TRANSFORMING TRIATOMIC MOLECULES INTO COMPLEX FUNCTIONAL MATERIALS

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By

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Perhaps because the dipole moment of CO₂ is equal to zero, a widely held misperception is that this triatomic gas is kinetically and thermodynamically stable under most reaction conditions. As a result, only recently has CO₂ been exploited as a useful and versatile reagent. Reactions involving it and other neutral triatomic molecules (most notably, CS₂) with substrates containing nucleophilic functional groups are based on Lewis acid-base equilibria. This simple chemistry can be used to form a variety of interesting new materials which are metastable or reversible in some cases, and able to be transformed into other materials, in other cases. In this way, molecules with controllable properties can be generated. Such molecules have been employed as cross-linkers, to initiate self-assembly¹ and to allow reversibility in functional soft materials (e.g., gel,² ionic liquids,³ supramolecular structures,⁴ catalysts,⁵ etc.) that are potentially useful in a wide variety of applications ranging from sensing and sequestration of environmentally deleterious molecules to the development of better materials for art conservation.⁶ In our work, greater emphasis will be placed on the chemistries of CO₂ and CS₂ (X=C=X type molecules in which the electronegativities of the X atoms are significantly larger than that of carbon); both molecules are linear and have large quadrupolar moments. The electrophilic nature of the carbon
atoms in molecules such as CO$_2$ and CS$_2$ makes them attractive reagents in organic syntheses as well.

In this dissertation, we investigate how and why these triatomic molecules react with other species and exploit the chemistries to synthesize complex molecules and aggregates, to change drastically the properties of materials, and to devise new processes.

First, the syntheses and properties of a new class of chiral, reversible, room-temperature, ionic liquids (RTILs) are investigated. They are made from easily synthesized, readily available materials and can be transformed reversibly to their nonionic liquid states. The nonionic liquids consist of equimolar mixtures of a $N'$-alkyl-$N,N$-dimethylacetamidine (L) and an alkyl ester (N) of a naturally occurring amino acid. When exposed to 1 atm of CO$_2$ gas, 1/1 (mole/mole) L/N solutions become cationic-anionic pairs, amidinium carbamates. Of the 50 L/N combinations examined, all except those involving the methyl ester of tyrosine (which was immiscible with the amidines) form RTIL states under a CO$_2$ atmosphere, and several remain liquids to at least -18 °C. Heating the ionic liquids in air to ca. 50 °C or bubbling N$_2$ gas through them at ambient temperatures for protracted periods displaces the CO$_2$ and re-establishes the nonionic L/N states. Thermal and spectroscopic properties of both the nonionic and ionic phases are reported and compared. Unlike many other ionic liquids, these need not be prepared and handled under scrupulously dry conditions and they can be cycled repeatedly between their high- and low-polarity states.

In addition, the properties of another class of reversible, room-temperature, chiral, ionic liquids (L-A-C) are studied. The L-A-C are prepared by passing CO$_2$ gas through equimolar mixtures of a simple amidine (L) and a chiral amino alcohol (A), L/A, derived from a naturally-
occurring amino acid, and they can be returned to their L/A states by passing a displacing gas, N\textsubscript{2}, through the ionic liquid; the process of passing from uncharged to charged states can be repeated several times without discernible degradation of each phase. All of the 40 L/A combinations examined form room-temperature ionic liquids (most stable to ca. 50 °C under one atmosphere of CO\textsubscript{2}) and they remain liquids to at least -20 °C. The L-A-C phases are more viscous than their corresponding L/A phases, the conductivities are much higher in the L-A-C phases than in the L/A phases, and the solubility characteristics of the liquids can be modulated significantly by exposing them to either CO\textsubscript{2} or N\textsubscript{2} gas. The spectroscopic characteristics of the L/A and L-A-C phases have been compared as well. Their reversibility, chirality, broad temperature ranges, tolerance to water, and, ease of preparation should make the L/A and L-A-C phases useful as solvents for several ‘green’ applications.

Also, by adding one equivalent of another triatomic molecule, CS\textsubscript{2} to an equimolar mixture of two non-ionic molecules, an amidine and an amine with diverse structures, amidinium dithiocarbamates salts are easily prepared. Many of the salts made in this way are RTILs and are thermally stable to ~80 °C, a temperature significantly higher than the decomposition temperatures of analogous amidinium carbamate RTILs. However, unlike the amidinium carbamates, the amidinium dithiocarbamates do not revert to their amidine/amine mixtures when they are heated. The thermal, rheological, conductance and spectroscopic properties of these RTILs are reported, comparisons between them and their non-ionic phases (as well as with their amidinium carbamate analogues) are made, and the thermolysis pathways of the ammonium dithiocarbamates are investigated. In addition, the above-mentioned \textit{in situ}-prepared, reversible
RTILs have been used as media for the syntheses of cyclic carbonates by addition of CO$_2$ to epoxides.

The similar approach has been explored to develop functional polymers. The physical properties of five siloxane polymers with different types and frequencies of amino functional groups along the polymer side-chains have been changed from flowing liquids to gels and to rubber-like materials by the simple addition or subtraction of CO$_2$ or CS$_2$ at room temperature. The chemical changes, formation of ammonium carbamates and ammonium dithiocarbamates, create materials whose properties are completely different from the parent polymers as a result of the introduction of ionic crosslinks. These materials can be returned to their original forms by heating (in the case of the CO$_2$ adducts) or to their protonated original forms by treatment with an acid (in the case of the CO$_2$ and CS$_2$ adducts). Heating the ammonium dithiocarbamates leads to loss of H$_2$S and permanent (covalent) thiourea crosslinks between the polymer chains. The new materials adhere strongly to other surfaces and can be swelled to several times of their original volumes by different liquids. The rheological, swelling, and physical properties of the new materials have been correlated with the structures of the original polymers to provide a comprehensive picture of how changes at the nanometric length scale are translated to macroscopic changes. At least for the polysiloxanes examined here, the properties of the adducts do not correlate with the molecular weights of the original polymers, but do with the frequency of amino groups. The results demonstrate a simple, new method to crosslink polysiloxanes (and, in principle, a wide range of other polymers), transforming them into materials with totally different and potentially commercially useful properties. Research on swelling-deswelling
behavior of crosslinked amino-polysiloxanes and possible applications for chemical spill containment and remediation were carried out as well.
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List of abbreviations and acronyms

Instrumentation

CD,circular dichroism
DSC…………………………differential scanning calorimetry
FT-IR………………………..Fourier transformed infrared spectroscopy
GC………………………….gas chromatography
GC-MS……………………..gas chromatography-mass spectrometry
NMR……………………...nuclear magnetic resonance
POM………………………polarized optical microscopy
TGA………………………thermogravimetric analysis
UV-Vis……………………..ultraviolet–visible spectroscopy

Amino acids, amino esters and amidines
A…………………………..amino alcohol
Cn…………………………aliphatic amidine, n represents the length of the chain
DBU……………………..1,8-diazabicyclo[5.4.0]undec-7-ene
GlyOH……………………glycinol
Ile…………………………..isoleucine
IleOH…………………….isoleucinol
IleC1………………………isoleucine methyl ester
L…………………………...N’-alkyl-N,N-dimethylacetamidine
Leu………………………..leucine
LeuOH…………………….leucinol
LeuC1……………………..leucine methyl ester
LeuC8……………………..leucine octyl ester
LeuC18……………………leucine octadecyl ester
Met..........................methionine
MetOH.....................methioninol
N..........................amino acid ester
Phe..........................phenylalanine
PheC₁......................phenylalanine methyl ester
Pro.........................proline
Pro.........................prolinol
tC₄..........................tetra-butyl amidine
Tyr.........................tyrosine
TMG........................1,1,3,3-tetramethylguanidine
Val..........................valine
ValOH......................valinol

Dye
DAPNE........................1-(p-dimethylaminophenyl)-2-nitroethylene
Eosin Y....................2’,4’,5’,7’-tetrabromofluorescein

Other chemicals
TMS..........................tetramethylsilane

Polysiloxanes
PDMS..........................poly(dimethylsiloxane)
nPSil..........................3-aminopropylmethyldimethylsiloxane-dimethylsiloxane copolymer with
                          n monomer % of amine functionality
nPSil-CO₂...................polysiloxanes cross-linked by CO₂
nPSil-CS$_2$………………polysiloxanes cross-linked by CS$_2$

nPSil-CS$_2$-H………………polysiloxanes cross-linked by CS$_2$, and heated to form the thiourea covalent crosslinks

Other acronyms and symbols

CCS………………carbon capture and storage

RTIL………………room-temperature ionic liquid

L-N-C …………………ionic liquid prepared by passing CO$_2$ through an equimolar mixture of an amidine (L) and a chiral amino acid ester (N)

L-A-C …………………ionic liquid prepared by passing CO$_2$ through an equimolar mixture of an amidine (L) and a chiral amino alcohol (A)

L-amine-C …………………ionic liquid prepared by passing CO$_2$ through an equimolar mixture of an amidine (L) and an aliphatic amine

C$_6$-cyclohexylamine-CS$_2$-N$_2$……exposing the C$_6$-cyclohexylamine-CS$_2$ amidinium dithiocarbamate to N$_2$ and gently heating at 50 °C

bp……………………boiling point

mp……………………melting point

pK$_a$……………………acid dissociation constant at logarithmic scale

pK$_b$……………………base dissociation constant at logarithmic scale

$\Delta H_f$……………………enthalpy of formation

$\Delta S$……………………entropy

$G'$……………………storage modulus
The goal of this thesis research

To the best of our knowledge, changing drastically the properties of materials by mild external perturbations is not easy. A potential method to do so is transformation of the materials between ionic and nonionic states. Following this concept, a goal of this thesis is to determine how selected simple reactions involving addition of neutral triatomic molecules can be utilized to create complex molecules and functional materials through self-assembly. This thesis will also explore in what ways the resulting materials have different physical and chemical properties, and will address the question of how to tune the physico-chemical properties by changing the various experimental parameters. A final goal is to develop structure-reactivity (or property) relationships among the materials.

In that regard, major accomplishments of this thesis include:

(1) Development of two classes of reversible, room-temperature, chiral ionic liquids

(2) Optimization of room-temperature ionic liquids to increase their thermostability
Dissertation Overview

This dissertation summarizes the author’s five years investigation in transforming triatomic molecules (CO$_2$ and CS$_2$) into functional, soft materials through self-assembly. In this work, classic chemical reactions, employing two triatomic molecules—CO$_2$, a “greenhouse gas”, and CS$_2$, a deleterious volatile liquid—as the key elements, transform charge-neutral molecules and polymers into self-assembled materials with interesting properties for a variety of applications. The basic reactions involved in the transformations have been integrated into approaches (1) to make new materials that can be reconverted into their original forms at will by benign physical methods and (2) that utilize environmentally controversial triatomic molecules.

In Chapter 1, background knowledge regarding soft materials, ionic liquids and triatomic molecules will be introduced. The goal and potential impact of this research will be explained as well.

Chapter 2 describes the syntheses and properties of reversible, room-temperature, chiral ionic liquids derived from carbon dioxide with amidines and amino-acid esters or amino alcohols. Also, thermally-stable, room-temperature ionic liquids from amidines and amines by adding CS$_2$, and comparison with CO$_2$ adducts will be discussed.
In Chapter 3, studies of reversibly crosslinking amino-polysiloxanes by simple triatomic molecules are reported. They describe facile methods for tuning thermal, rheological, and adhesive properties of polysiloxanes. In addition, swelling-deswelling behavior of crosslinked amino-polysiloxanes and possible applications will be illustrated.

Chapter 4 provides an application of the ionic liquids as a reaction media for cycloaddition reactions between epoxides and CO₂ to make cyclic carbonates.

A summary and conclusions will be addressed in Chapter 5.

Publications and patents resulting from this thesis research


CHAPTER 1. INTRODUCTION

Currently, our lives and activities are highly dependent on fossil fuels. As a result, extremely large amounts of neutral triatomic gases are released to the atmosphere as byproducts. Among those gases, carbon dioxide is considered to be a primary cause of the greenhouse effect. Whereas bulk absorption of CO₂ molecules into a bulk material involves its dissolution, CO₂ involves either chemisorption (covalent bonding) or physisorption (van der Waals interactions) between the gas molecules and the surface of a material. Carbon capture and storage (CCS) is a means of mitigating fossil fuel emissions. The process is based on capturing CO₂ from large point sources, such as fossil fuel power plants, and storing it in such a way that it does not enter the atmosphere again. Besides CO₂, other simple triatomic molecules also play a crucial role in the current climatic problems by contributing to environmental pollution. For example, sulfur dioxide (SO₂) is a major cause of acid rain and smog, oxides of nitrogen, especially nitrous oxide (N₂O), are an important contributor to the destruction of the ozone layer (as well as the aforementioned greenhouse effect), and carbon disulfide (CS₂) is a poisonous liquid that has been identified as a water contaminant from the viscose rayon industry. These and other neutral triatomic molecules have been produced by volcanic eruptions and the decay of plants and animals for more than a billion years on our planet. During that time, Nature has established an equilibrium in which such gases are captured by bodies of water, rocks, and plants (via photosynthesis) and are then slowly expelled back into the environment.

1.1 Soft matter

Soft matter, as the name suggests, is a subfield of condensed materials that are usually easily deformed by thermal stresses or thermal fluctuations. This field continues to attract more and more interest in systems, such as polymers, colloids, surfactants, gels, certain biomaterials, ionic liquids and liquid crystals. Many soft materials can be induced to flow.
under certain conditions and exist in metastable states. This weak ordering results from the lack of three-dimensional atomic long-range order found in a crystalline solid. Nevertheless, there is always a degree of local order at least as great as that of a liquid.\textsuperscript{17a,b} These unique properties result in soft matter being important for a wide variety of applications. In order to perform different functions, it is necessary to change the materials’ property by moderate changes. However, there are no general procedures of which we are aware that allow a common soft matter to change its properties by external changes. A potential solution to this problem that others\textsuperscript{18} and we\textsuperscript{3} are exploring is the development of soft matter that can be transformed easily, rapidly, and reversibly into uncharged, low-polarity analogs by the selective addition of gases. The selection of CO\textsubscript{2} and N\textsubscript{2} here is related to the fact that they are inexpensive, plentiful, nonflammable, nontoxic, environmentally benign, and easily removable.

Our group has explored reactions of primary and secondary alkylamines with CO\textsubscript{2} to obtain alkylammonium alkyl carbamates, which are gelators of a variety of organic liquids (Scheme 1-1).\textsuperscript{19} In those studies, the objective was to make solid ammonium carbamates which self-assemble into solid fibrillar networks and trap microscopically very large volumes of the organic liquids. In this thesis research, we have developed reversible, chiral room temperature ionic liquids and adhesive polymers by this method.

![Scheme 1-1. Use of primary amine-triatomic molecule adducts as gelators (Reproduced with permission from ref 90; copyright 2010, the Royal Society of Chemistry).\textsuperscript{90}](image-url)
1.2 Ionic liquids

While ordinary liquids such as water and molecular organic solvents are predominantly made of uncharged molecules, ionic liquids (ILs) are salts composed of ions and short-lived ion pairs. Ideally, ionic liquids have broad liquid and thermal stability ranges, spanning perhaps 300 °C (-100 °C ~ +200 °C). Most ILs are non-flammable or show very low flammability. During last decade, ionic liquids have become increasingly popular as solvents in academic and industrial applications because of their environmentally friendly characteristics, such as low vapor pressures and less toxic than molecular solvents, and ability to enhance the efficiencies of a large variety of solute reactions. In addition, different combinations of cations and anions of ILs result in different physical, chemical, and biological properties which can be tailored to specific purposes. Room-temperature ionic liquids (RTILs) are especially interesting in this regard. In addition, ionic liquids present a promising new technology for energy and cost efficient separation of CO₂ from post-combustion flue gas. In order to improve the selectivity of permeation of CO₂ separations of gas mixtures, Gin and coworkers developed an approach using imidazolium-based RTILs containing oligo(ethylene oxide), alkylnitrile, fluoroalkyl, polyalcohol, and oligo(siloxane) substituents on the cation.

1.3 Triatomic molecules

The triatomic molecules of interest here are uncharged and with a less electronegative atom flanked by one two more electronegative atoms. As such, the central atoms behave as electrophiles or Lewis acids. However, the simple structures of such neutral triatomic molecules mask the complexity of their many reactions. Several of them are involved with our life cycle, and an example of their importance is witnessed by the now recognized effect of the most common of these triatomic molecules, CO₂, on our climate. The attractiveness of CO₂ as a potential reagent in our research is enhanced by its abundance from renewable
carbon sources and lack of toxicity under most conditions.\textsuperscript{26} However, its high thermodynamic stability and low reactivity under many conditions have limited its industrial uses thus far. Also, because carbon of CO\textsubscript{2} is in the highest oxidation state, +4, of any neutral species (although other neutral molecules contain carbon atoms with equally high oxidation states), its reactions proceed more readily with mild reagents when the products are relatively stable and contain the carbon atom in a high oxidation state. Examples of such products are organic carbonates\textsuperscript{27} and carbamates.\textsuperscript{28} Catalysts are needed to allow reactions of CO\textsubscript{2} to proceed with other ‘stable’ species (such as molecular hydrogen) under mild conditions. Alternatively, CO\textsubscript{2} can be reacted with highly-energetic, very reactive reagents.

Some important physical properties of selected triatomic molecules are presented in Table 1-1. Triatomic molecules with the structure, X=Y=X or X=Y=Z may be linear or bent depending on the electronic distribution on the central atom. The nature of the three atoms and their spatial distribution determine the magnitude of the molecular dipole. CO\textsubscript{2} and CS\textsubscript{2} are linear molecules whose dipole moments are zero. The dipole moment of carbon oxysulfide (O=C=S) is directed toward the more electronegative oxygen atom and the C\rightarrow O and C\rightarrow S group dipoles of CO\textsubscript{2} and CS\textsubscript{2}, being diametrically opposed, are responsible for the zero molecular dipoles and non-zero quadrupoles. However, both molecules possess a large, non-zero quadrupole moment ($3.00 \times 10^{-26}$ esu·cm$^2$ (CO\textsubscript{2}) and $1.84 \times 10^{-26}$ esu·cm$^2$ (CS\textsubscript{2})).\textsuperscript{29} The reactivities of these molecules have a lot in common with those of some more complex molecules. An example is dicyclohexylcarbodiimide (DCC) which is commonly utilized to couple amino acids during peptide syntheses, and phenylthiocyanate, a reagent for making phenylthiohydantoins from peptides.
<table>
<thead>
<tr>
<th>Triatomic molecule</th>
<th>Bond length (Å)</th>
<th>Shape</th>
<th>Kinetic diameter$^{31}$ (Å)</th>
<th>boiling point (K)</th>
<th>$\Delta H_f^o$ a (kJ·mol$^{-1}$)</th>
<th>$\Delta G_f^o$ b (kJ·mol$^{-1}$)</th>
<th>Dipole moment (D)</th>
<th>Quadrupole moment (esu·cm$^2$)</th>
<th>Polarizability $\times 10^{25}$ (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ (g)</td>
<td>1.1600</td>
<td>linear</td>
<td>3.3</td>
<td>216.55</td>
<td>-393.5</td>
<td>-394.4</td>
<td>0</td>
<td>3.00 $\times 10^{-26}$</td>
<td>29.11</td>
</tr>
<tr>
<td>CS$_2$ (g)</td>
<td>1.5526</td>
<td>Linear</td>
<td>4.483</td>
<td>319.37</td>
<td>89.0</td>
<td>64.6</td>
<td>0</td>
<td>1.84 $\times 10^{-26}$</td>
<td>87.4 – 88.6</td>
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<tr>
<td>OCS$_{\text{(g)}}$</td>
<td>C-O</td>
<td>Linear</td>
<td>4.130</td>
<td>222.7</td>
<td>-142.0</td>
<td>-169.2</td>
<td>0.715</td>
<td>-</td>
<td>52 – 57.1</td>
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<tr>
<td>SO$_2$ (g)</td>
<td>1.4308</td>
<td>angular; C$_2$V (119.3°)</td>
<td>4.112</td>
<td>263.13</td>
<td>-296.8</td>
<td>-300.1</td>
<td>1.633</td>
<td>-</td>
<td>37.2 – 42.8</td>
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<td>N$_2$O (g)</td>
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<td>184.67</td>
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<td>103.7</td>
<td>0.161</td>
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</tr>
</tbody>
</table>

$^a$Enthalpy of formation.

$^b$Free energy of formation.
| NO$_2$(g) | 1.193 | angular, C$_2$V (134.1°) | 302.22 | 33.2 | 51.3 | 0.316 $\pm$0.010 | - | 30.2 |

$^a$ Standard molar enthalpy (heat) of formation at 298.15 K; $^b$ Standard molar Gibbs energy of formation at 298.15 K.
All of the molecules in Table 1 have at least one terminal atom that is more electronegative than the central one; the central atom has a partial positive charge. Some reactions of these molecules with nucleophilic species are important to maintaining life on our planet. For example, CO$_2$, despite its high thermodynamic stability, is in equilibrium with bicarbonate and carbonate in the oceans via reactions with water or hydroxide (Eq. 1-1). The process of solvation of CO$_2$ molecules in water, followed by reaction generating carbonic acid (H$_2$CO$_3$), is slightly exothermic (-19.7 kJ·mol$^{-1}$). The equilibrium between H$_2$CO$_3$ and bicarbonate (HCO$_3^-$) in water has a dissociation constant of $(1.72 \pm 0.05) \times 10^{-4}$ mol·kg$^{-1}$ at 25 °C, and more carbon atoms in our biosphere are in the form of HCO$_3^-$ than in any other molecule.

![Equilibrium Diagram]

The positions of the equilibria shown above are determined by (1) the nature of the nucleophile, (2) the reaction medium, (3) the temperature, and (4) the base strength. Although the oxygen atoms of alcohols react with CO$_2$ to give alkylcarbonic acids (R-O-CO$_2$H), they are less basic and nucleophilic than the analogous amines. To attain a significant amount of reaction like that shown in eq. 4, a strong base, such as an amidine (e.g., 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)), must be added. Thus, Hori and coworkers$^{33}$ demonstrated that the uptake of CO$_2$ by alcohol/DBU mixtures in toluene solutions is not quantitative at 1 atm of pressure, although reaction of CO$_2$ with alcohols and another base type, guanidines, is.$^{34}$ Primary aliphatic amine groups can react quantitatively with one atmosphere of CO$_2$ to generate alkylammonium alkylcarbamate salts (Eqs. 1-2 and 1-3, where Nu-H is a primary amine and XY$_2$ is CO$_2$) and amidinium carbamates in the presence of an amidine, guanidine, or other strong base of low nucleophilicity (Eq. 1-4, where Nu-H is a primary amine and XY$_2$ is CO$_2$).
Alkylammonium carbamates and amidinium carbamates are thermally stable at room temperature under one atmosphere of CO₂, but lose CO₂ at higher temperatures; a flow of an inert gas is able to displace CO₂ at room temperature (Eq. 1-5).

\[
XY_2 + \text{NuH} \rightleftharpoons \text{Nu-Y} \quad (1-2)
\]

\[
\text{Nu-Y} + \text{NuH} \rightleftharpoons \text{Nu-Y}^+ \text{NuH}_2 \quad (1-3)
\]

\[
\text{Nu-Y} + \text{Base (B)} \rightleftharpoons \text{Nu-Y}^+ \text{B-H} \quad (1-4)
\]

\[X = C, S, N \quad , \quad Y = O, S\]

\[\text{Nu-H} = \text{H}_2\text{O}, \text{NH}_3, \text{R-OH}, \text{NH}_2\text{R}, \text{NHHR'} \quad (R=\text{alkyl})\]

\[\text{Base (B)} = \text{amidine}, \text{DBU}, \text{guanidine}\]

For steric and other reasons, the usual order of reactivity of amines as nucleophiles with triatomic molecules is primary > secondary >> tertiary. Note that whereas primary and secondary amines can lose a proton from nitrogen after reacting with a molecule of CO₂ (thus generating carbamates), tertiary amines cannot and must remain as very unstable species that cannot be isolated at room temperature and under one atmosphere of CO₂.

\[
\text{CO}_2 + 2\text{RNH}_2 \rightarrow \text{R-N-CO}_2^\Theta \text{H}_3\text{N-R} \quad (1-5)
\]

\[
\text{CS}_2 + 2\text{RNH}_2 \rightarrow \text{R-N-S}_\Theta \text{H}_3\text{N-R} \rightarrow \text{R-N-S}^\Theta \text{H}_2\text{S} + \text{H}_2\text{S} \quad (1-6)
\]

Similar chemistry occurs with CS₂ as the triatomic molecule (Eq. 1-6). However,
heating ammonium dithiocarbamates from primary amines leads to thioureas and expulsion of H$_2$S.\textsuperscript{35} In a similar way, other electrophilic triatomic molecules such as SO$_2$, NO$_2$ and N$_2$O can react with nucleophilic species (Scheme 1-1). For example, SO$_2$ can form stable charge-transfer complexes with tertiary amines, and also reacts with primary amines to generate sulfamides.\textsuperscript{36} In the latter reaction, SO$_2$ (a strong Lewis acid) is activated first via formation of a donor-acceptor, non-covalent complex with an amine (base). It is noteworthy that both SO$_2$ and CS$_2$ have been shown to possess great versatility in interacting with metal complexes because of their sulfur atoms.\textsuperscript{35}

Recently, a new series of easily prepared, room-temperature ionic liquids (RTILs)—amidinium carbamates—has been developed by our group. They are made by bubbling CO$_2$ gas through a mixture of two non-ionic components, an aliphatic amidine and an aliphatic amine.\textsuperscript{3a} The resulting RTILs can be reconverted to their non-ionic forms by displacing the covalently bound CO$_2$ using N$_2$, and this process can occur repeatedly without detectable degradation. A very important attribute of these RTILs is their ability to be easily transformed between high-polarity, ionic states and low-polarity, uncharged states.

**CHAPTER 2: REVERSIBLE, ROOM-TEMPERATURE (CHIRAL) IONIC LIQUIDS**

**2.1.1 Introduction**

Their unique physical and chemical properties\textsuperscript{37} make room-temperature ionic liquids (RTILs)\textsuperscript{21, 38} attractive solvents for a wide variety of applications.\textsuperscript{39} Chiral ionic liquids\textsuperscript{40} present additional opportunities as media for enantioselective reactions of solutes,\textsuperscript{41} stereoselective polymerizations,\textsuperscript{42} and enantiomeric separations.\textsuperscript{43} However, there are no general procedures of which we are aware that separate products (or catalysts) from their host ionic liquids in a manner that allow the liquids (and catalysts) to be reused.\textsuperscript{44} Finding such procedures poses a serious challenge to expanded exploitation of these materials. A potential
solution to this problem that others\textsuperscript{18,45} and we\textsuperscript{3} are exploring is the development of ionic liquids that can be transformed easily, rapidly, and reversibly into uncharged, low-polarity analogs by the selective addition of gases. Another desirable attribute would be the ability to cycle easily and reversibly between an RTIL and a corresponding nonionic form because such materials allow easier separation of solvent mixtures, catalysts, etc. This goal has been achieved by alternating the bubbling of CO\textsubscript{2} and a displacing gas (N.B., argon or nitrogen) through mixtures of an amidine, 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), and 1-hexanol\textsuperscript{18a,46} or an amidine and an alkyl amine\textsuperscript{3a}.

In addition, although the benign nature of this switching process opens several potential applications for ionic liquids, such as reversible catalyst formation\textsuperscript{5,47} and CO\textsubscript{2} gas sequestration,\textsuperscript{25} the thermal instability of these ionic liquids above ca. 50 °C, even under one atmosphere pressure of CO\textsubscript{2}, imposes some limitations on their applicability. Thus, RTILs of similar structure, but with greater thermal stability, would expand greatly their potential uses.

\textbf{2.1.2 Materials}

Unless stated otherwise, all reagents were used as received. L-Proline (Pro; 99%), L-leucine (Leu; 99%), L-isoleucine (Ile; 99 %), L-phenylalanine (Phe; 98.5 %), L-tyrosine (Tyr; 99 %), and thionyl chloride (99.5 %) were from Acros; triethylamine (99.9 %) was from Alfa Aesor; 1-octanol (99 %), 1-octadecanol (95 %), L-valine (Val; 98 %), and p-toluenesulfonic acid monohydrate (98.5 %) were from Aldrich. Triethylamine (99.9%), methyl amine (40% aqueous solution) were from Alfa Aesor; (1\text{R}, 2\text{S})-(-)-norephedrine (Nor; 99%), ethanolamine (GlyOH; 99%), \textit{n}-decane (99%) and lithium aluminium hydride (LiAlH\textsubscript{4}, 95%) were from Aldrich; nitromethane (analytical grade) was from Fisher. Eosin Y (99%) was from Allied Chemical Co. Methanol (Aldrich, 99.8 %) was dried by Vogel’s method\textsuperscript{48}. Toluene (Aldrich, 99.9 %) was dried by refluxing over sodium metal for 5 h, followed by distillation. Carbon dioxide gas, generated by warming dry-ice, was dried by passing it
through a tube filled with indicating Drierite. Carbon disulfide (anhydrous, 99.9%) was purchased from Aldrich. *t*-Butyl amine (99.5%), *n*-hexylamine (99%), *n*-octylamine (99%), *n*-decylamine (99%), cyclohexylamine (99%), dibutylamine (99.5%), and 1,1,3,3-tetramethylguanidine (TMG) (99%) (all from Aldrich) were used as received. DBU (98% from Aldrich) was refluxed over CaH$_2$ (Acros) for 5 h and distilled at 67–68 °C/0.2 Torr onto activated 5Å molecular sieves (> 99.5% by GC). Chloroform-D (99.8% D) and deuterated water (99.9% D) were purchased from Cambridge Isotope Laboratory, Inc.

