nitric acids followed.
by potassium permanganate in sulfuric acid and copious water. The dodecane was then dried with magnesium sulfate and distillation purified. t-Butyl peroxide (Aldrich, 98%), phenyllithium (Alfa Aesar, 1.5-1.7 M in cyclohexane/ether), methyllithium (Sigma Aldrich, 1.6 M in diethyl ether), anhydrous heptane (Sigma Aldrich, 99%), tetrahydrofuran CHROMASOLV Plus for HPLC inhibitor free (Sigma Aldrich, >99.9%), and magnesium sulfate anhydrous (EMP Chemicals, >98%) were used as supplied. Carbon dioxide was SFC grade (Airgas, 99.999%) and further purified via a Matheson gas purifier and filter cartridge (Model 450B, Type 451 filter). Nitrogen (Airgas, Ultra high purity > 99.999%) was used as supplied.

4.2.2 Glassware Reactions

Dodecane (25 mL) and VTMS (5 wt%, 0.97 mL) were added into a round-bottom flask in the glovebox. The flask was then connected to a dry ice condenser and an argon line in a ventilated hood. The mixture was magnetically stirred. A solution of peroxide in dodecane was added so that the peroxide concentration was 750 ppm in the reaction mixture. A heating mantle was used to obtain the desired reaction temperature, 200°C. After reaction completion, the mixture was allowed to air cool to ambient temperature. Phenyllithium (4 equiv., 17 mL) was added and stirred in solution, typically for 24 hours. A saturated solution of ammonium chloride (10 mL) was used to quench the excess phenyllithium. The organic phase was separated from the aqueous phase and dried with magnesium sulfate. Before analysis, the sample was rotovaped to remove solvents and either Krugelrohr or short path distilled at 80°C. Samples were analyzed by gel permeation chromatography (GPC) (Water 2690 with two Varian Inc. columns PLgel 5μm and PLgel 3μm) using a UV detector (Water 996) with tetrahydrofuran (THF) as the
mobile phase (calibrated using polystyrene), matrix-assisted laser desorption/ionization (MALDI) mass spectrometer with a dithranol and AgTfa matrix (samples were sent to the Georgia Tech mass spec laboratory), and by $^1$H NMR and $^{13}$C NMR (Varian-Mercury VX400 MHz).

4.2.3 High Pressure Reactions

Dodecane reactions under gas pressure were run with the same chemical quantities and concentrations as glassware experiments. For reactions of heptane, heptane (25 mL) was added to VTMS (5 wt%, 0.93 mL) thereby using the same concentrations as dodecane experiments. A 316 stainless steel 100 mL Parr autoclave was used. The cell was evacuated prior to reagent addition. Reagents were introduced via an air-tight syringe. Gas pressure was introduced (either N$_2$ or CO$_2$) at ambient temperature, and the cell was then heated to the reaction temperature. Pressure was then further increased to reach the desired experiment value. After reaction, the cell was allowed to air cool to room temperature, and the vapor phase was bubbled through THF to collect any vapor-soluble reaction components. When CO$_2$ was used, the mixture was put under vacuum to ensure that all CO$_2$ was removed during venting. This eliminated the undesired reaction between CO$_2$ and PhLi. The remaining steps were performed following the procedure outlined for glassware experiments. Experiments were twice repeated to ensure reproducibility.
4.3. Results

4.3.1 Dodecane Model Reaction

Short straight chain alkanes were used as polyethylene mimics to ease analytical methods. Both heptane and dodecane were first reacted with VTMS, which was then capped with phenyl groups in order to increase the stability of the grafted product (Scheme 4.1). In glassware experiments, dodecane showed up to six grafts per molecule in the MALDI spectra. This result is consistent with literature and further verifies an intramolecular hydrogen atom abstraction as a contributing pathway as multiple grafts per molecule are not seen with an intermolecular path (See Figure 4.3). MALDI intensities give a semi-quantitative picture of the vinyltriphenylsilane (VTPS) grafted product mixture. The primary functionalized product has two silane groups attached per dodecane molecule based on the MALDI’s peak intensities. These results match those of the dodecane control experiment run in the Parr reactor, proving that the Parr’s material of construction did not affect the results.

