Design, Synthesis, and Evaluation of New Ionic Liquid-based Solvents, Polymers, and Composites for Enhanced Membranebased CO₂/Light Gas Separations

by

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B.S., Oregon State University, 2006

A dissertation submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment Of the requirement for the degree of Doctor of Philosophy Department of Chemical and Biological Engineering 2011 This thesis for the degree of Doctor of Philosophy entitled:

Design, Synthesis, and Evaluation of New Ionic Liquid-based Solvents, Polymers, and

Composites for Enhanced Membrane-based CO₂/Light Gas Separations

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The final copy of this thesis has been examined by the signatories, and we Find that both the content and the form meet acceptable presentation standards Of scholarly work in the above mentioned discipline.

ABSTRACT

Carlisle, Trevor Kenneth (Ph.D., Chemical and Biological Engineering)

Design, synthesis, and evaluation of new ionic liquid-based solvents, polymers, and composites for enhanced membrane-based CO₂/light gas separations

Thesis directed by Professors Douglas L. Gin and Richard D. Noble

Supported ionic liquid membranes (SILMs) possess very attractive CO₂ permeabilities and CO₂/light gas permeability selectivities. However, the liquid RTIL in SILMs is physically displaced at elevated trans-membrane pressures (e.g., > 1 atm). The RTIL component can, however, be "stabilized" by forming a solid, polymerized RTIL (poly(RTIL)) membrane. To compensate for a reduction in CO₂ permeability, "free" liquid RTIL can be incorporated into the poly(RTIL) to form a composite poly(RTIL)-RTIL material. Optimizing the performance of poly(RTIL)-RTIL membranes can be achieved by individually tailoring the liquid (i.e, RTIL) and solid (i.e., poly(RTIL)) components to maximize CO₂ permeability and CO₂/light gas permeability selectivity.

A thermodynamics-based, "rational" design guide for the synthesis of new, highly selective RTIL materials was presented and verified experimentally with CO₂ solubility and CO₂/light gas selectivity measurements. Appending the RTIL imidazolium cation with groups that possess large molar attraction constants (i.e., nitrile or propargyl) was found to increase the RTIL solubility parameter, reduce CO₂ solubility, and increase CO₂/light gas solubility selectivity relative to alkyl-functionalized RTIL analogues.

The synthesis and CO_2 separation characterization of several new RTIL-based polymeric membrane materials were also investigated. It was also found that composite structures formed by blending these polymers with liquid RTILs affords enhanced CO_2 flux and CO_2 light gas

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selectivity. For example, the CO₂ permeability and CO₂/N₂ permeability selectivity of a disiloxane-functionalized poly(RTIL)-RTIL (20 mol% liquid) composite were 190 barrers and 19, respectively. To maximize both CO₂ flux and CO₂/light gas selectivity, new cross-linked poly(RTIL)-RTIL gel membranes were developed, and the CO₂ separation performances of these membranes were studied. This membrane configuration effectively "stabilizes" the liquid RTIL component while maintaining a good degree of membrane mechanical stability. These materials demonstrated excellent CO₂/light gas separation performance. The CO₂ permeability of these membranes were found to range from 130 to 520 barrers with no change in CO₂/N₂ or CO₂/CH₄ selectivity (ca. 34 and 20, respectively). The CO₂/H₂ selectivity improved with RTIL content to a maximum of 12 at 75 wt. % liquid loading. As a new class of RTIL-based membrane materials, these next generation of RTIL-based membranes, cross-linked poly(RTIL)-RTIL gels were found to be very promising and potentially viable candidates for industrial CO₂ membrane separations.

DEDICATION

This work is dedicated to...

My wife and best friend, Amanda... words continue to fail me.

My parents, Richard and Wendy, to whom I owe a debt which can never be paid. All I can say is thank you, I am so lucky.

Ryan, Christie, and Matt, your love and support have kept me going.

And

Nicholas and Natalie.

ACKNOWLEDGEMENTS

Financial support for this dissertation research from the U.S. Army Research Office (Grants AB07CBT010 and HDTRA1-08-1-0028), the National Science Foundation (Grants DMR-0552399 and IIP1047356), and the Advanced Research Projects Agency Energy (Grant DE-AR0000098) is gratefully acknowledged. I also thank the U.S. Dept. of Education for two GAANN Fellowships during the course of this work.

I wish to thank my two thesis advisors, Douglas Gin and Richard Noble, for their dedication, guidance, and generosity throughout my thesis work. I also wish to thank them for the creative freedom they so willingly granted me throughout the course of my dissertation research. They provided me with so many wonderful opportunities, for which I will always be grateful.

I want to thank all of my post-doc and graduate student mentors for their willingness and guidance during my early stages of research. I wish to give special thanks to my grad-student mentor and friend, Jason Bara, who was eager to help me learn and succeed during my first year as a grad student. I also wish to thank my peers from both Doug Gin and Rich Noble's research groups for their support and friendship.

Much of this dissertation work was made possible by the expertise, dedication and valuable help from many of the technical Chemical Engineering staff members. I wish to give special thanks Dragan Mejic, Dana Hauschulz, Maria Toscano-Leary, and Hans Funke. I was fortunate to be able to count on people like them when I could not solve equipment and software problems on my own. It was a pleasure working with these talented people. I also wish to thank the CU NMR facility Director, Richard Shoemaker, for his willingness to help me succeed and for countless number of memorable conversations.

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I gratefully acknowledge two fellow graduate students, Paul Handke and Evan Hatakeyama, whom I became very close friends with over the course of my graduate studies. I wish to give them special thanks for their friendship and support over the years. My experience as a grad student would not have been as fulfilling without the times we had shared together. It is amazing what good beer and good friends can do for the soul. You two are pretty much family to me.

I want to thank my family for their love, support, and confidence during some of the darkest and most challenging times of my graduate experience. I am so lucky to have such a wonderful family that I have always been able to count on. You've always reminded me of what is important and helped me keep my focus. Most importantly, you make me laugh, smile and forget about the details.

Thank you to all of my friends – you get a choice in the matter, I'm lucky to be able to call you a friend. I have to give special thanks to Ben Degraff and Adam Richter – we go back a ways now. You know you are like family to me and I'm not sure what else to say. Even though we've been a few states apart the last five years, some of my best memories of these grad school-years are shared with you guys. You've been there to give me support and some really good times, thanks.

Lastly, I'd like to give an enormous thanks to my wife, Amanda. We shared the grad school experience only as few others dare to do. Under the shared hardships you were somehow there for me when I needed you the most. You are the most loving and selfless person I know. You lifted me up when I was down. You showed me reason when I was unreasonable. You gave me confidence when I had none. You are my best friend. I don't know how people finish grad school without an Amanda.

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Chapter 1

Introduction and Background

1.1. Motivation: CO₂/Light Gas Separations

The separation of carbon dioxide (CO₂) from mixtures of other light gases, such as nitrogen (N₂), methane (CH₄), and hydrogen (H₂), is paramount from both industrial and environmental standpoints. Specifically, the separation of CO₂ from N₂, CO₂ from CH₄, and CO₂ from H₂ are three distinct separation challenges faced by the electrical energy, natural gas, and syngas production sectors, respectively.

By far, one of the most challenging and well-documented CO_2 separation processes is the post-combustion removal of CO_2 from flue gas streams (i.e., the separation of CO_2 from N_2). Globally, coal and natural gas are among the cheapest and most abundant sources of fuel. Unfortunately, the combustion of these fuels for the production of electricity is inextricably linked to the release of large quantities of CO_2 both domestically and in other developed nations [1-3]. Climate- and oceanic-related issues associated with the buildup of anthropogenic CO_2 are anticipated to worsen as the global demand for cheap electricity and world population greatly increases [3]. To abate and, ultimately, eliminate the release of flue gas CO_2 , it will be imperative to develop CO_2/N_2 separation technologies that can effectively remove CO_2 from combustion exhaust in coal- and natural gas-based electrical power plants while minimally impacting the current cost of electricity. The ultimate fate of such large quantities of "captured" CO_2 , however, is certainly still a matter of debate. Current approaches under consideration

include pumping CO_2 into deep underground wells or into displaced or depleted oil wells [1, 4]. A distinct disadvantage of CO_2 as a chemical is that it is not a feedstock for any large commodity or commercial product (yet), due largely in part to its thermodynamic stability [5]. Storage of massive quantities of CO_2 could be avoided if CO_2 had commercial value (e.g., using CO_2 as a feedstock for polymeric building materials). Such enabling technologies may also accelerate the industrial interest and practice of CO_2 post-combustion capture. However, methods to utilize CO_2 in such a manner have proven difficult despite intense research efforts [5-7]. Regardless of the uncertainties associated with downstream processing of CO_2 captured from flue gas, there remains a great need to accelerate CO_2 separation technology to eventually make such "downstream processing" economically and technologically feasible.