2.1.3 Instrumentation

IR spectra were obtained on a Perkin-Elmer Spectrum One FTIR spectrometer interfaced to a PC, using an attenuated total reflection accessory or NaCl plates. NMR spectra were recorded on an Inova 400 MHz Spectrometer operating at 400 MHz ($^1$H), or 100.5 MHz ($^{13}$C), respectively. $^1$H and $^{13}$C spectra were indirectly referenced to TMS using residual solvent signals as internal standards and CDCl$_3$ as the solvent. Gas chromatographic (GC) analyses were performed Hewlett-Packard 5890A gas chromatograph equipped with flame ionization detectors and a DB-5 (15 m × 0.25 mm) column (J & W Scientific, Inc.). GC-MS was performed on a Varian Saturn 2100 instrument in the electron ionization (EI) mode using a DB-5 (15 m × 0.25 mm) column. UV-Vis spectra were recorded on a Varian CARY 300 Bio UV-Visible spectrophotometer in Hellma suprasil quartz cells with 0.1 or 0.2 mm pathlengths. Thermal gravimetric analysis (TGA) measurements were performed under a nitrogen atmosphere at a 5 °C/min heating rate on a TGA Q50 thermo-gravimetric analyzer (TA Instruments) interfaced to a computer. Some of the TGA tests were repeated and the deviation between measurements was ca. ±2%. Differential scanning calorimetry (DSC) measurements were recorded on a DSC Q200 calorimeter (TA Instruments, New Castle, DE) interfaced to a TA Thermal Analyst 3100 controller, and equipped with a refrigerated cooling system (RCS90) to control the cooling rates. Polarizing optical micrographs (POMs) of ionic
liquids sandwiched between thin cover slides were recorded on a Leitz 585 SM-LUX-POL microscope equipped with crossed polars, a Leitz 350 heating stage, a Photometrics CCD camera interfaced to a computer, and an Omega HH503 microprocessor thermometer connected to a J-K-T thermocouple. The samples were cooled by flushing cold nitrogen gas passing through a coil in liquid nitrogen. GC-MS measurements were recorded on a SHIMADZU GC-17A gas chromatograph connected SHIMADZU QP-5000 mass spectrometer instrument using an SGE BPX5 (15 m × 0.25 mm, 0.25 µm) column and a flame ionization detector. Viscosity experiments were performed on an Anton Paar Physica MCR 301 rheometer (Anton Paar GmbH, Graz, Austria) using a parallel plate (radius 25 mm, gap 0.5 mm). Samples were equilibrated at 25 °C for about 5 min before starting measurements (at 25 °C). Some of the tests were repeated twice and the error between each experiment is ±5%.

Optical rotations were recorded on a Rudolph Instruments DigiPal 781 automatic polarimeter at 589 nm in Hellma quartz cells with 0.1 or 0.2 mm pathlengths (l). Observed rotations, $\alpha$ ($\pm$ 0.0005°), were averaged from 5 determinations, each along 3 different axes of the cylindrical cells, and are corrected for residual rotations by the empty cells. Specific rotations of neat amino acid esters or amino acid ester/amidine mixtures, $[\alpha_{\text{total}}]$, are from eq 2-1 and of the optically active component in the mixtures, $[\alpha_{\text{opt}}]$, are from eq. 2-2. Densities, $\rho$ (g·cm$^{-3}$), were estimated from the slopes of graphs of sample weights versus volumes at ca. 25 °C and were used to calculate $c$ (g·dL$^{-1}$).

$$[\alpha_{\text{total}}] = \alpha / (l\rho)$$  \hspace{1cm} (2-1)

$$[\alpha_{\text{opt}}] = 100 \alpha / (lc)$$  \hspace{1cm} (2-2)

Conductivities were measured with a Yellow Spring Instrument Co. Model 31 conductivity meter using Au electrodes, supported by Teflon material (Figure 2-1). The distance between two electrodes is 8 mm. The cell was constructed by Prof. Robert de Levie.
The conductivity values were calibrated using various concentrations of standard KCl solutions in water purified with a Millipore Co. Milli-Q system (resistance 18.3 mΩ·cm; conductivity 50 μS/cm). The water was sealed in a flask until use to prevent adventitious absorption of CO₂ from the atmosphere. Some of the conductivity tests were repeated, and the reproducibility of the measurements was ±3%.

![Image](image_url)

**Figure 2-1.** Photograph of the Au electrode placed in a 1 cm glass cuvette and used in conductivity measurements.

### 2.2 Reversible, room-temperature chiral ionic liquids. Amidinium carbamates derived from amidines and amino-acid esters with carbon dioxide

#### 2.2.1 Introduction

Here, we describe a diverse class of RTILs which combine reversibility, chirality, and ease of formation. They are made by exposing a 1/1 mixture of an easily synthesized amidine (L) and an alkyl ester of a naturally occurring amino acid (N) to CO₂ gas (Scheme 2-1). When nitrogen gas is passed through these RTILs, they are reconverted to their nonionic forms. All of the 50 amidine/amino acid ester (L/N) combinations examined here form an RTIL (L-N-C) upon exposure to CO₂ and they can be reconverted isothermally to their non-ionic L/N states by bubbling with a displacing gas, such as N₂. In addition, many of these RTILs persist as liquids to far below 0 °C. Although we have examined esters of only 6 amino acids here (Pro,
Leu, Ile, Val, Phe and Tyr), clearly, many more (including the 20 “naturally-occurring” ones commonly found in most proteins) are available for study; each offers potentially different properties and applications.

2.2.2 Syntheses of amino esters and amidines

The general procedure for synthesis of the amino acid methyl esters is presented in detail for LeuC1; minor variations were adopted for syntheses of the other esters.

*L-Leucine methyl ester (LeuC1).* Under a dry atmosphere, thionyl chloride 15.0 g (126 mmol) was added dropwise, with stirring, over a period of 10 min to 50 mL of absolute methanol which was cooled by an ice-salt bath (ca. -10 °C). The solution was stirred for another 10 min, 10.0 g (76.0 mmol) of L-leucine was added, and the solution was slowly heated to reflux and left there for 5 h. Excess thionyl chloride was removed by distillation and then subsequent distillations in which 10 mL aliquots of dichloromethane were added. The residue was placed under house vacuum at 70-75 °C for 2 h. (A trap of crushed sodium hydroxide/Drierite was placed between the house vacuum and the drying apparatus to remove any acid vapors). The yellowish solid was dissolved in 20 mL of water and extracted with 25
mL of diethyl ether. The aqueous phase was placed under 50 mL of diethyl ether and 30 % aqueous sodium hydroxide was added until pH 8 was reached. Most of the liquid was removed on a rotary evaporator. The remaining material was distilled to yield 7.44 g (41.0 %) of L-leucine methyl ester bp 32-33 ºC/0.35 Torr, as a clear liquid of 99 % purity (GC). IR 3381, 3313, 2956, 2871, 1736, 1679, 1619, 1468, 1437 cm⁻¹. ¹H NMR 3.71 (s, 3H, C(=O)OCH₃), 3.48 (t, 1H, C*H), 1.77-1.36 (m, 5H, NH₂, CH₂CH(CH₃)₂), 0.93 (m, 6H, (CH₃)₂) (lit.⁵¹ 3.72 (3H), 3.48 (1H), 1.78 (1H), 1.56 (1H), 1.43 (1H), 0.94 (3H), 0.92 (3H)). ¹³C NMR 177.24, 52.92, 51.95, 44.23, 24.84, 23.01, 21.90.

L-Isoleucine methyl ester (IleC₃).⁵⁰ Yield 37 % of a clear liquid of 99 % purity (GC), GC-MS: 146 ([M]⁺); bp 34-35 ºC/0.5 Torr. IR 3386, 3313, 2963, 2935, 2877, 1735, 1619, 1459, 1436 cm⁻¹. ¹H NMR 3.72 (s, 3H, C(=O)OCH₃), 3.35 (d, 1H, C*H); 1.74 (m, 1H, C*H-CH); 1.45 (m, 2H, NH₂); 0.88-1.2 (m, 8H, CH(CH₃)CH₂CH₃). ¹³C NMR 176.13, 51.63, 39.20, 39.20, 24.67, 15.73, 11.63.

L-Proline methyl ester (ProC₃).⁵² Yield 36 % of a clear liquid, purity 99 % (GC). bp 30 ºC/0.15 Torr. IR 3351; 2955; 2876; 1733; 1436 cm⁻¹. ¹H NMR 3.73 (s, 3H, C(=O)OCH₃), 3.77-3.75 and 3.57-3.52 (m, 1H, C*H-); 2.87-2.95 and 3.04-3.12 (m, 2H, -CH₂-NH-); 2.61 (br, 1H, NH); 1.34-2.36 (m, 4H, CH₂CH₂-C*H) (lit.⁵¹ 3.77 (3H), 3.74 (3H), 3.03 (1H), 2.91 (1H), 2.13 (1H), 1.85 (1H), 1.76 (2H)). ¹³C NMR 175.76, 59.50, 51.93, 46.89, 45.07, 30.10, 25.40.

L-Valine methyl ester (ValC₃).⁵³ Yield 25 % of a clear liquid of 99 % purity (GC), bp < 21 ºC/0.1 Torr. IR 3387, 3319, 2960, 2848, 1732, 1606, 1467, 1436 cm⁻¹. ¹H NMR 3.72 (s, 3H, C(=O)OCH₃), 3.29 (d, 1H, C*H); 2.01 (m, 1H, C*H-CH); 1.42 (m, 2H, NH₂); 0.89-0.98 (d-d, 6H, CH(CH₃)₂) (lit.⁵¹ 3.72 (3H), 3.30 (1H), 2.02 (1H), 0.97 (3H), 0.91 (3H)). ¹³C NMR 176.06, 59.98, 51.73, 32.19, 19.30, 17.23.

L-Phenylalanine methyl ester (PheC₃).⁵⁴ Yield 45 % of a clear liquid of 99 % purity (GC), bp 84 ºC/0.25 Torr. IR 3381, 3313, 3029, 2951, 2852, 1734, 1603, 1496, 1455, 1437.
cm\(^{-1}\). \(^1\)H NMR 7.16-7.32 (m, 5H, phenyl), 3.71 (m, 1H, C*H), 3.6 (s, 3H, C(=O)OCH\(_3\)), 3.07 (d-d, 1H, CH\(_2\)-Phenyl), 2.84 (d-d, 1H, CH\(_2\)-Phenyl), 1.43 (br, 2H, NH\(_2\)). (lit.\(^{51}\) 7.31 (2H), 7.24 (1H), 7.19 (2H), 3.74 (1H), 3.72 (3H), 3.08 (1H), 2.87 (1H)). \(^13\)C NMR 175.34, 137.21, 129.19, 128.47, 126.72, 55.78, 51.86, 41.05.

**L-Tyrosine methyl ester (TyrC\(_1\)).**\(^{54}\) Yield 56.5 % of a white solid of 99 % purity (GC), mp 135 - 136 °C (lit\(^{54}\) 134 -135 °C). IR 3355, 3297, 1743, 1597, 1514, 1480, 1443 cm\(^{-1}\). \(^1\)H NMR 7.04 (d, 2H, phenyl), 6.74 (d-d, 2H, phenyl), 3.68 - 3.73 (m, 4H, C*HC(=O)OCH\(_3\)), 3.03 (d-d, 1H, CH\(_2\)-Phenyl), 2.89 (d-d, 1H, CH\(_2\)-Phenyl). (lit.\(^{51}\) 6.87, 6.65 (4 H), 3.59 - 3.53 (4H), 2.87 (1H), 2.67 (1H), 2.62 (3H), 3.08 (1H), 2.87 (1H)).

**L-Leucine octyl ester (LeuC\(_8\)).** Yield 52 % of 99 % purity (GC). GC-MS: 244 ([M+H]\(^+\)), bp 74 °C/ 0.5 Torr. IR 3379; 3313; 2955; 2926; 2857; 1733; 1606; 1468 cm\(^{-1}\). \(^1\)H-NMR 4.10 (t, 2H, C(=O)OCH\(_2\)); 3.11 (d-d, 1H, C*H); 1.28-1.80 (m, 17 H, NH\(_2\), (CH\(_2\))\(_6\)CH\(_3\), CHCH\(_2\)-C*H); 0.86-0.96 (m, 9H, CH\(_3\), CH(CH\(_2\))\(_2\)). \(^13\)C-NMR 176.95; 65.08; 53.07; 44.35; 31.91; 29.31; 28.74; 26.03; 24.94; 23.09; 22.78; 22.05; 14.23.

**L-Isoleucine octyl ester (IleC\(_8\)).** Yield 6.6 g (48 %) of a colorless liquid of purity 99 % (GC), bp 72 °C/0.5 Torr. GC-MS: 244 ([M+H]\(^+\)) IR 3385; 2929; 2858; 1733; 1606; 1465 cm\(^{-1}\). \(^1\)H-NMR 4.11 (m, 2H, C(=O)OCH\(_2\)); 3.34 (d, 1H, C*H); 1.13-1.79 (m, 17 H, NH\(_2\), (CH\(_2\))\(_6\)CH\(_3\), C*HCH\(_2\)CH\(_3\)); 0.86-0.96 (m, 9H, CH\(_3\), CH(CH\(_2\))\(_2\)CH\(_3\)). \(^13\)C-NMR 175.94, 64.95, 59.31, 39.34, 31.92, 29.32, 28.79, 26.10, 24.81, 22.78, 15.92, 14.23, 11.84.

**L-Leucine octadecyl ester (LeuC\(_{18}\)).** A colorless liquid, purity 99 % (GC), was obtained in 45 % yield. GC-MS: 384 ([M+H]\(^+\)) IR 3390; 3324; 2955; 2915; 2849; 1718; 1606; 1472 cm\(^{-1}\). \(^1\)H NMR 4.10 (t, 2H, C(=O)OCH\(_2\)), 3.45 (m, 1H, C*H); 1.79-1.25 (m, 39H, NH\(_2\), C*HCH\(_2\)CH\(_3\), (CH\(_2\))\(_{17}\)CH\(_3\)); 0.85-0.96 (m, 9H, CH\(_3\), CH(CH\(_3\))\(_2\)).

**L-Isoleucine octadecyl ester (IleC\(_{18}\)).** A colorless liquid, purity 99 %, was obtained in 54 % yield. GC-MS: 384 ([M+H]\(^+\)) IR 3385, 2924, 2854, 1735, 1621, 1645. \(^1\)H NMR 4.10 (t,
2H, C(=O)OCH₂), 3.45 (d, 1H, C*=H); 1.78-1.21 (m, 39H, NH₂, C*HCH₂CH₃, (CH₂)₁₇CH₃); 0.86-0.96 (m, 9H, CH₃, CH(CH₂CH₃)CH₃).

Synthesis of N,N-Dimethyl-N’-hexyl ethanimidamide (C6): 20.0 g (197 mmol) n-hexylamine and 19.9 g (197 mmol) of triethylamine were added to 30 mL of dichloromethane, then 15.5 g (197 mmol) of acetyl chloride was slowly added into the solution. The mixture was stirred for 24 h under a nitrogen atmosphere. The reaction mixture was added to 25 mL of water containing hydrochloric acid (pH < 2). The organic layer was separated from aqueous phase. The aqueous phase was extracted with dichloromethane (25 mL × 3). The organic phases were combined, and then dried with anhydrous sodium sulfate. The volatile materials were removed by rotary evaporator. The N-hexyl acetylamide was isolated by distillation of the residue bp 83-84 °C/0.15 Torr (Lit. 55 125 ºC/30 Torr) Yield was 23.8 g (70.9 %). GC-MS: 144 ([M+H]+) Purity was 99 % (GC). IR (neat) 3286; 3089; 2957; 2930; 2859; 1651; 1555; 1460; 1438; 725; 602 cm⁻¹. ¹H NMR 5.97 (br, 1H, CH₂-NH₂); 3.22 (q, 2H, CH₂-NH-); 1.98 (s, 3H, -C(=O)CH₃); 1.44-1.50 (m, 2H, CH₃-CH₂-NH); 1.2-1.4 (m, 4H, CH₃-(CH₂)₂); 0.88 (t, 3H, CH₃-CH₂). ¹³C NMR: 170.31; 39.82; 31.59; 29.63; 26.71; 23.34; 22.66; 14.10.

15.0 g (105 mmol) of N-hexyl acetamide was added to 15 mL of dry toluene, then 11.2 g (105 mmol) of dimethylcarbamyil chloride were slowly added and then the mixture was refluxed under a nitrogen atmosphere for 24 h. The volatile materials were removed by rotary evaporator and in vacuo. After the residue was dissolved in chloroform (30 mL), aqueous solution of 4.2 g of NaOH in 40 mL water was added and the mixture was vigorously stirred for 30 min. Calcium carbonate (2.8 g) was added to the mixture and stirring was continued for another 30 min. The organic phase was separated and the aqueous phase was extracted with dichloromethane (25 mL × 3). The organic phases were combined and dried with anhydrous calcium carbonate. The volatile materials were removed by rotary
evaporator. The product was isolated by distillation of the residue bp 52-54 °C/0.25 Torr (lit.\textsuperscript{55} 125 °C/30 Torr). GC-MS: 171 ([M+H]+); Purity 99 % (GC). IR 2955.4; 2926.0; 2855.5; 1626.0; 1342.6; 1007.3; 726.0 cm\textsuperscript{-1}. \textsuperscript{1}H NMR 3.18 (t, 2H, -CH\textsubscript{2}-N=), 2.87 (s, 6H, -N-(CH\textsubscript{3})\textsubscript{2}); 1.87 (s, 3H, -N=C(CH\textsubscript{3})=N); 1.49 (m, 2H, -CH\textsubscript{2}-CH\textsubscript{2}-N=); 1.25-1.4 (m, 6H, CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{3}-); 0.88 (t, 3H, CH\textsubscript{3}). \textsuperscript{13}C NMR: 158.79; 50.32; 38.07; 32.49; 32.00; 27.38; 22.80; 14.17; 12.45.

\textit{N,N-Dimethyl-N’-butyl ethanimidamide (C4)}. A colorless liquid, bp 28-30 °C/0.25 Torr (lit.\textsuperscript{56} bp 69-71 °C/13 Torr). GC-MS: 143 ([M+H]+); Purity 98 % (GC). IR (neat) 2956, 2929, 286 (C-H), 1629 (N=C) cm\textsuperscript{-1}. \textsuperscript{1}H NMR 3.17 (t, 2H, J\textsubscript{HH} 7.2 Hz, -CH\textsubscript{2}-N=), 2.86 (s, 6H, -N-(CH\textsubscript{3})\textsubscript{2}); 1.87 (s, 3H, -N=C(CH\textsubscript{3})=N); 1.5 (m, 2H, -CH\textsubscript{2}-CH\textsubscript{2}-N=); 1.25-1.4 (m, 6H, CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{3}-); 0.88 (t, 3H, J\textsubscript{HH} 7.2 Hz, CH\textsubscript{3}). \textsuperscript{13}C NMR: 158.73; 49.92; 38.02; 34.68; 20.74; 14.20; 12.40.

\textit{N,N-Dimethyl-N’-amyl ethanimidamide (C5)}. A colorless liquid, bp 40-41 °C/0.25 Torr. Purity 98.5 % (GC). GC-MS: 157 ([M+H]+); IR (neat) 2956, 2927, 2857 (C-H), 1626 (N=C) cm\textsuperscript{-1}. \textsuperscript{1}H NMR 3.18 (t, 2H, J\textsubscript{HH} 7.5 Hz, -CH\textsubscript{2}-N=), 2.87 (s, 6H, -N-(CH\textsubscript{3})\textsubscript{2}); 1.88 (s, 3H, -N=C(CH\textsubscript{3})=N); 1.51 (m, 2H, -CH\textsubscript{2}-CH\textsubscript{2}-N=); 1.25-1.4 (m, 4H, CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{2}-); 0.90 (t, 3H, J\textsubscript{HH} 6.9 Hz, CH\textsubscript{3}). \textsuperscript{13}C NMR: 158.90; 50.35; 38.15; 32.27; 29.98; 22.87; 14.31; 12.53.

\textit{N,N-Dimethyl-N’-heptyl ethanimidamide (C7)}. A colorless liquid, bp 63-64 °C/ 0.25 Torr. Purity 99 % (GC). GC-MS: 185([M+H]+); IR (neat) 2956, 2925, 2854 (C-H), 1626 (N=C) cm\textsuperscript{-1}. \textsuperscript{1}H NMR 3.18 (t, 2H, J\textsubscript{HH} 7.5 Hz, -CH\textsubscript{2}-N=), 2.86 (s, 6H, -N-(CH\textsubscript{3})\textsubscript{2}); 1.87 (s, 3H, -N=C(CH\textsubscript{3})=N); 1.5 (m, 2H, -CH\textsubscript{2}-CH\textsubscript{2}-N=); 1.25-1.4 (m, 4H, CH\textsubscript{3}-(CH\textsubscript{2})\textsubscript{2}-); 0.88 (t, 3H, J\textsubscript{HH} 7.2 Hz, CH\textsubscript{3}). \textsuperscript{13}C NMR: 158.89; 50.40; 38.14; 29.69; 32.08; 32.00; 27.71; 22.81; 14.26; 12.53.

\textit{N,N-Dimethyl-N’-octyl ethanimidamide (C8)}. A colorless liquid, bp 72-77 °C/0.25 Torr. Purity 99 % (GC). GC-MS: 199 ([M+H]+); IR (neat) 2955, 2924, 2853 (C-H), 1627 (N=C) cm\textsuperscript{-1}. \textsuperscript{1}H NMR 3.17 (t, 2H, J\textsubscript{HH} 6.9 Hz, -CH\textsubscript{2}-N=), 2.86 (s, 6H, -N-(CH\textsubscript{3})\textsubscript{2}); 1.87 (s, 3H,
-N=C(CH$_3$)-N); 1.5 (m, 2H, -CH$_2$-CH$_2$-N=); 1.25-1.4 (m, 10H, CH$_3$-(CH$_2$)$_5$-); 0.88 (t, 3H, $J_{HH}$ 6.1 Hz, CH$_3$). $^{13}$C NMR: 158.68; 50.26; 38.00; 32.49; 32.00; 29.69; 27.70; 27.64; 22.73; 14.14; 12.38.

1-(p-Dimethylaminophenyl)-2-nitroethylene (DAPNE).$^{57}$ Red crystals, mp 180.6–180.9 °C (lit$^{57}$ mp 181 °C). $^1$H NMR 3.08 (s, 6H, Ar-N(CH$_3$)$_2$); 6.68 (2H, d, $J_{HH}$ 8.7 Hz, Ar-H); 7.43 (2H, d, $J_{HH}$ 9.0 Hz, Ar-H); 7.50 (1H, d, $J_{HH}$ 13.2 Hz, Ar-CH); 7.97 (1H, d, $J_{HH}$ 13.5 Hz, CH-NO$_2$).

DAPNE

2.2.3 Preparation of ionic liquids and their reconversion to amidine/amine mixtures

Neat bulk samples. Dry CO$_2$ gas was bubbled for 30 min through neat (1/1, mol/mol) amidine/amine acid ester samples in a glass vessel immersed in a room-temperature water bath; the uptake of CO$_2$ is slightly exothermic.

NMR samples. Measured quantities of an amidine and an amine were dissolved in a known volume of CDCl$_3$. In an alternating fashion, CO$_2$ and N$_2$ gases were bubbled through the solutions for 30 min at room temperature. At the end of each bubbling period, an NMR spectrum was recorded.

2.2.4 Measurements of CO$_2$ uptake

A mercury burette$^{3a}$ was filled with CO$_2$ gas and the apparatus was purged by flushing CO$_2$ through it for > 30 min. Then, a flask with a weighed amount of neat amidine/amine ester mixture was attached to the burette, and the number of ccs of CO$_2$ gas taken up by the amidine/amine ester mixture was recorded as a function of time and converted to molar equivalents assuming that the ideal gas law applies approximately. Readings on the burette
were recorded when two burettes’ mercury levels maintained the same height after moving the mercury container. The liquid was stirred with a Teflon-coated spin bar while the volume of CO$_2$ adsorbed was recorded as a function of time until no volume change was discernible. This procedure was repeated 3 times for each mixture using different aliquots of a sample and the average is reported here.

The percentage of the theoretical amount of CO$_2$ taken up ($\%$CO$_2$) was calculated as follows. The volume of CO$_2$ taken up by the amine/amidine solution ($V$) was calculated from eq. 2-3, where $V_{\text{blank}}$ is the volume decrease in the burette when the flask contained only CO$_2$ and $V_{\text{obs}}$ is the total volume decrease measured by the burette.

$$V = (V_{\text{obs}} - V_{\text{blank}}) \quad (2-3)$$

The theoretical volume of CO$_2$ ($V_{P,T}$) taken up by $M$ moles of amidine/amine at a known temperature ($T$, K) and pressure ($P$, Torr), assuming complete conversion to amidinium carbamate, was calculated using eq. 2-4, and assuming that CO$_2$ exhibits nearly ideal gas behavior at room temperature and one atmosphere of pressure.

$$V_{P,T} = \left[22.4 \times \frac{760}{P} \times \frac{T}{273.15}\right] \times M \quad (2-4)$$

Then,

$$\%\text{CO}_2 = \left[\frac{V}{V_{P,T}}\right] \times 100 \quad (2-5)$$

2.2.5 Results and discussion

The various L/N combinations examined are shown in Table 2-1. All 50 yield ionic liquids at room temperature after exposure to CO$_2$ gas despite the fact that some of the original mixtures are not liquids and all but those containing the amino acids with octadecyl esters remain liquids to -18 °C (vide infra). The maximum temperatures at which the L-N-C persist without losing CO$_2$ is ca. 50 °C according to thermal gravimetric analyses (vide infra). By contrast, all but one of the amino acid esters investigated solidified when they were exposed as neat liquids to CO$_2$. This solidification behavior has been observed during the
transformation of many simple achiral amines to ammonium carbamates upon the addition of CO₂, as well (Eq. 1-5 in Chapter 1).¹⁹

The diversity of the RTILs which can be formed with the amidines is demonstrated by the fact that the phenyl substituted amino acid methyl ester, PheC₁, also yields liquids, although they appeared qualitatively to be more viscous than those with the alkyl-substituted amino acid methyl esters. Clearly, there are many more possibilities for other L-N-C just from the list of naturally occurring amino acids. Although the list is too extensive to be studied exhaustively here, each is capable of imparting a different set of characteristics to its L-N-C and of affecting the stereo-chemical consequences of solute reactions, for instance. Furthermore, although the reactions to form the L-N-C and the L/N from them were performed under dry conditions, the systems appear to be able to tolerate a significant amount of water: addition of 3 wt% of H₂O to a C₆/LeuC₁ mixture did not impede its formation of an RTIL when it was exposed to CO₂ (yielding C₆-LeuC₁-CO₂). The results in Table 2-1 with IleC₈, LeuC₈, IleC₁₈, and LeuC₁₈ illustrate the ability of RTILs to be formed in which the amino acids have very long alkyl ester chains. None of the octyl or octadecyl esters exhibited a birefringent pattern when observed under a polarizing microscope before or after shearing, and therefore, none is liquid crystalline. Taken in toto, these results indicate that an exceedingly wide variety of RTILs can be made easily from much more diverse L/N mixtures than the structures in Scheme 2-1.
Table 2-1. Phases of neat 1/1 (mol/mol) L/N mixtures at room temperature and –18 °C (in parentheses) before (B) and after (A) CO₂ bubbling. L, S, W, and M indicate (respectively) liquid, solid, wax, and a turbid liquid mixture which eventually separated into solid and liquid components.

<table>
<thead>
<tr>
<th>Amidine</th>
<th>Amino acid methyl ester</th>
<th>Amino acid octyl ester</th>
<th>Amino acid octadecyl ester</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ProC₁</td>
<td>LeuC₁</td>
<td>IleC₁</td>
</tr>
<tr>
<td>C₄</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>C₅</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>C₆</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>C₇</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>C₈</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>none</td>
<td>L</td>
<td>L</td>
<td>S</td>
</tr>
</tbody>
</table>
The time dependence of CO\textsubscript{2} uptake by some of the amidine/primary acid ester mixtures was followed using a gas burette containing one atmosphere pressure of CO\textsubscript{2}. As was observed for the uptake of CO\textsubscript{2} by amidine/alkyl amine mixtures,\textsuperscript{3} \textit{C8/IleC\textsubscript{1}} added CO\textsubscript{2} rapidly,\textsuperscript{58} reaching a constant value near 100 % (Figure 2-2), as expected if the reaction in Scheme 2-1 (leading to RTIL formation) goes to completion. In addition, \textit{C8/IleC\textsubscript{8}} system showed similar CO\textsubscript{2} uptake plots as \textit{C8/IleC\textsubscript{1}} system, which indicates CO\textsubscript{2} uptake by the \textit{L/N} system was not disturbed by much longer alkyl chain length of amino acid ester. Uptake of CO\textsubscript{2} by the \textit{C8/ProC\textsubscript{1}} system, containing a secondary amino acid methyl ester, stopped after ca. 90 % of the amount calculated for one equivalence. Regardless, 90% uptake indicates that the \textit{C8/ProC\textsubscript{1}} system produces a useful RTIL. A lower affinity for CO\textsubscript{2} by the \textit{L/ProC\textsubscript{1}} systems was expected because primary amines are known to react more readily with CO\textsubscript{2} than secondary (or tertiary) amines.\textsuperscript{59} For that reason, we anticipated a much lower uptake of CO\textsubscript{2}.

![Figure 2-2](image.png)

**Figure 2-2.** Percentage uptake of CO\textsubscript{2} (%CO\textsubscript{2}) by \textit{C8/IleC\textsubscript{1}} (●), \textit{C8/IleC\textsubscript{8}} (○), and \textit{C8/ProC\textsubscript{1}} (▲) as a function of time upon exposure to 1 atm pressure of CO\textsubscript{2}. 

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TGA measurements of weight loss from heating $\text{C8/LeuC}_1$ and $\text{C8-LeuC}_1-\text{CO}_2$ are shown in Figure 2-3. They indicate that some of the amidine and amino acid ester evaporated in the stream of nitrogen gas which passed over the sample at elevated temperatures. The subtracted curve, Figure 2-3(c), has a plateau-like region above ca. 50 °C, corresponding to loss of 10.9 % sample weight. This amount is in excellent agreement with the calculated weight for loss of one molar equivalent of CO$_2$, 11.5 %. These results demonstrate that loss of CO$_2$ gas from the L-N-C becomes important in air atmospheres well above room temperature. The RTILs are more stable to heating when placed under CO$_2$ atmospheres.

We have also explored the temperatures at which some of the L-N-C RTILs crystallize. Except for those from amidine/octadecyl esters, all of the L-N-C remained liquids at -18 °C. Solidification of $\text{C6-LeuC}_{18}-\text{CO}_2$ and $\text{C6-IleC}_{18}-\text{CO}_2$ was observed.
by polarizing optical microscopy (Figure 2-4) as samples were cooled from room temperature and then heated subsequently from below their melting temperatures. For **C6-LeuC18-CO2**, solidification and melting occurred at 14.3–12.6 °C and 11.8–12.5 °C, respectively; for **C6-IleC18-CO2**, the corresponding temperatures were 9.2–11.6 °C and 9.5–11.0 °C. The freezing and melting temperatures for **C6-LeuC18-CO2** are in reasonably good agreement with the values determined by DSC (Figure 2-5) where the onsets of the cooling exotherm (-24.0 J/g) and heating endotherm (19.2 J/g) were at 7.6 and -3.1 °C, respectively; for **C6-IleC18-CO2**, the corresponding temperatures were 9.0 °C (22.0 J/g) and -5.5 °C (24.9 J/g). In subsequent cooling and heating cycles, the heats of transitions became progressively lower. We ascribe this behavior to loss of some CO2 while the sample was heated to 30 °C. Furthermore, **C6-LeuC1-CO2** to which had been added 3 wt% of water also remained a liquid at -18 °C after remaining in a freezer for 1 h, the sample was turned upside down and it flowed (rather than remaining at the top or falling as a solid would) due to gravity.