Scheme 4.1. Two step radical initiated reaction between VTMS and alkanes
CO₂ was added to the dodecane reaction to determine if this small molecule would contribute to changing the distribution of reaction products. Three pressures of CO₂ were used: 70 bar, 100 bar, and 150 bar. By MALDI, the only change from the Parr control experiment was seen at the highest CO₂ pressure, 150 bar. In this case, only up to five grafts per molecule were seen on the product (See Figure 4.4). This finding is significant because fewer grafts per dodecane enable more efficient use of VTMS, therefore, only a few grafts per molecule are industrially desired. The MALDI spectrum also shows shadow peaks that follow each product peak by 46 amu. We are currently trying to conclude the cause of these peaks.
In contrast, GPC detected no change between any of the CO₂ reactions and the Parr control or glassware experiments (Figure 4.7 vs. Figure 4.5 or Figure 4.6). Table 4.2 shows that the percent change in the grafted product’s spectra between the Parr dodecane experiment both with and without CO₂ fell within experimental error. We attribute this to the GPC not detecting VTPS-g-dodecane with more than three grafts per chain, which is where we see the change in results. Therefore, MALDI provided the best picture into the product.
Mass:
1) 891 (3 grafts 1030)
2) 730 (2 grafts 743)
3) 519 (1 graft 457)
4) 310 (VTPS 286)
5) 199
6) 154 (dodecane 170)
7) 89
8) 61

Figure 4.5. GPC spectrum of dodecane glassware reaction

Mass:
1) 925 (3 grafts 1030)
2) 739 (2 grafts 743)
3) 519 (1 graft 519)
4) 352
5) 236 (VTPS 286)
6) 132 (dodecane 170)
7) 86

Figure 4.6. GPC spectrum of dodecane Parr control reaction
Figure 4.7. GPC spectrum of dodecane reaction in Parr autoclave with 150 bar CO₂

**Mass:**
1) 882 (3 grafts 1030)
2) 713 (2 grafts 743)
3) 503 (1 graft 456)
4) 313 (VTPS 286)
5) 227
6) 183 (dodecane 170)
7) 120
8) 78
Table 4.2. GPC results of VTPS-g-dodecane from 1) glassware 2) Parr control and 3) Parr with 150 bar CO2 experiments

<table>
<thead>
<tr>
<th>MW of product</th>
<th>Glassware</th>
<th>Parr control</th>
<th>% difference from glassware</th>
<th>Parr with 150 bar CO2</th>
<th>% difference from control</th>
</tr>
</thead>
<tbody>
<tr>
<td>891</td>
<td>925</td>
<td>3.8</td>
<td>882</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>730</td>
<td>739</td>
<td>1.2</td>
<td>713</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>519</td>
<td>519</td>
<td>0.0</td>
<td>503</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>352</td>
<td>13.5</td>
<td>313</td>
<td>11.1</td>
<td></td>
</tr>
<tr>
<td>199</td>
<td>236</td>
<td>18.6</td>
<td>227</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>154</td>
<td>132</td>
<td>14.3</td>
<td>183</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>89</td>
<td>86</td>
<td>3.4</td>
<td>120</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>Not seen</td>
<td>N/A</td>
<td>78</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>7.8</td>
<td>Average</td>
<td>6.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The change seen in the grafting distribution when high pressures of CO2 were used could be due to the following reasons:

1) a dilution effect from CO2 expanding the dodecane phase, thereby causing the concentration of the VTMS and peroxide in the liquid phase to decrease,

2) a change in solvent polarity due to CO2 dissolving into the dodecane phase,

3) head space pressure of CO2,

4) change in solvent viscosity with CO2,

5) or an altered radical reaction rate due to a change in the radical cage.

The change in dodecane’s polarity as a function of CO2 pressure was explored using Nile red as a polarity probe. A mixture of dodecane and Nile red was charged into a high pressure UV-Vis cell equipped with quartz windows. Figure 4.8 shows that although the concentration of Nile red decreased with increasing pressure due to dilution of the dye, the maximum absorbance of Nile red remained constant at 492 nm. This implies that the change in dodecane’s polarity is not significant enough (at the
temperature and pressures tested) to be detected by the probe, Nile red. Therefore, it is unlikely that polarity changes can explain the change in grafting distribution. The other possible causes of the product’s change are still under investigation.

![Figure 4.8. Nile red absorbance in CO2-expanded dodecane](image)

It was suspected that the standard literature procedure, which requires a 24 hour phenyllithium quench, did not replace all of the alkoxy groups on VTMS-g-dodecane. The incomplete reaction was observed from product decomposition over prolonged exposure to the atmosphere as well as small alkoxy peaks in the grafted products’ $^1$H NMR spectra. The steric bulk introduced by phenyl groups into the grafted molecules structure inhibits all methoxy groups from being protected. This hypothesis was experimentally proven by reacting the product with phenyllithium for an extended time period.