A second challenging and highly important CO_2 separation process is the efficient removal of CO_2 from mined natural gas sources (i.e., the separation of CO_2 from CH_4). Natural gas (i.e., CH_4) combustion is certainly cleaner and produces significantly lower amounts of SO_x , NO_x and CO_2 when compared to the combustion of coal [3, 8]. This fuel source also lessens the United States' dependence on foreign energy sources, since almost 90% of all natural gas consumed in 2009 was produced domestically [8]. In that same year, the United States consumed natural gas at an estimated rate of 22.8 trillion cubic feet per year $(tcf/yr)^X$. Current projections estimate that this rate will only increase in the coming years, particularly as shale gas becomes increasingly utilized [8]. The acid gas impurities typically present in natural gas wells (e.g., CO_2 , SO_2 and H_2S) must be brought to minimal levels prior to CH_4 transport and combustion for power generation) [8, 9]. This type of separation or purification process is typically referred to as "natural gas sweetening". Specifically, the level of CO_2 in natural gas pipelines is restricted to less than 1–2 mol % [8, 9]. This is to ensure that the hydrocarbon fuel can ultimately be combusted cleanly and efficiently as well as to limit the amount of equipment corrosion during transport and distribution. Similar to CO_2/N_2 separation, there is a need for CO_2/CH_4 separation technologies that can efficiently remove CO_2 to the required levels while affording little-to-no increase in the cost of piped natural gas and CH_4 -generated electricity. These new CO_2 separation technologies will prove critical as this domestic resource is increasingly utilized in the coming decades.

A third and related industrially important CO_2 separation process is the efficient removal of CO_2 from H_2 in the production of syngas. In addition to its use as a combustible fuel, methane is also an incredibly important feedstock chemical for the production of H_2 (i.e., syngas), which is then used for clean power generation in the form of combustion or H_2 fuel cells. H_2 is also a feedstock chemical for numerous chemical products, most notably NH_3 . The production of H_2 from CH_4 is performed in a two-step reaction process referred to as (1) steam methane reforming and (2) water gas shift (Scheme 1.1).

> Steam methane reforming (1) $CH_4 + H_2O \longrightarrow CO + 3H_2$ Water gas shift (2) $CO + H_2O \longrightarrow CO_2 + H_2$

Scheme 1.1. Production of H_2 from CH_4 via steam methane reforming followed by water gas shift.

The CO₂ produced over the two-step process is an impurity and must be reduced to minimal levels before the H₂ can be used as a fuel or transported for other chemical feedstocks [10, 11]. Technologies that can efficiently separate H₂ from CO₂ to high levels of purity are very desirable

[10, 12]. Ideally, such a technology would selectively remove CO_2 , leaving the purified H_2 at high pressure and ready for transport or combustion without the need for further compression. This type of separation is technically difficult to achieve based on traditional CO_2/H_2 separation processes.

 CO_2 removal technology has advanced greatly over the last 60 years largely due to intense research efforts in the petrochemical, chemical, and academic sectors. Despite these advancements, current industrial CO_2 separation technology is faced with many challenges – most notably the need to keep up with growing separation demands while minimizing operating/capital costs. The current industrial practices for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 separations are similar and take on one of three basic forms: (1) absorption using a liquid solvent, (2) adsorption using a solid media, or (3) cryogenic distillation. In every case, the ultimate separation is driven and achieved by thermodynamic equilibrium and subsequent phase change(s). Each of these CO_2 separation methods possesses inherent drawbacks that limit their wide-spread use and feasibility. Cryogenic distillation, for example, requires incredibly pure feed streams to be viable. More notably, it requires an enormous energy input to carry out the separation at such low temperatures. For the CO_2 separation methods described below (i.e., for flue gas, natural gas and syngas), cryogenic distillation is simply not feasible and is utilized only for very specific applications that will not be discussed here.

Pressure swing adsorption (PSA) for the selective separation of CO₂ is a viable but still developing technology [2, 13]. The basic operating principle involves a high pressure process stream containing product and impurities (e.g., CO₂, SO₂, or H₂S) pass through a column containing a porous, high surface area solid media, such as zeolites or metal-organic-frameworks (MOFs), which selectively adsorb CO₂. Once the adsorption media has been saturated, the

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column pressure is greatly reduced (with the possible addition of elevated temperature), and the CO_2 is liberated from the adsorbed surface sites. This process is capable of removing CO_2 to extremely low levels, but its industrial viability is contingent upon a large quantity of extremely high surface area materials that can be perfectly regenerated over many cycles. Furthermore, the energy requirement due to repeated compression/vacuum cycles of a PSA process will be significant and may lead to high operating costs.

A common practice, particularly for CO_2/CH_4 , is the use of a scrubbing column with an aqueous amine as the solvent to physically absorb and react with CO₂ [11, 14-16]. Amines, typically monoethanolamine (MEA), reversibly react with CO₂ in water to form a carbamate salt. To regenerate the aqueous amine solution and liberate the bound CO₂, the solution must be heated to elevated temperatures and subsequently cooled for further CO2 scrubbing. This process is inherently energy intensive and current estimates suggest that approximately 20% of electricity generated by a coal-based power plant would be required to operate the amine-based CO₂/N₂ flue gas separation [15, 17]. In addition to excessive operating cost, the corrosive nature of aqueous amine solutions requires special equipment and materials of construction, greatly increasing capital costs [18]. The aqueous amine process also suffers from solvent loss and toxicity issues, since the amine is typically a volatile organic compound (VOC) [19]. This fact only serves to compound the issues the process already faces with excessive operating costs. Despite these well-known drawbacks, amine-based CO_2 removal is perhaps one of the most promising separation technologies to be utilized during the interim where newer technologies advance beyond the developmental stage, particularly in the case of CO_2/N_2 separation.

There are two other primary solvent-based absorption processes that have found successful industrial use for CO₂ removal from hydrocarbon and syngas streams. "Rectisol" is a

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process that has been established for quite some time in the petrochemical sector [11]. It uses refrigerated methanol (typically at -40 to -60 °C) as the physical solvent for the removal of acid gasses, such as CO₂ and H₂S [11]. Similar to the Rectisol process, the "Selexol" process has primarily been established for use in IGCC (Integrated Gasification Combined Cycle) power plants for the cleanup of syngas streams [11]. Selexol uses a considerably viscous poly(ethylene glycol) solution (as opposed to methanol) as the physical solvent [11]. This proprietary glycol solution has the specific advantages of chemical inertness and high resistance to degradation. Selexol also avoids the use of a VOC (i.e., MeOH), and the solvent loss issues that are integral to the Rectisol process. In addition to sizable energy requirements associated with solvent regeneration and cooling, both the Rectisol and Selexol processes require large equipment, immense amounts of solvent and considerably sophisticated operation and training.

1.2. Membrane-Based Materials for CO₂/Light Gas Separations

Membrane-based gas separations have the potential to overcome many of the disadvantages associated with traditional CO_2 separation technologies, most notably high operating and capital costs. As mentioned above, traditional separations are equilibrium-based processes that can involve multiple phase changes (i.e., gas to liquid, liquid to solid) and subsequently cause high energy costs. Membranes, on the other hand, achieve gas separation based on relative differences in gas transport, where no phase change occurs. On a basic level, membrane-based separations are significantly simpler than the industrial practices discussed above: two gas streams are physically separated by a selective organic or inorganic film (i.e., a membrane) that allows one gas to transport from one side to the other preferentially over other gases in a mixture. Transmembrane diffusion is driven by the partial pressure (or chemical

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activity) difference of a species between the upstream and downstream sides of the membrane. Selective transport of that species occurs spontaneously from the upstream side of high partial pressure to the downstream side of low partial pressure, where the species concentration is subsequently enriched. Of course in reality, membrane separations are not quite as simple as this idealization, but their "simplicity" is nonetheless a major attraction compared to conventional technologies. Membrane-based processes have the advantages of scalability and small plant footprint in addition to ease of operation. Most notably, the amount of "functional" material (i.e., a membrane material) is infinitesimally smaller compared to the large amount of solvent needed for the traditional separations described above. If the membrane materials are very effective in removing CO₂, then less surface area will be required to perform a separation. In practice then, one could use a very small amount considerably expensive membrane material.

Gas separation membranes can be divided into three general classes of materials: (1) inorganic (e.g., ceramic or zeolite) membranes, (2) polymeric (e.g., carbonaceous organic) membranes, and (3) physical blends of materials from classes 1 and 2 (i.e., "mixed-matrix-membranes"). Regardless of the type of material used, membranes cannot be considered to be competitive with traditional separations if they do not possess both *high flux* CO₂ (i.e., a high rate of gas transport) and CO₂ *high selectivity* (i.e., a high preferential transport of one species over others). Selective gas separation and transport is accomplished by distinctly different mechanisms in each of these three classes. A detailed discussion of the first and third class of membrane materials (mixed-matrix-membranes) is not pertinent to this body of work and will not be discussed here. By far, the majority of industrial, membrane-based processes utilize polymeric materials [20]. However, ceramic and mixed matrix materials are better suited for

unique applications that demand high temperature and robust chemical stability in addition to membrane separation performance [20].