**Figure 2-4.** Optical micrograph of solidified **C6-LeuC18-CO2** (left) and **C6-IleC18-CO2** (right) at 8 °C. Scale bar is 400 μm.
Figure 2-5. DSC thermograms of C6-LeuC18-CO2 and C6-IleC18-CO2 from first cooling and heating protocols. The heats of each subsequent cooling/heating cycle were lower than the last, indicating progressively greater loss of CO2.

Formation of amidinium carbamate is also evidenced by IR spectral measurements. The typical N=C amidine stretch at 1629 cm\(^{-1}\) in the FT-IR spectrum of a neat mixture of C8/IleC1 \(^{60}\) was replaced by bands at 1646 cm\(^{-1}\) and 1575 cm\(^{-1}\), assigned to protonated amidine \(^{60}\) and carbamate stretches, \(^{19d}\) respectively, of C8-IleC1-CO2 (Figure 2-6).
Figure 2-6. IR spectra of neat C8/IleC1 (a) before and (b) after exposure to CO2.

Because the amino acid esters are optical active, we have investigated the changes that occur in their specific optical rotations at 589 nm before and after addition of CO2 (Table 2-2). As expected, the $[\alpha]_{\text{total}}$ of achiral amidine/amine mixtures remain within experimental error of 0° before and after addition of CO2. However, $[\alpha]_{\text{total}}$ of the mixtures with an amino acid ester, especially those with leucine, changed significantly in magnitude and changed sign upon addition of CO2. Although this behavior can be attributed to the interactions between amino esters and amidines after adding CO2 to form the ionic liquids, the nature of those specific interactions is not known at this time. Somewhat surprisingly, the $[\alpha]_{\text{opt}}$ values of C6/LeuC1 and C6/IleC1 are lower than the $[\alpha]_{\text{total}}$ values of their neat optically active components, LeuC1 and IleC1, respectively. This result suggests that even before the addition of CO2 to the L/N mixtures, amidine and amino acid ester molecules interact strongly. The specific nature of that interaction is not obvious from any of the other measurements we have made. However, we suspect that there is a strong interaction between the relatively acidic amino protons and the basic amidine functionality. An H-bonding interaction of this sort could alter the conformation at the chiral center of the amino acid esters and lead to the changes observed.61

Table 2-2. Specific rotations of alkyl amines and amino acid ester, and their amidine mixtures before and after exposure to 1 atm CO2.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\alpha]_{\text{total}}$</th>
<th>$[\alpha]_{\text{opt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LeuC1</td>
<td>17.10</td>
<td></td>
</tr>
<tr>
<td>C6/LeuC1</td>
<td>6.15</td>
<td>8.86</td>
</tr>
<tr>
<td>C6-LeuC1-CO2</td>
<td>-9.06</td>
<td>-13.05</td>
</tr>
<tr>
<td>IleC1</td>
<td>44.72</td>
<td></td>
</tr>
<tr>
<td>C6/IleC1</td>
<td>16.67</td>
<td>19.81</td>
</tr>
<tr>
<td>C6-IleC1-CO2</td>
<td>-0.98</td>
<td>-1.17</td>
</tr>
<tr>
<td>LeuC8</td>
<td>6.23</td>
<td></td>
</tr>
<tr>
<td>C6/LeuC8</td>
<td>6.53</td>
<td>2.71</td>
</tr>
<tr>
<td>C6-LeuC8-CO2</td>
<td>-12.87</td>
<td>-5.34</td>
</tr>
</tbody>
</table>

$[\alpha]_{\text{total}}$: Specific optical rotation for neat samples and mixtures; $[\alpha]_{\text{opt}}$: Specific optical rotation for the optical active component in amidine/amino acid ester ester mixtures.

A significantly different (and stronger) interaction between the two molecular components upon addition of CO$_2$ (and amidinium carbamate formation) is signaled by the change from positive to negative $[\alpha]_{\text{total}}$ values for the C6/LeuC1 and C6-LeuC1-CO$_2$ systems and the large decrease of $[\alpha]_{\text{total}}$ to nearly 0$^\circ$ for the C6/IleC1 system. In addition, the $[\alpha]_{\text{total}}$ values of C6/LeuC1 and C6/LeuC8 before and after CO$_2$ exposure indicate that the conformation at the chiral center of the amino acid ester is affected grossly by the absence or presence of CO$_2$, but not by the length of the alkyl ester chain.

Attempts to investigate the chirality of the RTILs and their L/N precursors by circular dichroism (CD) were unsuccessful because the achiral amidines absorb much more strongly in the UV than do the chiral amino acid esters. Apparently, the aforementioned interactions between the amidines and the amino acid esters, as well as those between the amidinium and carbamate components of the RTILs, do not induce significant chirality in the (planar) amidine parts or the aggregate intermolecular interactions attenuate the bulk chirality. Thus, both C6/IleC1 and
C6/LeuC1 showed no clear CD bands at wavelengths corresponding to their absorption bands at wavelengths where the optical densities were <1. Attempts to detect induced chirality\textsuperscript{61} in the uncharged (achiral) dye, 1-(p-dimethylaminophenyl)-2-methylene (DAPNE), and the anionic dye, Eosin Y, by adding them as solutes to C6/IleC1 and C6/LeuC1 and their RTILs, were unsuccessful; there were no discernible induced CD bands. Both dyes absorb above 290 nm, where absorption by the L/N and L-N-C are minimal.

A major attribute of these systems is their large polarity changes when exposed to CO\textsubscript{2} and N\textsubscript{2} gases\textsuperscript{3}. As an example, the polarity of one of our reversible amidine/amino acid ester systems was estimated using the solvatochromic dye\textsuperscript{62}, DAPNE, as a probe. Its 425 nm absorbance maximum in C8/IleC1 indicates an environment like that afforded by toluene (\(\lambda_{\text{max}} = 425\) nm).\textsuperscript{57} After CO\textsubscript{2} exposure, the \(\lambda_{\text{max}}\) is shifted to 443 nm, indicating a medium slightly less polar than N,N-dimethylformamide (DMF; \(\lambda_{\text{max}} = 446\) nm).\textsuperscript{57} Consistent with the presence of the ester functionality in the C8/IleC1 system, it is slightly more polar than the C8/1-hexylamine system in which DAPNE exhibited \(\lambda_{\text{max}} = 423\) nm before and 438 nm after addition of CO\textsubscript{2} (Table 2-3).\textsuperscript{3}

<table>
<thead>
<tr>
<th>solvent</th>
<th>(\lambda_{\text{max}}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)-heptane</td>
<td>393</td>
</tr>
<tr>
<td>(n)-decane</td>
<td>396</td>
</tr>
<tr>
<td>C8/hexylamine</td>
<td>423</td>
</tr>
<tr>
<td>C8/IleC1</td>
<td>425</td>
</tr>
</tbody>
</table>

Table 2-3. Absorption maxima (\(\lambda_{\text{max}}\)) of DAPNE\textsuperscript{57} in various solvents and RTILs.\textsuperscript{3a}
<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>425</td>
</tr>
<tr>
<td>THF</td>
<td>427</td>
</tr>
<tr>
<td>acetone</td>
<td>433</td>
</tr>
<tr>
<td>C8-hexylamine-CO₂</td>
<td>438</td>
</tr>
<tr>
<td>C8-IleC₁-CO₂</td>
<td>443</td>
</tr>
<tr>
<td>DMF</td>
<td>446</td>
</tr>
<tr>
<td>DMSO</td>
<td>456</td>
</tr>
<tr>
<td>Water</td>
<td>496</td>
</tr>
</tbody>
</table>

As such, it is possible to dissolve, reversibility, a low polar material into the L/N and separate them from the L-N-C phase or, by bubbling through N₂ gas, redissolve them into the L/N phase. An example of this strategy is shown in Figure 2-7. A solution of C8/LeuC₁ and n-decane containing Eosin Y became opaque after bubbling CO₂ through it for < 1 min. When centrifuged for ca. 10 min, the liquid separated into two phases, with the anionic dye isolated in the ionic liquid layer (as indicated by the color in it and the lack of discernible UV-vis absorption from Eosin Y in the n-decane layer). The two layers were reconverted to a single liquid phase by bubbling N₂ gas through and warming to ca. 40 °C to accelerate the displacement of CO₂. This RTIL appears to be very stable in n-decane at room temperature; it did not reconvert to a single layer after N₂ bubbling for 60 min at room temperature.
As found in the amidine/alkyl amine systems,$^3$ the chemical shifts of selected $^1$H and $^{13}$C resonances in NMR spectra of L-N-C, but not of the corresponding nuclei in the L/N mixtures, were sensitive to concentration in the range, 10–1500 mM (Figure 2-8). This dependence has been attributed to aggregation of the amidinium carbamates and must play a significant role in the optical rotation measurements noted above. A detailed study of the concentration dependence of CDCl$_3$ solutions of C$_8$/IleC$_1$ and C$_8$-IleC$_1$-CO$_2$ was performed. The nuclei of IleC$_1$ most affected, the protons of the geminal $N$-dimethyl groups (N=C-N(CH$_3$)$_2$), the C-methyl protons (N=C(CH$_3$)-N), the $\alpha$-methylene protons (-CH$_2$N=C-N), and the amidine carbon atom (N=C(CH$_3$)-N), exhibited only small peak shifts upon addition of CO$_2$. The resonances were shifted downfield when the concentration was increased up to 750 mM. By bubbling N$_2$ gas through the solutions with higher concentrations of C$_8$-IleC$_1$-CO$_2$ (350 mM; Figure 2-9), the proton and carbon signals could be returned to their C$_8$/IleC$_1$ values. The system was cycled 3 times between C$_8$/IleC$_1$ and C$_8$-
IleC$_1$-CO$_2$, with no or little discernible degradation of the sample. These results and the aforementioned partitioning of added $n$-decane provide strong evidence that the L/N $\Leftrightarrow$ L-N-C conversions are reversible and can be used to effect separations of solvents and solutes.

**Figure 2-8.** Concentration dependence of chemical shifts of key protons for C8/IleC$_1$ (open symbols) and C8-IleC$_1$-CO$_2$ (closed symbols) in CDCl$_3$: CH$_2$N=C-N (◇, ■ : 3.15-3.35 ppm), N=C-N(CH$_3$)$_2$ (○, ● : 2.85–3.15 ppm), N=C(CH$_3$)$_2$-N (Δ, ▲ : 1.85–2.1 ppm).
Figure 2-9. Chemical shifts in CDCl₃ solution of the protons and ¹³C nuclei of 350 mM C₈/IleC₁ which are most sensitive to the addition and removal (by N₂ bubbling) of CO₂. -CH₂N=C-N (●, 3.15 – 3.35 ppm), N=C-N(CH₃)₂ (▲, 2.85 – 3.15 ppm), N=C(CH₃)-N (■, 1.85 – 2.1 ppm), and N=¹³C-N (○, 158.7 – 161.2 ppm). The scale at left is for the filled data symbols; the scale at right is for the open circles.

In summary, we have described variety of reversible chiral RTILs derived from addition of carbon dioxide to a 1/1 mixture of an amidine and an ester derivative of a naturally occurring amino acid. They have an excellent ability for forming chiral RTILs. Also, it is anticipated that changing the alkyl chain length of the ester groups may enhance the solubility characteristics for different solutes and may influence chiral interactions with those solutes. Clearly, the chemical and physical properties,
such as density, and viscosity, of the RTILs can be adjusted with the choice of functional groups near the amine.

2.3 Carbon dioxide and molecular nitrogen as switches between ionic and uncharged room-temperature liquids comprised of amidines and chiral amino alcohols

2.3.1 Introduction

In this part, we report the properties of amidinium carbamates—reversible, room-temperature, chiral ionic liquids that are easily made from readily available amidines and chiral amino alcohols. Results from this work are compared with those from mixtures of amidines and alcohols and of amidines and achiral amines or chiral amino acid esters. Among their other attributes, the ionic liquids reported here persist over very wide temperature ranges, are much more tolerant to added water than an analogous reversible ionic liquid made from amidine and hexanol (that must be kept dry to avoid the formation of solids), and lack chromophores absorbing in the visible and the near UV region. Although several ILs and RTILs employing amino acids and their derivatives are known, none of which we are aware (except our own involving amino acid esters), including one which employs CO$_2$, has been reported to have switchable capability between non-ionic and ionic states.

The ionic liquid phases are prepared by exposing a 1/1 (mol/mol) mixture of an easily synthesized amidine ($N'$-alkyl-$N,N$-dimethylacetamidine; \textbf{L}) and an amino alcohol (\textbf{A}), obtained in one step by reduction of a naturally-occurring amino acid, to CO$_2$ gas (\textbf{C}) (Scheme 2-2); one commercially available amino alcohol with two chiral centers, (1$R$, 2$S$)-(-)-norephedrine, and one achiral amino alcohol, glycino (i.e., 2-aminoethanol; \textbf{GlyOH}), have been employed as well. All of the possible 40 combinations from the \textbf{L/A} mixtures in Scheme 2-2 form room-temperature ionic
liquids (L-A-C) in this way. They are stable indefinitely at room temperature under an atmosphere of CO₂ and all of them remain liquids to -20 °C. The L-A-C can be reconverted to their non-ionic (L/A) states after an inert gas (such as N₂) is bubbled through them at room temperature or, more rapidly, at slightly elevated temperatures.

Scheme 2-2

2.3.2 Syntheses of amino alcohols

The general procedure for synthesis of the amino alcohols is presented in detail for L-leucinol (LeuOH); minor variations were adopted for the other amino alcohols.

Over a 30 min period, lithium aluminum hydride 4.0 g (0.10 mol) was added to a cooled (ice-bath) suspension of L-leucine 10 g (0.076 mol) in 100 mL of THF under a nitrogen atmosphere. The ice bath was removed and the reaction mixture was warmed to room temperature, then refluxed for 24 h under a nitrogen atmosphere, and quenched by slowly adding sequentially water (4.0 mL), aqueous 15% of sodium hydroxide (4.0 mL), and water (12 mL). The mixture was stirred for 30 min and a white precipitate was separated by filtration. The filter cake was extracted with dichloromethane and the combined organic layers were dried with sodium sulfate, concentrated under reduced pressure, and distilled at bp 90 °C /0.9 Torr (lit.66 bp 64-65
ºC /1.5 Torr) to yield 5.3 g (60%) of a colorless liquid. Purity 98% (GC). \(^1\)H NMR: δ 3.56 (d-d, 1H, J\(^HH\) 10.5 Hz, 3.9 Hz, CH\(_2\)-OH); 3.23 (d-d, 1H, J\(^HH\) 10.5 Hz, 5.1 Hz, CH\(_2\)-OH); 2.87 (m, 1H, H\(_2\)N-C*H); 1.8-2.4 (br, 3H, NH\(_2\) and OH); 1.68 (m, 1H, CH\(_2\)-CH(CH\(_3\))\(_2\)); 1.21 (t, 2H, J\(^HH\) 10.5 Hz, C*H-CH\(_2\)-CH); 0.89-0.94 (m, 6H, CH(CH\(_3\))\(_2\)). \(^{13}\)C NMR: δ 67.12, 50.83, 43.68, 24.89, 23.58, 22.38.

**L-Prolinol (ProOH).** Yield: 48% of a yellowish clear liquid; Purity 99% (GC); bp 46-47 ºC/0.2 Torr (lit 67-89 ºC/6 Torr); \(^1\)H NMR: δ 3.22-3.58 (m, 5H, -NH-C*-CH\(_2\)-OH); 2.90 (t, 2H, J\(^HH\) 6.8 Hz, -CH\(_2\)-CH\(_2\)-NH-); 1.65-1.88 and 1.34-1.46 (m, 4H, CH\(_2\)-CH\(_2\)-C*H). \(^{13}\)C NMR: δ 64.90, 59.92, 46.50, 27.65, 26.01.

**L-Valinol (ValOH).** Yield: 50.2% of a colorless solid. Purity 98% (GC); mp 31.3-33.6 ºC (lit\(^{12}\) mp 32 ºC); bp 38-39 ºC /0.15 Torr (lit\(^{12}\) 55-57 ºC /2 Torr); \(^1\)H NMR: δ 3.64 (d-d, 1H, J\(^HH\) 13.5 Hz, 3.9 Hz, CH\(_2\)-OH); 3.28 (d-d, 1H, J\(^HH\) 13.5 Hz, 8.7 Hz, CH\(_2\)-OH); 2.56 (m, 1H, H\(_2\)N-C*H); 1.7-2.2 (br, 3H, NH\(_2\) and OH); 1.57 (m, 1H, C*H-CH(CH\(_3\))\(_2\)); 0.92 (m, 6H, CH(CH\(_3\))\(_2\)). \(^{13}\)C NMR: δ 64.89, 58.64, 31.71, 19.48, 18.56.

**L-Isoleucinol (IleOH).** Yield: 54% of a colorless solid. Purity 98% (GC). mp 32.5-37.3 ºC (lit\(^{68}\) mp 38-40 ºC); bp 61 ºC /0.5 Torr (lit\(^{68}\) 100-101 ºC /5 Torr); \(^1\)H NMR: δ 3.64 (d-d, 1H, J\(^HH\) 10.5 Hz, 3.9 Hz, CH\(_2\)-OH); 3.28 (d-d, 1H, J\(^HH\) 10.5 Hz, 9.0 Hz, CH\(_2\)-OH); 2.64 (m, 1H, H\(_2\)N-C*H); 1.48-1.57 (m, 1H, C*H-CH-); 1.12-1.39 (m, 2H, CH-CH\(_2\)-CH\(_3\)); 1.87 (br, 3H, NH\(_2\) and OH), 0.87-1.12 (m, 6H, CH(CH\(_3\))\(_2\)). \(^{13}\)C NMR: δ 64.52, 57.19, 38.79, 25.50, 15.29, 11.48.

**L-Methioninol (MetOH).** Yield: 83.5% of a yellowish solid. Purity 98% (GC). mp 33.1-34.6 ºC. (lit\(^{67}\) mp 34-35 ºC). \(^1\)H NMR: δ 3.60 (d-d, 1H, J\(^HH\) 10.5 Hz, 3.9 Hz, CH\(_2\)-OH); 3.34 (d-d, 1H, J\(^HH\) 10.5 Hz, 7.5 Hz, CH\(_2\)-OH); 2.95 (m, 1H, H\(_2\)N-C*H); 2.62 (m, 2H, CH\(_2\)-S-CH\(_3\)); 2.11(s, 3H, CH\(_2\)-S-CH\(_3\)); 2.0-2.3 (br, 3H, NH\(_2\) and OH)
1.73 and 1.54 (m, 2H, CH$_2$- CH$_2$-S-CH$_3$). $^{13}$C NMR: δ 66.92, 52.16, 33.83, 31.26, 15.83.

*L-Phenylalaninol (PheOH).* Yield: 62% of a colorless solid. Purity 99% (GC). mp 92.5-94.4 °C (lit$^{69}$ mp 91-93 °C). $^1$H NMR: δ 7.18-7.34 (m, 5H, Ph-H); 3.64 (d-d, 1H, $J_{HH}$ 13.5 Hz, 3.9 Hz, CH$_2$-OH); 3.36 (d-d, 1H, $J_{HH}$ 13.5 Hz, 7.5 Hz, CH$_2$-OH); 3.12, (m, 1H, H$_2$N-C*H); 2.80 (d-d, 1H, $J_{HH}$ 10.5 Hz, 5.1 Hz, CH$_2$-Ph); 2.53 (d-d, 1H, $J_{HH}$ 10.5 Hz, 8.5 Hz, CH$_2$-Ph); 1.64 (br, 3H, NH$_2$ and OH$^\ominus$). $^{13}$C NMR: δ138.95, 129.47, 128.85, 126.69, 66.64, 54.43, 41.22.

The acyclic amidines and DAPNE were available from previous studies. Their preparation methods and purities are mentioned in Section 2.1. Methods for the preparation of the ionic liquids, their reversion to their non-ionic states, the preparation of samples for NMR investigations, the measurement and calculation of optical rotations, and the measurement of CO$_2$ uptake as a function of time have been reported in Section 2.1 as well.

### 2.3.3 Conductivity measurements

The conductivity ($\sigma$) of the ionic liquids are obtained from the measured resistance (R) by the following eq. 2-6:

$$\sigma = l/AR$$

Where $l$ is the distance between the two electrodes in the impedance cell and $A$ is the area of the electrodes. The term $l/A$ is referred to as the cell constant and the conductivity values were calibrated using various concentrations of standard KCl solutions in water purified with a Millipore Co. Milli-Q system (resistance 18.3 m$\Omega$-cm; conductivity 50 $\mu$S/cm).$^{49}$ The water was sealed in a flask until use to prevent adventitious absorption of CO$_2$ from the atmosphere. The conductivity tests were repeated, and the absolute values differed by ca. ±3%.
2.3.4 Results and Discussion

The appearances of the phases of the L/A combinations at room temperature and at -20 °C, both before and after bubbling CO₂, are collected in Table 2-4. All the L/A combinations formed clear, nearly colorless ionic liquids after exposure to CO₂ at room temperature and remained so to -20 °C. By comparison, exposure of mixtures of the same amidines and either a simple amine³ᵃ or simple esters of the amino acids³ᵇ from which the amino alcohols were derived led to liquids in many cases, but to solids in others, even at room temperature. As expected, the L/A mixtures were qualitatively less viscous than the corresponding L-A-C ionic liquids (with their added electrostatic interactions), and those with the phenyl-substituted amino alcohols, PheOH and NorOH, were more viscous than the ionic liquids with alkyl-substituted amino alcohols. The ionic liquids are stable indefinitely at room temperature under one atmosphere of CO₂ pressure at room temperature and some are stable for very long periods in the air. However, TGA measurements indicate that the loss of CO₂ occurs very rapidly at ca. 50 °C in air.

Consistent with our observations on analogous systems employing an amidine and either a simple amine or an amino acid ester, the L/A and L-A-C retain their general phase characteristics when as much as 10% of water is added; the addition of water to an L/A mixtures did not impede the formation of L-A-C upon bubbling CO₂ and no precipitate or cloudiness was observed. To assure quantitative reproducibility, all experiments reported here were conducted under dry conditions unless stated otherwise.
Table 2-4. Appearances of 1/1 (mol/mol) amidine/amino alcohol mixtures at room temperature and at -20 °C (in parentheses) before (B) and after (A) exposure to CO₂.

<table>
<thead>
<tr>
<th>Amino alcohol</th>
<th>Glycinol</th>
<th>Prolinol</th>
<th>Leucinol</th>
<th>Isoleucinol&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Valinol&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Methioninol&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Phenylalaninol&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Norephedrine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amidine</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>C4</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L&lt;sup&gt;b&lt;/sup&gt; (L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
</tr>
<tr>
<td>C5</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
</tr>
<tr>
<td>C6</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L&lt;sup&gt;b&lt;/sup&gt; (L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
</tr>
<tr>
<td>C7</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
</tr>
<tr>
<td>C8</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L&lt;sup&gt;b&lt;/sup&gt; (L)</td>
<td>L(L)</td>
<td>L(L)</td>
<td>L(L)</td>
</tr>
<tr>
<td>none</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>

<sup>L</sup> and <sup>S</sup> indicate liquid and solid, respectively, at room temperature. <sup>a</sup> Samples were heated slightly above 50 °C until amino alcohols were dissolved before CO₂ bubbling. <sup>b</sup> Samples were initially a milky-white mixture that became a totally clear liquid upon further exposure to CO₂.
Figure 2-10. Percentage uptake of CO$_2$ (\%CO$_2$; based upon a presumed 1/1 stoichiometry for CO$_2$ and amino alcohol) by 1/1(mol/mol) C$_8$/ProOH (■), C$_8$/LeuOH (△), and C$_8$/ValOH (●) as a function of time upon their exposure to one atmosphere pressure of dry CO$_2$ gas at room temperature. Samples were stirred to increase the rate of molecular exchange at the gas-liquid interfaces.

The existence of amidinium carbamates was confirmed by the quantitative determination of \%CO$_2$ uptake by the L/A systems as a function of time using the mercury burette apparatus described above\textsuperscript{70} and, independently, by FT-IR, TGA, and $^1$H and $^{13}$C NMR measurements before and after samples were exposed to CO$_2$. The examples in Figure 2-10 show that the rates of CO$_2$ uptake during the first 10 min are fast, and reached plateau values after approximately 50 min. For C$_8$/LeuOH and C$_8$/ValOH mixtures, the theoretical amount is absorbed after ca. 30 min and another ca. 10\% was absorbed thereafter. These results indicate that both chemically-fixed and physically adsorbed CO$_2$ are present.\textsuperscript{71} The initial absorption is probably the result of the conversion of L/A to L-A-C phases, and the ca. 10\% excess is the physically
adsorbed part. Only 87% uptake of CO₂ was observed in the C8/ProOH system; the fractions that are chemically and physically absorbed are not known. It is known that the efficiency of CO₂ uptake by secondary amines, such as ProOH, is much less than that of primary amines. Because hydroxyl groups are also capable of reacting with CO₂ and then with an amidine, the %CO₂ uptake by 2/1 C8/LeuOH and C8/ValOH systems was examined to determine whether 2 molecules of gas can react per molecule of amino alcohol when 2 equivalents of amidine is present. In both cases, ca. 1.5 equivalents of CO₂ were absorbed, indicating that conversion of the hydroxyl groups to carbonates was not complete.

Figure 2-11. FT-IR spectra of C8/ValOH (a) and C8-ValOH-CO₂ (b).

Figure 2-11 shows the spectra of a C8/ValOH sample before and after bubbling CO₂ through it. After bubbling, the typical N=C stretching band of the C8 component
at 1629 cm\(^{-1}\) \(^{73}\) is replaced by bands at 1646 and 1575 cm\(^{-1}\) which can be assigned, respectively, to protonated amidine and carbamate stretching modes.\(^ {73}\) In addition, a broad band, centered at 3380 cm\(^{-1}\), from amidinium and carbamate N-H stretching modes, is found after bubbling.

Because each of the A components is optically active, the changes of the specific optical rotations ([\(\alpha\)]) upon changing from L/A to L-A-C phases could be investigated (Table 2-5). The specific rotations of the molecular mixtures, [\(\alpha\)]\(_{\text{total}}\), changed sign and magnitude during the L/A to L-A-C transformations. Furthermore, the specific rotations of the A components of the L/A mixtures, [\(\alpha\)]\(_{\text{opt}}\), were lower than the [\(\alpha\)] values of the corresponding neat amino alcohols. These results are consistent with our observations on systems with amidines and amino-acid esters, and can be attributed to the interactions between amino alcohols and amidines even before CO\(_2\) is added to form the ionic liquids. A manifestation of those interactions is the qualitatively higher viscosity of the L/A mixtures than of either of the components alone. We conjecture that the protons of the amino and hydroxyl groups of the A become strongly associated with the basic amidine functionalities. Such interactions can alter the conformations of the amino alcohols and lead to the observed changes of optical rotations. Although additional experimentation will be required to determine whether and to what extent the alkyl chains of amidinium cations associate in micro-heterogeneous domains within the L-A-C ionic liquids,\(^ {74}\) we suspect that they do and that such associations will lead to additional changes of the optical rotations. The self-association of surfactants in other ionic liquids has been demonstrated.\(^ {75}\)

However, attempts to observe solvent-induced dichroism in guest dye molecules\(^ {76}\) have been unsuccessful thus far. For example, addition of the uncharged dye, DAPNE, or the anionic dye, Eosin Y, to an L/C and the corresponding L-A-C did not result in
discernible CD signals in the region where the dyes absorb. These results indicate that it will be necessary to increase the specificity of the interactions between a guest and one of the host molecules if induced CD signals are to be observed.

Table 2-5. Specific rotations$^a$ of amino alcohols, and of amino alcohol/amidine mixtures before and after exposure to 1 atm CO$_2$ gas at 25 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\alpha_{\text{total}}$</th>
<th>$\alpha_{\text{opt}}$</th>
<th>Sample</th>
<th>$\alpha_{\text{total}}$</th>
<th>$\alpha_{\text{opt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ProOH</td>
<td>36.7</td>
<td></td>
<td>LeuOH</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>C6/ProOH</td>
<td>10.9</td>
<td>27.4</td>
<td>C6/LeuOH</td>
<td>2.7</td>
<td>3.8</td>
</tr>
<tr>
<td>C6-ProOH-CO$_2$</td>
<td>-20.1</td>
<td>-20.5</td>
<td>C6-LeuOH-CO$_2$</td>
<td>-21.5</td>
<td>-23.7</td>
</tr>
</tbody>
</table>

$^a$ $\alpha_{\text{total}}$ = specific optical rotation of neat samples and mixtures; $\alpha_{\text{opt}}$ = specific optical rotation of the amino alcohol component in mixtures. $\alpha$ values are ± 0.1°.

The concentration dependence of the NMR chemical shifts of selected $^1$H and $^{13}$C resonances in chloroform-$_d$ solutions of the L-A-C (but not the L/A mixtures) provides evidence that is consistent with the aggregation of amidinium-carbamate ionic pairs and microdomains of amidinium alkyl chains. As an example, the concentration dependence of the resonances from C6/IleOH and C6-IleOH-CO$_2$ in CDCl$_3$ at room temperature is shown in Figure 2-12. The L-A-C protons that are closest to ionic centers (N.B., the $N$-dimethyl groups ($N=C-N(CH_3)_2$), the C-methyl protons ($N=C(CH_3)_2-N$), and the $\alpha$-methylene protons ($-CH_2N=C-N$)) exhibited slight, but reproducible, downfield shifts as concentration was increased to 350 mM.
Figure 2-12. Chemical shifts of protons in equimolar mixtures of C6 and IleOH (open symbols) and the corresponding amidinium carbamate (closed symbols) that are most sensitive to concentration in CDCl₃ solutions: \(CH₂N=C-N\) (□, ■: 3.20–3.35 ppm), \(N=C-N(CH₃)₂\) (○, ●: 2.89–3.18 ppm), \(N=C(CH₃)-N\) (△, ▲: 1.89–2.12 ppm).

An interesting and potentially very useful attribute of these \(L/A ⇔ L-A-C\) systems is their ease of reversibility. The \(L-A-C\) ionic liquids were reconverted slowly to their non-ionic \(L/C\) phases by bubbling \(N₂\) through them at room temperature or, more rapidly, by bubbling the gas at slightly elevated temperatures. Clearly, other inert gases should be able to effect the \(L-A-C \rightarrow L/A\) phase transformations.
Figure 2-13. Chemical shifts of the protons and a carbon atom of 350mM C6/ProOH in CDCl3 by alternating the bubbling of CO2 and N2 over three cycles. (a) -C\textsubscript{6}H\textsubscript{2}N=\text{C}-N (●), (b) N=C-N(CH\textsubscript{3})\textsubscript{2} (▲), (c) N=C(CH\textsubscript{3})-N (■), and N=\textsuperscript{13}C-N (○). The scale at left is for the filled symbols; the scale at right is for the open circles.