After reacting VTMS with dodecane following the standard procedure, however, using a 48 hour phenyllithium capping time, both a liquid and solid product were collected. The MALDI spectrum of the liquid looked as expected, with a distribution of
up to six grafts per dodecane, and the primary component containing two grafts per chain. However, as Figure 4.9 shows, the solid contained up to eight grafts, and the distribution is skewed towards a larger number of grafts per chain. This result proves that the literature accepted 24 hour capping reaction is not sufficient. Also, the presence of more than six grafts per chain suggests that in addition to the anticipated 1,5 intramolecular hydrogen atom abstraction, a 1,4 abstraction is a contributing pathway. The 1,4 radical pathway has not been highlighted in literature.

![Figure 4.9. MALDI spectrum of solid product collected after reaction of VTMS-g-dodecane with PhLi for 48 hours](image)

Due to the steric hindrance associated with phenyllithium and the length of time required for efficiently capping the product, a sterically unencumbered lithium salt, methyllithium (MeLi), was investigated. The reaction was run following the standard procedure with a 24 hour MeLi cap time. The $^1$H NMR spectrum of the grafted product (See Figure 4.10), shows peaks for dodecane, the CH$_2$ groups on the product adjacent to silicon, and the CH$_3$ groups on the product adjacent to silicon. By comparing the area of the CH$_3$-Si peak to the CH$_2$-Si peak, a nine to two ratio is obtained, which is what would
be expected for complete alkoxy substitution. However, other analytical techniques were complicated by the use of MeLi to replace PhLi. In particular, the molecular weight of the grafted products was too low for MALDI spectrometry, and the loss of aromatic groups prevents UV-detection methods. For these reasons, the use of MeLi was abandoned.

![Figure 4.10. ¹H NMR spectrum of VTMS-g-dodecane capped by MeLi](image)

4.3.2 Heptane Model Reaction

Heptane was used as a simple model for polyethylene in order to ease quantitative analysis. These reactions were run in a Parr reactor because the boiling point of the reagents is lower than the operating temperature. The standard reaction of heptane with VTMS surprisingly showed up to five grafts per heptane molecule in the MALDI spectra (Figure 4.11). This finding is consistent with an intramolecular 1,4 hydrogen shift contributing as a pathway. This pathway has not been shown as contributing in literature. Again, shadow peaks were seen; however, these peaks were 22 amu from the main peak.
Figure 4.11. MALDI spectrum of VTPS-g-heptane
4.4. Conclusions

In conclusion, we have demonstrated successful radical initiated grafting of silanes onto long chain hydrocarbon (polymer mimic) molecules. We have shown both experimentally and theoretically that a 1,4 intramolecular hydrogen atom abstraction is a contributing pathway. This finding has not been highlighted in the literature. We investigated the use of CO₂ as a method for tuning the grafted product distribution. At moderate pressures of CO₂, a shift to the lower grafted fractions occurs. We have discovered that this change does not arise from a polarity effect, but are still working on pinpointing the cause. We also have shown that literature precedent for a one day phenyllithium capping reaction is not sufficient to substitute all of the alkoxy groups due to the steric bulk of the phenyl rings.
4.5. References


CHAPTER 5. RECOMMENDATIONS

5.1. Chapter 2: One-Component, Switchable Ionic Liquids Derived from Silylated Amines

5.1.1 Coupling Reactions and Separations in Single-Component Reversible Ionic Liquids

Single-component reversible ionic liquids can be utilized to couple reactions and separations. This capability arises from the switch in solvent polarity between the molecular and ionic liquid forms of the solvent. Following a homogeneous reaction in the molecular liquid precursor, CO₂ is added to react with the amine and generate the ionic liquid. Nonpolar organic products and unreacted reagents can phase split from the polar ionic liquid and subsequently be decanted. After separation, the ionic liquid can be heated and reversed back to its corresponding molecular precursor and the reaction cycle can be repeated. Figure 5.1 portrays the process diagram for this recyclable system for the general reaction of A+B going to product C. Catalytic reactions will especially benefit from this process because the catalyst can be tailored to remain in the ionic liquid phase during separation.