Transport and separation in the second class of materials is typically described by a solution-diffusion mechanism [20-23]. As the name implies, this mechanism has two components: the affinity of a membrane material for a gas (i.e., gas solubility) as well as gas mobility within the membrane matrix (i.e., diffusivity). Both aspects of the solution-diffusion mechanism determine the overall transport properties of a gas. The selectivity of a penetrant species is determined as the relative ratio of transport rates to other species in a mixture. As discussed above, membrane gas transport is a pressure (or concentration) driven process, and for dense polymeric membranes is very well described by Fick's first law [20-23]:

$$J_i = -D_i(c_i)\frac{dc_i}{dx} \qquad (1)$$

In Eq. 1, J_i is the flux of gaseous species *i*, D_i is the diffusion coefficient of species *i*, c_i is the local concentration of *i*, and *x* is the transmembrane length. The gas permeability is the membrane thickness and pressure-drop normalized flux of gas species *i*:

$$P_i = \frac{J_i}{\Delta f_i} l \qquad (2)$$

where, *l* is the membrane thickness and Δf_i is the transmembrane fugacity difference of species *i*. If ideal gas conditions exist, Δf_i can be replaced by Δp_i , where p_i is the partial pressure of species *i*. By substituting Eq. 2 into Eq. 1, the permeability can be expressed as [20-22]:

$$P_i = -D_i(c_i) \frac{dc_i}{dx} \frac{l}{\Delta f_i} \quad (3)$$

Separation and integration of Eq. 3 from limits of x = 0 to x = l and $c_i = 0$ to $c_i = c_l$ (i.e., the case of zero concentration of species *i* at the downstream side of the membrane) result in the general equation form [20-22]:

$$P_i \equiv D_i \times S_i \tag{4}$$

where D_i is the average diffusivity of species *i* (the mobility component) in the membrane and S_i is the average solubility of species *i* (i.e., the thermodynamic, equilibrium component) in the membrane. The units of permeability are typically given in barrer, e.g.,

$$P[=]barrer, 1 \ barrer = 10^{-10} \frac{cm^3(STP) \cdot cm}{cm^2 \cdot s \cdot cm \ Hg}$$

Solution-diffusion transport is simplified and described schematically in Fig. 1.1. As can be seen in Fig. 1.1, it involves a five-step theoretical process consisting of (1) convective diffusion to the membrane surface, (2) adsorption and subsequent absorption (i.e., dissolution) on the upstream side of the membrane, (3) diffusion through the dense membrane, (4) de-solvation and de-adsorption on the downstream side of the membrane, and finally (5) convective diffusion away from the downstream membrane surface.



Figure 1.1. The theoretical steps involved with solution-diffusion transport across dense polymeric membranes. (1) Convective diffusion to upstream membrane surface; (2) Adsorption and dissolution into the membrane; (3) Diffusion of gas through the polymer; (4) De-solvation and de-adsorption; and (5) Convective diffusion away from downstream membrane surface.

As both diffusivity and solubility are properties inherent to the chemistry and morphology of polymeric membrane materials, an important implication can be inferred from Eq. 4: The permeability of a particular species can be improved by enhancement of D_i and/or S_i through tuning of the material properties of the membrane. Membrane permeability, however, is only one of two important factors that define ultimate separation performance. The permeability selectivity or, simply, selectivity is the other critical factor and is defined as:

Permeability Selectivity
$$(\alpha_{i/j}) = \frac{P_i}{P_j} = \frac{D_i}{D_j} \times \frac{S_i}{S_j}$$
 (5)

As shown in Eq. 5, the permeability selectivity of species *i* over species *j* ($a_{i/j}$) is the ratio of permeabilities of the two gases. Using the definition of Eq. 4, the permeability selectivity can also be written as the product of the solubility selectivity (S_i/S_j) and the diffusivity selectivity (D_i/D_j). This, of course, implies that the ultimate selectivity of a membrane is based on how well it discriminates between one gas species over another (solubility selectivity) and how easily it permits one gas to pass through compared to others (diffusivity selectivity).

As mentioned above, membranes must possess both high CO_2 flux and high CO_2 selectivity before they can be considered competitive with traditional CO₂ gas separation methods [20-22]. Ideally, one would strive to simultaneously improve membrane CO₂ permeability (i.e., enhance CO₂ diffusivity and CO₂ solubility, Eq. 4) as well as CO₂ permeability selectivity. It is extremely difficult, however, to reformulate polymer chemistries and morphologies in ways that will enhance both permeability and permeability selectivity. Membrane permeability may be enhanced, but at the expense of lower selectivity and vice versa. In the field of polymer-based membrane separations this phenomenon has been widely studied (both theoretically and experimentally) and is known ubiquitously as the so called "fluxselectivity tradeoff' [24]. For example, glassy polymers tend to be very selective because of their ability discriminate between gases of differing size (high diffusivity selectivity), but also tend to have low diffusivity and, subsequently, permeability because of a rigid polymer matrix [20-22, 24]. On the other hand, polymers in the rubbery state tend to have high permeability (i.e., diffusivity), but rather low selectivity because the rubbery polymer matrix allows accommodation of gases of all sizes (low diffusivity selectivity) [20-22, 24]. Comparison of the CO_2/CH_4 separation performance between silicone rubber (PDMS) and polycarbonate (PC) in

Table 1.1 exemplifies this flux-selectivity tradeoff. PC is incredibly glassy, while PDMS is entirely rubbery [22, 25, 26].

Table 1.1 Glass transition temperature (T_g) , CO₂ permeability, and CO₂/CH₄ permeability selectivity of PC and PDMS [22, 25, 26].

Polymer	T _g (°C)	P(CO ₂)	P(CO ₂)/P(CH ₄)
PDMS	-123	4550	3.37
PC	145	6.5	23.2

The drastic difference in both polymer chemistry and morphology between PC and PDMS contributes to such wildly different gas separation properties. Although comparison of these two specific polymers represents the "extremes" in terms of the flux-selectivity tradeoff, a large body of work has shown that intermediate materials tend to follow the same trend. A convenient way to plot gas separation performance is on what is known as a "Robeson Plot" [24]. This is a log-log plot of the permeability selectivity of a particular gas pair vs. the permeability (i.e. throughput) of the more permeable gas. Robeson plots for CO_2/N_2 and CO_2/CH_4 are shown in Figs. 1.2a-b [24].



Figure 1.2. Robeson plots of (a) CO_2/N_2 and (b) CO_2/CH_4 with polymer data (^O) data from Robeson [24].

These plots contain data from a broad range of membrane materials and research groups and they perfectly exemplify the flux-selectivity tradeoff. As can be seen in each plot, the more permeable a membrane is (i.e., as you go to the right), the less selective the material becomes and vice-

versa. The solid lines labeled "upper bound 2008" represent the current limit in flux selectivity performance. The negative slope of this line represents the general tradeoff trend for a specific separation pair [24]. The upper bounds were determined by statistical analysis of very large data sets and serve as good benchmarks by which to gauge the performance of newly-tested membrane materials [24]. At this point, however, it is important to point out that the so called "flux-selectivity tradeoff" trend is the general rule to which there are certainly exceptions. It is also important to point out that the "upper bounds" are only current day empirical bench marks and by no means demark any theoretical upper limit. As Fig. 1.2 suggests, there are hundreds if not thousands of polymer materials that can be used for the separation of specific CO₂/light gas pairs. It is desirable to design new polymer membrane materials that fall in the upper right quadrant of the Robeson Plots (Fig. 1.2) (i.e., demonstrate improved CO₂ permeability and selectivity).

Polyamide- and polycarbonate-based membranes have been exhaustively studied for their CO_2 separation properties[2, 9, 16, 27]. Even to this day, these inherently glassy polymers are studied by many researchers. However, there is still a need to develop new polymeric membrane materials that push the conventional limits of CO_2 permeability and CO_2 /light gas selectivity. As seen in Fig. 1.2, very few polymer materials have demonstrated CO_2 separation performances that approach or surpass Robeson's Upper Bounds. One class of materials, in particular, that has shown much promise are poly(ethylene oxide) (PEO)-based materials [12, 28-36]. Many groups have exploited the enhanced CO_2 solubility inherent to PEO to produce membranes that not only possess excellent CO_2 permeability (ca. 100–1000 barrers) but promising CO_2 selectivity as well [12, 28-36]. It is widely accepted that the inherently good CO_2 selectivity of PEO is due to favorable interactions of the polar ether units with the quadrapole moment of CO_2 [29]. PEO-

based polymers can also be tuned to possess rather low values of T_g (i.e., to be very rubbery) and high values for CO₂ diffusivity leading to high CO₂ permeability [28, 33, 37]. Very few new membrane materials have emerged that are able to compete with the performance of PEO-based materials. However, room-temperature ionic liquids (RTILs) have recently arisen as a new class of highly CO₂-selective and CO₂-permeable materials for membrane applications.