A demonstration of this reversibility for the C6/ProOH system is shown by the NMR data in Figure 2-13. The amidinium carbamate was formed as a chloroform solution upon exposure to CO2 and the non-ionic components, C6 and ProOH, were reformed by bubbling N2 through the chloroform solution at 50 °C for 3 min. The chemical shift data indicate little or no discernible changes to the amidinium carbamate or the uncharged precursors upon repeated cycling. The FT-IR spectra in Figure 2-14, recorded during 2 bubbling cycles, provide additional evidence for the reversibility of the C6/ProOH system in the absence of chloroform as a diluent. The N=C stretch at 1629 cm\textsuperscript{-1} was replaced by peaks attributable to amidinium and
carbamate at 1646 and 1575 cm$^{-1}$ after exposure to CO$_2$. The changes in the frequencies were noted during two bubbling cycles.

![Figure 2-14](image)

**Figure 2-14.** Vertically offset IR spectra recorded sequentially for neat C6/ProOH (a), after bubbling CO$_2$ (i.e., C6-ProOH-CO$_2$) (b), the compound in (b) after bubbling with N$_2$ (c) at 50 °C, and the compound in (c) after bubbling with CO$_2$ (d).
Figure 2-15. Viscosities (Pa·s) at 25 °C of C8-IleOH-CO2, C8-LeuOH-CO2, C4-IleOH-CO2, C4-LeuOH-CO2, C8/IleOH and C8/LeuOH (from top to bottom) as a function of shear stress (Pa).

As shown in Figure 2-15, the viscosities of the L/A and L-A-C are virtually independent of shear rate; they exhibit Newtonian behavior. Shear rate versus shear stress plots are shown in Figure 2-16. The average viscosities over the ranges of shear stress for the L/A mixtures, C8/LeuOH and C8/IleOH, are 0.020 and 0.036 Pa·s, respectively. After exposure to CO2, the viscosities of these samples increase by orders of magnitude to 3.8 (C8-LeuOH-CO2) and 6.5 Pa·s (C8-IleOH-CO2). With the shorter chained amidine, C4, the L-A-C viscosities are somewhat lower—0.28 Pa·s for C4-LeuOH-CO2 and 1.5 Pa·s for C4-IleOH-CO2—but both are higher than the viscosities the more common ionic liquids.

Figure 2-16. Shear stress (Pa) versus shear rate (s⁻¹) plots of C4-LeuOH-CO2 (green), C4-IleOH-CO2 (black), C8-IleOH-CO2 (blue), C8-LeuOH-CO2 (red) at room temperature.
We have also measured the electronic conductivity (σ) of chloroform solutions of some mixtures that were cycled between their L/A and L-A-C forms by bubbling with CO₂ and N₂. Chloroform was added to reduce the viscosity, thereby allowing more rapid flow of ions, and decreasing the amount of aggregation among the ions.⁷⁷

The conductivity of the neat chloroform employed remained < 0.1 µS/cm after bubbling CO₂ through it for 30 min. As expected, addition of an uncharged L/A mixture, C₈/IleOH (Figure 2-17), did not increase the conductivity to a much higher level. However, the conductivity increased rapidly as CO₂ was bubbled through the solution and the ionic C₈-IleOH-CO₂ formed; at the C₈/IleOH concentration employed, the conductivity reached a plateau value of 268 µS/cm. When N₂ was passed subsequently through the solution, the conductivity decreased to 25 µS/cm, a value nearly identical to the conductivity of the original C₈/IleOH solution. The inset in Figure 2-17 shows the conductivity changes during two bubbling cycles. Combined with the results shown in Figure 2-18, we attribute the small decrease after the second CO₂ bubbling to evaporation of some of the chloroform (and resultant increase in viscosity and ion aggregation) that occurs during the bubbling procedures.
Figure 2-17. Conductivity at 25 °C of 50 wt % C8/IleOH in CHCl₃ as a function of time of bubbling CO₂. The inset shows maximum conductivities at 25 °C when CO₂ (at 25 °C) and N₂ (at 50 °C) were bubbled through sequentially. The N₂ bubbling was conducted at 50 °C to accelerate the loss of CO₂.

The conductivity values at room temperature of three neat C8 amidine and amino alcohol combinations, before and after exposing them to CO₂ for 30 min, are shown in Table 2-6. The conductivity values of the L-A-C phases are similar to those of related ionic liquids, but are less than those of imidazolium-based ionic liquids. The mobilities of the ions in the L-A-C phases are attenuated by the relatively high viscosities as well as the aforementioned ion aggregation.

Table 2-6. Conductivities of three neat equimolar C8/amino alcohol combinations before (L/A) and after (L-A-C) exposing them to CO₂ for 30 min at room temperature.
<table>
<thead>
<tr>
<th>amino alcohol (A)</th>
<th>conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L/A</td>
</tr>
<tr>
<td>ProOH</td>
<td>22</td>
</tr>
<tr>
<td>MetOH</td>
<td>15</td>
</tr>
<tr>
<td>IleOH</td>
<td>14</td>
</tr>
</tbody>
</table>

To explore further the influences of viscosity and ion-pairing on conductivity of the L-A-C, various concentrations of C8/IleOH and C8-IleOH-CO₂ were prepared in chloroform and water and their conductivities were measured at room temperature (Figure 2-18). As expected, the conductivities of the C8/IleOH remained low at all concentrations in chloroform but increased significantly with increasing water content, to a plateau value of ca. 2.1 mS/cm.

In contrast, the conductivity of C8-IleOH-CO₂ increased dramatically when small amounts of either chloroform or water were added; a maximum of 319 µS/cm, about 5.5 times higher than the conductivity of neat C8-IleOH-CO₂, was reached at 80 wt% of CHCl₃, and the maximum conductivity, at 70 wt % water, was 7.1 mS/cm. Clearly, the net effect of adding chloroform or water is a convolution of two factors that increase conductivity—higher ion mobilities and less ion pairing—and one that decreases it—lower ion concentrations. Separation of these factors and quantification of each are not trivial. Furthermore, the very large conductivities when water is added to C8-IleOH-CO₂ must be due, in part, to reaction of water and CO₂ to form carbonates.
Figure 2-18. Conductivity of C8/IleOH as a function of CHCl₃ (a) and H₂O (b) concentrations before (○) and after (●) bubbling CO₂ through their solutions at room temperature.

Knowledge of the degree of miscibility of ionic liquids with other solvents is important for several applications, including their use in liquid-liquid extraction processes.⁷⁹ As with many other types of RTILs, our L-A-C phases are miscible with highly polar solvents, such as water, DMSO and ethanol (Table 2-7). Although the polarity of most ionic liquids depends on the length of the alkyl chains on (what is
usually) the cationic portion, the length of the amidine alkyl chain does not appear to influence strongly the miscibility of the L-A-C phases we have investigated. Instead, the structural differences among the carbamates derived from the amino alcohols seem to be the most important determinant of L-A-C polarity. When the L-A-C are mixed with lower polarity solvents, such as hexane, toluene and diethyl ether, two phases, whose volumes were similar to the amounts of each added, were observed. The L-A-C RTILs prepared from the phenyl-substituted amino alcohols, NorOH and PheOH, were immiscible or only partially miscible with dichloromethane and ethyl acetate, and C6-NorOH-CO2 was also only partially miscible with chloroform. The other L-A-C RTILs investigated here were completely miscible with dichloromethane, ethyl acetate and chloroform.
### Table 2-7. Miscibility behavior of various 1/1 (vol/vol) L-A-C/organic solvent mixtures at room temperature.\(^a\)

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>C4-IleOH-(\text{CO}_2)</th>
<th>C5-IleOH-(\text{CO}_2)</th>
<th>C6-ProOH-(\text{CO}_2)</th>
<th>C6-NorOH-(\text{CO}_2)</th>
<th>C8-PheOH-(\text{CO}_2)</th>
<th>C8-ProOH-(\text{CO}_2)</th>
<th>C8-ValOH-(\text{CO}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexane</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
</tr>
<tr>
<td>toluene</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
<td>(I)</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(I)</td>
<td>(I)</td>
<td>(M)</td>
<td>(M)</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(I)</td>
<td>(P)</td>
<td>(M)</td>
<td>(M)</td>
</tr>
<tr>
<td>chloroform</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(P)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
</tr>
<tr>
<td>ethanol</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
</tr>
<tr>
<td>DMSO</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
</tr>
<tr>
<td>water</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
<td>(M)</td>
</tr>
</tbody>
</table>

\(^a\)\(I\)=immiscible, \(M\)=miscible, \(P\)=partially miscible (i.e., only part of this solid amino alcohol was dissolved; most of the amino alcohols are liquids at room temperature.).
The L/A and L-A-C are potentially interesting hosts for optical spectroscopic studies. Neat 1.0 mm pathlength samples of both with A molecules containing acyclic, saturated side groups are almost completely transparent above 300 nm, and others are transparent at > 400 nm. As a demonstration of this utility, the changes in solvent polarity induced by bubbling CO₂ through an L/A sample or N₂ through an L-A-C sample were investigated using the uncharged solvatochromic dye,\textsuperscript{62} DAPNE.\textsuperscript{57}

The $\lambda_{\text{max}}$ of this dye in C8/ValOH, 424 nm, indicates a polarity like that of toluene (425 nm) (Table 2-8). Upon exposure to CO₂, the $\lambda_{\text{max}}$ value was shifted bathochromically to 443 nm, indicating an environment whose polarity is between that of acetone ($\lambda_{\text{max}} = 433$ nm) and DMF ($\lambda_{\text{max}} = 446$ nm). In general, the L/A and L-A-C polarities reported by DAPNE are somewhat higher than and similar to, respectively, those found for mixtures of L-A-C in which the A component is an amino acid ester. The difference between the polarities of the two sets of L/A can be attributed to the polar hydroxyl groups in the amino alcohols. Regardless, the L-A-C appear to be less polar than imidazolium-based RTILs; for example, the spectroscopically determined polarities of 1-butyl-3-methyl imidazolium ionic liquids are like those of methanol and ethanol.\textsuperscript{81}

Table 2-8. Absorption maxima ($\lambda_{\text{max}}$) of 2.4 mM DAPNE\textsuperscript{57} in various solvents and RTILs.\textsuperscript{3}

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>393</td>
</tr>
<tr>
<td>n-decane</td>
<td>396</td>
</tr>
<tr>
<td>C6/ProOH</td>
<td>424</td>
</tr>
</tbody>
</table>
The ability of the **L/A** and **L-A-C** to interconvert without adding liquid or solid reagents opens the possibility for these RTILs to be used to solubilize and precipitate/(phase separate) added species selectively. Figure 2-19 shows an example of how such a system can be employed. After exposure to CO₂ for 1 min and followed by centrifugation for 3 min, an initial solution of *n*-decane and **C6-ProOH** (containing a very low concentration of Eosin Y as a marker) separated into two phases, with *n*-decane on top and the much more polar **C6-ProOH-CO₂** (with the dye) on the bottom. When N₂ was bubbled through the two-phase system (at room or slightly elevated temperatures) to displace the CO₂, the one-phase (low-polarity) solution was reformed.

<table>
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<th>Compound</th>
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<tr>
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<tr>
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<td>DMSO</td>
<td>456</td>
</tr>
<tr>
<td>Water</td>
<td>496</td>
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</tbody>
</table>
Figure 2-19. Photographs of a 1/1 (v/v) \( n \)-decane/(\( C_6 / \text{ProOH} \)) solution containing 0.3 μM Eosin Y (left) and after CO\(_2\) bubbling for 1 min and centrifugation for 3 min (right). The two-phase system became one phase again by bubbling through N\(_2\) for 5 min at 50 ºC.

2.3.5 Conclusions

A series of easily-prepared, chiral, room-temperature ionic liquids has been made and characterized. A very important attribute of these liquids is their ability to be transformed from high-polarity, ionic states to low-polarity, uncharged phases by exposure to an inert gas such as N\(_2\) and to reconver the low-polarity phases to their high-polarity phases by adding CO\(_2\) gas. It was somewhat surprising, but gratifying, that all of the combinations of amidines and amino alcohols examined form room-temperature ionic liquids when exposed to CO\(_2\). They appear to remain liquids with larger structural variations and over wider temperature ranges—generally from below -20 ºC to ca. 50 ºC under one atmosphere of CO\(_2\)—than the amidine-alkylamine\(^a\) and amidine-amino acid ester\(^b\) systems examined. The L-A-C phases are more viscous than their corresponding L/A phases, the conductivities increase dramatically between

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the L/A and L-A-C phases, and the solubility characteristics of the liquids can be modulated significantly by the gas to which they are exposed.

Also, the amino alcohols provide a chiral center and a potentially useful hydroxyl functionality for future applications (i.e., as task-specific RTILs). In addition, L-A-C system is much less sensitive to water than other reversible RTILs that have been reported. Thus, experiments need not be performed under scrupulously dry conditions. Additionally, the components of these RTILs are biodegradable and have low toxicity. Their reversibility, chirality, broad temperature ranges, tolerance to water, and, ease of preparation should make the combination of L/A and L-A-C phases useful as solvents for several ‘green’ applications.

In that regard, the addition of a second chiral center, as in (1R, 2S)(−)-norephedrine, may improve the affinity of an amino alcohol for CO₂ and the ability of its L-A-C phases to act as chiral inductors for guest reactions, separations, etc. The reversibility of these liquids is especially promising for the easy separation of components of reactions in which the products are soluble in low-polarity media and their formation depends on contact with a metal catalyst soluble only in high-polarity media; the catalyst should be easily recoverable if it precipitates when N₂ is bubbled through the L-A-C phase in which the reaction was conducted. Future work will focus on such applications, on their use as hosts for optical spectroscopic studies (because they lack chromophores absorbing in the visible and into the near UV region), and on increasing their upper temperature limits. Possible strategies for accomplishing the latter are to place the ionic liquids under several atmospheres of CO₂ pressure or to use CS₂ in place of CO₂ (yielding more thermally stable dithiocarbamates) as a means to convert the L/A into ionic liquids.
2.4 In situ formation of thermally stable, room-temperature ionic liquids from
CS₂ and amidine/amine mixtures.

2.4.1 Introduction

Research from this laboratory has demonstrated that the gel networks⁶ made
when a triatomic molecule is added to a ‘latent’ alkylamine gelator and the ionic
crosslinks formed similarly within amino-polysiloxanes (vide infra)⁸⁵ are thermally
more stable with CS₂ (an environmentally harmful liquid⁸⁶) than with CO₂. In addition,
others have investigated the properties of functional materials made by adding CS₂ to
liquid-like mixtures.⁸⁷,⁸⁸,⁸⁹,⁹⁰ It is reasonable to assume that formation of an
isothiocyanate (R-NCS) is involved in the first step leading to the thiourea.⁹¹ The
difference in reactivity of carbamates and dithiocarbamate is a consequence of the
lower bond strength of N-CO₂ than in N-CS₂ and the greater thermodynamic stability
of CO₂. In both the carbamate and dithiocarbamate anions, the oxygen-carbon or
sulphur-carbon and carbon-nitrogen bonds have some double bond character.
Although reactions of amines with either CO₂ or CS₂ are exothermic, the enthalpy of
formation of dithiocarbamates is more favored. In a simple example, thiourea
formation from ammonia and CS₂ is more energetically favorable than is the
formation of urea from ammonia and CO₂,⁹⁰ see data in Section 2.5.
Here, we describe the properties of the RTILs obtained when CS₂ is added to L/A mixtures (Scheme 2-3). As expected, the amidinium dithiocarbamates (L-A-S) are more thermally stable (to ~80 °C under air atmospheres) than the corresponding ammonium carbamates (to ~50 °C under CO₂ atmospheres) and have other attractive features, but they are not thermally reversible. However, loss of CS₂ can be accomplished at room temperature by adding a small amount of a solution of dilute aqueous carboxylic acid.

Here, the pathways for reaction of the neat L-A-S above 80 °C are inferred from their thermolysis products. The thermal, conductive, and spectroscopic properties of these RTILs are presented and compared with those of their non-ionic phases and of the corresponding amidinium carbamates. The latter comparison addresses the extent to which changing the triatomic molecular adduct influences the properties of the RTILs and demonstrates further that environmentally deleterious triatomic molecules can have beneficial purposes in materials science.
2.4.2 Amidinium dithiocarbamate sample preparation

CS$_2$ liquid (1 mole equivalent) was added slowly to a stirred amidine and amine sample in a glass vial in the air. The vial was placed in an ice-water bath during the CS$_2$ addition to dissipate the heat from the exothermic reaction. (Warning: CS$_2$ is a toxic liquid and H$_2$S is a very toxic gas that should be handled carefully.) The vials were closed once addition of the CS$_2$ was completed.

2.4.3 Thermolyses

General procedure for synthesis of tC$_4$-t-butylamine-CS$_2$ and separation of its thermolysis products. CS$_2$ liquid 0.76 g (10 mmol) was added slowly to a stirred solution of 1.3 g (10 mmol) tC$_4$ and 0.73 g (10 mmol) tert-butylamine in 4.0 mL chloroform in a round bottom flask. The flask was placed in an ice-water bath during the CS$_2$ addition to dissipate the heat from the exothermic reaction. The mixture was stirred for 1 h at room temperature in a closed vessel. Then, the temperature was raised to 120 °C for 2 h. The products were separated by column chromatography (silica gel; 3:1 and 2:1 hexanes: ethyl acetate as eluants) and were identified spectroscopically, using literature assignments for comparison; the literature citations are noted after the name of each compound; the spectroscopic data below are for the isolated products. Before separation by column, the data from the $^1$H NMR spectra of the thermolysis mixture indicated a molar ratio of 58:42 N-tert-butyl-N',N'-dimethylthiourea (D):N,N'-di-tert-butylthiourea (E).

Tert-butyl isothiocyanate $^{92}$ (AA): a liquid, C$_3$H$_9$NS. $^1$H NMR (400MHz, CDCl$_3$) $\delta = 1.37$ (9H, s, C(CH$_3$)$_3$); $^{13}$C NMR (100MHz, CDCl$_3$) $\delta = 131$ (C=S), 57 (C(CH$_3$)$_3$), 30. 7 (C(CH$_3$)$_3$); IR (thin film) $\nu = 2981, 2081, 1975, 1368, 1207$ cm$^{-1}$; MS (EI) m/z (M$^+$) 115.
Tert-butyl thioformamide\(^93\) (B): a liquid, C\(_{5}\)H\(_{11}\)NS. \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta = 1.36\) (9H, s, C(CH\(_3\))\(_3\)), 7.6-8.0 (1H, br, s, NH), 9.25-9.28 (1H, d, J=7.8Hz, CH); \(^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta = 187.7\) (C=S), 55.8 (C(CH\(_3\))\(_3\)), 29.8 (C(CH\(_3\))\(_3\)); IR (thin film) \(\nu = 1567, 1369, 1041\) cm\(^{-1}\); MS m/z (M\(^+\)) 117.

\(N,N\)-Dimethyl thioformamide\(^94\) (C): a liquid, C\(_{7}\)H\(_{13}\)NS. \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta = 3.27-3.29\) (6H, d, J=4.6 Hz, N(CH\(_3\))\(_2\)), 9.2 (1H, s, CH); \(^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta = 188.2\) (C=S), 45.3 (N(CH\(_3\))\(_2\)), 37.2 N(CH\(_3\))\(_2\)); IR (thin film) \(\nu = 1540, 1397, 1130, 1040\) cm\(^{-1}\); MS m/z (M\(^+\)) 89.

\(N\text{-Tert-butyl-}\,N\text{'-dimethylthiourea}\(^95\) (D): a white solid, mp 85-88 °C (no reported lit value); C\(_{7}\)H\(_{16}\)N\(_2\)S. \(^1\)H NMR (400MHz, CDCl\(_3\)) \(\delta = 1.54\) (9H, s, C(CH\(_3\))\(_3\)), 3.21 (6H, s, N(CH\(_3\))\(_2\)) 5.1-5.3 (1H, br, s, NH); \(^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta = 181.2\) (C=S), 56.0 (C(CH\(_3\))\(_3\)), 29.7 (C(CH\(_3\))\(_3\)); IR (ATR) \(\nu = 1548, 1393, 1346, 1131, 1050\) cm\(^{-1}\); MS m/z (M\(^+\)) 160.

\(N\text{-N'-Di-tert-butylthiourea}\(^96\) (E): a white solid, mp 128–130 °C (lit.\(^96\) mp 131–132 °C); C\(_{9}\)H\(_{20}\)N\(_2\)S. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 1.48\) (18H, s, C(CH\(_3\))\(_3\)), 5.7-5.8 (2H, br, NH); \(^{13}\)C NMR (100MHz, CDCl\(_3\)) \(\delta = 180.2\) (C=S), 54.0 (N(CH\(_3\))\(_2\)); IR (ATR) \(\nu = 3300, 1540, 1320, 1210\) cm\(^{-1}\). MS m/z (M\(^+\)) 188.

Procedures for identification of dimethylamine and t-butylamine upon thermolyses of tC\(_4\)-t-butylamine-CS\(_2\). A HCl/D\(_2\)O solution was prepared by bubbling HCl gas (generated by dropping sulfuric acid into hydrochloric acid and passing the vapors through a Drierite tube) into D\(_2\)O in a round-bottom flask (to which a Drierite drying tube was attached at the exit side). Then, the vapor from thermolysis of 1.0 g (3.6 mmol) tC\(_4\)-t-butylamine-CS\(_2\) was introduced into the HCl/D\(_2\)O solution that had been cooled in an ice-water bath. The peaks characteristic of the hydrochloride salts
of dimethylamine and t-butylamine were found in the $^1$H NMR and $^{13}$C NMR spectra (reported below) and are consistent with values reported in the literature.

*Dimethylammonium chloride.* $^{97}$ $^1$H NMR (400 MHz, CDCl$_3$): δ = 2.88 (6H, s, N(CH$_3$)$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 32.6 (N(CH$_3$)$_2$).

*Tert-butyllammonium chloride.* $^{98}$ $^1$H NMR (400 MHz, CDCl$_3$): δ = 1.10 (9H, s, C(CH$_3$)$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 26.5 (C(CH$_3$)$_3$), 48.8 (C(CH$_3$)$_3$).

2.4.4 Density measurements

Densities were measured by a method that yields only approximate values.$^{99}$ For the purpose that they were used, to construct Walden plots,$^{111}$ the values obtained are adequate. An aliquot of **C4-hexylamine-CS$_2$** was weighed in a 1.00 mL volumetric flask that was filled to the mark initially at room temperature. The flask was heated in stages to progressively higher temperatures in a GC oven and equilibrated at each temperature for 15 min before the excess volume from thermal expansion was removed rapidly by syringe and the flask was reweighed. Because the density changes are small over the temperature range investigated, the probable experimental errors have little effect on the overall conclusions derived from them.

2.4.5 Transformation from ammonium dithiocarbamates to amidinium dithiocarbamates

CS$_2$ liquid 0.16 g (21 mmol) was added slowly to a round-bottom flask containing a stirred solution of 0.43 g (42 mmol) $n$-hexylamine in 2.0 mL chloroform-$d$. The solution was stirred for 30 min at room temperature in a dry atmosphere. $^1$H and $^{13}$C NMR spectra of an aliquot were recorded and shown to be consistent with the ammonium dithiocarbamate (Figure 2-21a). Then, 0.71 g (42 mmol) **C6 amidine** and 0.16 g (21 mmol) CS$_2$ were added. After another 30 min of stirring, $^1$H and $^{13}$C NMR (Figure 2-21b) of an aliquot were recorded. They demonstrated that the product was
the amidinium dithiocarbamate without any detectable amount of ammonium
dithiocarbamate.

2.4.6 Results and Discussion

Table 2-9. Phases\(^a\) of neat 1/1 (mol/mol) L/A mixtures before \((b)\) and after \((a)\) adding
CS\(_2\) at room temperature and phase appearances at -20 °C in parentheses; melting
points (°C) of ammonium dithiocarbamates which are solids at room temperature are
presented numerically.
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<tr>
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\* L = liquid, S = solid.
The appearances of the phase of the L/A combinations at room temperature, both before and after adding CS₂, are collected in Table 2-9. Primary amines, secondary amines, amino esters and amino alcohols were tested as A components. Aliphatic amidines, DBU and 1,1,3,3-tetramethylguanidine (TMG) were employed as the L components. A large number of the combinations remain liquids at room temperature after adding CS₂. However, none of the combinations with the longest-chained linear amidine, C₁₆, produced a liquid dithiocarbamate at room temperature; in general, the shorter chained L appear to favor the formation of liquid L-A-S, probably as a result of less ordering by London dispersion forces. All of the amidinium dithiocarbamates which are solids at room temperature have melting points < 65 °C, well below 80 °C, the approximate temperature at which the amidinium dithiocarbamates decompose according to TGA measurements (Figure 2-22). Furthermore, many of the RTILs remain non-crystalline and flowing (albeit very viscous fluids) to at least -20 °C; they have a broad and synthetically useful liquid range.

As expected, the L/A mixtures were qualitatively less viscous than the corresponding L-A-S ionic liquids due to the introduction of strong electrostatic interactions in the latter. The additional hydrogen bonding and dipolar interactions available to the RTILs with an amino alcohol or an amino ester component made them more viscous than the ionic liquids with aliphatic amines. In addition, there was no evidence by polarized optical microscopy for liquid crystallinity in any of the amidinium dithiocarbamates made from hexadecyl amidine (C₁₆) and several different aliphatic amines, amino esters and amino alcohols. Unlike the amidinium carbamates (i.e., the RTILs made by adding CO₂ to L/A mixtures) which remain clear and uncolored, the amidinium dithiocarbamates are a yellow or orange color that can be attributed to n-π* electronic transitions of the dithiocarbamate group.¹⁰⁰
Figure 2-20. FT-IR spectra of C6/cyclohexylamine (a) and C6-cyclohexylamine-CS2 (b).

The structures of the amidinium dithiocarbamates were confirmed by comparisons of thermal gravimetric analyses (TGA) and FT-IR and 1H and 13C NMR spectral data of samples before and after the addition of CS2. Figure 2-20 shows the FT-IR spectra of a representative sample, C6/cyclohexylamine, before and after adding CS2. After addition of CS2, the typical N=C stretching band of the amidine at 1629 cm⁻¹ is replaced by a band at 1645 cm⁻¹ which can be assigned to protonated amidine. In addition, the bands at 1088 and 977 cm⁻¹ are assigned to C=S and C–S stretchings, respectively.101

The 1H NMR spectrum of C6/cyclohexylamine changes markedly upon addition of CS2 (Figure 2-21a). Exposing the C6-cyclohexylamine-CS2 (amidinium dithiocarbamate) to N2 and gently heating at 50 °C for 30 min (C6-cyclohexylamine-CS2-N2), conditions which reconvert the analogous amidinium carbamate to its uncharged amidine/amine mixture, results in no discernible changes. Upon addition of
CS₂, the ¹³C resonance of the central carbon of the amidine in C6 shifted downfield from 156 ppm to 162 ppm and the resonance of CS₂ moved from 193 ppm to 210 ppm (Figure 2-21b).

**Figure 2-21.** NMR spectra: (a) ¹H spectra of C6-cyclohexylamine (black), C6-cyclohexylamine-CS₂ (red) and C6-cyclohexylamine-CS₂-N₂ (blue) in CDCl₃ with peak assignments in the inset; (b) ¹³C spectrum of C6-cyclohexylamine-CS₂ in CDCl₃.
Adding CS₂ to the amine itself is known to form ammonium dithiocarbamate salts (RNHCS₂⁻ H₃N⁺R’)². To demonstrate the absence of ammonium dithiocarbamates in L-A-S, one equivalent of amidine and CS₂ were added to RNHCS₂⁻ H₃N⁺R’ solution, and NMR spectra (Figure 2-22) were collected. They are nearly identical to the spectra obtained from directly prepared L-A-S, showing that amidinium dithiocarbamates is the thermally favorable product.¹⁰²
Figure 2-22. (a) $^1$H NMR spectra in CDCl$_3$ of $n$-hexylamine-CS$_2$ before (red) and after (black) adding 1.0 equivalent C6 and 0.5 equivalent CS$_2$. The blue spectrum was obtained by adding one drop of D$_2$O to the $n$-hexylamine-CS$_2$ in CDCl$_3$ sample as a means to verify the locations of the N—H peaks in the red spectrum. (b) $^{13}$C NMR
spectra in CDCl$_3$ of $n$-hexylamine-CS$_2$ before (red) and after (black) adding 1.0 equivalent C6 and 0.5 equivalent CS$_2$. The concentrations are lower than described above.

![Graph](image)

**Figure 2-23.** (a) TGA curves of C8/IleC8 (grey) and C8-IleC8-CS$_2$ (black). (b) Isothermal TGA curve of C8-IleC8-CS$_2$ at 25 °C for 60 min.

A higher boiling amine, IleC8, was selected for TGA studies. Based on the data in Figure 2-23a, the L-A-S are stable to at least 80 °C under a nitrogen atmosphere and weight losses indicate that decomposition above 150 °C does not involve either CS$_2$ or H$_2$S as the exclusive species expelled. The theoretical weight loss from C8-IleC8-CS$_2$ if one molecule of CS$_2$ or H$_2$S (the molecule lost when ammonium dithiocarbamates are heated to their decomposition temperatures$^{19a}$) is 14.7 % or 6.6 %, respectively. Furthermore, only 0.18 % weight was lost from C8-IleC8-CS$_2$ when it was kept at 25 °C under a dry nitrogen gas flow of 60 cc/min during a 60 min period (Figure 2-23b), and only 1.7 % of the initial weight was lost after heating the sample to ca. 100 °C at a rate of 5 °C/min; nearly 16% more weight was lost when C8/IleC8 was heated under the same conditions. As mentioned, the thermal behaviors of this and other L-A-S are in contrast with those of the corresponding ammonium carbamates and amidinium
carbamates (which are thermally reversible, losing a molecule of CO₂ when heated to ca. 50 °C).19 Also, when heated, an amidinium dithiocarbonate (Eq. 2-7) has been found to lose a molecule of CS₂,87 and we established that ammonium dithiocarbamates lose one molecule of H₂S and become thioureas when heated to ca. 100 °C.19c

\[
\begin{array}{c}
\text{RN} = \text{N(CH₃)₂} + \text{R₁OH} \underset{Δ}{\overset{\text{CS}_2}{\rightleftharpoons}} \text{RN} = \text{N(CH₃)₂}^\cdot \text{S} = \text{C} = \text{O} \quad \text{(2-7)}
\end{array}
\]

**Scheme 2-4.** Thermolysis of tC₄-t-butylamine-CS₂.

To the best of our knowledge, the mechanism of thermolysis of amidinium dithiocarbamates has not been investigated.103 To gain insights into the process, we
have isolated and identified the thermolysis products from one amidinium dithiocarbamate, tC4-t-butylamine-CS2. From them, it is possible to infer a plausible mechanistic pathway for the thermally induced reactions (Scheme 2-4). Reaction commences with formation of a covalent bond between the amidinium carbon atom and a sulfur from the dithiocarbamate followed by (or synchronous with) addition of a proton from the amine moiety of the dithiocarbamate (blue) to one of the nitrogen atoms of the amidine. Note that two parallel pathways ensue based upon which of the amidine nitrogen atoms is the proton acceptor. Some of these steps are reminiscent of the reactions between carbodiimides and carboxylates in Merrifield peptide syntheses. Cleavage of the original C–S bond of the CS2 molecule results in an isothiocyanate (AA) and a zwitterionic species (III or IV) which cleaves into a thioformamide (B or C) and an amine. Cleavage of the original C–S bond of the CS2 molecule results in an isothiocyanate (AA) and a zwitterionic species (III or IV) which cleaves into a thioformamide (B or C) and an amine. The resulting amines can then react with the t-butyl isothiocyanate (AA), generating N-tert-butyl-N',N'-dimethylthiourea (D) or N,N'-di-tert-butylthiourea (E). The proposed pathways are consistent with the presence of dimethylamine and t-butylamine which were captured as their hydrochloride salts. Furthermore, the relative yields of D and E suggest that the thermolysis prefers slightly the pathway through intermediate I.