C-C bond forming reactions, such as the Miyaura-Suzuki and Mizoroki-Heck, are central to organometallic chemistry [1]. Reversible ionic liquids can advance the application of this sector of synthetic chemistry by enabling efficient post-reaction product separation and catalyst recycle. The products of many carbon-carbon coupling reactions, e.g. biphenyls and alkenes, are relatively nonpolar and therefore subjected to separation from the polar ionic liquid phase. Also, a carefully designed
palladium catalyst could favorably partition into the ionic liquid phase. In addition, our amine precursors are basic and may act as *in-situ* base catalysts for C-C coupling reactions. The need for traditional base catalysts and the associated waste management could be eliminated.

Figure 5.1. Coupling reaction and separation using one-component reversible ionic liquids

The built-in separation of our reversible ionic liquids was used for the transesterification of glyceryl trioleate (model ester due to chemical availability in the laboratory) with methanol. This reaction is shown in Scheme 5.1. Transesterifications are central to biodiesel production, which is gaining attention due to a depletion of conventional petroleum oil resources, concern for energy independence, and increased global warming awareness. The polarity of glycerol (byproduct) may cause it to separate from the reaction phase, while the large organic character of the ester product may cause
it to phase separate from the ionic liquid. In addition, the solvent may act as an *in-situ* base catalyst.

Unfortunately, when testing the solubility of both the reactants and products for this reaction in the siloxylated ionic liquids and ionic liquid precursors, a noticeable undesired side reaction between the solvents with both glycerol and methanol occurred. The reaction was evidenced by an exotherm and color change upon mixing. We propose the side reaction shown in Scheme 5.2. However, chemically inert versions of the siloxylated solvents (e.g. TEtSAC) may provide successful alternatives for transesterifications as they will not suffer from these reactivity problems.

![Scheme 5.2. Reaction of siloxylated amine precursors with glycerol]
5.1.2 Designing Molecular Structure for Enhanced Carbon Capture Capacity

The following molecules might improve the carbon capture capacity of our first generation designs (Figure 5.2). The increased capacity of these precursors arises from either their incorporation of multiple sites for chemical absorption of CO$_2$ and/or their polyethyleneoxide units which can provide enhanced physical absorption. Polyethylene oxides, such as crown ethers, have been shown to selectively encompass or complex inorganic molecules and ions of specific diameters [2-3]. The polymer’s repeating unit, $n$, can be adjusted to improve physical absorption specificity by selectively encompassing CO$_2$ over other flue gas stream components. However, this is complicated by the similar size of CO$_2$ and N$_2$ with molecular volumes of 34.0 m$^3$/kgmol and 31.2 m$^3$/kgmol respectively [4]. Also, the enhanced capacity needs to be proven on a gravimetric basis since the molecular weight of the proposed precursors has increased.
The steric and electronic characteristics of the sidechain groups attached to the silicon center of our generation one, single component, reversible ionic liquids can be altered to create new solvent properties. For example, the precursor’s electronic environment could be modified as shown in Figure 5.3, where an aromatic, electron withdrawing group replaces one of the side chain units. In addition, this molecule is assymmetric, thereby decreasing its ionic packing efficiency and solvent viscosity. These types of structural changes provide insight into how properties trend with structure (See following section on structure-property relationships).
5.1.3 Structure-Property Relationships

We now possess a qualitative understanding of how the properties of reversible ionic liquids can be altered by structural modifications. To generalize and quantify our findings, creating structure-property relationships is compulsory. This has been done in literature using linear solvation energy relationships (LSER)[5-7]. With this approach we can quantify how the property of interest is affected by a solvent’s characteristics, such as hydrogen bond donating ability and polarizability. Correlations reduce the synthetic demand and/or number of experiments required when trying to pick the best solvent for any given application.

5.1.4 One-Component, Reversible Ionic Liquids Using SO₂

Silylated amine precursors also react with SO₂ (See Scheme 5.3).

CO₂. Specifically, there is a larger polarity jump between the precursor and the ionic liquid. Using Nile red as a polarity probe, the \( \lambda_{\text{max}} \) jump between TMSA and its corresponding SO₂ derived IL was about 25 nm (from 528.1 to 553.3 nm). The jump between TESA and its corresponding SO₂ derived IL was 24 nm (from 522.6 to 546.6 nm). These jumps are even larger than those seen in our two-component reversible ionic liquids based on amidines or guanidines with alcohols (maximum switch was 16 nm) [8]. The increased polarity change results from either physically dissolved SO₂ (which is
polar, especially when compared with CO2) or to sulfur’s lone electron pair. For applications requiring a polarity switch of this magnitude, ionic liquids generated from SO2 will work best. For this reason, it is beneficial to characterize these solvents in more detail. For example, running DSC/TGA experiments to determine ionic liquid reversal temperatures and obtaining ionic liquid viscosity measurements. When fully characterized, these solvents can be directly compared to their CO2 analogues and can contribute to structure-property relationship equations. Also, the properties of one component SO2 based ionic liquids are important because like CO2, SO2 is a post combustion gas stream component.