1.3. RTILs as Selective and Tunable Solvents for CO₂ Capture

RTILs are liquids at ambient conditions (i.e., near-room-temperature) and are composed only of ions in the absence of a molecular co-solvent [38-40]. RTILs typically possess bulky, organic cations and organic or inorganic anion pairs [38-40]. A selection of some common RTILs is shown in Fig. 1.3. RTILs are a very unique class of "designer solvents" that possess distinctive properties that set them apart from traditional organic solvents. The most notable of these qualities is an inherently low (i.e., vanishingly small) vapor pressure [38-42]. The ability to uniquely tailor RTILs and their properties by choice of substituent (R in Fig. 1.3), cation, and anion is certainly the most unique quality that distinguishes RTILs from any other known class of solvents [38-40, 42]. It has been estimated that millions or more cation-anion possibilities can exist, making for a seemingly limitless number of possible RTIL structures and properties [38-40, 42]. Many RTILs also possess inherently good CO₂ solubility and excellent CO₂/light gas solubility selectivity [40, 43-51]. Similar to PEO, these observations are attributed to favorable interactions between the quadrapole moment of CO₂ and the ionic components of RTILs [45]. A considerable effort by many groups has been undertaken to understand and improve upon CO₂ solubility and selectivity for a wide range of RTILs [43, 44, 46-52].



Figure 1.3. Chemical structures and names of a selection of common RTIL cations and anions.

The imidazolium moiety (Fig. 1.3) has, however, been one of the most widely studied RTIL component structures. It has two points of functionality (**R** and **R'**, Fig. 3), is considerably straightforward to synthesize, and is based on the relatively inexpensive starting material 1-Himidazole. More notably, imidazolium-based RTILs have repeatedly demonstrated some of the most promising CO₂ solubility and selectivity performances [43, 44, 46-52]. Many researchers quickly realized the value of RTILs as possible replacements for VOCs that are used in solventbased CO₂ separations (e.g., Rectisol or amine-scrubbing [11, 15]) [40, 42, 53]. However, the considerable cost and high viscosity associated with most RTILs has cast some doubt on their ability to assume the same role as organic solvents in traditional CO₂ separation processes. Many researchers have found that the most rational approach is to employ RTILs in a membrane configuration known as a supported ionic liquid membrane (SILM) [43, 46, 52, 54-60]. Thus, exploiting their most their unique properties (e.g., vanishingly low vapor pressure and high CO₂ selectivity) while eliminating the need for large amounts of RTIL and high pump cost (due to high liquid viscosity).

1.4. SILMs for Membrane-Based CO₂ Separations

SILMs are fabricated by saturating an inert, highly porous polymer (or inorganic) support material with a RTIL [43, 46, 52, 54-60]. Porous poly(ether sulfone) or poly(sulfone) are commonly used supports for SILM fabrication [43, 46, 52, 54-60]. Obviously, the liquid nature of these membranes is highly advantageous in terms of CO_2 diffusivity and, subsequently, CO_2 permeability. Combined with the good CO_2 /light gas solubility selectivity inherent to many RTILs, SILM performances have certainly been impressive [43, 46, 52, 54-57, 59, 60]. A selection of imidazolium-based SILM CO_2/N_2 performances is summarized in Fig. 1.4 [59].


Figure 1.4. CO_2/N_2 Robeson Plot with polymer data ($^{\bigcirc}$) adapted from Robeson [24] and a selection of SILM data (\blacksquare) measured in our lab and adapted from a prior review [59].

SILMs clearly possess very competitive CO₂ permeability and selectivity performance that sets them apart as viable and promising candidates for industrial membrane applications. However, separation performance alone (i.e., CO₂ permeability and selectivity) is not the only metric by which new membrane materials are gauged. Ultimate feasibility will depend highly on long-term chemical stability and robustness of membrane materials. Despite their excellent separation performance, "blowout" of the liquid RTIL component of SILMs typically occurs at transmembrane pressure drops (TPDs) of \geq 1 atm, since capillary/hydrostatic forces alone retain the RTIL in the porous support [43, 59]. As nearly all large-scale membrane-based CO₂ separations will involve a TPD much greater than any SILM can withstand, there is little doubt that SILMs are not an industrially viable membrane configuration. SILMs, however, can offer a very useful method and test platform to quickly gain diffusivity and selectivity data for newly synthesized RTILs.

1.5 Poly(RTIL) Membranes for CO₂/Light Gas Separations

SILMs have clearly demonstrated the potential in using RTIL-based materials for membrane-based CO₂ separations. Researchers have demonstrated that the RTIL component can be stabilized through the formation of a solid RTIL analogue [61, 62]. This was accomplished by functionalization of RTILs with polymerizable groups (e.g., styrene), which were subsequently polymerized to form solid poly(RTIL) membranes [61, 62]. Examples of imidazolium-based RTIL monomers are shown in Fig. 1.5.



Figure 1.5. Examples of (1a) styrene-, (2a) acrylate-, and (3a) vinyl-based imidazolium photopolymerizable RTIL monomers and resulting polymers (1b, 2b, and 3b). X = bistriflamide (Fig. 1.3)

The resulting polymers (i.e., poly(RTIL)s) are chemically analogous to liquid RTILs (i.e., SILMs), but the cationic units are covalently linked during the polymerization reaction of the pendant C=C double bond (Fig. 1.5). The general structure of the poly(RTIL)s will depend on the structure of the RTIL monomer, and examples of resulting polymers are also shown in Fig.

1.5. Previous research found that polymerization of the RTIL monomer certainly resulted in highly stable, polymer materials [61, 62]. In fact, poly(RTIL) materials were generally found to have improved CO₂/light gas permeability selectivity compared to analogous SILMs [61, 62]. The diffusivity and permeability of poly(RTIL) membranes was, however, several orders of magnitude lower than analogous pure RTIL performance [46, 59, 61, 62]. The lower diffusivity was obviously a consequence of the solid, more dense nature of the poly(RTIL) membranes (i.e., gas diffusivity in liquids >> gas diffusivity in solids). To illustrate the large observed decrease in permeability performance, a selection of representative poly(RTIL) performances has been plotted in Fig. 1.6. Considerable efforts have been made to understand and improve upon acrylate- and styrene-based poly(RTIL) permeability and selectivity by functionalization of the imidazolium cation with a variety of *n*-alkyl or polar substituents [61, 63]. For example, the permeability of a *n*-hexyl-functionalized poly(RTIL) was found to be considerably higher than an analogous methyl-functionalized poly(RTIL) [61]. Additionally, improvements in CO₂/N₂ and CO₂/CH₄ selectivity were accomplished by incorporation of polar substituents, such as oligo(ethylene glycol) sidechains [63]. However, any improvements in permeability and/or selectivity brought on by functionalization of the imidazolium cation were somewhat incremental (Fig. 1.6). Although poly(RTIL)s are advantageously more mechanically stable than SILMs, their lower CO₂ separation performance (i.e., low CO₂ permeability) does not qualify them as strong candidates for membrane-based industrial CO_2 separations. However, researchers have recently realized that there is potential to maximize RTIL-based membrane performance by blending solid, poly(RTIL)s with liquid RTILs to form stable solid-liquid composite structures [64-66].



Figure 1.6. CO_2/N_2 Robeson Plot with polymer data (\bigcirc) adapted from Robeson [24] and a selection of representative poly(RTIL) (\square) and SILM data (\blacksquare) [59, 61, 63]. Some SILM data was measured in our lab.

1.6 Composite Poly(RTIL)-RTIL Membranes for Improved CO₂ Separation Performance

Poly(RTIL)-RTIL composite films have been fabricated by incorporating a nonpolymerizable RTIL into the RTIL monomer mixture and then polymerizing the RTIL monomer in situ [64-66]. Upon photo-initiated radical polymerization, the formed poly(RTIL) matrix would contain "free" liquid RTIL [64-66]. The RTIL component acts essentially as a nonvolatile, CO₂-selective, plasticizing agent that has a dramatic effect on gas penetrant permeability. For example, incorporation of 20 mol % of "free RTIL" into a poly(RTIL) membranes was found to increase CO₂ permeability by a factor of 4, with little-to-no change in CO_2/N_2 or CO_2/CH_4 permeability selectivity [64-66]. As discussed above, it is considerably rare to observe improvements in membrane permeability without a loss in selectivity. The "free RTIL" imparts more "liquid-like" diffusivity to the membrane but does not sacrifice in CO₂ selectivity because the free liquid is inherently selective for CO₂. Perhaps the most significant conclusion from these works was that the ionic interaction between the polymer and the RTIL enhances the stability of the liquid component, since no liquid "blow out" is observed [64-66]. Other researchers have also pointed out the potential value of using ionic polymers with ionic liquids [67]. Entrapment of the liquid RTIL is dominantly accomplished through the strong ion-ion interactions between the liquid RTIL and solid poly(RTIL) components. This will perhaps prove to be a valuable characteristic of poly(RTIL)-RTIL that is not achievable with other (non-ionic) polymer-RTIL composite systems.