Acid treatment of dithiocarbamates is known to result in formation of ammonium ions and CS2. Depending on the pK_B of the parent amine, acid-derived decomposition of alkyl dithiocarbamates can occur by two different mechanisms. For parent amines with pK_B > 10.5, the decompositions occur by a concerted intramolecular S-to-N hydrogen transfer with C–N bond cleavage. When pK_B < 10.5, alkyl dithiocarbamates decompose via zwitterionic intermediates whose N-
protonation is slower than the C-N bond breaking (Eq. 2-8). The same mechanism should obtain when an L-A-S is treated with an acid (such as dilute aqueous acetic acid). Evidence for that chemistry, shown in eq. 2-9, comes from $^{13}$C NMR spectroscopy (Figure 2-24).

$$\begin{align*}
    \text{R-N-C-S}^+ + \text{H}^+ & \xrightarrow{k_1} \text{R-N-C-S}^2 + \text{H}_2 \text{O} \\
    \text{R-N-C-S}^+ & \xrightarrow{k_2} \text{R-NH}_2 + \text{CS}_2
\end{align*}
$$

(2-8)

$$\begin{align*}
    \text{R-N^+N(CH}_3)_2^+ \text{S-C-N-R''} & \xrightarrow{\text{CF}_3\text{COOH}} \text{R-N^+N(CH}_3)_2^+ \text{O-C-CF}_3 + \text{R''N}_3^+ \text{O-C-CF}_3 + \text{CS}_2
\end{align*}
$$

(2-9)

![Figure 2-24. $^{13}$C NMR of tC4-t-butylamine-CS$_2$ in D$_2$O (black) and tC4-t-butylamine-CS$_2$ after treatment with acetic acid (red) in D$_2$O.](image)

The conductivity ($\sigma$) of some of the L-A-S and their mixtures with CHCl$_3$ was investigated at room temperature. The effect on conductivity of the high ion concentrations upon adding CS$_2$ to L/A combinations were offset to a large extent in
the neat RTILs by large viscosity increases (Table 2-10). However, conductivities increased significantly when CS$_2$ was added to L/A mixtures in 50 wt % CHCl$_3$ solutions. The increases were slightly smaller than observed when CO$_2$ was added to either neat or chloroform solutions of an L/A. $^3$ These observations can be attributed to the higher viscosities of the dithiocarbamates ($\textit{vide infra}$), and less ion pairing $^{78,108}$ in the carbamates.

### Table 2-10. Conductivities before ($b$) and after ($a$) adding CS$_2$ to neat and 50 wt% CHCl$_3$ solutions of neat L/A combinations at room temperature.

<table>
<thead>
<tr>
<th>L/A</th>
<th>Triatomic molecule</th>
<th>Conductivity ($\mu$s/cm)</th>
<th>mol% of L-A-S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$b$</td>
<td>$a$ (neat)</td>
</tr>
<tr>
<td>C$_8$/hexylamine</td>
<td>CS$_2$</td>
<td>22</td>
<td>39</td>
</tr>
<tr>
<td>C$_8$/hexylamine</td>
<td>CO$_2$</td>
<td>22</td>
<td>58</td>
</tr>
<tr>
<td>DBU/LeuOH</td>
<td>CS$_2$</td>
<td>31</td>
<td>46</td>
</tr>
<tr>
<td>DBU/LeuOH</td>
<td>CO$_2$</td>
<td>31</td>
<td>54</td>
</tr>
</tbody>
</table>

As shown in Figure 2-25, for example, the conductivity of neat C$_8$/hexylamine changed very little as it was diluted with CHCl$_3$. After adding CS$_2$, the conductivity of the C$_8$-hexylamine-CS$_2$ only doubled, but it increased further as small increments of CHCl$_3$ were added, reached a maximum at ca. 10 mol% $^{109}$ (ca. 20-30 wt% of C$_8$-hexylamine-CS$_2$) and decreased at still lower concentrations (higher dilutions) in CHCl$_3$ (Figure 2-25a). As mentioned, the rise in conductivity upon initial addition of CHCl$_3$ is attributed to a convolution of decreasing viscosity (i.e., higher ion mobility) and less ion pairing (i.e., leading to an increase in the concentration of free ions). $^{77,110}$
Eventually, the decreased viscosity and ion pairing that accompany the addition of more CHCl₃ are offset by the lower concentration of mobile ions, and the conductivity decreases. Increased conductivity with decreasing viscosity is also seen in neat L-A-S as temperature is raised (Figure 2-25b).⁹⁹

![Graph](image)

**Figure 2-25.** (a) Conductivities of C₈/hexylamine mixtures at room temperature as a function of mol % substrate before (▲) and after saturating the mixture with CO₂ (○) or adding one equiv of CS₂ (●). (b) Conductivities of neat C₈-hexylamine-CS₂ (●) and DBU-LeuOH-CS₂ (○) as a function of temperature.
A Walden plot\textsuperscript{111} has been used to evaluate further the ion mobilities of the ionic liquids. It is based on Walden’s observation for aqueous solutions of strong electrolytes that the equivalent conductivity (i.e., the conductivity per mole of charge), $\Lambda = \sigma V_E$ (where $V_E$ is the volume containing one Faraday of positive charge), of electrolytes is large, depends inversely on viscosity, and changes with temperature in parallel with the inverse of viscosity. According to Walden’s Rule, $\Lambda \eta = k$, where $\eta$ is the viscosity and $k$ is a temperature dependent constant. From the Walden plot in Figure 2-27, \textbf{C4-hexylamine-CS$_2$} can be classified as a ‘good ionic liquid’ because it lies very close to the ideal line described by aqueous KCl.\textsuperscript{112} However, because of their relatively high viscosities, the ammonium dithiocarbamates exhibit lower conductivities than many other classes of ionic liquids.\textsuperscript{112}
Figure 2-27. Log-log plot of equivalent conductivity ($\Lambda$) versus fluidity ($\eta^{-1}$) for C4-hexylamine-CS$_2$. The straight line is determined by data for 1 M aqueous KCl.$^{113}$

Initially, the miscibility of the samples in their L/A and L-A-S states were determined empirically as a measure of their polarity.$^{114}$ Before adding CS$_2$, L/A mixtures with all solvents examined were solutions (Table 2-11). Similar to many other types of classical RTILs, including amidinium carbamates, our L-A-S phases are miscible with very polar solvents, such as DMSO and ethanol, but not with lower polarity solvents, such as hexane, toluene, and diethyl ether. Furthermore, the length of the C$_n$ amidine alkyl chain appears to influence somewhat the miscibility behavior: C8-hexylamine-CS$_2$ is partially miscible with diethyl ether and C6-hexylamine-CS$_2$ or C4-hexylamine-CS$_2$ is immiscible with it.

The solvatochromic dye, DAPNE$^{57,62}$ was utilized to estimate the polarity of the L/A and L-A-S. For example, $\lambda_{\text{max}} = 423$ nm for C8-hexylamine and 438 and 440 nm for C8-hexylamine-CO$_2$ and C8-hexylamine-CS$_2$, respectively (Table 2-12); the $\lambda_{\text{max}}$ of toluene and $N,N$-dimethylformamide are 425 and 446 nm, respectively. According
to this probe, the L/A are much less polar than their RTILs, whether they be generated by addition of CS₂ or CO₂, but are less polar than many imidazolium-based ILs.¹¹⁵

**Table 2-11.** Miscibility behavior² of various mixtures of 50 vol % L-A-S ionic liquids and organic solvents at room temperature.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>hexane</th>
<th>toluene</th>
<th>diethyl ether</th>
<th>CH₂Cl₂</th>
<th>ethyl acetate</th>
<th>ethanol</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄-hexylamine-CS₂</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>C₆-hexylamine-CS₂</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>C₈-hexylamine-CS₂</td>
<td>I</td>
<td>I</td>
<td>P</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>C₄-IleC₈-CS₂</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>C₆-IleC₈-CS₂</td>
<td>I</td>
<td>I</td>
<td>P</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
<tr>
<td>C₈-IleC₈-CS₂</td>
<td>I</td>
<td>I</td>
<td>P</td>
<td>M</td>
<td>M</td>
<td>M</td>
<td>M</td>
</tr>
</tbody>
</table>

²I = immiscible, M = miscible, P = partially miscible.

**Table 2-12.** Absorption maxima (λ_max, nm) of 2.4 mM DAPNE⁵⁷ in various solvents and RTILs.³

<table>
<thead>
<tr>
<th>solvent</th>
<th>λ_max (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>393</td>
</tr>
<tr>
<td>n-decane</td>
<td>396</td>
</tr>
<tr>
<td>C₈/Hexylamine</td>
<td>423</td>
</tr>
<tr>
<td>C₈/LeuOH</td>
<td>424</td>
</tr>
<tr>
<td>Toluene</td>
<td>425</td>
</tr>
<tr>
<td>THF</td>
<td>427</td>
</tr>
<tr>
<td>Acetone</td>
<td>433</td>
</tr>
<tr>
<td>C8-Hexylamine-CO$_2$</td>
<td>438</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----</td>
</tr>
<tr>
<td>C8-Hexylamine-CS$_2$</td>
<td>440</td>
</tr>
<tr>
<td>C8-ValOH-CO$_2$</td>
<td>443</td>
</tr>
<tr>
<td>C8-LeuOH-CS$_2$</td>
<td>444</td>
</tr>
<tr>
<td>DMF</td>
<td>446</td>
</tr>
<tr>
<td>DMSO</td>
<td>456</td>
</tr>
<tr>
<td>Water</td>
<td>496</td>
</tr>
</tbody>
</table>

**Figure 2-28.** (a) Viscosities (Pa·s) at 25 °C of neat C$_n$/cyclohexylamine before (white) and after addition of saturating the mixture with CO$_2$ (grey) or adding one equiv of CS$_2$ (black). (b) Viscosities (Pa·s) of C$_8$-cyclohexylamine-CS$_2$ (white) and C$_8$-IleC$_8$-CS$_2$ (black) as a function of temperature.$^{116}$

The viscosities increase with increasing chain length of the C$_n$: for example, C$_4$-cyclohexylamine-CS$_2$, C$_6$-cyclohexylamine-CS$_2$, and C$_8$-cyclohexylamine-CS$_2$ have viscosities 8.6, 19 and 69 Pa·s, respectively. As expected, the viscosities of the amidinium dithiocarbamate ionic liquids decrease significantly as temperature is...
increased within the range below their decomposition temperatures (Figure 2-28b and Figure 2-28): the viscosity of C8-IleC8-CS₂ at 45 °C is 1.6 Pa·s, almost 25 times lower than that at 25 °C (43 Pa·s), which is also lower than the viscosity of C8-IleC8-CO₂ (7.1 Pa·s) at 25 °C.

![Viscosity vs Temperature](image)

**Figure 2-29.** Viscosities of neat C4-hexylamine-CS₂ as a function of temperature.

### 2.4.7 Conclusions

Equimolar mixtures of an amidine and an amine can be transformed easily into a new class of room-temperature ionic liquids, amidinium dithiocarbamates, upon addition of one molar equivalent of CS₂. The amidinium dithiocarbamates are more stable thermally than their amidinium carbamate analogues, made by adding another triatomic molecule, CO₂, to amidine/amine mixtures. In general, the dithiocarbamates remain stable to higher temperatures than their amidine-amine mixtures, even in air. Unlike their amidinium carbamate analogues (which lose a molecule of CO₂ near their decomposition temperatures, ca. 50 °C under one atmosphere pressure of CO₂), the amidinium dithiocarbamates do not lose a molecule of CS₂ when heated above their decomposition temperatures, ca. 80 °C. Instead, they undergo a series of structural
changes that lead to several products, including thioureas and thioformamides, which provide insights into the thermolysis mechanism. However, CS₂ can be expelled from the amidinium dithiocarbamates in the presence of a weak acid.

The thermal, polar, viscous and conductance properties of the liquid amidinium dithiocarbamates have been characterized and compared with both their amidine-amine precursor mixtures and with the analogous amidinium carbamates. The results show that these physical and chemical properties can be tuned by changing the L/A combinations and the nature of the triatomic molecule added. Viscosities of the Cn-amine-CS₂ systems increase as the amidine chain length n increases and are more viscous than the corresponding Cn-amine-CO₂ RTILs. Although the C₄ amidine provided RTILs when combined with CS₂ and all of the amines examined in this work, only the amidinium dithiocarbamates composed of an amino alcohol were liquids at room temperature when the amidine was the bulky and short-chained guanidine TMG.

According to the spectroscopic probe DAPNE, the dithiocarbamates and carbamates have similar polarities and are much more polar than their corresponding non-ionic L/A mixtures. However, as noted by miscibility studies, the polarities of the dithiocarbamates do change subtly when the chain length of the Cn amidine or the amine structure is changed. As expected, the conductivities of the structurally analogous neat dithiocarbamates and carbamates are very similar, they remain similar at the same dilution factors in chloroform, and they are significantly higher than the conductivities of their L/A component mixtures.

Attractive attributes of the amidinium dithiocarbamate RTILs (when compared to many other types of ionic liquids) include their ease of preparation from commercially available or easily synthesized precursors, their diversity of structures, and their broad temperature ranges (commencing at subambient temperatures). This work provides a
facile, one-step approach to utilize CS$_2$, an environmentally unattractive liquid, to prepare useful and very attractive chemical materials by very simple manipulations and reactions. These RTILs are expected to find extensive use as media for a broad range of guest molecule reactions, including some that involve the creation of chiral centers or the recuperation of expensive metal catalysts.$^{117}$ Future research will focus on such applications.

2.5 Comparisons of the RTILs

Comparisons of the structural differences between amidinium dithiocarbamates and amidinium carbamates offer a means to gain insights about how they support formation of RTILs. The data in Table 2-13 demonstrate that the appearances of some of the L/A ionic liquids depend upon whether CO$_2$ or CS$_2$ is added. For example, DBU-hexylamine-CO$_2$$^{3a}$ is a liquid while DBU-hexylamine-CS$_2$ is a solid. Obviously, these differences are a manifestation of the properties of the carbamate and dithiocarbamate anions. To some extent, those properties can be related to the physical properties of the triatomic molecules from which the anions derive, CO$_2$ and CS$_2$. Both are linear molecules and have zero dipoles.$^{30}$ However, they possess large quadrupole moments (Table 1-1).$^{118}$ In addition, both the bond lengths and kinetic diameter of CS$_2$ are larger than those of CO$_2$.$^{90}$

Table 2-13. Phases$^a$ of neat 1/1 (mol/mol) L/A mixtures at room temperature after treating them with saturating the mixture with CO$_2$ or adding one equiv of CS$_2$.

<table>
<thead>
<tr>
<th>Amidine (L)</th>
<th>Leucinol (LeuOH)</th>
<th>Isoleucine octyl ester (IleC8)</th>
<th>Hexylamine</th>
<th>Cyclohexylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine (A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

83
As mentioned above, whereas the amidinium dithiocarbamates cannot be heated to expel CS₂ and regenerate the non-ionic L/A states, gentle heating or passing nitrogen gas through an amidinium carbamate does result in the loss of CO₂. This grossly different chemical behavior can be understood from the enthalpies of formation of dithiocarbamates and carbamates. The heats of formation $\Delta H_f$ are -393.5 kJ·mol⁻¹ for CO₂ and 115.7 kJ·mol⁻¹ for CS₂ in the gas phase. Thus, it is expected from the Hammond Postulate that the enthalpy of formation of a dithiocarbamate will be more favored energetically, although reactions of amines with both CO₂ and CS₂ are exothermic. These results indicate that the addition of CO₂ and CS₂ can tune the physicochemical properties of the RTILs, although they may do so in different ways.

In this work, DAPNE, a solvatochromic dye was utilized to estimate the polarity of ionic liquids. For example, $\lambda_{\text{max}} = 424$ nm for **C8-LeuOH** and 443 and 444 nm for **C8-LeuOH-CO₂** and **C8-LeuOH-CS₂**, respectively (Table 2-14). According to this probe, in any cases, nonionic mixtures are much less polar than their RTILs, whether they will be generated by addition of CS₂ or CO₂, but are less polar than many imidazolium-based ILs. However, L/N and L/A have similar polarities before and after saturating the mixture with CO₂ or adding one equiv of CS₂.

<table>
<thead>
<tr>
<th></th>
<th>CO₂</th>
<th>CS₂</th>
<th>CO₂</th>
<th>CS₂</th>
<th>CO₂</th>
<th>CS₂</th>
<th>CO₂</th>
<th>CS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>S</td>
<td>L</td>
</tr>
<tr>
<td>C8</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>S</td>
<td>L</td>
</tr>
<tr>
<td>DBU</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>S</td>
<td>L</td>
<td>S</td>
<td>L</td>
<td>S</td>
</tr>
</tbody>
</table>

\(a\) L = liquid, S = solid
Table 2-14. Absorption maxima ($\lambda_{\text{max}}$) of 2.4 mM DAPNE\textsuperscript{57} in various solvents and RTILs.\textsuperscript{3}

<table>
<thead>
<tr>
<th>solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-decane</td>
<td>396</td>
</tr>
<tr>
<td>C6/Hexylamine</td>
<td>423</td>
</tr>
<tr>
<td>C6/IleC\textsubscript{1}</td>
<td>425</td>
</tr>
<tr>
<td>C8/LeuOH</td>
<td>424</td>
</tr>
<tr>
<td>Toluene</td>
<td>425</td>
</tr>
<tr>
<td>Acetone</td>
<td>433</td>
</tr>
<tr>
<td>C6-Hexylamine-CO\textsubscript{2}</td>
<td>438</td>
</tr>
<tr>
<td>C8-Hexylamine-CS\textsubscript{2}</td>
<td>440</td>
</tr>
<tr>
<td>C6-IleC\textsubscript{1}-CO\textsubscript{2}</td>
<td>443</td>
</tr>
<tr>
<td>C6-IleC\textsubscript{1}-CS\textsubscript{2}</td>
<td>444</td>
</tr>
<tr>
<td>C8-LeuOH-CO\textsubscript{2}</td>
<td>443</td>
</tr>
<tr>
<td>C8-LeuOH-CS\textsubscript{2}</td>
<td>444</td>
</tr>
<tr>
<td>DMF</td>
<td>446</td>
</tr>
<tr>
<td>DMSO</td>
<td>456</td>
</tr>
<tr>
<td>Water</td>
<td>496</td>
</tr>
</tbody>
</table>

Consistent with their CO\textsubscript{2} analogues, the L/A and L-A-S exhibit viscosities which are virtually independent of shear rate; they behave like Newtonian liquids (Figure 2-30).\textsuperscript{121} As shown in Figure 2-28a, the average viscosity over the range of shear stress values for C6/cyclohexylamine is 0.010 Pa·s at room temperature. After exposure to CO\textsubscript{2}, the viscosities of these samples increase by orders of magnitude to 3.8 Pa·s (C6-cyclohexylamine-CO\textsubscript{2}), but the viscosity of the corresponding C6-cyclohexylamine-
CS2 is much higher still, ca. 19 Pa·s. The higher viscosities of the dithiocarbamates can be explained on the basis of their higher polarizabilities and hard-soft/acid-base\(^{122}\) (HSAB) theory: dithiocarbamate is a softer base than a carbamate and amidinium is a soft acid.

![Graph showing viscosities (Pa·s) at 25 °C of C8-LeuOH-CS2, C8-LeuOH-CO2 and C8/LeuOH as a function of shear stress (Pa).]

**Figure 2-30.** Viscosities (Pa·s) at 25 °C of C8-LeuOH-CS2, C8-LeuOH-CO2 and C8/LeuOH (from top to bottom) as a function of shear stress (Pa).

3. PREPARATION AND CHARACTERIZATIONS OF CROSSLINKED AMINO-SUBSTITUTED POLYSILOXANES AND THEIR APPLICATIONS

3.1 Reversibly crosslinking amino-substituted polysiloxanes by simple triatomic molecules. Facile methods for tuning thermal, rheological, and adhesive properties

3.1.1 Introduction

Polysiloxanes are among the most studied and commercially important partially inorganic polymers in use today.\(^{123}\) Their backbones are very flexible, allowing easy interconversion of conformers. They also have interesting gas permeability and
unusual surface properties.\textsuperscript{124} As a result, they are used in a myriad of applications, such as drug-delivery systems,\textsuperscript{125} high performance elastomers,\textsuperscript{126} membranes,\textsuperscript{127} adhesives,\textsuperscript{128} coatings,\textsuperscript{129} soft lithography stamps,\textsuperscript{130} and self-healing materials.\textsuperscript{131} The low energy of interaction among polysiloxane chains is responsible for two of their interesting attributes, high malleability and relatively low viscosity. These can also be disadvantageous because polysiloxanes cannot be made into fibers and immobilized films without significant structural modifications (N. B., crosslinks between chains). It would be advantageous to be able to interconvert polysiloxanes between low and high interaction energy states so that they can be processed for different purposes without expending a large effort or expense.

Many modifications of the parent polysiloxane structure are known. Usually, a fraction of the methyl groups of the most common polysiloxane, poly(dimethylsiloxane) (PDMS) are substituted by a group containing a different length or functionality (i.e., a one-dimensional structural change).\textsuperscript{132} Ladder polysiloxanes possess two-dimensional structural features,\textsuperscript{133} while crosslinked polysiloxanes,\textsuperscript{134} including tubular and pseudo-sieve plate polysiloxanes are three-dimensional structures.\textsuperscript{135} The nature and extent of the chain crosslinks can be varied and each change leads to materials with different chemical and physical properties. The crosslinks can be covalent or non-covalent (e.g., hydrogen bonding,\textsuperscript{136} metal coordination,\textsuperscript{137} etc.). Although the crosslinking can be reversed in some cases, it does not yield the original materials without performing significant physical or chemical manipulations. Clearly, a \textit{reversible} crosslinking strategy that requires benign changes to the material mild conditions, and allows the non-crosslinked and crosslinked forms to be recovered intact without significant effort would be desirable. Such strategies
are described here and differences between the properties of the non-crosslinked and crosslinked states are explored.

The basis for our approaches is grounded in simple organic chemical transformations that have led to the development of reversible organogels,\textsuperscript{2, 138} ionic liquids,\textsuperscript{3} and reversible solvents\textsuperscript{18, 45} CO\textsubscript{2} fixation-release systems\textsuperscript{139, 140} and supermolecular polymers.\textsuperscript{1} It is known that simple, neutral X=Y=X triatomic molecules, in which the X atoms are much more electronegative than the Y atom (e.g. CO\textsubscript{2} and CS\textsubscript{2}), can become “bridge-linkers” for amino groups.\textsuperscript{28, 33} It should be possible to exploit the general chemistry shown in eqs. 3-1 and 3-2 to transform weakly interacting chains of uncharged polysiloxanes with substituent amino groups into strongly interacting chains via attractive electrostatic attractions between positive and negative charged centers that lead to crosslinks. In a medium of low polarity, such electrostatic forces can be very strong because they vary with the inverse of dielectric constant,\textsuperscript{141} and the dielectric constant of silicone polymer is only 3.0-3.5.\textsuperscript{142}

\[
\text{CO}_2 + 2\text{RNH}_2 \xrightleftharpoons[N_2]{\Delta}\text{R-N}_2\text{O}^+\text{H}_3\text{N}-\text{R} \tag{3-1}
\]

\[
\text{CS}_2 + 2\text{RNH}_2 \xrightarrow[\Delta]{\text{R-N-R}}\text{R-N}_2\text{S}^+\text{H}_3\text{N}-\text{R} \tag{3-2}
\]

Reversal of the CO\textsubscript{2}-generated ammonium carbamate crosslinks can be effected by warming the material under air or, more rapidly, by bubbling an inert (displacing) gas, such as molecular nitrogen, through the sample (Eq. 3-1). Our experience is that the analogous ionic crosslinks achieved with CS\textsubscript{2}, ammonium dithiocarbamates, are not amenable to reversal, but heating produces (permanent) covalent thiourea crosslinks instead (Eq. 3-2).\textsuperscript{35} Clearly, the degree of crosslinking can be controlled by the amount of amine functionality of polysiloxanes (as well as by the amount of the
triatomic molecule added to the polymer; *vide infra*). In this way, the thermal and rheological properties of the polysiloxanes can be tuned easily. Compared with conventional crosslinking methods, this strategy has the advantages of being rapid, isothermal, inexpensive, and (with CO$_2$) reversible.

Here, we describe how these simple crosslinking methods change the thermal, rheological, and adhesive properties of polysiloxanes with up to 15% (by monomer content) of amino-functional groups (PSil). The resulting polymers after addition of a triatomic, PSil-CO$_2$ or PSil-CS$_2$, possess viscosities and adhesive properties that are several orders of magnitude higher than those of the PSil. As expected, the PSil-CO$_2$ can be reconverted to their PSil forms by warming and bubbling N$_2$ through them (Scheme 3-1); this cycle has been repeated three times without detectable degradation. Also, as expected, warming the PSil-CS$_2$ results in permanent thiourea crosslinks and loss of H$_2$S. However, the triatomic adduct can be removed from both the PSil-CS$_2$ and the PSil-CO$_2$ by treatment with an acid such as acetic acid or trifluoroacetic acid, to produce protonated PSil that are flowing liquids. The results demonstrate that the simple chemical changes effected by addition or removal of a triatomic molecule to one of the PSil as a bulk polymer can change its properties in extraordinary fashions of both fundamental an applied interest. Furthermore, the magnitude of those changes can be tuned by the amount of amino functionalities in the PSil.

### 3.1.2 Instrumentation.

Unless stated otherwise, all instruments are the same with the instruments described in Section 2.1.3. Rheological experiments were performed on an Anton Paar Physica MCR 301 rheometer (Anton Paar GmbH, Graz, Austria) using a parallel plate (radius 25 mm, gap 0.5 mm) or cone-and-plate (radius 25 mm, gap 0.5 mm, cone angle 1°, truncation 49 μm) geometry. Samples were equilibrated at 25 °C for about 5 min
before starting measurements (at 25 °C) in order to eliminate any mechanical hysteresis. Dynamic frequency-sweep spectra were conducted in the linear viscoelastic regime of each sample as determined by dynamic stress-sweep tests. All measurements were carried out within one week of sample preparation. The percentage of CO$_2$ uptake (%CO$_2$, based upon the stoichiometric amount calculated from the amino content of a PSil) was measured with a mercury burette apparatus that is based on a design described in ref. $^{70}$ Samples were weighed on an OHaus E01140 balance (precision 0.1 mg). Some of the rheological studies were repeated two or three times; the differences among the measurements were <5%.

3.1.3 Materials

(6-7% Aminopropylmethyldifluorosiloxane)-dimethylsiloxane copolymer ((6-7)PSil; structure below) (Gelest, Inc; boiling point >205 °C, melting point: <-60 °C, molecular weight 3000~6000, viscosity 80~120 cST, clear to pale yellow liquid with a mild ammonia odor) was used as received.

(2-4% Aminopropylmethoxysiloxane)-dimethylsiloxane copolymer ((2-4)PSil; structure below) (Gelest, Inc; boiling point >205 °C, melting point <-60 °C, molecular weight not reported by manufacturer, viscosity 200-300 cST, clear liquid) was used as received.
Aminofunctional siloxane 20869-146 (10PSil) (Synthesized and characterized by Dr. Dimitri Katsoulis and Mr. Kenneth E. Zimmerman from Dow-Corning. According to Dow-Corning: molecular weight ca. 9950, PDI (polydispersity): 1.71, viscosity 100 mPa·s, 1.33 milli-equivalents of amine per gram. The polymer was clear white to yellow liquid with amine-like odor; it was used as received.

\[
\text{Si} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{O} \\
\text{Si} \quad \text{O} \\
\text{H}_2 \text{C} \quad \text{C} \\
\text{H}_2 \quad \text{C} \\
\text{NH}_2
\]

Aminofunctional Siloxane 20869-145 (15PSil) (Synthesized and characterized by Dr. Dimitri Katsoulis and Mr. Kenneth E. Zimmerman from Dow-Corning. According to Dow-Corning: molecular weight ca. 9650, PDI (polydispersity) 1.71, viscosity 100 mPa·s, 2.33 milli-equivalents of amine per gram. The polymer was clear white to yellow liquid with amine-like odor; it was used as received.

\[
\text{Si} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{O} \\
\text{Si} \quad \text{O} \\
\text{H}_2 \text{C} \quad \text{C} \\
\text{H}_2 \quad \text{C} \\
\text{NH}_2
\]

Other organic solvents are the same as described in Section 2.1.2.

3.1.4 Preparation of cross-linking polysiloxanes

**Sample preparations. Syntheses of Ammonium Carbamate Polysiloxanes (PSil-CO$_2$).**

Dry CO$_2$ gas (prepared as described in Section 2.1.2) was bubbled gently through a stirred PSil sample in a glass vial for 1 h. The vial was placed in a water bath at room temperature during the CO$_2$ addition to dissipate the heat from the exothermic reaction.
Syntheses of Ammonium Dithiocarbamate Polysiloxanes (PSil-CS₂). Two molar equivalents of carbon disulfide were slowly added to a PSil in a closed glass vial. The vial was sonicated in a Bransonic 1210 ultrasonic cleaner with water in the bath for 1 h, allowed to stand for 2 days, and the contents were placed under a house vacuum for 24 h to remove excess CS₂.

Syntheses of Thiourea Crosslinked Polysiloxanes (PSil-CS₂-H). After the procedure above (minus the removal of excess CS₂ under house vacuum), the sample was heated to 120 °C for 1 h and cooled to room temperature. The heating and cooling were repeated twice more. The resulting material was kept in a vacuum oven with house vacuum 250 Torr at 40 °C for 24 h to remove any dissolved H₂S and residual CS₂. The thiourea-containing samples were slightly yellow. (WARNING: H₂S is a highly toxic gas.)