5.2. Chapter 3: Homogeneous Catalysis Coupled with Benign Separation in Polyethylene Glycol-Organic-Tunable Solvent Systems

5.2.1 PEG-Alcohol-CO2 Tunable Solvents

There is industrial interest in replacing tunable solvents based on organics with those based on alcohols, due to their increased sustainability. This alteration would increase the benign character of POTS which would then consist of PEG, CO2, and an alcohol. Also, some alcohols, including isopropanol, provide increased enzyme stability over organic solvents for biocatalytic reactions [9]. Based on the Pfizer solvent selection guide, dioxane ranks as an undesirable pharma solvent choice whereas alcohols rank on the preferred list [10]. The phase behavior of high molecular weight PEGs (PEG 1000, PEG 6000, and PEG 20000) with CO2 and alcohols has been studied by other groups [11-12]. However, at room temperature PEGs at these molecular weights are solids which may pose processing issues. In addition, the phase split or cloud point pressures increase with the molecular weight of PEG. This increase is a problem for industries that are
uncomfortable using high pressures. On the other hand, as in the case of PEG/dioxane/CO₂, a minimal amount of PEG was found in the gas-expanded organic phase. The phase behavior of tunable systems based on low molecular weight PEGs and alcohols needs to be calculated in order to outline the operating conditions and efficiency for liquid-liquid-vapor equilibrium.

5.2.2 Ligand Design

Through molecular design of the model monophosphine ligand used for the reactions presented in Chapter 3 (L1), enhanced catalyst retention in the PEG-rich phase can be achieved. Bulky alkyl groups increase the catalyst’s, PdL₁₂, CO₂/organic solubility. Therefore the ligand’s bulky nonpolar side chains (i.e. t-butyl and i-propyl groups) should be replaced with polar constituents. Although a few polar monophosphine ligand variations were unsuccessful in catalyzing the reaction, it is expected that with further investigation other bulky polar analogues will work and should decrease the catalyst’s solubility in the organic-rich phase. There are reports in biological literature of proteins which have been PEGylated to enhance their solubility in polar phases, such as water [13]. A PEGylated phosphine ligand would improve the catalyst’s retention in the solvent phase, PEG 400, due to like interactions.

5.2.3 Propane as a Tunable Solvent Miscibility Switch

Due to the benefits of using CO₂ as an antisolvent for tunable solvent systems, only a few reports have been made on other small gas molecules that could serve the same purpose [14-15]. However, using propane as a miscibility switch has several advantages over CO₂ including: drastically lower phase split/operating pressures,
elimination of carbonic acid formation from the equilibrium between CO₂ and water for pH sensitive reactions, and decreased product (organic) phase contamination [16]. Additionally, because the phase split pressure between propane and organics is low, decanting the gas-expanded organic phase is made simpler: approximately the entire volume of the organic-rich phase can be removed before the phases merge. With CO₂, after removing some portion of the organic-rich phase, a single liquid phase remains over a large CO₂ pressure range. Therefore, a fraction of the product is not extracted. This result was qualitatively observed when sampling the organic-rich phase of a propane based OATS system verse that of a POTS system.

PEG and water react with CO₂ to form acids. Although water is not directly a POTS component, removing water from the equation is difficult as it is present in the atmosphere and absorbed by many liquids. Results from Chapter 3 indicate that water improves the separation of products for some POTS systems. Enzymes, which are often used for enantioselective reactions, are denatured in the presence of acids. Because propane does not form an acid when in contact with water or alcohols, it provides a superior solvent switch to CO₂ for enzymatic reactions. With propane the use of buffers to control solution pH is eliminated. Buffers introduce the processing issues associated with solids handling. Consequently, an ideal use of propane-POTS would be for biocatalytic reactions. Still, before an application of this solvent system can be examined, phase behavior measurements are needed to provide insight into the quality of separation. The advantages of using propane may or may not substantiate the use of a flammable gas.
5.3. Chapter 4: Functionalization of Ethylenic Polymers with Silanes

5.3.1 Advanced NMR and Chromatography Techniques for Quantifying Grafted Products

The analytical techniques used in Chapter 4 to determine the extent of grafting of the model compounds provided good semi-quantitative data. Quantitative analysis of polymer and polymer model mixtures is challenging; however, there are a few quantitative techniques. These include DEPT (Distortion Enhancement by Polarization Transfer) NMR, 2D-NMR, and liquid chromatography-mass spectrometry (LC-MS).