1.7 Thesis Objectives: The Design of Selective RTILs and Functional RTIL-based Polymers to Form Composite Structures with Enhanced CO₂ Separation Capability

As described above, there is certainly much promise and merit in pursuing RTIL-based membrane materials for CO_2 /light gas separations. Toward the ultimate goal of creating industrially-viable RTIL-based membrane materials, poly(RTIL)s or SILMs on their own are clearly not viable configurations. SILMs certainly possess the separation performance, but suffer from mechanical instability. On the other hand, poly(RTIL)s have demonstrated excellent pressure stability but do not possess large enough CO_2 permeability to merit industrial viability. Only recently have researchers in CO_2 separations begun to find that the maximum in RTILbased membrane performance potential can be realized upon incorporation of solid and liquid RTIL components. For some time, researchers in the electrochemical field have understood the value of incorporating liquid RTILs with solid poly(RTIL)s to obtain nearly liquid-like ion conductivities [67-73]. This was perhaps due to a more natural extension of materials like Nafion in this field. However, in the field of gas separation membranes, the use of solid-liquid composite films is still a relatively novel, perhaps radical, approach. Limited studies have existed for some time in the use of supported liquid membranes [74], but these configurations have not found widespread application due to pressure stability and evaporation issues. As those in the electrochemical field have found for ion conductivity, there is potential for obtaining nearly liquid-like membrane properties for CO₂ permeability and CO₂ selectivity with poly(RTIL)-RTIL composite structures [67, 75-78].

The overall objective of this thesis work is to advance the state-of-the-art for poly(RTIL)-RTIL composites with respect to membrane composition and CO_2 separation performance. Since these structures contain two distinct components, the RTIL and the ionic polymer, a rational design approach was to investigate and/or improve upon individual component performance prior to fabricating and optimizing composite materials and performance. Chapter 2 investigates methods to optimize and design tailored RTILs for enhanced CO_2 separation performance (i.e., improved CO_2 solubility and solubility selectivity). Chapters 3 and 4 investigate new, RTILcompatible, ionic polymer structures and their inherent separation performance as well as composite separation performance. In Chapter 5, the composite structure design approach between the two components (RTIL and poly(RTIL)) is pushed to physical limits to attain maximum potential in measured CO_2 separation performance (permeability and selectivity). Performances of poly(RTIL)-RTIL membranes were shown to approach and exceed Robeson's upper limits. Furthermore, Chapter 5 demonstrates the unique ability of poly(RTIL)-RTIL membranes to be highly selective for CO_2/H_2 separation, a rarity among membrane materials.

Prior to this work, the design approach toward more CO_2 -selective RTILs was relatively heuristic in nature. As discussed above, there are perhaps millions or more possibilities of RTIL structures based on the various combinations of functionalized cations and anions. It would be incredibly useful to have a rational, quantitative design approach that could dramatically narrow the scope and guide the design toward new, promising RTILs (i.e., ones that possess desirable CO_2 separation properties). In Chapter 2, one such design approach is presented and validated through experimental CO_2 solubility and selectivity testing of new nitrile-functionalized and previously studied oligo(ethylene glycol)-functionalized RTILs.

Limited numbers of RTIL-based ionic polymers (i.e., ones that contain RTIL moieties such as imidazolium) exist in the current literature. For the most part, these are chain-addition polymers derived from unsaturated RTIL monomers (Fig. 1.5). Polymers of this type possess carbonaceous backbones and all functionality as pendant side groups (Fig. 1.5). There have been no gas separations studies investigating ionic step-growth polymers, or "ionenes" where the ionic moiety and all functionality are contained along the polymer backbone. Chapter 3 investigates the synthesis of new imidazolium-based ionenes and their preliminary CO₂/light gas separation performance as neat polymers and as composite structures with an added RTIL. Additionally, there has been very little work investigating vinyl-based, chain addition poly(RTIL)s (3a and 3b, Fig. 1.5) for neat or composite CO₂ separation performance. Chapter 4 investigates the structure-property relationships of these vinyl-based polymers as well as the CO₂ separation performance of composite films.

There is a considerable amount of work in the electrochemistry field that has involved the fabrication of cross-linked poly(RTIL)-RTIL gel membranes for ion conductivity [70-73]. Ion conductivity in these membranes was considerably high do to rather high loading of the RTIL

component. Those membranes presented a very promising composite design for highly permeable and selective poly(RTIL)-RTIL membranes. There are limited studies where researchers have explored the CO₂ separation performance of polymer-RTIL gels [67, 75, 76, 78], but practically no studies have been performed with cross-linked poly(RTIL)-RTIL membranes [77]. Chapter 5 presents some important structure-property relationships of crosslinked poly(RTIL)-RTIL gel membranes in terms of CO₂ permeability and selectivity. Furthermore, the efficacy of these membranes for CO₂/H₂, CO₂/N₂, and CO₂/CH₄ separation is demonstrated.

1.8 References

- 1. *Basic research needs for geosciences: Facilitating 21st century energy systems*, 2007, Office of Basic Energy Sciences of the U.S. Dept. of Energy.
- 2. Jones, C.W. and Maginn, E.J., "Materials and processes for carbon capture and sequestration." ChemSusChem **2010**, *3*, 863-864.
- 3. Goodell, J., *Big coal: The dirty secret behind america's energy future* 2006, New York, NY: Houghton Mifflin Co,.
- 4. Shackley, S. and Gough, C., *Carbon capture and its storage: An integrated assessment* 2006, Aldershot, UK: Ashgate.
- 5. Havran, V., Duduković, M.P., Lo, C.S., "Conversion of methane and carbon dioxide to higher value products." Ind. Eng. Chem. Res. **2011**, *50*, 7089-7100.
- Dorner, R.W., Hardy, D.R., Williams, F.W., Willauer, H.D., "Heterogeneous catalytic CO₂ conversion to value-added hydrocarbons." Energy & Environmental Science 2010, 3, 884-890.

- Climate change 2007: Synthesis report. Contribution of working groups i, ii and iii to the fourth assessment report of the intergovernmental panel on climate change, Pachauri, R.K. and Reisinger, A., Editors. 2007: IPCC, Geneva, Switzerland. p. 104.
- 8. *Review of emerging resources: U.S. Shale gas and shale plays.* 2011 [cited 2011 August]; Available from: <u>http://www.eia.gov</u>.
- 9. Sridhar, S., Smitha, B., Aminabhavi, T.M., "Separation of carbon dioxide from natural gas mixtures through polymeric membranes—a review." Separ. Purif. Rev. **2007**, *36*, 113-174.
- 10. Descamps, C., Bouallou, C., Kanniche, M., "Efficiency of an integrated gasification combined cycle (igcc) power plant including CO₂ removal." Energy **2008**, *33*, 874-881.
- 11. Kohl, A.L. and Nielsen, R.B., *Gas purification (5th edition)*, Elsevier.
- 12. Lin, H., Van Wagner, E., Freeman, B.D., Toy, L.G., Gupta, R.P., "Plasticizationenhanced hydrogen purification using polymeric membranes." Science **2006**, *311*, 639-642.
- 13. Ho, M.T., Allinson, G.W., Wiley, D.E., "Reducing the cost of CO₂ capture from flue gases using pressure swing adsorption." Ind. Eng. Chem. Res. **2008**, *47*, 4883-4890.
- 14. Oyenekan, B.A. and Rochelle, G.T., "Energy performance of stripper configurations for CO₂ capture by aqueous amines." Ind. Eng. Chem. Res. **2005**, *45*, 2457-2464.
- 15. Rochelle, G.T., "Amine scrubbing for CO₂ capture." Science **2009**, *325*, 1652-1654.
- 16. Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R.B., Bland, A.E., Wright, I., "Progress in carbon dioxide separation and capture: A review." J. Env. Sci. **2008**, *20*, 14-27.
- 17. Rao, A.B. and Rubin, E.S., "A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control." Env. Sci. Technol. **2002**, *36*, 4467-4475.
- 18. Wong, S. and Bioletti, R., *Carbon dioxide separation technologies*, 2002, Alberta Research Council Report; Alberta Research Council: Edmonton, AB,.