Acidification experiments. Either acetic acid or trifluoroacetic acid (1.0 mL) was added to 1.0 g of PSil-CO₂ or PSil-CS₂ in a closed glass vial and the mixture was stirred for 1 h before removing a weighed aliquot for NMR studies.

Procedure for swelling. A weighed aliquot (ca. 50 mg) of polymer and 3.0 mL of a liquid were placed in a closed screw-cap glass vial for 24 h. The polymer was removed, its surface was dried quickly on a piece of filter paper, and it was reweighed. The swelling ratio (S%) was calculated by eq 3-3, where Wg and Wp are the weights of swelled and dry polymer, respectively. The temporal uptake of liquid was determined by removing the polymer at different times from the liquid, weighing it, and placing it anew into the liquid until no weight increase could be detected.

\[ S\% = \frac{(W_g-W_p)}{W_p} \times 100\% \]  
(3-3)

Adhesion test procedures. An aliquot of polymer was placed on the steel base plate of the rheometer, and the upper parallel (flat) steel plate was moved into contact with the
upper surface of the polymer. The initial gap was set at 0.15 mm. The system was left undisturbed for 10 min to form an equilibrated interfacial contact. Then, the top plate was lifted vertically to a plate gap of 0.50 mm at a velocity of 0.01 mm/s. The normal force response in this process was recorded by the rheometer. All measurements were performed at 25 °C.

3.1.5 Results and Discussion

Scheme 3-1. Structures of polysiloxane samples and a general scheme for their reactions with CO₂ and CS₂.
Bubbling CO$_2$ through the stirred polysiloxanes for a few minutes resulted in a noticeable and significant increase in viscosity (Figure 3-1). The crosslinking from formation of ionic pairs, as ammonium and carbamate centers are created (Scheme 3-1), can be monitored conveniently by FT-IR spectroscopy (Figure 3-2 with 15PSil as an example). After CO$_2$ bubbling, a C=O stretching band at 1640 cm$^{-1}$, typical of a carbamate,$^{73}$ was observed as a shoulder. In addition, a medium strong band centered at 1586 cm$^{-1}$ can be assigned to the N-H bending; $^{143}$ the corresponding peak was located at 1598 cm$^{-1}$ in 15PSil before CO$_2$ bubbling and after passing N$_2$ through 15PSil-CO$_2$. Also, a band ascribed to the asymmetric vibration of C-Si-C shifted to 1472 cm$^{-1}$ upon bubbling CO$_2$ through the 15PSil. The changes in the IR frequencies, in combination with the qualitative evidence from the Hg burette measurements (as shown on page 101), demonstrate that a chemical change occurred, and it is reasonable to ascribe it to the uptake of CO$_2$. 

**Figure 3-1.** Before (left) and after (right) bubbling CO$_2$ through neat (6-7)PSil at 25 °C.
Similarly, exposure of the amino-terminated polysiloxane 3PSil to CO₂ led to a rapid increase in its viscosity. The infrared spectrum in Figure 3-3 for the product of the reaction is consistent with the 3PSil-CO₂ structure; its new absorption bands are almost the same as those found in the spectrum of 15PSil-CO₂. The formation of ammonium dithiocarbamates in polysiloxanes upon addition of CS₂ is also indicated by FT-IR spectra. An N-H bending band was found at 1552 cm⁻¹, and the bands at 1370 and 945 cm⁻¹ can be assigned to C=S and C-S stretchings, respectively. Upon heating a 3PSil-CS₂ sample to 120 °C (to form 3PSil-CS₂-H), the N-H stretching band shifts from 3190 cm⁻¹ to 3068 cm⁻¹ as a result of H-bonding interactions (Figure 3-3). The C-S stretching band at 945 cm⁻¹ is no longer present and the C=S stretching band shifts to 1348 cm⁻¹. The IR frequencies for the thiourea groups in 3PSil-CS₂-H are very similar to those found in the spectrum of N, N’-dialkylthioureas obtained by heating alkylammonium alkylthiocarbamates.
Figure 3-3. Vertically offset IR spectra of 3PSil (a), 3PSil-CO$_2$ (b), 3PSil-CS$_2$ (c) and 3PSil-CS$_2$-H (d).

The temporal course of uptake of (1 atm) CO$_2$ by the polysiloxanes has been followed. Because the uptake rate is dependent on the surface area of the polysiloxanes exposed to the CO$_2$ gas and the rate of stirring, neither of which can be reproduced exactly, no attempt has been made to compare quantitatively rates of uptake by the different PSil polymers. However, the surface area and stirring rate in each run were nearly the same, so that the order of rates among the PSil can be approximated. The plateau (saturation) values for uptake are independent of both variables and, therefore, are reproducible quantitatively.

A typical plot for (6-7)PSil is shown in Figure 3-4. The other polysiloxanes behaved in an analogous fashion. The uptake was rapid during the first 5 min and reached its maximum, ~130% of the expected amount for complete reaction, after ca. 60 min. The 30% excess is ascribed to physically adsorbed CO$_2$.$^{146}$
Figure 3-4. Weight percentage uptake of CO$_2$ (%CO$_2$) by neat (6-7)PSil as a function of time upon exposure to 1 atm pressure of CO$_2$. Data from two separate runs and their average are shown.

Examples of the weight losses from heating 3PSil, 3PSil-CO$_2$, 3PSil-CS$_2$ and 3PSil-CS$_2$-H by TGA are collected in Figure 3-5. The difference curve between 3PSil-CO$_2$ and 3PSil shows a 4.0% higher loss at 80 °C from 3PSil-CO$_2$ than from 3PSil; the calculated weight of CO$_2$ in 3PSil-CO$_2$, assuming complete conversion, is ca. 4.0%. We assume that the excess (i.e., physically adsorbed) CO$_2$ is lost over time as the 3PSil-CO$_2$ samples equilibrate with air.

Heating 3PSil-CS$_2$ according to the same protocol resulted in a 2.8% weight loss at 120 °C. This value is close to the 3.1% loss predicted if each of the ammonium dithiocarbamate ion pairs loses one molecule of H$_2$S. As expected, the thiourea-containing polysiloxane, 3PSil-CS$_2$-H, is more stable thermally than its electrostatically crosslinked analogue, 3PSil-CS$_2$. 


Figure 3-5. TGA curves of 3PSil-CS$_2$-H (a) heated from room temperature, neat 3PSil (b), 3PSil-CO$_2$ (c) and 3PSil-CS$_2$ (d). Difference curves between 3PSil and 3PSil-CO$_2$ curves (e) and between 3PSil and 3PSil-CS$_2$ curves (f) are shown as well.

Representative DSC thermograms of polysiloxanes are collected in Figures 3-6 and 3-7. The first-heating thermogram of 15PSil-CO$_2$ includes a broad endotherm that extends from 60 to 120 °C which is attributed to loss of CO$_2$. The first-heating thermogram of 15PSil-CS$_2$ has a broad endotherm from 75 to 150 °C that is in good agreement with the expectation from the TGA results that H$_2$S is being lost. No subsequent exotherms or endotherms were detected during the first cooling or second heating of the sample; conversion of ammonium dithiocarbamate to thiourea is complete after the initial heating to 350 °C.
**Figure 3-6.** DSC thermograms of 15PSil-CO$_2$. The arrows indicate starting point of the experiment and the direction of initial temperature change.

**Figure 3-7.** DSC thermograms of 15PSil-CS$_2$. The arrows indicate the starting point of the experiment and the direction of initial temperature change. The black curve is the first heating-cooling cycle and the red curve is the second cycle.

The isothermal stability of 15PSil-CO$_2$ was monitored by TGA. The reversion of the ionic-to-uncharged forms of the polysiloxanes is very slow at 25 °C in the presence of a dry nitrogen gas flow of 60 cc/min (0.70% weight, corresponding to ~0.16 equivalents of CO$_2$, was lost during 60 min) and is even slower in the absence
of a wind (0.08% or ~2×10⁻² equivalents of CO₂ was lost during 60 min) (Figure 3-8b). At 75 or 100 °C, 96% of the weight loss calculated for total removal of the CO₂ is achieved after less than 5 min with N₂ flow. (Figure 3-8a).

**Figure 3-8.** (a) Isothermal TGA weight loss curves of 15PSiL-CO₂ at various temperatures under a nitrogen flow of 60 ml/min. From top to bottom: 25, 50, 75 and 100 °C. (b) TGA weight loss curve of 15PSiL-CO₂ at 25 °C without nitrogen flow.

Taken together, these results clearly demonstrate that the PSiL-CO₂ have good thermal stability at room temperature without nitrogen flow, and good reversibility at elevated temperatures with nitrogen flow. The ionic cross-links allow the PSiL-CO₂ and PSiL-CO₂ to retain three-dimensional networks even as they imbibe large amounts of liquid. Therefore, the PSiLS can be swelled by a variety of organic liquids to create gel states. An example, a photo of the increase in size of 10PSiL-CS₂ swelled by hexane, is displayed in Figure 3-9. The details of the swelling studies will be discussed in Section 3.2.
**Figure 3-9.** Photographs of (6-7)PSil-CS$_2$ before (left) and after (right) swelling with hexane at room temperature.

**Figure 3-10.** Viscosities (Pa·s) of samples before and after bubbling CO$_2$ as a function of shear rate (S$^{-1}$) at 25 °C. From top to bottom: 15PSil-CO$_2$ (●), 10PSil-CO$_2$ (▼), (6-7)PSil-CO$_2$ (■), (2-4)PSil-CO$_2$ (▲), 3PSil-CO$_2$ (♦), 15PSil (∗), 10PSil (∇), (2-4)PSil (□), (6-7)PSil (△) and 3PSil (≡).

**Rheological properties.** In order to determine the relationships among amine content, polymer structure, and viscoelastic properties, both static and dynamic rheological studies have been conducted on the polysiloxanes before and after exposing them to one of the triatomic molecules. At low molecular weights, linear polydimethylsiloxane (PDMS) polymers behave essentially as Newtonian liquids—their viscosity is not influenced by shear rate. At molecular weights above 10,000, PDMS polymer chains become entangled and exhibit a viscoelastic response and shear-thinning behavior at modest shear rates.$^{123}$ Esmail and coworkers$^{147}$ found that the Newtonian viscosity of poly(dimethylsiloxane) solutions generally decreases with
temperature from 10 °C to 50 °C. The viscosity of their PDMS was ca. 1.0 Pa·s at 20 °C, which is 10 fold higher than the viscosity of 15PSil. However, the viscosity of 15PSil-CO₂, ca. 300 Pa·s, is significantly higher than that of the PDMS. Figure 3-10 displays steady-shear rheological data for the polysiloxanes before and after crosslinking by CO₂. The viscosities $\eta$ (Pa·s) are independent of shear rate, as expected of Newtonian liquids. However, the $\eta$ increase by ca. 3 orders of magnitude after each PSil is exposed to CO₂. The increase in viscosity is especially noticeable in the two polysiloxanes with the highest amino group contents, 10PSil-CO₂ and 15PSil-CO₂.

The viscosities of the PSil-CO₂ increase in a regular fashion with increasing amino group content (Figure 3-11). Although there is no apparent relationship between amino group content and the ratio of the PSil-CO₂ and PSil viscosities (Table 3-1), the viscosities of the neat PSil polymers are known to be proportional to their molecular weights. We emphasize here that crosslinks within the 3PSil-CO₂ network do not result in a true 3-dimensional network—the amino end-groups can extend the lengths of the chains only and, thus, produce 1-dimensional topological networks that can appear to be pseudo 3-dimensional networks if the chains intertwine or their cation-anion pairs aggregate in pairs, providing quadrupolar interactions.

The PSils, became highly viscous liquids upon adding CS₂, and eventually transformed into elastic materials after 48 h, as a result of the slow diffusion of CS₂ in the resulting, highly viscous environment. This result can be attributed to the stronger electrostatic interaction of ammonium dithiocarbamate than ammonium carbamate and the higher polarizability of the dithiocarbamate. Their gel-like rheological behavior is shown in Figure 3-18 and Figure 3-19 and discussed on page 108.
Table 3-1. Viscosities (Pa·s) of PSils before (B) and after (A) bubbling CO₂ at 25 °C.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Viscosity (Pa·s)</th>
<th>A/B viscosity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>3PSil</td>
<td>0.020</td>
<td>18</td>
</tr>
<tr>
<td>(2-4)PSil</td>
<td>0.030</td>
<td>48</td>
</tr>
<tr>
<td>(6-7)PSil</td>
<td>0.024</td>
<td>95</td>
</tr>
<tr>
<td>10PSil</td>
<td>0.067</td>
<td>168</td>
</tr>
<tr>
<td>15PSil</td>
<td>0.098</td>
<td>290</td>
</tr>
</tbody>
</table>

Figure 3-11. Viscosities of PSil (□, right Y-axis) and PSil-CO₂ (■, left Y-axis) versus % amine functionality at room temperature.

The rheological properties of two polysiloxanes containing comparable frequencies of amino groups but one, (2-4)PSil, capable of making 3-D crosslinked networks and the other, 3PSil, capable of making only extended 1-D structures with increased molecular weights, have been compared. Addition of CO₂ or CS₂ increased
the viscosities of both (Figure 3-12). Also, the stronger attachment of CS$_2$ than CO$_2$ to the amine groups and the greater polarizability of the dithiocarbamate make the viscosity of 3PSil-CS$_2$ higher than that of 3PSil-CO$_2$, but both are less viscous than their (2-4)PSil analogues which can form 3-dimensional crosslinked networks in the presence of one of the triatomic molecules.

![Viscosity vs Shear Stress](image)

**Figure 3-12.** Steady-shear rheology of polysiloxane samples at room temperature (25 °C): the apparent viscosities (Pa·s) of 3PSil-CS$_2$-H (▲), 3PSil-CS$_2$ (●), 3PSil-CO$_2$ (▼) and 3PSil (■).

The viscosity of the (thiourea-containing) 3PSil-CS$_2$-H, made by heating 3PSil-CS$_2$ to ca. 120 °C, is ca. 20X that of its immediate precursor. The large increase can be attributed to the covalent nature of the thiourea links between 3PSil chains and the ability of the thiourea groups to establish strong H-bonding networks.$^{150,151}$ The viscous modulus $G''$ of 3PSil-CS$_2$ exceeds the elastic modulus $G'$ over the entire range of frequencies examined and is strong function of frequency (Figure 3-13), whereas $G'$ is nearly independent of frequency, which indicate that this material is like both a viscous liquid and a gel.$^{152}$
Figure 3-13. Dynamic rheology of polysiloxane samples at room temperature (25 °C): storage modulus ($G'$, solid) and loss modulus ($G''$, open) of $3\text{PSil-CS}_2$ (▲, △), $3\text{PSil-CO}_2$ (■, □) and $3\text{PSil-CS}_2$-H (●, ○).

Figure 3-14. Storage modulus ($G'$, solid symbols) and loss modulus ($G''$, open symbols) of $15\text{PSil-CO}_2$ (▲, △), $10\text{PSil-CO}_2$ (▼, ▽), (6-7)$\text{PSil-CO}_2$ (●, ○), and (2-4)$\text{PSil-CO}_2$ (♦, ◇) at 25 °C.
However, (2-4)PSiL-CS₂ exhibited a different rheological behavior from the other polysiloxane samples, whether they were treated with CO₂ or CS₂ (Figure 3-15). Its viscoelastic response can be divided into two regimes: at lower frequencies, $G''$ exceeds $G'$ (a viscous response); at higher frequencies, above the crossing point ($\omega_c$, where the system relaxation time, $t_R \sim 1/\omega_c$), $G''$ becomes lower than $G'$ (an elastic response of a transient entangled network). Its steady-shear rheology differs from those of the other CO₂- and CS₂-treated polysiloxanes as well (Figure 3-16): at low angular frequencies, viscosity increases with increasing shear stress (Pa); above the critical shear stress, the viscosity becomes independent of shear stress, as expected for a Newtonian liquid—in behavior typical of viscous liquids, both $G'$ and $G''$ increase with increasing angular frequencies. These are extremely viscous fluids that are not true gels.
The partial reaction of 15PSil with CS$_2$ to effect crosslinks has a different consequence than when a polysiloxane with amino groups of a different type and in a different distribution along a chain, such as (2-4)PSil, in which each side-chain contains one primary and one secondary amino group, is completely reacted with CS$_2$. As shown in Figure 3-17, addition of 0.2 equivalents of CS$_2$ to 15PSil, in which each side chain contains only one primary amino group, to simulate the frequency of ammonium dithiocarbamate groups in (2-4)PSil-CS$_2$, led to polymers with very different rheological properties than those of (2-4)PSil-CS$_2$. Specifically, $G'$ and $G''$ of (2-4)PSil-CS$_2$ cross at a specific shear strain, as expected for an elastic response of a transient entangled network.$^{153}$ By contrast, $G'$ of 15PSil-0.2CS$_2$ exceeds $G''$ at low shear strains and, eventually, $G'$ and $G''$ overlap at very high shear strain. In addition, very similar swelling ratios in hexane were found for 15PSil-0.4CS$_2$ (329%) and (6-7)PSil-CS$_2$ (362%). These rheological and swelling results demonstrate that the structure (i.e., the nature of amino substitution on side chains) of the PSils must be considered carefully when attempting to understand the consequences of adding an

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**Figure 3-16.** Steady-shear rheology of (2-4)PSil-CS$_2$ at 25 °C as apparent viscosities (Pa·s).
X=Y=X crosslinker to the PSils. The details of the swelling studies will be presented in section 3.2.

**Figure 3-17.** Storage modulus ($G'$, ●) and loss modulus ($G''$, ○) at 25 °C of 15PSil with 0.2 equivalents of CS$_2$. This amount of CS$_2$ corresponds approximately to the same concentration of ammonium dithiocarbamate units as in fully reacted 3PSil (i.e., when it is treated with 0.5 equivalent of CS$_2$).

**Figure 3-18.** Storage ($G'$, ●) and loss ($G''$, ○) moduli of (6-7)PSil-CS$_2$ at 25 °C.
According to the dynamic strain sweep measurements in Figure 3-18, (6-7)PSil-CS$_2$ is a soft elastic material (a gel; *vide infra*); $G'$ decreases as shear strain increases. However, $G''$ increases and then decreases in the high-strain region. This behavior, a “weak strain overshoot,” arises from the strain-induced imbalance between the formation and destruction of network junctions.$^{154}$ If the polysiloxane backbones with ammonium dithiocarbamate groups (as well as those with ammonium carbamate groups) are highly extended as a result of the electrostatic repulsion from the charged centers, the resultant microstructure networks can resist deformation while a weak strain is imposed and $G''$ increases. However, the microstructures are destroyed by large strains, decreasing $G''$.

![Figure 3-19](image.png)

**Figure 3-19.** Storage ($G'$, ○) and loss ($G''$, ○) moduli of (6-7)PSil-CS$_2$ at 25 °C (left Y axis). The loss tangent, $\tan \delta (G''/G')$ as a function of angular frequency of the same data (▲, right Y axis).
Based upon the observations in Figure 3-18, the dynamic rheological data for (6-7)\textit{PSil-CS}_2 in Figure 3-19, showing a gel-like behavior—the elastic modulus $G'$ greatly exceeds the viscous modulus $G''$ over the entire range of frequencies and both moduli and the loss tangent $\delta (G''/G')^{155}$ are almost independent of angular frequencies—is not surprising. The lack of frequency dependence indicates that the sample does not relax in the timeframe of $\leq 100$ s. The value of tan $\delta$, in the range of 0.1 at angular frequencies from 0.1 to 3 rad/s, indicates that (6-7)\textit{PSil-CS}_2 is a strong gel.$^{19b}$ The (6-7)\textit{PSil-CS}_2 swollen by chloroform and ethyl acetate and \textit{PSil-CS}_2-H swollen by hexane also behave rheologically like gels (Figures 3-20 and 3-21).

![Figure 3-20](image)

**Figure 3-20.** Storage ($G'$, ●, ▼) and loss ($G''$, ○, ▼) moduli at 25 °C of (6-7)\textit{PSil-CS}_2 swelled with CHCl$_3$ (●, ○) and with ethyl acetate (▼, ▼).
Figure 3-21. Storage ($G'$, ●, ▲) and loss ($G''$, ○, △) moduli at 25 °C of 15PSil-CS$_2$-H (●, ○) and 10PSil-CS$_2$-H (▲, △) after swelling with hexane.

PSil-CO$_2$ samples adhered$^{156}$ strongly to several different surfaces. Figure 3-22 provides quantitative data for the adhesion to steel as a function of amino group content. Although adhesion is highest for 15PSil-CO$_2$, the dependence on amino group content is not linear. The ability of the PSil-CO$_2$ to adhere to other rigid substrates has been examined only qualitatively as a result of instrumental limitations. The results indicate that the PSil-CO$_2$ have strong adhesive forces to glass in the opening mode (i.e., pulling the plates apart by applying a force perpendicular to the plate surfaces); the forces are weaker for Teflon, paper, cardboard, and copper, but all are substantial. Adhesion to any of the materials tested was much stronger for the PSil-CO$_2$ than for the corresponding PSil. It is noted that adhesion of 15PSil-CO$_2$ even to Teflon was rather strong.
We also evaluated the qualitative adhesiveness of the PSil-CO₂ under different environmental conditions. There was no discernible difference in the adhesion of 15PSil-CO₂ to copper plates during 24 h when the sandwiched samples were left in air or submerged under tap water. In both cases, the contact surface area of the polymer to the outside environment was very small, conditions that disfavor loss of CO₂ via out-diffusion and entry of water via in-diffusion. However, the substrates could be separated much more easily when a sandwich was warmed for several minutes to 40 °C (i.e., below the CO₂ loss temperature according to DSC and TGA measurements); recooling the same sandwich to room temperature increased again the adhesive strength. However, both the aged PSil-CS₂ and (heated) PSil-CS₂-H are gel-like materials and exhibit very little adhesion to the same substrates. Very recently,
Zhang and coworkers\textsuperscript{157} reported the use of PDMS as a substrate combined with 3-aminopropyl-triethoxysilane as a bonding agent for the separation of semiconducting (s) and metallic (m) single-walled carbon nanotubes. In essence, the polymer is acting like a selective adhesive. Although the essential character of these interactions is still unclear, the lone pair of electrons on the amino nitrogen is implicated as an important contributor to the adhesion.\textsuperscript{158}

It is known that protonation of carbamate of dithiocarbamate group results in a rapid loss of their triatomic moieties and formation of ammonium groups.\textsuperscript{19} When the ammonium carbamate being treated is part of a polymeric material, addition of acid causes a precipitous decrease in viscosity, analogous to that experienced by ammonium carbamates when they are heated to remove CO\textsubscript{2}.\textsuperscript{159} Thus, the viscosities of the PSil-CO\textsubscript{2} were reduced and small bubbles (presumably CO\textsubscript{2}) were formed in them when glacial acetic acid ($pK_a$ 4.8) was added. However, the PSil-CS\textsubscript{2} was converted to flowing liquids only after addition of the stronger trifluoroacetic acid ($pK_a$ 0.5) in its neat form.

3.1.6 Conclusions

A facile method has been developed for crosslinking polysiloxanes with amino functionalities via addition of an uncharged triatomic molecule, CO\textsubscript{2} or CS\textsubscript{2}. The crosslinking with CO\textsubscript{2} can be reversed easily by mild heating while that with CS\textsubscript{2} cannot be—warming the ammonium dithiocarbamates that are formed upon exposure of the PSil to CS\textsubscript{2} results in covalent thiourea crosslinks and expulsion of H\textsubscript{2}S. The physical, rheological and adhesive properties of the polysiloxanes before and after ionic and covalent crosslinking can be ‘tuned’ by varying the amino substitution along the polymer chains. A remarkable aspect of this work is the extremely large increases in the viscosity and adhesiveness that can be attained simply by bubbling CO\textsubscript{2} through
the polymers. Although there is a direct relationship between the absolute viscosity and the amount of amine functionality in the polymers after addition of a triatomic, no correlation was obvious in the PSils, themselves. There, molecular weight of the polymer chains appears to be the most important factor in determining the viscosities. The strong adhesion of the PSil-CO2 polymers to various substrates, combined with their reversibility to the original PSils (and loss of adhesive strength), opens prospects for creating reversible, stimuli-responsive adhesives or sealants in which adhesion can be controlled by environmental conditions.

The PSil-CS2 and the PSil-CS2-H materials (that the PSil-CS2 yield upon heat treatments) are able to be swelled to several fold their original volumes by some organic solvents. Again, this ability to be swelled and deswelled may lead to interesting new applications for polysiloxanes. Although heating the PSil-CS2 cannot reconvert them to their PSil forms (as it can the PSil-CO2), exposing them to a strong acid produces ammonium groups along the chains (i.e., a protonated PSil) that allow the PSils to flow again like low viscosity liquids. These materials do not possess the gel-like or the strong adhesive properties of the PSil-CS2.

In summary, simple organic chemistry can be applied to a set of complex polymers to change enormously their macroscopic properties. The natures of those changes have been documented step-by-step through a combination of spectroscopic and rheological measurements. This facile strategy provides not only an effective alternate to the more classical method to crosslink polymers, but it also affords an easily accessed route to two classes of novel materials with interesting physical and chemical properties.

Potential new applications include the use of polysiloxanes as cleaning agents in art conservation, where rheoreversibility and swelling by organic liquids are highly
desirable attributes. In addition, our swollen polysiloxanes may be useful packing materials for chromatography and as aligning media for NMR measurements. This approach may also be useful in the syntheses of new polymers from monomers pre-treated with CO₂ or CS₂. Experiments to exploit some of these uses are underway.

3.2 Swelling-deswelling behavior of crosslinked amino-substituted polysiloxanes.

Possible applications for chemical spill containment and remediation

3.2.1 Introduction

Swelling of cross-linked polymer networks is an important topic, given the wide variety of applications of such materials, including stimuli-responsive materials, membranes, templates for inorganic morphologies, and drug delivery systems. Polymeric materials such as poly(dimethylsiloxane) (PDMS) are known to swell in various organic solvents, and their swelling properties have been extensively investigated. Several types of ionically and covalently crosslinked amino-functionalized polysiloxanes (PSils), prepared by simple addition of CS₂ (PSil-CS₂) and heating (PSil-CS₂-H) have been prepared by our group (Scheme 3-1). These PSils were shown to imbibe large volumes of several organic liquids, especially those of low polarity, without dissolving.

Here, we report a detailed investigation of the swelling and deswelling kinetics of PSil-CS₂ and PSil-CS₂-H at different temperatures using neat and mixed solvents as the swelling agents. (Although the corresponding PSil-CO₂ materials must swell organic liquids in a similar fashion, we have not examined their swelling ability because the experiments must be conducted under industrially unrealistic conditions—one atmosphere of CO₂—in order to maintain the integrity of the crosslinks over long times and ensure reproducibility.) The swelling ability can be
tuned by varying the degree of crosslinking (i.e., the frequency of amino functionalities along a polymer chain). These investigations allow the rate-limiting step for entry into or exit from PSils to be identified. Furthermore, the swelling/deswelling cycle could be repeated several times without significant loss of swelling capacity. Based upon these observations and the density of the polymers (<1 g/cm³), a procedure for recovery of oils or chemicals from spills (that includes reuse of the PSils) has been developed.

3.2.2 Materials

87-octane gasoline was obtained from a commercial gas station; VM-46 Naphtha was from VM&P; Xylol was from Xylol Parts, Inc. Other chemicals used in this study are described in Section 3.1.3.

3.2.3 Procedure for swelling/deswelling

Procedure for swelling. A weighed aliquot (ca. 30 mg) of cross-linked PSil and 3.0 mL of a liquid were for 24 h. During this time, the PSil and the solvents were kept in closed, screw-capped glass vials with Teflon inserts in the caps to ensure no loss of solvent. Then, the polymer was removed, its surface was dried quickly on a piece of filter paper, and it was reweighed on a precision balance. The swelling ratio (S%) was calculated by eq. 3-3 in section 3.1.4. The swelling and deswelling cycle was repeated at least three times and the average data are reported. The reproducibility of the swelling kinetics was ± 5%.

Procedure for swelling kinetics. For swelling, a polymer was removed from the organic solvent at pre-determined time intervals, weighed after drying it with a piece of filter paper rapidly, and placed anew into the liquid until no weight increase could be detected between successive determinations. For deswelling, a known amount fully swollen polymer was placed on a precision balance, and the loss of weight was
recorded at pre-determined time intervals. The swelling and deswelling cycle was conducted at least three times, and the reproducibility of the kinetics of deswelling was ± 3%.

Selective swelling capacity. 33 mg of 10PSiL-CS₂ and an equimolar mixture (0.62 mmol) of 0.52 g dichloromethane and 0.29 g ethanol were placed into a closed screw-capped glass vial at room temperature. After 2 h, the swelled polymer was removed with a spatula and its surface was dried quickly on filter paper and weighed immediately. Integration of selective protons of the two organic liquids in ¹H NMR spectra of the solvent mixture remaining in the vial (Table 3-2) was used to calculate the molar ratio of the remaining solvents in the vial and, thereby, knowing the weight of the solvent imbibed into the 10PSiL-CS₂, the molar ratio of solvents taken into the 10PSiL-CS₂. The estimated error in the measurements is ± 5%.

Procedure for determining total swelling capacity and selectivity of swelling in ethanol-dichloromethane mixtures. In closed screw-capped glass vials, ca. 30 mg of 10PSiL-CS₂ were added to ca 1.0 g mixtures of dichloromethane and ethanol. The mol % of ethanol was 0% (1.0 g CH₂Cl₂), 20% (0.88 g CH₂Cl₂ and 0.12 g ethanol), 40% (0.74 g CH₂Cl₂ and 0.26 g ethanol), 50% (0.65 g CH₂Cl₂ and 0.35 g ethanol), 60% (0.55 g CH₂Cl₂ and 0.45 g ethanol), 80% (0.32 g CH₂Cl₂ and 0.68 g ethanol) and 100% (1.1 g ethanol). The swelled polymers were removed after 2 h by spatula, their surfaces were dried quickly on filter paper, and they were reweighed immediately. The swelling ratios (S %) were calculated eq. 3-3 in section 3.1.4. The estimated error in the measurements is ± 5%.

Also, a weighed amount (ca. 40 mg) of 10PSiL-CS₂ was placed in a water and gasoline mixture in a closed screw-cap glass vial. The polymer was removed was and reweighed as described above. Deswelling of the gasoline from the polymer was
monitored by placing it on a piece of filter paper, removing it at different times, weighing it, and placing it anew on the filter paper until no additional weight decrease could be detected. The estimated error in the measurements is ± 5%.