DEPT NMR can differentiate carbons based on the number of attached hydrogen atoms. Because this carbon NMR method uses polarization transfer, it can be run quantitatively and is more sensitive than traditional $^{13}$C NMR [17]. DEBT NMR will benefit analysis of the grafted products as only they bear CH carbons as shown in Figure 5.4.

![Figure 5.4. VTPS-g-heptane demonstrating 1, 2 and 3 grafts per heptane chain](image)

DEPT will highlight the CH carbons found on the grafted product and allow one to quantify them, but the major challenge is the atom assignment of each signal. Therefore, starting with a simple model such as heptane, with less possible grafts per molecule, and then extending to larger models will provide for a step-wise approach. As
a guide, the NMR spectra of VTPS-g-heptane was simulated using Spartan (Hartree Fock (HF)-6.31G* data set) (See Figure 5.5). The simulated $^{13}$C signals assignments (ppm) are underlined. With three VTPS grafts per heptane, although the molecule appears symmetrical in 2-D, the minimum energy configuration is not symmetrical in 3-D space. This explains the differences between the shifts on carbon two and six.

![Figure 5.5. Spartan-predicted $^{13}$C NMR shifts for 1, 2 and 3 grafts on VTPS-g-heptane](image)

Preliminary NMR experiments were performed on a grafted heptane crude reaction product. The $^{13}$C NMR indicates that un-reacted heptane is present, which was expected as heptane was used as both the solvent and the reagent. More importantly, the DEPT 135 experiment was promising. In a DEPT 135, the CH and CH$_3$ signals point upward and the CH$_2$ signal points downward. We can clearly distinguished 5 peaks pointing upward in Figure 5.6. The first and most intense peak is attributed to the CH$_3$ of un-reacted heptane. However the four other upward peaks are attributed to the grafted heptane products. Based on chemical shift, the peak at around 20 ppm is most likely a CH$_3$ signal while the three peaks between 30-40 ppm are most likely CH signals. In addition to DEPT 135, DEPT 90 will provide insight into our products because in this experiment only CH signals show.
Two-dimensional NMR such as Heteronuclear Single Quantum Correlation (HSQC) can correlate carbon and hydrogen NMR spectra [17]. This gives information regarding which hydrogen atoms are attached to each carbon. In addition, HSQC is sensitive because it is proton detected as opposed to carbon detected. A preliminary HSQC experiment for VTPS-g-heptane was run and the results are shown in Figure 5.7. The red dashed lines in this figure are used as an example to demonstrate that the hydrogen peak at 1 ppm corresponds to carbon peak near 15 ppm. These peaks are attributed to CH₃ groups based on their chemical shifts. Overall, a combination of advanced NMR techniques will provide quantitative information.
Using a silica column to separate each grafted fraction from the mixture will aid with peak assignment in the NMR spectra. Literature precedent verifies that the fractions could be separated by column chromatography using a 10% ethyl acetate, 90% hexanes eluent [18]. Ideally a liquid chromatography-mass spectrometer (LC-MS) run with a silica column could be used to simultaneously separate, identify, and quantify each component of the mixture. However, because the grafted molecules are difficult to ionize, this is not as straightforward as expected. Adding AgTfa to the eluent will help ionize our products as it was proven effective for MALDI analysis.
5.4. References


A.1. Introduction

In Chapter 3, we explored a tunable solvent system based on PEG/organic/CO₂ mixtures. This tunable solvent system achieved the goal of coupling homogeneous catalysis with heterogeneous separation. Another tunable solvent system of interest is based on fluorous/organic/CO₂ mixtures. In these systems, catalysts tagged with fluorous groups can be easily separated from the reaction mixture. At standard conditions fluorous solvents and organic solvents are immiscible. However, at moderate pressures of CO₂ these solvents become soluble. Reactions are run in this single liquid phase followed by depressurization which regenerates the two liquid phase system and allows catalyst recycle and product separation. Therefore, fluorous/organic/CO₂ tunable solvents operate in a reverse manner to that of PEG/organic/CO₂.