- 19. Hook, R.J., "An investigation of some sterically hindered amines as potential carbon dioxide scrubbing compounds." Ind. Eng. Chem. Res. **1997**, *36*, 1779-1790.
- 20. Baker, R.W., *Membrane technology and applications*. 2nd ed 2004, West Sussex, England: John Wiley & Sons, Ltd.
- 21. Petropoulos, J.H., in *Polymeric gas separation membranes*, Paul, R.D. and Yampol'skii, Y.P., Editors. 1994, CRC Press, Inc.: Boca Raton, FL. p. 17.
- 22. Zolandz, R.R. and Fleming, G.K., *Membane handbook* 1992, New York, NY: Chapman & Hall.
- 23. Daynes, H.A., "The process of diffusion through a rubber membrane." Proceedings of the Royal Society of London. Series A **1920**, *97*, 286-307.
- 24. Robeson, L.M., "The upper bound revisited." J. Membr. Sci. 2008, 320, 390-400.
- 25. Bauwens-Crowet, C. and Bauwens, J.C., "Annealing of polycarbonate below the glass transition: Quantitative interpretation of the effect on yield stress and differential scanning calorimetry measurements." Polymer **1982**, *23*, 1599-1604.
- 26. Goodwin, A.A., Beevers, M.S., Clarson, S.J., Semlyen, J.A., "Studies of cyclic and linear polydimethylsiloxanes: 32. Dielectric relaxation investigations." Polymer **1996**, *37*, 2603-2607.
- 27. Powell, C.E. and Qiao, G.G., "Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases." J. Membr. Sci. **2006**, *279*, 1-49.
- 28. Kusuma, V.A., Freeman, B.D., Borns, M.A., Kalika, D.S., "Influence of chemical structure of short chain pendant groups on gas transport properties of cross-linked poly(ethylene oxide) copolymers." J. Membr. Sci. **2009**, *327*, 195-207.
- 29. Lin, H. and Freeman, B.D., "Gas solubility, diffusivity and permeability in poly(ethylene oxide)." J. Membr. Sci. **2004**, *239*, 105-117.
- 30. Lin, H. and Freeman, B.D., "Gas and vapor solubility in cross-linked poly(ethylene glycol diacrylate)." Macromolecules **2005**, *38*, 8394-8407.

- 31. Lin, H. and Freeman, B.D., "Gas permeation and diffusion in cross-linked poly(ethylene glycol diacrylate)." Macromolecules **2006**, *39*, 3568-3580.
- 32. Lin, H., Freeman, B.D., Kalakkunnath, S., Kalika, D.S., "Effect of copolymer composition, temperature, and carbon dioxide fugacity on pure- and mixed-gas permeability in poly(ethylene glycol)-based materials: Free volume interpretation." J. Membr. Sci. **2007**, *291*, 131-139.
- Lin, H., Kai, T., Freeman, B.D., Kalakkunnath, S., Kalika, D.S., "The effect of crosslinking on gas permeability in cross-linked poly(ethylene glycol diacrylate)." Macromolecules 2005, *38*, 8381-8393.
- 34. Lin, H., Van Wagner, E., Raharjo, R., Freeman, B.D., Roman, I., "High-performance polymer membranes for natural-gas sweetening." Adv. Mater. **2006**, *18*, 39-44.
- 35. Lin, H., Wagner, E.V., Swinnea, J.S., Freeman, B.D., Pas, S.J., Hill, A.J., Kalakkunnath, S., Kalika, D.S., "Transport and structural characteristics of crosslinked poly(ethylene oxide) rubbers." J. Membr. Sci. **2006**, *276*, 145-161.
- 36. Patel, N.P., Miller, A.C., Spontak, R.J., "Highly CO₂-permeable and selective polymer nanocomposite membranes." Adv. Mater. **2003**, *15*, 729-733.
- Kalakkunnath, S., Kalika, D.S., Lin, H., Freeman, B.D., "Segmental relaxation characteristics of cross-linked poly(ethylene oxide) copolymer networks." Macromolecules 2005, 38, 9679-9687.
- Gordon, C.M., Muldoon, M.J., Wagner, M., Hilgers, C., Davis, J.H., Wasserscheid, P., Synthesis and purification, in Ionic liquids in synthesis 2008, Wiley-VCH Verlag GmbH & Co. KGaA. p. 7-55.
- 39. Wilkes, J.S., Wasserscheid, P., Welton, T., *Introduction*, in *Ionic liquids in synthesis* 2008, Wiley-VCH Verlag GmbH & Co. KGaA. p. 1-6.
- 40. Brennecke, J.F. and Maginn, E.J., "Ionic liquids: Innovative fluids for chemical processing." AIChE J. **2001**, *47*, 2384-2389.
- 41. Earle, M.J., Esperanca, J.M.S.S., Gilea, M.A., Canongia Lopes, J.N., Rebelo, L.P.N., Magee, J.W., Seddon, K.R., Widegren, J.A., "The distillation and volatility of ionic liquids." Nature **2006**, *439*, 831-834.

- 42. Rogers, R.D. and Seddon, K.R., *Ionic liquids: Industrial applications for green chemistry.* Proceedings of the american chemical society meeting 2002, Washington, DC: American Chemical Society.
- Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L., Noble,
 R.D., "Guide to CO₂ separations in imidazolium-based room-temperature ionic liquids." Ind. Eng. Chem. Res. 2009, 48, 2739-2751.
- 44. Bara, J.E., Gabriel, C.J., Lessmann, S., Carlisle, T.K., Finotello, A., Gin, D.L., Noble, R.D., "Enhanced CO₂ separation selectivity in oligo(ethylene glycol) functionalized room-temperature ionic liquids." Ind. Eng. Chem. Res. **2007**, *46*, 5380-5386.
- 45. Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F., Maginn, E.J., "Why is CO₂ so soluble in imidazolium-based ionic liquids?" J. Am. Chem. Soc. **2004**, *126*, 5300-5308.
- 46. Camper, D., Bara, J., Koval, C., Noble, R., "Bulk-fluid solubility and membrane feasibility of rmim-based room-temperature ionic liquids." Ind. Eng. Chem. Res. **2006**, *45*, 6279-6283.
- 47. Carlisle, T.K., Bara, J.E., Gabriel, C.J., Noble, R.D., Gin, D.L., "Interpretation of CO₂ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach." Ind. Eng. Chem. Res. **2008**, *47*, 7005-7012.
- 48. Finotello, A., Bara, J.E., Camper, D., Noble, R.D., "Room-temperature ionic liquids: Temperature dependence of gas solubility selectivity." Ind. Eng. Chem. Res. **2007**, *47*, 3453-3459.
- 49. Muldoon, M.J., Aki, S.N.V.K., Anderson, J.L., Dixon, J.K., Brennecke, J.F., "Improving carbon dioxide solubility in ionic liquids." J. Phys. Chem. B **2007**, *111*, 9001-9009.
- 50. Raeissi, S. and Peters, C.J., "A potential ionic liquid for CO₂-separating gas membranes: Selection and gas solubility studies." Green Chem. **2009**, *11*, 185-192.
- 51. Yokozeki, A. and Shiflett, M.B., "Hydrogen purification using room-temperature ionic liquids." Applied Energy **2007**, *84*, 351-361.

- 52. Mahurin, S.M., Lee, J.S., Baker, G.A., Luo, H., Dai, S., "Performance of nitrilecontaining anions in task-specific ionic liquids for improved CO₂/n₂ separation." J. Membr. Sci. **2010**, *353*, 177-183.
- 53. Maase, M., *Industrial applications of ionic liquids*, in *Ionic liquids in synthesis* 2008, Wiley-VCH Verlag GmbH & Co. KGaA. p. 663-687.
- 54. Bara, J.E., Gabriel, C.J., Carlisle, T.K., Camper, D.E., Finotello, A., Gin, D.L., Noble, R.D., "Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes." Chem. Eng. J. **2009**, *147*, 43-50.
- 55. Hanioka, S., Maruyama, T., Sotani, T., Teramoto, M., Matsuyama, H., Nakashima, K., Hanaki, M., Kubota, F., Goto, M., "CO₂ separation facilitated by task-specific ionic liquids using a supported liquid membrane." J. Membr. Sci. **2008**, *314*, 1-4.
- 56. Morgan, D., Ferguson, L., Scovazzo, P., "Diffusivities of gases in room-temperature ionic liquids: Data and correlations obtained using a lag-time technique." Ind. Eng. Chem. Res. **2005**, *44*, 4815-4823.
- 57. Myers, C., Pennline, H., Luebke, D., Ilconich, J., Dixon, J.K., Maginn, E.J., Brennecke, J.F., "High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes." J. Membr. Sci. **2008**, *322*, 28-31.
- 58. Riisagera, A., Fehrmanna, R., Haumann, M., Wasserscheid, P., "Supported ionic liquids: Versatile reaction and separation media." Top. Catal. **2006**, *40*, 91-102.
- 59. Scovazzo, P., "Determination of the upper limits, benchmarks, and critical properties for gas separations using stabilized room temperature ionic liquid membranes (silms) for the purpose of guiding future research." J. Membr. Sci. **2009**, *343*, 199-211.
- 60. Scovazzo, P., Kieft, J., Finan, D.A., Koval, C., DuBois, D., Noble, R., "Gas separations using non-hexafluorophosphate [pf₆]⁻ anion supported ionic liquid membranes." J. Membr. Sci. **2004**, *238*, 57-63.
- 61. Bara, J.E., Lessmann, S., Gabriel, C.J., Hatakeyama, E.S., Noble, R.D., Gin, D.L., "Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes." Ind. Eng. Chem. Res. **2007**, *46*, 5397-5404.