3.2.4 Results and discussion

The crosslinker frequency is known to affect significantly the ability of a polymer to be swelled because it determines the porosity and flexibility of the polymer networks. Okay and coworkers reported that the total volume of the pores first increases with increasing crosslinker content up to 20 mol% in a 2-hydroxyethyl methacrylate/ethylene glycol dimethacrylate copolymer, the total volume of the pores first increases with increasing crosslinker content up to 20 mol%, but then it decreases continuously at higher crosslinker concentrations. The effect of the crosslinking density on swelling ability in various organic liquids is shown for six types of PSil-CS$_2$ in Figure 3-23. Water is not included because it did not perceptibly swell any of the PSil-CS$_2$. 

![Swelling ratio S%](image-url)
**Figure 3-23.** Swelling ratios of (6-7)PSil-CS$_2$ (red), 10PSil-CS$_2$ (blue), 15PSil-CS$_2$ (yellow) and their PSil-CS$_2$-H (stripe) in 4 liquids at room temperature.

The swelling ratios of PSil-CS$_2$ gels show no discernible relationship with increasing frequency of amine functionality; 10PSil-CS$_2$ is clearly the most efficient. We hypothesize that the three-dimensional networks of 10PSil-CS$_2$ offer the best balance between crosslinking density and network flexibility. Osmotic pressure balance between solvent molecules and a polymer surface is critical to the equilibrium swelling capacity. Physically, the liquid molecules must enter initially near the surface of a polymer and then move into the interior regions as other molecules of liquid occupy sites near the surface. Therefore, it is understandable that the degree of rubbery elasticity of the cross-linked network will affect the osmotic pressure balance. This theory is consistent with the results shown in Figure 3-23, where an even higher (15%) crosslinking percentage leads to a decrease in the swelling capability. The more highly crosslinked polymeric network is more rigid and has more interactions between polymer chains. At lower crosslinking densities, the network is looser with larger spaces between chains, allowing more solvent to be incorporated. However, the relative stabilities of three-dimensional networks need to be taken into account, as well. Too few crosslinks do not lead to stable gel networks after swelling. These results indicate that the swelling process is a convolution of network stability and space between chains.

Note also in Figure 3-23 that each of the PSil-CS$_2$ is able to imbibe more of a liquid than its corresponding (covalently) thiourea crosslinked analogue PSil-CS$_2$-H. This observation is attributed to the ability of the ionic crosslinks to ‘float’ from one position to another in a manner that maximizes the network stability in the presence of a liquid; covalent crosslinks are ‘fixed’ and, therefore, unable to readjust to the
presence of a swelling liquid. Even before swelling, the \textit{PSil-CS}_2-\text{H} are a much stiffer materials than the \textit{PSil-CS}_2. As a result of the longer side chains in the \textit{PSil-CS}_2 than \textit{PDMS} and the triatomic crosslinkers, which leave the 3-D networks more flexible (i.e., the cationic and anionic centers remain paired, but the specific groups constituting the pairs can change with time and degree of swelling), the swelling ratios reported here are larger than those from other crosslinked \textit{PDMS} gels in the same liquid.\textsuperscript{166,178}

As mentioned above, the degree of crosslinking can be controlled also by the amount of the triatomic molecule added to the polymer. Thus, 0.4 equivalents of CS\textsubscript{2} were added to 15\textit{PSil} in order to simulate the degree of crosslinking in fully reacted (6-7)\textit{PSil}. Under these conditions, swelling ratios in hexane were 329\% for 15\textit{PSil}-0.4CS\textsubscript{2} and 252\% for 15\textit{PSil}-0.4CS\textsubscript{2}-H (i.e., the sample of 15\textit{PSil}-0.4CS\textsubscript{2} that was heated and then swelled). The corresponding (6-7)\textit{PSil} samples have swelling ratios in hexane, 362\% and 278 \%, that are very near these values. From this observation, we conclude that the ammonium dithiocarbamate crosslinks are not affected in an important fashion by the presence of free amino groups on the polymer chains. However, when the nature of the amino groups differ, as they do between (2-4)\textit{PSil}, in which each side-chain contains one primary and one secondary amino group, and 15\textit{PSil}, in which each side chain contains only one primary amino group, the properties of the partially reacted 15\textit{PSil} do not match those in which all of the amino groups of (2-4)\textit{PSil} are thought to be reacted.
3.2.5 Swelling kinetic model and diffusion

Figure 3-24. Time-dependent swelling (blue) and deswelling (red) behaviors of 15PSil-CS2 (filled circles) and 15PSil-CS2-H (open circles) in THF at room temperature.

Figure 3-25. Time-dependent swelling of (6-7)PSil-CS2 (●), 10PSil-CS2 (●) and 15PSil-CS2 (●) in hexane at room temperature.
To understand the swelling process, the kinetics of swelling and deswelling behavior of PSil-CS$_2$ has been systematically investigated.$^{179, 180}$ In general, the swelling process of polymers involves three steps: (1) diffusion of the solvent molecules into polymer networks; (2) relaxation of the polymer chains due to salvation by solvent molecules; (3) diffusion of the polymer chains into the solvent.$^{181}$ Time-dependent swelling and deswelling behaviors of (6-7)PSil-CS$_2$, 10PSil-CS$_2$ and 15PSil-CS$_2$ in CHCl$_3$ are shown in Figure 3-24. Swelling of (6-7)PSil-CS$_2$ is rapid during the first several minutes and reaches an equilibrium after ca. 2 h; its rate is faster and, as mentioned above, its equilibrium value is higher than those of (6-7)PSil-CS$_2$-H. The lower flexibility and mobility of the polymer chains and the smaller spaces available to liquid molecules between 3-D networks in the permanently (covalently) crosslinked (6-7)PSil-CS$_2$-H explain both results. It is noted that there is no rate difference among the three investigated PSil-CS$_2$ in the first several minutes (Figure 3-26), showing cross-linker densities have no or little impact on the swelling rate.

### 3.2.6 Swelling kinetics

\[
\frac{dS}{dt} = k_s (S_e - S)^2 \quad (3-4)
\]

\[
t/S = A + Bt \quad (3-5)
\]

In eq. 3-4, $k_s$ is the rate constant and $S_e$ and $S$ are the equilibrium swelling ratio and the swelling ratio at time = $t$, respectively. Eq. 3-4 can be presented in its integrated form as eq. 3-5 where $A=1/k_s \cdot S_e^2$ is reciprocal of the initial swelling rate and $B = 1/S_e$ is the inverse of the equilibrium swelling ratio.
Figure 3-26. Best linear fits of data in Figure 3-25 according to plots of $t/S$ versus $t$ for swelling $15\text{PSil-CS}_2$ (black) and $15\text{PSil-CS}_2$-H (blue) by THF at room temperature.

Schott\textsuperscript{182} has proposed a theoretical model for the polymer swelling system, considering that the swelling follows second-order swelling kinetics. Figure 3-26 displays plots of the reciprocal of the average swelling rate ($t/S$) versus swelling time ($t$), showing a straight linear relation which indicates $15\text{PSil-CS}_2$ and $15\text{PSil-CS}_2$-H swelling processes follow a second-order swelling model.\textsuperscript{183} This result indicates that there are many types of polymer-solvent interactions occurring in this system. Therefore the swelling process failed to follow first-order swelling kinetics.\textsuperscript{173a} In eq. 2, the swelling rate depends on the two constants of $A$ and $B$—the initial rate of swelling and the equilibrium swelling ratio, respectively. As discussed in section 3.2.4, the initial swelling rate is related to the relaxation rate of the chain segments in the polymer networks.

$$- \frac{dS}{dt} = k_s (S_e - S) \quad (3-6)$$
$$\ln \left(1 - \frac{S}{S_c}\right) = -Kst \quad (3-7)$$

Figure 3-27. Rate analysis of the swelling properties of (6-7)PSil-CS$_2$ in THF at room temperature.

Also, we investigated whether the swelling follow the first-order kinetics as illustrated by eqs 3-6 and 3-7. The semi-log graph as a fist-order rate analysis swelling behavior of (6-7)PSil-CS$_2$ was plotted and showed in Figure 3-27. The swelling rate constants of the gels can be obtained from the slopes of these fitting lines. The linear correlation of the data was poor especially in the first five minutes, showing that the swelling process does not follow the first-order kinetics.

3.2.7 Binary system$^{184, 185}$

Most of the current research concerning swelling and diffusion in cross-linked polymers has focused on single component solvent systems. From the standpoint of applications, such as a binary liquid mixture separation by polymer membranes, swelling investigations in the presence of a binary or multi-component solvent is important as well. Two theoretical models to describe the swelling of polymer networks in binary solvents have been developed by Okeowo and coworkers.$^{186}$ Also, the Flory-Rehner theory$^{187}$ has been modified to describe multi-component sorption in cross-linked polymer films. Here, we report a simple experiment to investigate the
selectivity of solvent uptake from dichloromethane and ethanol solvent mixtures in 10PSiL-CS₂ at room temperature.

As shown in Figure 3-28, in the 4:6 (mol:mol) CH₂Cl₂:ethanol mixture, 10PSiL-CS₂ was swelled to 310 % its original weight. However, the swelling ratio of 10PSiL-CS₂ in solvent mixtures is ca. 200 wt% lower than in a pure CH₂Cl₂ solvent under identical condition. Table 3-2 illustrates that 10PSiL-CS₂ takes up 4.2 times as many moles of CH₂Cl₂ as ethanol from an equimolar mixture of CH₂Cl₂ and ethanol.

The data show that the equilibrium swelling ratio is decreased by the presence of a ‘bad’ solvent and that 10PSiL-CS₂ is selective in its uptake of solvents in mixtures. These results indicate that ability of CH₂Cl₂ to diffuse into a PSiL-CS₂ (or other PSiL material) is affected considerably by the presence of ethanol. The most probable cause for this effect is a decrease in the concentration of the ‘good’ solvent at the surface of the 10PSiL-CS₂ rather than a change in the partition coefficient.¹⁸⁸
Table 3-2. Selectivity tests of sorption of 1:1 (mol:mol) CH\textsubscript{2}Cl\textsubscript{2}:CH\textsubscript{3}CH\textsubscript{2}OH into 10PSi\textsubscript{l}-CS\textsubscript{2} at room temperature.a

<table>
<thead>
<tr>
<th>Sample status</th>
<th>Solvent composition</th>
<th>Solvent in polymer g (mmols)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH\textsubscript{2}Cl\textsubscript{2} g (mmoles)</td>
<td>CH\textsubscript{3}CH\textsubscript{2}OH g (mmoles)</td>
</tr>
<tr>
<td>Before adding 10PSi\textsubscript{l}-CS\textsubscript{2} (33.3 mg)</td>
<td>0.52 (6.2)</td>
<td>0.29 (6.2)</td>
</tr>
<tr>
<td>After 10PSi\textsubscript{l}-CS\textsubscript{2} swelling: S% = 575% (225 mg)</td>
<td>0.35 (4.1)</td>
<td>0.26 (5.7)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Calculated from integration of $^1$H NMR peak areas of protons (indicated in italics) of CH\textsubscript{2}Cl\textsubscript{2} and CH\textsubscript{3}CH\textsubscript{2}OH and adjusted for the different populations per molecule.

3.2.8 Influence of temperatures<sup>189</sup>

A systematic study of the influence of temperature on the swelling extent of PDMS networks was reported by Favre,<sup>166</sup> in which data were interpreted according to Arrhenius and Flory-Huggins theories.<sup>190</sup> Here, different swelling ratios were measured for experiments conducted from 0 °C to 45 °C.

Different swelling ratios of 10PSi\textsubscript{l}-CS\textsubscript{2} were obtained from 0 °C to 45 °C, as shown in Figure 3-29. The swelling ratios increase with increasing temperature. For example, 10PSi\textsubscript{l}-CS\textsubscript{2} can take up 320 wt% and 405 wt% of hexane, at 0 °C and 45 °C, respectively. The 85 wt% uptake indicates that the polysiloxane networks become more extendable at elevated temperatures, thereby, allowing the uptake of more
solvent. In addition, the surface properties, such as charge density (in the case of PSil-CS$_2$), and “softness” (i.e., the elasticity of the cross-linked network) of the polymers change with temperature. They are other factors that affect the swelling capacity.$^{191}$ Studies of the temperature dependence of swelling of polystyrene networks, reported by Baysal and coworkers,$^{192}$ show a 3-4 fold increase in the swelling ratio, depending on the degree of cross-linking, between 16 and 45 °C.,

![Swelling Ratio Changes](image)

**Figure 3-29.** Swelling ratio changes of 10PSil-CS$_2$ in hexane (●) and THF (○) at as a function of temperature.

### 3.2.9 Chemical spill containment and remediation

Recent events in the Caribbean Sea have made the development of new and more efficient functional materials to mediate the deleterious effects of oil spills a high priority. Surprisingly, many of the initiatives have focused on dispersion of the spilled oil rather than its recovery. Here, we describe a potential method to contain and recover spilled oil that appears to be superior in several aspects to recently devised methods.$^{193, 194}$ As described in section 3.1.5, the PSil-CS$_2$s can absorb hydrocarbon compounds efficiently, do not absorb water to an appreciable extent, and
are less dense than water. Therefore, a potential application of the PSil-CS$_2$ systems is
the recovery of chemicals and/or crude oil spilled in bodies of water.\textsuperscript{195} Here, the
swelling capabilities of 10PSil-CS$_2$ with gasoline (I), naphtha (II), and xylol (III)
have been investigated. The S (wt\%) values are ca. 205\% (I), 240\% (II), and 235\%
(III), respectively. Under ambient conditions (room temperature in the air), a naphtha-
swelled 10PSil-CS$_2$ polymer was able to be scooped out with a spatula, and placed on
a piece of filter paper. It lost solvent gradually and returned to its original weight in ca.
3h. Elevating the temperature to 50 °C or placing the naphtha-swelled 10PSil-CS$_2$
polymer under reduced pressure (250 Torr) at ambient temperature, the 10PSil-CS$_2$
returned to its unswelled weight in ca. 15 min or 45 min, respectively. To mimic the
real scenario of a chemical spill in water, a demonstration of how such a system can
be employed is shown in Figure 3-30. Furthermore, this swelling/deswelling cycle has
been repeated three times without significant loss of swelling capacity (Figure 3-31).

\textbf{Figure 3-30.} Photographs of water (1.05g) and 87 octane gasoline (0.2g) mixture
(left), and after adding 10PSil-CS$_2$ (60 mg) into the mixture for 30 min (middle). The
top gasoline layer is indicated by an added dye, perylene. The swelling ratio is ca. 208
wt %. As indicated by the photographs above the arrow, the width of the 10PSil-CS$_2$
sample before and after swelling is ca. 0.50 and 0.75 cm, respectively. Swelled PSil
was removed from the mixture and only a small amount of gasoline could be observed in the vial (right). The appearances of 10PSi-CS$_2$ before (left) and after (right) swelling are shown in the photographs above the arrows.

![Swelling Ratio Graph]

**Figure 3-31.** Three swelling/deswelling cycles of 38 mg 10PSi-CS$_2$ by 0.75 g naphtha (II) in a layer over 1.5 g water.

### 3.2.10 Conclusions

We present a detailed study of PSi-CS$_2$ and PSi-CS$_2$-H swelling properties and their swelling/deswelling kinetic behavior. The polymer swelling is dependent on polymer chain relaxation and solvent molecule diffusion. The swelling processes of PSi-CS$_2$ and PSi-CS$_2$-H followed Schott’s second-order diffusion kinetics which is based on the stress-relaxation model for polymer chains. Swelling investigations in a binary solvent system show that the equilibrium swelling ratio of a ‘good’ is decreased by the presence of a second ‘poor’ solvent and that the PSi-CS$_2$ display selective uptake from the mixture. In addition, we demonstrate how a potential application for recovery by PSi-CS$_2$ polymers of chemicals and crude oil on water surfaces might function. These polymers are easily prepared and exhibit the ability to
uptake selectively chemicals from water. Also, the PSi-CS$_2$ can be recovered and used multiple times for this purpose. We believe this is a promising method for the containment and remediation of oil or chemical spills from aqueous layers.

Future work will focus on determining the nature of the diffusion process by using the Fickian diffusion model.\textsuperscript{196} To do so will require \textit{in situ} monitoring of the uptake by the polymer gels.

4. SYNTHESES OF CYCLIC CARBONATES IN REUSABLE, REVERSIBLE ROOM-TEMPERATURE IONIC LIQUIDS

4.1 Introduction

Due to the growing concern about the deleterious effects of greenhouse gases on our environment, chemical fixation of CO$_2$ and its use as an inexpensive, single carbon atom building block have gained considerable attention during last two decades.\textsuperscript{197} From the standpoint of resource utilization, the syntheses of five-membered cyclic carbonates from CO$_2$ and epoxides (Eqs. 4-3 ~ 4-6) is a promising methodology because cyclic carbonates are widely used for a variety of applications, such as polar aprotic solvents, precursors of polymeric materials, and intermediates in the syntheses of pharmaceuticals.\textsuperscript{198, 199, 200} Numerous catalysts, including metal halides, metal oxides, and metal complexes have been developed and investigated to facilitate the reactions.\textsuperscript{201} However, the problem of how to separate easily the products from the solvents and catalysts after reaction still needs to be solved. Also, the nature of the solvent can be a critical element in the ease of reaction.\textsuperscript{202}

Although ionic liquids, by themselves, are not necessarily ‘greener’ than other solvents, they can offer intrinsic advantages in catalytic reactions over many other organic solvents in reactions involving CO$_2$,\textsuperscript{203} especially in the steps leading to
isolation of the products and to minimize byproducts such as polycarbonates\textsuperscript{204} or polyesters.\textsuperscript{205} In addition, high temperatures (>100 °C) and high pressures of CO\textsubscript{2} are generally required to obtain high yields of cyclic carbonates from epoxides.\textsuperscript{206, 207}

The reversibility of the RTILs described in sections 2.2, 2.3 and 2.4 offer significant potential benefits as solvents in the syntheses and separations of products which are soluble in low-polarity media and whose mechanisms of formation depend on catalysts soluble only in high-polarity media.

Here a prototype reaction, the synthesis of cyclic carbonates by addition of CO\textsubscript{2} to epoxides, utilizing the \textit{in situ}-reversibility of the RTILs, is described. Amidinium carbamate RTILs (L-amine-C) were prepared as described previously.\textsuperscript{3a} For comparison purposes, amidinium dithiocarbamates were employed as the RTILs\textsuperscript{208} in some experiments. Reaction between CO\textsubscript{2}, present at 25-50 atmospheres of pressure, and a number of epoxides in the RTILs, occurs in good yields (> 90% in many cases) at ambient or slightly elevated temperatures in the presence of an amidinium halide catalyst. The cyclic carbonate products and any remaining epoxide could be extracted easily upon addition of an immiscible, lower density liquid (an alkane or ether) to an RTIL reaction mixture. Protracted bubbling of CO\textsubscript{2} through the L-amine-C was sufficient to remove any dissolved extracting liquid so that the RTIL could be reused. Thereafter, another substrate was added and its reaction was conducted as before. The influence of the type of catalyst, CO\textsubscript{2} pressure, reaction time and temperature on the reaction yields will be reported.
Scheme 4-1. Reaction mechanism for carbonate syntheses from epoxides and CO$_2$.

Importantly, these reversible RTILs can be used repeatedly with little or no decrease of product yield, and no metal catalyst need be employed. The relatively mild reaction conditions, ease of separation of products from the L-amine-Cs, and the ability to use the L-amine-Cs repeatedly make this an attractive alternative to other procedures for the syntheses of cyclic carbonates. In addition, this reaction demonstrates a beneficial use of CO$_2$, a greenhouse gas.

4.2 Materials.

Epichlorohydrin (99%), 1,2-epoxy-3-phenoxypropane (99%), styrene oxide (97%), cyclohexene oxide (98%), tetraethylammonium bromide (98%) and lithium bromide (>99%) were purchased from Sigma-Aldrich and used as received. Carbon dioxide (CO$_2$) was supplied by GT & S with a purity > 99.9%. Sodium bromide (99.9%), zinc chloride (99.2%) and Zinc iodide (99.9%) were from Fisher. Zinc Bromide (99.9%) was from Baker. Hydrochloric acid (HCl, 99%, 37 wt% in water), hydroiodic acid (HI, 99.95%, 57 wt% in water), hydrobromic acid (HBr, 99.9%, 48 wt% in water) are from Baker. CH$_3$CN was dried by 4A molecular sieve before using. All organic solvents
were HPLC grade (Fisher or Aldrich). Other chemicals have been reported in section 2.1.2.³a, b

4.3 Instrumentation.

Unless stated otherwise, all instruments are the same as described in section 2.1.3. High pressure generators (Model: 50-6-15; Pressure rating: 15,000 psi; Capacity per stroke: 20 mL), valves and tubings were purchased from High Pressure Equipment Company (HIP), Pennsylvania. The pressure gauge was purchased from McDaniel Controls, Inc. (Ni Span C Tube 316SS Socket, 0-25000 psi). A stainless steel reaction cell with three quartz windows was manufactured at the University of Buenos Aires under the supervision of Prof. Pedro F. Aramendía and Prof. Laura Japas. The apparatus was assembled with the help of Dr. Rodrigo Cristiano and is shown in Figure 4-1. The highest pressure achieved using a gas cylinder was 80.2 atm.

Super-ambient temperatures are achieved with four cartridge electric heating elements and a rheostat in a system designed by Mr. William Craig (shown in Figure 4-1 upper right). Temperature is monitored by an Omega HH503 microprocessor thermometer connected to a J-K-T thermocouple. The temperature variation throughout the cell is estimated to be ca. 1.5 °C based upon measurements of the internal and external temperatures of the cell at various points.
Figure 4-1. High pressure CO\textsubscript{2} generator and reaction cell (upper left) and temperature control setup (upper right). The reaction cell is indicated by the arrow in both figures. The layout of the components of the high pressure instrument is shown in the diagram at the bottom.

4.4 General experimental procedure

Procedure for the syntheses of cyclic carbonates:

A typical reaction procedure is described for the synthesis of 4-phenoxyethyl-1,3-dioxolan-2-one (2b) from CO\textsubscript{2} and 1,2-epoxy-3-phenoxy propane (2a) using
LiBr as a catalyst in C⁶-hexylamine-CO₂ ionic liquid, as shown in eq 4-4. Cn-HX catalyst was used in an analogous fashion for this reaction. In all cases, \(^1\)H, \(^{13}\)C NMR and MS spectra of the products were consistent with those in the literature.

In an open glass vial with a 1 cm teflon stir bar, LiBr (1.2 mg, 1.4×10⁻² mmol) was added to a solution of 1,2-epoxy-3-phenoxypropane (2a) (0.10 g, 0.70 mmol) in 0.50 mL of C⁶-hexylamine-CO₂ ionic liquid, prepared by bubbling CO₂ through a C⁶/hexylamine mixture for 10 min. The glass vial was placed into the stainless steel high pressure cell. Then, CO₂ gas was introduced to a suitable pressure and temperature. After stirring the reaction mixture for several hours, the pressure was brought slowly back to one atmosphere and diethyl ether (3.0 mL×3) was used to extract the products and any unreacted epoxide from the reaction mixture. To purify the product, in some cases, the residues after removal of the combined etherates under vacuum were analyzed and separated by column chromatography using 2:3 hexane:EtOAc as the eluent. Product yields were calculated from the weight of the residues (which were a combination of product and starting material whose proportion was calculated by integration of characteristic peaks in \(^1\)H NMR spectra Some of the reactions were repeated and the reproducibility of the yields was ± 3%. In a few runs, the yield was calculated by the weight of isolated product after column chromatography.

4-Phenoxyethyl-1,3-dioxolan-2-one (2b): \(^1\)H NMR: 4.15 (dd, \(J = 3.6, 3.6\) Hz 1H, OCH₂), 4.24 (dd, \(J = 4.4, 4.4\) Hz 1H, OCH₂), 4.55 (dd, 1H, PhOCH₂), 4.62 (t, \(J = 8.4\) Hz, 1H, PhOCH₂), 5.03 (m, 1H, OCH), 6.91 (d, \(J = 8.8\) Hz, 2H, Ph), 7.02 (t, \(J = 8.0\) Hz, 1H, Ph), 7.31 (t, \(J = 8.0\) Hz, 2H, Ph); \(^{13}\)C NMR: \(\delta\) 66.25, 66.88, 74.03, 114.55, 122.03, 129.70, 154.57, 157.73 ppm; IR: 1786 cm⁻¹ (C=O); MS (m/z 194, M⁺).
4-Chloromethyl-1,3-dioxolan-2-one (1b): $^1$H NMR: $d = 3.75 - 3.81$ (m, 2 H, ClCH$_2$), 4.41 (dd, $J = 6.0, 9.0$ Hz, 1 H, OCH$_2$), 4.59 (dd, $J = 8.4, 9.0$ Hz, 1H, OCH$_2$), 4.93 – 4.96 (m, 1 H, CHO); $^{13}$C NMR: $\delta$ 43.71, 66.90, 74.35, 154.30 ppm; IR: 1786 cm$^{-1}$ (C=O); MS (m/z 137 M$^+$).

4-Phenyl-1,3-dioxolan-2-one (3b): $^1$H NMR: $d = 4.36$ (t, $J = 8.4$ Hz, 1 H, OCH$_2$), 4.82 (t, $J = 8.4$ Hz, 1 H, OCH$_2$), 5.72 (t, $J = 8.4$ Hz, 1 H, OCH), 7.36 (m, 2 H, Ph), 7.44 (m, 3 H, Ph); $^{13}$C NMR: $\delta$ 71.15, 77.97, 125.85, 129.25, 129.75, 135.80, 154.76 ppm; IR: 1780 cm$^{-1}$ (C=O); MS (m/z 164 M$^+$).

4,5-Tetramethylene-1,3-dioxolan-2-one (4b): $^1$H NMR: $d = 4.65 – 4.70$ (m, 2 H, CHO), 1.86 – 1.90 (m, 4 H, CH$_2$CHO), 1.58–1.64 (m, 2 H, CH$_2$CH$_2$), 1.38–1.44 (m, 2 H, CH$_2$CH$_2$); $^{13}$C NMR: $\delta$ 19.13, 26.75, 75.67, 155.27 ppm; IR: 1790 cm$^{-1}$; MS (m/z 142 M$^+$).

**Procedure for the synthesis of C6-HX**

![Reaction Scheme](image)

$R = C_6H_{13}$

$X = \text{Cl, Br or I}$

The reaction scheme for C6-HX preparation is shown in eq. 4-1. A detailed example is presented for the synthesis of dried C6-HBr. C6-HCl and C6-HI were prepared in analogous fashions using 37% aqueous HCl and 57% aqueous HI. To a solution of C6 amidine (0.34 g, 2.0 mmol) in a stirred round bottom flask, 48% aqueous HBr (0.69 g, 4.0 mmol HBr) was added dropwise. After stirring the reaction mixture for 2 h at room temperature, the water component was removed on a rotary evaporator. The residue was placed in a vacuum oven at 250 Torr and 50 °C for 48 h.
In some reactions, the ‘wet’ (undried) catalysts were employed as well (see below).

Yield 0.79 g (95%) of a yellowish liquid; $^1$H NMR (CDCl$_3$): 3.56 (t, 2H, -CH$_2$-N=); 3.50 (s, 3H, -N-(CH$_3$)$_2$); 3.30 (s, 3H, -N-(CH$_3$)$_2$); 2.15 (s, 3H, -N=C(CH$_3$)-N); 1.43 (m, 2H, -CH$_2$-CH$_2$-N=); 1.15-1.2 (m, 6H, CH$_3$-(CH$_2$)$_3$-); 0.72 (t, 3H, CH$_3$). $^{13}$C NMR (D$_2$O): 164.56; 44.31; 40.57; 37.95; 30.57; 29.09; 25.26; 21.78; 13.92 ppm; MS(m/z 172 M–Cl$^+$); IR: 1646 cm$^{-1}$ (C=N$^+$).

C$_6$-HCl: Yield: 88% of a yellowish liquid; $^1$H NMR (CDCl$_3$): 3.52 (t, 2H, -CH$_2$-N=); 3.50 (s, 3H, -N-(CH$_3$)$_2$); 3.22 (s, 3H, -N-(CH$_3$)$_2$); 2.16(s, 3H, -N=C(CH$_3$)-N); 1.45 (m, 2H, -CH$_2$-CH$_2$-N=); 1.15-1.23 (m, 6H, CH$_3$-(CH$_2$)$_3$-); 0.73 (t, 3H, CH$_3$). $^{13}$C NMR (CDCl$_3$): 164.73; 44.48; 40.67; 37.88; 30.68; 29.21; 25.32; 21.86; 13.99 ppm; MS(m/z 172 M–Br$^+$); IR: 1646 cm$^{-1}$ (C=N$^+$).

C$_6$-HI: Yield: 85% of a dark orange color solid, mp 33.5-34.8 ºC; $^1$H NMR (CDCl$_3$): 3.54 (t, 2H, -CH$_2$-N=); 3.52 (s, 3H, -N-(CH$_3$)$_2$); 3.30 (s, 3H, -N-(CH$_3$)$_2$); 2.17 (s, 3H, -N=C(CH$_3$)-N); 1.46 (m, 2H, -CH$_2$-CH$_2$-N=); 1.18-1.23 (m, 6H, CH$_3$-(CH$_2$)$_3$-); 0.74 (t, 3H, CH$_3$). $^{13}$C NMR (CDCl$_3$): 164.66; 44.49; 40.63; 37.82; 30.78; 29.28; 25.38; 21.88; 14.05 ppm; MS(m/z 172 M–I$^+$); IR: 1646 cm$^{-1}$ (C=N$^+$).

**Procedure for recycling test**

The recycling procedure is illustrated in Scheme 4-3. LiBr 1.2 mg (1.4×10$^{-2}$ mmol) was added to a solution of 1,2-epoxy-3-phenoxypropane (2a) 0.10g (0.70 mmol) in 0.50 mL of **C$_6$-hexylamine-CO$_2$** ionic liquid in a glass vial,. The glass vial was placed into the stainless steel high pressure cell. Then CO$_2$ (25 atm) was introduced to a suitable pressure and temperature was maintained at room temperature or 50 ºC. After 8 h, diethyl ether (3.0 mL×3) was used to extract products from the reaction mixture. CO$_2$ at 1 atm was bubbled into the solvent for 10 min to regenerate the RTIL and to remove any residual ether; according to $^1$H NMR spectra, no ether
remained after this procedure. Then, same amount of 1,2-epoxy-3-phenoxypropane (2a) was added to the reaction mixture again to start the next cycle.