A previous group member has studied the phase behavior of perfluorohexane (PFH) with methanol, toluene, and acetone [1]. Subsequently, we have experimentally measured the cloud point pressure of equal volume mixtures of perfluorohexane and FC-43 (mixed perfluorinated compounds: primarily C12) with 14 different common organic solvents to expand upon previous findings. These solvents include: toluene, ethyl acetate, tetrahydrofuran, chloroform, acetone, cyclohexane, propionic acid, acetic acid, decane, acetonitrile, dimethylformamide, nitromethane, ethanol, and methanol. Solvents were chosen to span the range from nonpolar to polar and from protic to aprotic.
A.2. Experimental Methods

Following the procedure developed by Hallett [2], equal volumes of fluorous and organic solvents were added to a 60 mL fixed volume Jerguson® pressure cell. CO₂ was added to the system by an ISCO Model 500D syringe pump until the two liquid phases began to merge. The cell was temperature controlled via an airbath. After equilibration, the mutual solubility pressure was determined by removing and reintroducing CO₂, through a hand pump, over the cloud point. This cycle was repeated three times and an average pressure was recorded.

A.3. Results

Figure A1 shows the miscibility pressures of 14 different common organic solvents with FC-43 at 40°C, and PFH at both 25°C and 40°C. Polar solvents, such as methanol, require the largest amount of CO₂ to induce homogeneity. The temperature trend is difficult to analyze because two competing effects occur. As temperature is increased and volume remains constant pressure is increased, which would make the solubility pressures high. However; as temperature is increased, the solubility of the two liquid phases is increased, therefore lowering the pressure required for inducing homogeneity. These competing effects give rise to the mixed solubility pressure trends with temperature. FC-43 requires a greater CO₂ pressure than PFH to generate a single liquid phase because its structure is more fluorinated and therefore nonpolar.
A1. Solubility pressures of common organic solvents with fluorinated organics
A.4. References


APPENDIX B. Nucleophilic Displacement Reactions In Catalytic Room Temperature Ionic Liquids

B.1. Introduction

Nucleophilic substitution reactions between organic reactants and inorganic ionic salts can be facilitated by using phase transfer catalysts (PTCs) to shuttle salt anions into the organic reactant phase. Good PTCs, such as quaternary ammonium salts and ionic liquids, not only increase reactant contact, but also activate the salt’s anion for reaction by binding it less tightly than the salt’s cation. Many examples of ionic liquid phase transfer catalyzed nucleophilic displacement reactions can be found [1-3]. Here we investigate how the presence of water and supercritical carbon dioxide affect the kinetics of solid-liquid PTC displacement reactions.

B.2. Kinetic Effect of Supercritical Carbon Dioxide

The nucleophilic displacement of benzyl chloride (BzCl) with potassium cyanide in [bmim][PF₆] was chosen as a model solid-liquid PTC reaction for this study (Scheme B1). [Bmim][PF₆] was chosen as the model ionic liquid because it is commercially available and has well characterized properties. Previously published results have indicated that at lower temperatures (40ºC) this reaction appears to be mass transfer limited rather than pseudo first order and kinetically limited [1]. Although this behavior may appear to be non-intuitive, it was speculated that the high viscosity of the ionic liquid- especially at lower temperatures- was the cause of transport issues. Supercritical carbon dioxide has been shown to lower the viscosity of ionic liquids without changing their solvent properties [4]. For this reason, it was hypothesized that adding scCO₂ to the
reaction would alleviate mass transfer issues without diminishing the ionic liquid’s solvent power.

\[
\text{Scheme B1. Reaction of benzyl chloride with potassium cyanide}
\]

Reactions were performed in a 100 mL Parr pressure reactor at 40°C and quenched by cooling and venting CO₂ into a beaker of cold acetonitrile. KCN was stirred at temperature in the solvent for an hour prior to addition of the substrate. Reactant conversions were determined by GC-MS. Table B1 displays the conversion to benzylcyanide at various times with varying compositions of carbon dioxide. The results show an unexpected carbon dioxide effect. Increasing CO₂ pressure decreases reaction conversion. This outcome is consistent with the absence of mass transfer limitations at 40°C, however not conclusive. The decrease in reaction conversion could be attributed to all or any of the following three factors:

1) A decrease in polarity of the ionic liquid with added carbon dioxide. The polarizability (\(\pi^*\)) probe used in previously published reports is extremely polar and is therefore preferentially solvated by the ionic liquid [4]. Therefore, the probe may not see the effect of CO₂. Also, the study of polarity is very probe dependent. The reactant used for this study is less polar than the \(\pi^*\) probe that was used and can be preferentially solvated by CO₂, a less effective solvent for PTC.
2) CO₂ affects the solubility of the cyanide salt and crashes it out of the ionic liquid.