- 62. Bara, J.E., Hatakeyama, E.S., Gabriel, C.J., Zeng, X., Lessmann, S., Gin, D.L., Noble, R.D., "Synthesis and light gas separations in cross-linked gemini room temperature ionic liquid polymer membranes." J. Membr. Sci. **2008**, *316*, 186-191.
- 63. Bara, J.E., Gabriel, C.J., Hatakeyama, E.S., Carlisle, T.K., Lessmann, S., Noble, R.D., Gin, D.L., "Improving CO₂ selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents." J. Membr. Sci. **2008**, *321*, 3-7.
- 64. Bara, J.E., Gin, D.L., Noble, R.D., "Effect of anion on gas separation performance of polymer–room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. **2008**, *47*, 9919-9924.
- 65. Bara, J.E., Hatakeyama, E.S., Gin, D.L., Noble, R.D., "Improving CO₂ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid." Polym. Adv. Technol. **2008**, *19*, 1415-1420.
- 66. Bara, J.E., Noble, R.D., Gin, D.L., "Effect of "free" cation substituent on gas separation performance of polymer–room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. **2009**, *48*, 4607-4610.
- 67. Lodge, T.P., "A unique platform for materials design." Science 2008, 321, 50-51.
- 68. Jin, X., Tao, J., Yang, Y., "Synthesis and characterization of poly(1-vinyl-3propylimidazolium) iodide for quasi-solid polymer electrolyte in dye-sensitized solar cells." J. Appl. Polym. Sci. **2010**, *118*, 1455-1461.
- 69. Mizumo, T., Watanabe, T., Matsumi, N., Ohno, H., "Preparation of ion conductive inorganic–organic composite systems by in situ sol–gel reaction of polymerizable ionic liquids." Polym. Adv. Technol. **2008**, *19*, 1445-1450.
- 70. Nakajima, H. and Ohno, H., "Preparation of thermally stable polymer electrolytes from imidazolium-type ionic liquid derivatives." Polymer **2005**, *46*, 11499-11504.
- 71. Ohno, H., "Design of ion conductive polymers based on ionic liquids." Macromol. Symp. **2007**, *249-250*, 551-556.

- 72. Ohno, H., Yoshizawa, M., Ogihara, W., "Development of new class of ion conductive polymers based on ionic liquids." Electrochim. Acta **2004**, *50*, 255-261.
- 73. Washiro, S., Yoshizawa, M., Nakajima, H., Ohno, H., "Highly ion conductive flexible films composed of network polymers based on polymerizable ionic liquids." Polymer **2004**, *45*, 1577-1582.
- 74. Majumdar, S. and Sirkar, K.K., in *Membrane handbook*, Ho, W.S.W. and Sirkar, K.K., Editors. 1992, Chapman and Hall: New York, NY. p. 764.
- 75. Gu, Y. and Lodge, T.P., "Synthesis and gas separation performance of triblock copolymer ion gels with a polymerized ionic liquid mid-block." Macromolecules **2011**, *44*, 1732-1736.
- 76. Jansen, J.C., Friess, K., Clarizia, G., Schauer, J., Izák, P., "High ionic liquid content polymeric gel membranes: Preparation and performance." Macromolecules **2011**, *44*, 39-45.
- Li, P., Pramoda, K.P., Chung, T.-S., "CO₂ separation from flue gas using polyvinyl-(room temperature ionic liquid)–room temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. 2011, 50, 9344-9353.
- 78. Uk Hong, S., Park, D., Ko, Y., Baek, I., "Polymer-ionic liquid gels for enhanced gas transport." Chem. Commun. **2009**, 7227-7229.

Chapter 2

Interpretation of CO₂ Solubility and Selectivity in Nitrile-Functionalized Room-Temperature Ionic Liquids Using a Group Contribution Approach

(As seen in: Carlisle, T. K. et al, Ind. Eng. Chem. Res., 2008, 47 8496-8498)

Summary

In this work the idea of tuning the solubility parameter of room-temperature ionic liquids (RTILs) with appended functional groups was explored using a combination of experiment and theory. By predictably altering the solubility parameters of several RTIL solvents, their gas solubility and separation performance were tailored. This concept was demonstrated by synthesizing and characterizing imidazolium-based RTILs that incorporate nitrile and acetylenic functional substituents. The ideal solubility and selectivity values of CO₂, N₂, and CH₄ at near ambient temperature and pressure were measured for these RTILs. These functionalized RTIL solvents exhibited lower CO₂, N₂, and CH₄ solubility values but improved CO₂/N₂ and CO₂/CH₄ solubility selectivity when compared to analogous non-functionalized, alkyl-substituted RTILs. A group contribution method was used to predict the solubility parameters of the functionalized RTILs, and regular solution theory was employed to predict the solubility and selectivity of the three gases. These predicted gas solubility values were found to be in good agreement with those measured experimentally. Furthermore, the predictions from the group contribution method indicated that inclusion of the nitrile and acetylenic functional groups increased the solubility parameter relative to the analogous, alkyl-substituted

RTILs. These initial results show that the group contribution method offers a valuable guide for systematically designing functionalized RTILs with specific gas solubility and selectivity performance.

2.1. Introduction

There are many schemes currently employed in industrial processes to capture CO₂ emissions,[1, 2] which are largely due to the increasing need to reduce and regulate the atmospheric buildup of this greenhouse gas.[2] One conventional and widely employed method is the use of a CO₂-scrubbing solvent as a gas absorption medium in a packed bed or bubble column to remove CO₂ from flue gas.[1, 2] However, many effective solvents currently used are volatile organic compounds (VOCs), such as monoethanolamine or methanol, which is used in the Rectisol process.[1-4] The use of VOCs is typically accompanied by several issues such as high flammability, volatility, and varying degrees of toxicity.[3-7] Consequently, suitable replacement solvents that exhibit low volatility and "green" chemistry are highly desirable.[1, 3-7] Room-temperature ionic liquids (RTILs) have recently been found to be promising candidates for CO₂ absorption and separation, and they show exceptional promise for these applications.[8-13]

In general, RTILs are organic salts that are molten at or below ambient temperature. Typically, an RTIL is a neat liquid composed solely of a bulky organic cation and an organic or inorganic anion, in the absence of any molecular co-solvent.⁷ RTILs have recently attracted a great deal of interest as a new class of solvents for CO_2 sorption due to their unique combination of properties, such as negligible vapor pressure, thermal stability, low flammability, and in many cases, high CO_2 solubility.[3, 7, 9, 14]

Several studies have shown that imidazolium-based RTILs (Fig. 2.1) are the most promising for CO_2 -capture applications due to their tunable chemistry, low viscosity, good CO_2 solubility, and good CO_2/N_2 and CO_2/CH_4 selectivities.[8-10, 15] Currently, for large-scale industrial applications, it remains impractical to replace VOC solvents with RTILs because RTILs are more costly and have comparable or worse solubility performance. Thus, much work remains to improve upon the CO_2 solubility and selectivity of RTILs if they are to become attractive and viable replacements for VOCs in industrial CO_2 -scrubbing processes.

$$R_1 \xrightarrow{N} \stackrel{N}{\underset{\bigcirc}{\oplus}} N_{-}R_2$$

Figure 2.1. General structure of imidazolium-based RTILs.

Perhaps the most promising characteristic of imidazolium-based RTILs is that their chemical and physical properties can be readily altered by the inclusion of specific functional groups on the cation unit, or by the choice of cation or anion.[16-18] Many recent studies have shown that the solubilities of certain gases in RTILs, particularly CO₂, are highly dependent on the chemical composition of the RTIL.[9, 10, 12, 15] The choice of cation and, more notably, anion has been shown to have a large impact on RTIL gas solubility.[8-10, 16]. Fluorination of the RTIL cation has been shown to be effective at increasing gas solubility but often results in highly viscous RTILs that are chemically less benign.[9] Variation of the substituent alkyl chain length on an imidazolium cation was demonstrated to be another successful method to modify RTIL gas solubility.[15] can chemically react to bind CO_2 .[19] Inclusion of non-reactive, polar functional groups on RTIL cations, such as ether linkages, has also recently been shown to improve CO_2/N_2 and CO_2/CH_4 solubility selectivity.[13] Unfortunately, a systematic, rational, nonempirical approach to the design of functionalized RTILs with specific gas solubility properties has yet to be developed.