**Procedures for attempted polymerization of cyclohexene oxide**

*Attempted polymerization in CH$_3$CN:* In an open glass vial with a 1 cm teflon stir bar, C$_6$-HBr (10 mg, 4.0×10$^{-5}$ mol) was added to a solution of cyclohexene oxide (3a) (0.20 g, 2.0×10$^{-3}$ mol) in 0.25 mL of CH$_3$CN. The glass vial was placed into the stainless steel high pressure cell under 25 atm CO$_2$ gas and the temperature was increased to 50 °C. After stirring the reaction mixture for 24 h, and returning the vessel to room temperature, the pressure was brought slowly back to one atmosphere. The reaction mixture was added to 5.0 mL of water and the aqueous phase was extracted with diethyl ether (5.0 mL × 3). The organic phases were combined, and dried with anhydrous sodium sulfate. The volatile materials were removed on a rotary evaporator and the residue was placed under a house vacuum (250 Torr) at 50 °C for 24 h to remove any remaining solvent before characterization by FTIR and NMR (see below).

*Attempted polymerization in solvent-free conditions.* In an open glass vial with a 1 cm teflon stir bar, C$_6$-HBr (10 mg, 4.0×10$^{-5}$ mol) as a solute, was added to a solution of cyclohexene oxide (3a) (0.20 g, 2.0×10$^{-3}$ mol). The glass vial was placed into the stainless steel high pressure cell under 25 atm CO$_2$ gas and the temperature was increased to 50 °C. After stirring the reaction mixture for 24 h and returning the vessel to room temperature, the pressure was brought slowly back to one atmosphere. The reaction mixture was added to 5.0 mL of water and the aqueous phase was extracted with diethyl ether (5.0 mL × 3). The organic phases were combined, and dried with anhydrous sodium sulfate. The volatile materials were removed on a rotary evaporator and the residue was placed under a house vacuum (250 Torr) at 50 °C for 24 h to
remove any remaining solvent before characterization by NMR and FTIR (see below).

**GC response factor calculations**

\[
F_i(R\text{-molar}) = \frac{(\text{area}_{\text{refer}}/\text{mol}_{\text{refer}})}{(\text{area}_{\text{comp}}/\text{mol}_{\text{comp}})} \quad (4-2)
\]

The response factor was calculated according to eq 4-2. Here, \(\text{area}_{\text{refer}}\) and \(\text{area}_{\text{comp}}\) are the areas of the peaks of a reference compound (biphenyl) and 2a or 2b, respectively. \(\text{mol}_{\text{refer}}\) and \(\text{mol}_{\text{comp}}\) represent the known (by preparation) concentrations of the biphenyl and 2a or 2b, respectively. From a plot of area ratios versus composition ratios in samples with known amounts of each (Figure 4-2), \(F_i\) (biphenyl/2b) = 1.18 \((R^2 = 0.998)\) and \(F_i\) (biphenyl/2a) = 1.20 \((R^2 = 0.999)\) were calculated.
Figure 4-2. Linear fit of weight and GC peak ratios for biphenyl/2b (a) and biphenyl/2a (b). The respective formulas are: \( Y = -0.02 + 1.18X \) for (2a) and \( Y = 0.01 + 1.20X \) for (2b).

4.5 Results and discussion

In this study, three mono-substituted epoxides—epichlorohydrin (1a), 1,2-epoxy-3-phenoxypropane (2a), styrene oxide (3a)—and one sterically hindered disubstituted epoxide, cyclohexene oxide (4a), have been used as substrates, and the reactions are shown in Scheme 4-3. The miscibility tests described in section 2.3 show that both hexane and diethyl ether are almost completely immiscible with our RTILs. Therefore, these two solvents were selected to extract products from the RTILs in our experiments. These reactions were carried out from room temperature to 50 °C, which are much lower than the temperatures reported for the syntheses of cyclic carbonates from epoxides and CO\(_2\) in almost all literature examples.\(^{197}\) However, very recently, Endo and coworkers reported that an amidine-mediated system, MTHP-CO\(_2\) is capable of catalyzing cyclic carbonate syntheses.\(^{210}\) In their case, the amidine was a
successful CO₂ delivery agent. Under a high concentration of LiBr catalyst (25 mol%), high yields (100% in some cases) were obtained at room temperature and 1 atm of CO₂ pressure.

\[
\text{MTHP-CO}_2
\]

Scheme 4-3. Syntheses of various cyclic carbonates from cycloaddition of CO₂ to epoxides.

Table 4-1. Syntheses of cyclic carbonate (2b) from CO₂ and 1.40 mol/L 1, 2-epoxy-3-phenoxypropane (2a) in C₆-hexylamine-CO₂ with various 2 mol% of metal halide catalysts.

<table>
<thead>
<tr>
<th>Catalyst (mol%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr</td>
<td>70 (65)</td>
</tr>
</tbody>
</table>
Table 4-1. Substrate (1.40 mol/L) reactivity under the same reaction conditions in C6-hexylamine-CO2 as solvent in cycloaddition reaction

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Epoxides</th>
<th>Products</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr (2 %)</td>
<td>1a</td>
<td>1b</td>
<td>75</td>
</tr>
</tbody>
</table>

* Time = 12 h; \( T = 50 \, ^\circ C; \) \( P_{CO_2} = 40 \, \text{atm}. \) Yields by \(^1\text{H} \) NMR spectroscopy or isolated by column chromatography (in parentheses).

The catalytic activities of various salt catalysts in our RTILs were evaluated and results are listed in Table 4-1. When the anion is the same (Br\(^-\)), Li\(^+\) is the most efficient of the cations examined. Although Zn\(^{2+}\) is a stronger Lewis acid than Li\(^+\), its catalytic activity is lower here. The type of anion is important to the yield as well. Of the catalysts with Zn\(^{2+}\) as the cation, the one with Br\(^-\) shows the highest catalytic activity. Polarity of the salts and their solubility in RTILs may also affect the reaction yields. These results are consistent with literature results that indicate the lithium salt has higher catalytic activity under these conditions. Note that no reaction occurs in the absence of a catalyst. Also, no byproducts, such as polycarbonates or polyesters, were detected by GC-MS in the isolated products by column chromatography. The limit of detectability of the GC-MS is \( \leq 0.1\% \).
LiBr (2 %)  2a  2b  85 (84)
LiBr (2 %)  3a  3b  82 (79)
LiBr (2 %)  4a  4b  80

\(^a\) Time = 8 h; \(T = 50 \, ^\circ C; \) \(P_{\text{CO}_2} = 25 \, \text{atm.}\) Yields by \(^1\text{H}\) NMR. Isolated (by column) yields are shown in parentheses.

The cycloaddition yields using LiBr as a catalyst are shown in Table 4-2. The relatively lower yields of the products, as compared with the conversions reported using other reaction conditions\(^{214}\) can be attributed to the slower diffusion of the important bromide anion in the RTILs, and poor ion separation in the system, due to the relatively high local viscosity of RTILs, especially at room temperature. Ammonium salts, including tetramethyl, tetraethyl and tetrapropyl ammonium bromides, have also been investigated.\(^{215}\) Supported on silica, all three of the salts gave yields \(\geq 96\%\) of cyclic carbonate. In our previous work,\(^3a\) we also demonstrated that amidine can capture CO\(_2\) molecules, forming amidinium carbamate salts after reacting with a second component containing an amino group. To extend further the versatility of this reaction, we explored the use of \textit{in situ} prepared organic salts, amidinium halides (C\textsubscript{n}-HX) to catalyze the reaction. This preparation is convenient for conducting the reactions and results in much higher yields (by \(~15\%) of the products from 1a-4a than when metal halides are employed as the catalysts (Table 4-3). The enhancement of catalyst performance is attributed to the ability of amidine to capture CO\(_2\) molecules from the gas phase and deliver them to the reactive site in a catalytic cycle (Scheme 4-1). The pKa of protonated DBU is ca. 12,\(^{216}\) and the proton on the amidinium part of the C\textsubscript{6}-HX, assuming a similar pKa, may form a hydrogen bond with the oxygen atom of an epoxide thereby activating it for nucleophilic attack.
during the reaction. Note also that commercially available amidines, such as DBU, can be used as amidinium catalysts. As shown in Table 4-4, C6-HBr and C6-HI are better catalysts than C6-HCl in this system, indicating the substitution in the amidinium salt of a Cl ion by a more nucleophilic Br or I ion would yield better results such as an increase of reaction rate.\textsuperscript{217} Given the experimental error of the operation, it is difficult to compare the catalytic activity of C6-HBr and C6-HI.

**Table 4-3.** Syntheses of cyclic carbonates with C6-HBr (2 mol\%) as catalyst in RTILs\textsuperscript{a} and CH\textsubscript{3}CN.\textsuperscript{b}

<table>
<thead>
<tr>
<th>Epoxide</th>
<th>Product</th>
<th>Yield (%) in RTIL\textsuperscript{c}</th>
<th>Yield (%) in CH\textsubscript{3}CN\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>1b</td>
<td>94</td>
<td>91</td>
</tr>
<tr>
<td>2a</td>
<td>2b</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td>3a</td>
<td>3b</td>
<td>99</td>
<td>96</td>
</tr>
<tr>
<td>4a</td>
<td>4b</td>
<td>91</td>
<td>90</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Time = 8 h; $T = 50 ^\circ \text{C}$; $P_{\text{CO}_2} = 25$ atm; C6-hexylamine-CO\textsubscript{2}: 0.5 mL; concentration of 1a-4a: 1.40 mol/L.

\textsuperscript{b} Time = 8 h; $T = 50 ^\circ \text{C}$; $P_{\text{CO}_2} = 25$ atm; CH\textsubscript{3}CN: 0.5 mL; concentration of 1a-4a: 1.40 mol/L.

\textsuperscript{c} Yields determined by GC-MS a using biphenyl as an internal standard.

**Table 4-4.** Syntheses of cyclic carbonate 2b from 1.40 mol/L 2a with 2 mol\% dry and ‘wet’ amidinium halide (C6-HX) catalysts.\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
</table>

144
<table>
<thead>
<tr>
<th></th>
<th>from dry catalyst</th>
<th>from wet catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6-HCl</td>
<td>90</td>
<td>82</td>
</tr>
<tr>
<td>C6-HBr</td>
<td>98</td>
<td>87</td>
</tr>
<tr>
<td>C6-HI</td>
<td>99</td>
<td>90</td>
</tr>
</tbody>
</table>

\(^a\) Time = 8 h; \(T = 50 ^\circ C\); \(P_{\text{CO}_2} = 25\) atm; 0.5 mL \textbf{C6-hexylamine-CO}_2. Yields determined by GC-MS using biphenyl as an internal standard.

\(^b\) See Experimental section 4.4 on page 135 for a description of the dry and wet catalysts.

In addition, the amidinium halide, prepared by the addition of C6 to an equimolar amount of an HX (X = Cl, Br, and I) as a concentrated aqueous solution, was used as the catalyst for the conversion of 2a to 2b. Other procedures were the same as those described on page 134. As shown in Table 4-4, the yields of 2b with ‘wet’ C6-HX were ca. 8-11 % lower than when 2 mol% of dry C6-HX were employed. Specifically, the yield difference under dry and ‘wet’ C6-HCl conditions is ca. 8% while the differences under C6-HBr and C6-HI are 11% and 9%, respectively. Because the experimental error of the yields in these experiments was ± 3%, water has about the same impact on the catalytic activities of each of the C6-HX and does not affect significantly the yield of cyclo adduct. Also, the trend of the ‘wet’ Cn-HX catalytic activities are the same as those of the dry catalysts: in both sets, C6-HI or C6-HBr is a better catalyst than C6-HCl. These results demonstrate that the \textbf{L-amine-C} medium remains effective even in the presence of water. As mentioned on page 21, the presence of 3 wt% H\textsubscript{2}O in a \textbf{C6/LeuC}_1 mixture did not impede formation of the \textbf{L-N-C} upon exposure to CO\textsubscript{2}. It is known from reaction between wet DBU and CO\textsubscript{2} that
[DBUH]$^+$HCO$_3^-$ (shown below) is formed. Analogous reactions, resulting in amidinium bicarbonate salts from a Cn amidine and water, must occur and bicarbonate rather than CO$_2$ may be involved in the formation of the cyclic carbonates; it has been reported that 0.3 equivalents of water promoted the syntheses of cyclic carbonates from CO$_2$ and epoxides. As shown in ref , a water molecule and the anion of a Lewis base (PPh$_3$BuI) can play a synergistic role in opening an epoxy ring and in stabilizing the carbonate intermediates. Thus, a 95% yield of the cyclic carbonate from reaction of styrene oxide under 20 atm of CO$_2$ at 125 °C for 1 h in the presence of water and only 25% in its absence.

The influence of CO$_2$ pressure on reaction yields were compared using LiBr and C$_6$-HBr as the catalyst. As shown in Table 4-5, the carbonate yield increased with increasing pressure from 0 atm to 20 atm CO$_2$. However, the yields decreased as pressure was increased further to 60 atm. Similar trends have been reported and explained in other media used to effect CO$_2$ cycloadditions. The initial increase of yield as pressure is increased between 0 and 20 atm can be attributed to the increase in CO$_2$ concentration within the RTIL; the decreases in yield experienced at yet higher pressures is presumably a consequence of dilution of the substrate and catalyst as they are partitioned between the RTIL and a pre-supercritical phase of CO$_2$ that dissolves some of the reactant throughout the total volume of the stainless steel cell.
In other words, excessive CO₂ pressure causes a low concentration of epoxide in the vicinity of the catalyst and hinders their interaction, resulting in a lower yield. In the experiments conducted here, a small amount of liquid was observed outside the glass vial after the reactions, especially in the cases with higher pressures of CO₂; CO₂ can extract reaction liquids out of the vial under high pressures. Although the reproducibility of the yields in these experiments was ± 3%, the trend of the yields changed at different CO₂ pressures (Table 4-5) is still obvious: the highest yields were obtained at 25 atm of CO₂.

Table 4-5. Influence of CO₂ pressure on the yields of cyclic carbonate 2b in C₆-hexylamine-CO₂.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pressure (atm)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>78</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>80</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>85</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>80</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>76</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>69</td>
<td>86</td>
</tr>
</tbody>
</table>

<sup>a</sup> Time = 8 h; T = 50 °C; LiBr (2 mol%), 2a (1.40 mol/L), and yields were determined by <sup>1</sup>H NMR.

<sup>b</sup> Time = 8 h; T = 50 °C; C₆-HBr (2 mol%), 2a (1.40 mol/L), and yields were determined by <sup>1</sup>H NMR.
The yield of carbonate product 3b in the cycloaddition reaction was investigated as a function of reaction time. As expected, longer reaction times resulted in increased yields of cyclic carbonate. For example, the yield reached 92 % when the reaction time was extended to 10 h. Particularly, during the first 5 h, the yield increased rapidly and gradually reached a plateau value after 12 h (Figure 4-3).

![Graph showing the influence of reaction time on yield of cyclic carbonate 3b.](image)

**Figure 4-3.** Influence of time on the yield of cyclic carbonate 3b from 1.40 mol/L 3a in C6-hexylamine-CO₂ at 50 °C, 25 atm of CO₂ using 2mol% of LiBr (○) or C6-HBr (●) as catalyst. Yields were calculated by ¹H NMR.
Figure 4-4. Influence of temperature on the yield of cyclic carbonate $3b$ from 1.40 mol/L $3a$ after 8 h, 25 atm of CO$_2$ in C$_6$-hexylamine-CO$_2$ using 2 mol% of LiBr (○) or C$_6$-HBr (●) as catalyst. Yields were calculated by $^1$H NMR.

In order to investigate the influence of temperature on product yields, the relatively low yield reaction $4a$-$4b$ was selected. Even at room temperature, decent yields of $4b$ were obtained (Figure 4-4). The increased yields of cyclic carbonate at higher temperatures is attributed to the lower viscosity of the RTILs, and, subsequently, higher rates of diffusion of cations and ions which allow more efficient capture of CO$_2$ by the critical intermediate (A) shown in Scheme 4-1 before it loses the nucleophile (X group) and reverts to epoxide.

**Table 4-6.** Comparison of carbamate and dithiocarbamates RTILs on the yield of cyclic carbonate catalyzed by C$_6$-HBr (2 mol%).
<table>
<thead>
<tr>
<th>Epoxide</th>
<th>Product</th>
<th>Yield (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(carbamate) (^a)</td>
<td>(dithiocarbamate) (^b)</td>
</tr>
<tr>
<td>1a</td>
<td>1b</td>
<td>95</td>
<td>75</td>
</tr>
<tr>
<td>2a</td>
<td>2b</td>
<td>97</td>
<td>82</td>
</tr>
<tr>
<td>3a</td>
<td>3b</td>
<td>97</td>
<td>77</td>
</tr>
<tr>
<td>4a</td>
<td>4b</td>
<td>93</td>
<td>72</td>
</tr>
</tbody>
</table>

\(^a\) Time = 8 h; \(T = 50^\circ\text{C}; \ P_{\text{CO}_2} = 25\ \text{atm}; \) RTIL (a) C\(_6\)-hexylamine-\text{CO}_2; 1\text{a}-4\text{a} (1.40 mol/L), and yields were determined by \(^1\text{H} \text{NMR.}\)

\(^b\) Time = 8 h; \(T = 50^\circ\text{C}; \ P_{\text{CO}_2} = 25\ \text{atm}; \) RTIL (b) C\(_6\)-hexylamine-\text{CS}_2; 1\text{a}-4\text{a} (1.40 mol/L), and yields were determined by \(^1\text{H} \text{NMR.}\)

According to our previous studies\(^{208}\), RTILs prepared by adding \text{CS}_2 (L-amine-S) to amidine/amine mixtures usually have higher viscosities and better thermal stabilities than their \text{CO}_2 analogues (L-amine-C). However, as a result of their lower viscosities, the amidinium carbamate results in higher product yields (Table 4-6). The differences between the polarities of amidinium carbamate and dithiocarbamate RTILs (Table 2-14) are very small, and apparently do not play an important role here.
Scheme 4-4. Diagram of the recycling procedure employed in reuse of RTIL/catalyst mixtures in the syntheses of cyclic carbonates from CO$_2$ and an epoxide.

As mentioned above, the reversibility of these ionic liquids is a significant benefit for the easy separation of components of reactions in which the products are soluble in low-polarity media and their formation depends on contact with a catalyst soluble only in high-polarity media. Thus, the recyclability of the RTIL/catalytic system using the procedures outlined in Scheme 4-4 was explored. The results in Table 4-7 show that the efficiency of the system decreased slightly upon reuse, but still remained effective after 3 runs. In that regard, the product extraction was performed at room temperature under 1 atm pressure of air, in which RTILs are relatively unstable according to the TGA studies reported in section 2.2. Because lithium salts have a high affinity for carbonates, the gradual decrease of LiBr catalyst during product
separation by repeated extracting with diethyl ether may be responsible for the
decrease of the reaction efficiency upon recycling the ionic liquid. Jessop and
coworkers\textsuperscript{45} reported a switchable ionic liquid that could be used and reused as a
reaction and separation medium for the copolymerization of cyclohexene oxide (2a)
and CO\textsubscript{2}, but that the yield of polycarbonate was reduced by ca. 20\% during the
second run and the polydispersity increased from 1.06 to 1.10. Our attempts to
copolymerize 2a and CO\textsubscript{2} using C\textsubscript{6}-HBr as a catalyst (Eq. 4-7) in acetonitrile and
solvent-free condition were unsuccessful. Analysis of the reaction mixture revealed
2b (55 \% yield in acetonitrile and 42 \% yield under neat conditions) as the only
product formed. The FT-IR and \textsuperscript{1}H NMR spectra showed no peaks attributable to a
polycarbonate.\textsuperscript{204a} Therefore, different conditions will have to be explored in the
future to effect polymerizations of this type using our catalysts.

\begin{equation}
\begin{array}{c}
\text{O} \\
\text{C}_6-\text{HBr}
\end{array}
\begin{array}{c}
\text{CO}_2 \\
50 \, ^\circ\text{C}, 24 \, \text{h}
\end{array}
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{n}
\end{array}
\end{equation}

(4-7)

Despite the unsuccessful co-polymerizations, it is interesting and synthetically
useful that a good yield of 2b was obtained under the solvent-free conditions; the C\textsubscript{n}-
HX catalyzes the cycloaddition reaction even in neat epoxide to the exclusion of side
reactions! Also, increasing the reaction time or temperature should increase the
reaction yield even further. In this case, the epoxide, as well as the resulting cyclic
carbonate, act as the solvent.\textsuperscript{26}

Previously, a Zeolite-based organic--inorganic hybrid catalyst has been reported to
give 86-100 \% yields of cyclic carbonate for the same reaction under ‘mild’
conditions—6.8 atm of CO\textsubscript{2} and 120 \, ^\circ\text{C} for 8 h without organic solvents.\textsuperscript{225} Also,
bis(triphenylphosphine)immmium (PPN) salts, [PPN]\textsuperscript{+}Cl\textsuperscript{–}, and PPN-manganese
carbonylates, $[\text{PPN}^+]\text{[Mn(CO)₄L]}^-\ (L = \text{CO, PPh}_3)$, were found to be good catalysts for cyclic carbonate syntheses under solvent-free conditions. The reactions had no polycarbonate contamination when conducted under 5 atm of CO₂ and at 100 °C. The relatively low solubility of CO₂ in conventional solvents is a primary reason to search for alternatives to the reaction between CO₂ and epoxides. Supercritical CO₂ has also been found to be an effective solvent, although very high pressures are necessary. For example, in the presence of a Re(CO)₅Br catalyst, the reaction of epoxides with supercritical CO₂ without an organic solvent at 110 °C has afforded good yields. Thus, our catalyst appears to be competitive with all of the others reported to date for the cycloadditions, and it is superior to most in terms of cost and required temperature.

Table 4-7. Recycling tests using C₆-hexylamine-CO₂ and 2 mol% of LiBr or C₆-HBr as catalyst to convert 2a and CO₂ to 2b.\(^a\)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Yield (%) with LiBr as catalyst</th>
<th>Yield (%) with C₆-HBr as catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>85</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>82</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>78</td>
<td>94</td>
</tr>
</tbody>
</table>

\(^a\) Time = 8 h; \(T = 50^\circ\text{C}; \ P_{\text{CO}_2} = 25\ \text{atm}; \ 2\text{a} (1.40 \text{mol/L}).\) Yields were determined \(^1\text{H}\) NMR.

Also, it is necessary to consider the mechanism of the cyclic addition reaction in our RTIL and amidinium halide system (Scheme 4-1). A plausible mechanism involves the ring opening of the epoxide by means of a nucleophilic attack to the less
hindered carbon atom by the bromide ion, which leads to an oxy anion intermediate. Then, CO₂ reacts with the oxy anion and subsequently forms the carbonate products upon ring closure. An experiment, in which the product (2b) was placed into C₆-hexylamine-CO₂ at 1 atm CO₂ pressure and room temperature for 24 h, and showed no epoxide (2a) was obtained due to the loss of CO₂ from 2b, based on the GC result. This experiment demonstrates the conversion from epoxide to cyclic carbonates is kinetically favorable in RTIL system.

4.6 Conclusions

In summary, an approach has been reported for utilizing reversible room-temperature ionic liquids (RTILs) to synthesize five-membered cyclic carbonates by the addition of CO₂ to epoxides. Four epoxide substrates were used, and the product mixtures indicate that the reactions proceed under the experimental conditions employed to give only the desired cyclic carbonates. Also, the effects of RTIL compositions, CO₂ pressure, reaction time, and temperature on the reaction yields were investigated and compared in a systematical manner. High yields (> 90%) were achieved in most cases. Notably, no metal catalyst is required in our RTIL systems to effect reaction.

Amidinium halide salts have been found to be efficient catalysts for preparing cyclic carbonates in our RTILs. This system broadens the scope of such reactions by providing an interesting approach to overcome the high activation barrier. More significantly, the ionic liquid/catalyst systems can be reused several times without significant decrease in product yields. Because the RTILs and catalysts can be reused and the temperatures needed are much lower than in most other solvent/catalyst systems reported in the literature, this approach is an effective method for preparing cyclic carbonates.
There are several other reactions in which these RTILs may be advantageous to effect additions of CO$_2$, such as synthesis of oxazolidinones from aziridines and CO$_2$,\textsuperscript{232} and the preparation of polycarbonates from epoxide and CO$_2$.\textsuperscript{204} Lewis base ionic liquids have been developed as recyclable and efficient catalysts for selective syntheses of oxazolidinones from aziridines and CO$_2$ without utilization of any organic solvent or additive.\textsuperscript{233} Others of our group will explore some of these reactions in the future.

5. SUMMARY AND CONCLUSIONS

Methodologies to convert reversibly a variety of non-ionic molecules and polymers with amino groups into gels, room-temperature ionic liquids, and rubbery polymers have been reported. Throughout this thesis, classic, simple chemistry, involving triatomic molecules as chemical reagents, has been used to convert simple molecules into complex materials. In our approaches, CO$_2$ and CS$_2$ are stoichiometric reagents that stimulate specific conversions and assemblies of otherwise disorganized aggregates or solutions of molecules; the increased value by adding CO$_2$ (or CS$_2$) to simple molecules is potentially enormous. For example, two classes of ‘green’ solvents, chiral, reversible room-temperature ionic liquids (RTILs), have been made by simple addition of CO$_2$ or CS$_2$ to mixtures of two non-ionic molecules, an aliphatic amidine and an amino acid ester or an amino alcohol. The resulting chemical transformation leads to ion pairs, amidinium carbamates or amidinium dithiocarbamates. The reactions with CO$_2$ can be reversed at will by heating or passing N$_2$ through the amidinium carbamates.

This strategy has also allowed us to make reversibly crosslinked polysiloxanes with amino functional groups. Crosslinking occurs when the amino groups on different polymer chains react with one molecule of CO$_2$ or CS$_2$. The changes to the
bulk properties of the polysiloxanes by these simple reactions are enormous. The flowing polymers become rubbery, adhere strongly to many surfaces, and can be swelled to several times their original volumes by a variety of organic liquids.

In addition, the non-ionic/ionic reversibility, chirality, broad temperature ranges over which they are stable, tolerance to water, and ease of preparation should make several of these materials very useful for applications as ‘green’ solvents, adhesives, and (as has been demonstrated with similar materials), cleaning agents for works of art.234 These systems may be useful as sensors and switches as well.235 The low cost and easy access of the constituent, non-ionic molecules and polymers and the abundance of CO\textsubscript{2} add to the attractive features of these systems. There are many opportunities for discovering additional methods to ‘fix’ CO\textsubscript{2} and other triatomic molecules and to use them to create other sophisticated materials. Here, \textit{in situ}-prepared, reversible, RTILs have been used as media for the syntheses of cyclic carbonates by addition of CO\textsubscript{2} to epoxides.

Overall, the simple chemistry of these reactions offers an effective approach to construct a diverse range of materials. The basic chemical theory behind these reactions and applications has been summarized, so that the link between the basic chemistry and the materials obtained should stimulate others to envision new strategies. Most neutral triatomic molecules are considered environmentally harmful. Because their transformation into new materials under very mild reaction conditions has been demonstrated, and there are numerous combinations of cations and anions that yield RTILs, this flexibility can be used to tune chemical and physical properties for RTILs. We consider this chemistry a scientific example of the adage, “changing a pig’s ear into a silk purse”.236
AUTOBIOGRAPHY

Tao Yu was born in 1981 in Hangzhou, Zhejiang Province, China. He received a B.S. degree in Chemistry from Fudan University (Shanghai, China) in 2004. Then, he joined Professor Wei Huang’s group for graduate study, at the Institute of Advanced Materials, Fudan University. He began his Ph.D. studies with Professor Richard G. Weiss at Georgetown University (Washington, DC) in the summer of 2006. His research interests include the syntheses and properties of reversible room-temperature ionic liquids and functional polymers. His Ph.D. degree is being awarded in Organic Chemistry under the mentorship of Prof. Richard G. Weiss in 2011.
REFERENCE


(21) (a) Rogers, R. D.; Seddon, K. R., Eds. Ionic Liquids: Industrial Applications to Green


(46) Unfortunately, the uptake of CO₂ in DBU/alcohol systems is not quantitative at one atmosphere of pressure, at least in toluene solutions.


(58) The slope difference between C8/IleC1 and C8/ProC1 samples is dependent on the surface area of the liquid samples (which depends, in part, on stirring speed of the sample and size of the vessel). In fact, C8/IleC1 showed more rapid CO₂ uptake, but the same %CO₂ plateau when a smaller vessel was applied.


(60) The wavenumber assignment of the protonated amidine was confirmed by the IR spectrum of a 1/1 C8/trifluoroacetic acid mixture which showed a C=N stretch at 1648 cm⁻¹. IR spectra of protonated amidines have been reported: Corset, C.; Froment, F. J. Phys. Chem. 1990, 94, 6908–163


(71) Previously, we have found that 1:1 amidine:alkylamine and 1:1 amidine:amino acid esters take up more than one equivalent of CO₂, as well. Both of those amines lack a hydroxyl group.
(capable for forming a carbonate upon reaction with a second molecule of CO$_2$). Also, simple electrostatic arguments disfavor the production of proximal carbamate and carbonate groups on one amino alcohol. If the ionic state is a mixture of two different compounds, the second (an amidinium carbonate) must be a very small amount with respect to the first (an amidinium carbamate).


(81) It should be recognized, however, that the heterogeneous nature of ILs makes determinations of their polarity by solvatochromic probes less reliable than in ‘normal’ liquids. Jin, H.; Baker, G. A.; Arzhantsev, S.; Dong, J.; Maroncelli, M. J. Phys. Chem. B 2007, 111, 7291-7302.


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(102) As shown in Figure 2-20, three protons from C$_6$H$_{13}$NH$_3$ of ammonium the dithiocarbamate at 7.9 ppm, proved (by adding a drop of D$_2$O to an ammonium dithiocarbamate sample in chloroform-$d$), disappear after adding amidine and CS$_2$, and peaks corresponding to protons on protonated amidinium moiety appear.


(104) To simplify our study, tC4 (which lacks a methyl group at the amidine carbon) and t–butylamine were selected as substrates. These molecules simplify the spectral identification of
the thermolysis products. As indicated by the proposed mechanism in Scheme 2-4, these substrates should react like the others in Scheme 2-3.


(109) The concentrations are expressed in mol % in order to normalize the concentrations of ionic liquids and amidine/amine.


(116) Some of the viscosity tests were repeated twice, and the differences of the absolute value are ca. 5%.


(119) \( \Delta H_{f0} \) (gas) = \( \Delta H_{f0} \) (liquid) + \( \Delta v_{ap} H_{f0} \) (tb) = 89.0 + 26.7 = 115.7 kJ·mol\(^{-1}\). Ref 30, pp 5–20 and 6–117.


(143) Lobo, H.; Bonilla, J. V. Handbook of Plastics Analysis; Routledge: USA 2003


(157) Hong, G.; Zhou, M.; Zhang, R. X.; Hou, S. M.; Choi, W. M.; Woo, Y. S.; Choi, J. Y.; Liu,
We envision that these polysiloxanes can be employed as reversible, temperature–dependent adhesives. Specifically, substrates strongly adhere at room temperature to the polysiloxanes exposed to CO$_2$, and their adhesive strength can be tuned by changing the temperature.


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