3) The volume expansion of the ionic liquid, approximately 35%, upon CO₂ addition decreases the concentration of the limiting reactant and slows the reaction.
The effect of stirring speed on the reaction kinetics was analyzed in order to conclusively determine whether mass transfer limitations exist in this system at 40°C. Reactions were carried out in a 100 mL round bottom flask submerged in an oil temperature bath and connected to an overhead stirrer. Samples were drawn and analyzed by GC-MS. Figure B1 displays the pseudo-first order kinetic results of varying stirring speed from 410 to 750 rpm. At the two stirring speeds tested, the reaction rate does not appear to be affected by stirring rate. Moreover, the data fits a pseudo first order rate plot. It is concluded that at stirring speeds above 410 rpm and in the absence of water the reaction is rate limited. Previous reports on this system did not specify stirring speed or water content in the ionic liquid and this could explain the disparity in results.
B.3. **Kinetic Effect of Water**

It is known that ionic liquids are hygroscopic and purifying them of water is extremely difficult. The viscosity of ionic liquids is decreased when water is present. The viscosity of [bmim][PF₆] in the presence of water follows equation (1) which was established by Seddon et al.:

\[
\eta = \eta_o 10^{(-\chi/0.19)}
\]  

(1)

where \(\eta_o\) is the pure ionic liquid viscosity and \(\chi\) is the water mol fraction [5]. Water is known to have a dramatic effect on the kinetics of this and other solid-liquid phase transfer catalyzed reactions. Liotta et al. showed the drastic effects of water for the nucleophilic displacement of benzyl bromide with potassium cyanide using a crown ether PTC [6]. This reaction followed zero order kinetics in the absence of water and pseudo first order kinetics in the presence of water. However, literature involving a quantitative analysis of how water content effects reactions run in ionic liquids is sparse.
Reactions were run with varying amounts of water added before the onset of reaction at 40°C, 60°C, and 80°C. Figure B2 is an example of the kinetic pseudo first order plot for the effect of water content ranging from 0-13% by mass at 40°C. At this temperature and these water concentrations, the viscosity of \([\text{bmim}][\text{PF}_6]\) ranges from 0.02 cP- 120 cP. It appears that adding small amounts of water (0.76 wt%) has a marked increase in reaction rate which is not further increased by addition of more water. Organic co-solvents (acetonitrile (ACN) and 1,4-dioxane) were used to prove the unique impact of water. These co-solvents did not alter the kinetics, although they would decrease the ionic liquids viscosity. This suggests that water is playing a role. Table B2 shows the activation energy of this reaction with and without water. The addition of water to the system decreases the activation energy by over 1 kcal/mol.

![Figure B2. Pseudo-first order plot on the effect of water at 40°C and 750rpm on kinetics](image-url)
Table B2. Activation energy for displacement reaction w/ and w/o water

<table>
<thead>
<tr>
<th>Water added (vol %)</th>
<th>Activation Energy (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.2</td>
</tr>
<tr>
<td>1</td>
<td>12.0</td>
</tr>
</tbody>
</table>

These trends emulate those found by Yadav et. al. when studying the solid-liquid phase transfer catalyzed nucleophilic substitution reaction of isobutyl phenyl ethyl chloride with cyanide in toluene [7]. He explains his results by the presence of an aqueous omega phase which increases the local concentration of nucleophile available to the PTC. Therefore, the omega phase present in our system creates an increased reaction rate.
B.4. References


APPENDIX C. Phenol and Ether Calibration Curves

Figure C1. Calibration curve for 3,5-di-tert-butylphenol

\[ y = 0.1128x - 0.0228 \]
\[ R^2 = 0.9995 \]
Figure C2. Calibration curve for o-tolyl-3,5-xylyl ether

\[ y = 1.79E+08x + 3.95E+07 \]

\[ R^2 = 9.95E-01 \]
VITA

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PUBLICATIONS


PRESENTATIONS


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**INVENTION DISCLOSURES**