It has recently been shown that regular solution theory (RST) (Eqn. 1) is a very useful model for predicting and interpreting gas solubility in many 1-alkyl-3methylimidazolium RTIL systems.[12, 15, 20] A major advantage of RST is that it does not rely on computational simulations. Although less exhaustive than any computational model, RST still has much utility in first-order engineering approximations, such as process design calculations. RST requires only the input of tabulated values and estimated empirical constants:

$$\frac{1}{x_2} = \frac{f_{pure2}^L}{f_2^G} \exp\left[\frac{v_2^L(\delta_1 - \delta_2)^2 \Phi_1^2}{RT}\right]$$
(1)

In the RST equation (Eqn. 1), 1 represents the solvent, 2 represents the gas solute, $f_{pure,2}^{L}$ is the theoretical liquid solute fugacity, f_2^{G} is the solute gas fugacity, v_2^{L} is the theoretical liquid molar volume of the solute, δ is the solubility parameter, Φ is the volume fraction, *R* is the ideal gas constant, and *T* is the absolute temperature.[21] It has been shown that groups of similar RTILs can be modeled with a modified version of Eqn. 1 when $f_{pure,2}^{L}$ and v_2^{L} are not accurately known (see Eqn. 2 below):

$$\ln(H_{2,1}(atm)) = a + b(\delta_1 - \delta_2)^2$$
 (2)

In this equation, *a* and *b* are empirically determined constants that depend only on the gas and temperature (unique for a specific set of RTILs), and $H_{2,1}$ is the Henry's constant of the gas in the RTIL.[12, 20] The solubility parameter, δ , is defined as the square root of the cohesive energy density (see Eqn. 3) [27]:

$$\delta = \sqrt{\frac{E_{vap}}{V_m}} \tag{3}$$

In Eqn. 3, E_{vap} is the energy of vaporization of the saturated liquid to the ideal gas state (vacuum) and V_m is the molar volume of the liquid. This definition applies to all chemical species. Success in utilizing and extending Eqns. 1 and 2 to the design of tailored, functionalized RTILs for gas absorption relies on knowing accurate values for δ_1 and δ_2 , the solubility parameters of the RTIL and gas, respectively. The cohesive energy densities are typically determined by obtaining energies of vaporization for volatile solvents, and as such, values for δ_2 are widely tabulated. However, the experimental determination of δ_1 for RTILs is very difficult since RTILs are very difficult to vaporize. Recently, it was demonstrated that one may circumvent this problem by estimating the energy of vaporization of an RTIL using the Kapustinskii Equation (Eqn. 4) and the relationship shown in Eqn. 5:[15, 20]

$$U = 2.56 \times 10^{6} \left(\frac{z_{1} z_{2}}{V_{1}^{L}} \right) \left(1 - \frac{0.367}{V_{1}^{L}} \right)$$
(4)

 $\delta = \left(\frac{U}{V_1^L}\right)^{1/2} \tag{5}$

In Eqns. 4 and 5, V_1^{L} is the RTIL molar volume, and z_1 and z_2 are the charges of the cation and anion, respectively. With this simplification, it was found that the solubility parameter of the RTIL is proportional to its molar volume [15, 20]. However, the solubility parameters of RTILs reported in that prior work are much higher than those reported in a recent handful of studies.[22-25] The Kapustinskii approximation does not account for the solvent polarizability; it is merely an approximation that has been used for higher melting organic and inorganic salts.

The value of the term $(\delta_1 - \delta_2)^2$ in Eqns. 1 and 2 is of key importance in the RST model, as well as other thermodynamic mixing models[21, 26, 27]. This enthalpic difference between the solvent and solute is clearly a dominating factor when considering the degree of solvent-solute miscibility (Eqns. 1 and 2). Furthermore, the term $(\delta_1 - \delta_2)^2$ is a quantity that can be modified via choice of solvent (i.e., by tuning of δ_1). Given the modular nature of RTILs,[7] it is believed that the cohesive energy density of RTIL solvents can be readily altered by choice of anion, cation, and/or appended functional groups on the imidazolium cation. By focusing on chemically tuning the appended functional groups on the RTIL cation, it appears possible to adjust the RTIL solubility parameter in a predictive manner through the inclusion of specific functional groups. The degree to which a functional group on the RTIL cation impacts the solubility parameter is related to its contribution to the cohesive energy of the solvent. Fortunately, well-established methods that implement the ideas behind a "group contribution" approach have already been developed.[26-28]

It has been shown that solubility parameters for both polymers and solvents can be estimated using a group contribution method (Eqn. 6):[27, 28]

$$\delta_i = \frac{\sum_j F_j}{V_{mi}} \qquad (6)$$

In Eqn. 6, *i* represents the solvent, *j* represents each substituent chemical group, *F* is the molar attraction constant of chemical group *j*, and V_m is the molar volume of the solvent. The group contribution method is based on the idea that the total cohesive energy of a molecule is the sum of the individual cohesive energies (molar attraction constants) associated with each substituent group on the molecule. This method also assumes that molar attraction constants are considered constant regardless of the chemical nature of the molecule or of the surrounding chemical environment. Molar attraction constants of several organic functional groups relevant to this study were taken from the Polymer Handbook [28] and references therein, and presented in Table 2.1.

Table 2.1. Relevant Organic Functional Groups and their Molar Attraction Constants

Group	$F (\mathrm{MPa}^{1/2} \mathrm{cm}^3 \mathrm{mol}^{-1})$
H ₃ C-	303
$-CH_{2}$	269
НС≡С—	583
N≡C—	725

The group contribution method is useful for predicting the degree of solventsolute mixing, in addition to guiding the design of tailored molecules with specific solubility parameters.[26-28] Group molar attraction constants have been tabulated for many chemical groups by various investigators.[26-28] Thus, the use of chemical group contributions in combination with RST may offer valuable insight into the design and

performance of RTIL gas solvents with functional groups that have not yet been synthesized. It has been well-established in the coating and polymer industries that the quantity $(\delta_1 - \delta_2)^2$ is of key importance to achieving a desired miscibility of solute and solvent.[26] Often, this quantity is tuned by mixing of various solvents to achieve a desired composite value of δ_1 . This approach, however, may have limitations due to miscibility issues of disparate RTILs.[29, 30] As mentioned previously, given the highly modular nature of RTILs, a desired value for δ_1 may be achieved through the inclusion of particular functional groups on the cation or anion. However, tuning of the RTIL cation appears to be more readily achieved than chemical modification of the largely inorganic anions typically used to form RTILs.[7, 31] Implementing a group contribution approach to designing and screening new RTILs has much promise for gas separation applications. Given a particular mixture of gases, RTILs can be tailored to possess a specific value of δ_1 , ideally achieving the desired solubility and/or solubility selectivity for a specific gas. Given the wide range of current and potential uses of RTILs as solvents, this approach is by no means limited solely to gas separations.[3, 14]

Herein, we show that it is possible to systematically design a more CO₂-selective RTIL solvent using the group contribution method as a guide. We demonstrate this through experimentally measuring the solubilities of CO₂, N₂, and CH₄ in imidazoliumbased RTILs that incorporate either nitrile-terminated *n*-alkyl groups or a propargyl group, and interpreting these results with respect to group contributions and RST. To our knowledge, nitrile- and acetylene-terminated *n*-alkyl-imidazoliums have yet to be studied for gas solubility and solubility selectivity. 1-Alkylnitrile-3-methylimidazolium salts have, to date, only been investigated as reaction solvents and electrolytes for dyesensitized solar cells.[32-39]

2.2. Experimental

2.2.1. Materials and General Procedures

All reagents and solvents were purchased from Sigma-Aldrich (Milwaukee, WI, USA) in the highest purities available and used as received, except for lithium trifluoromethanesulfonimide, (LiTf₂N), which was purchased from 3M (St. Paul, MN, USA) and used as received. All gases were at least 99.99% purity and were purchased from AirGas (Radnor, PA, USA). All syntheses and work-up procedures were performed in air.

2.2.2. Instrumentation

High-resolution mass spectrometry was performed with a PE SCIEX/ Applied Biosystems API QSTAR[™] Pulsar i quadrupole time-of-flight mass spectrometer. Proton and carbon–13 NMR spectra were obtained with a Varian INOVA 400 spectrometer (400 MHz and 100 MHz, respectively). Fourier-transform infrared (FT-IR) spectra were obtained with a Mattson Satellite FT-IR spectrometer. Samples were prepared as thin, liquid films on a Ge crystal substrate. The water content of the RTILs in this study was determined with a Mettler Toledo DL32 Karl Fischer Coulometer. The equipment used for gas solubility experiments is identical to that thoroughly described in a previous work by our group [13].

2.2.3. Synthesis of Functionalized RTILs

The RTILs used in this study were synthesized according to Scheme 2.1:

$$\sqrt{N} \frac{R-X}{CH_{3}CN, 65-85 \ ^{\circ}C, 16 \ h}} \sqrt{H} \frac{R-X}{X^{\odot}} R^{-}R = \frac{R-X}{Br} = \frac{Br}{N} n = 3, 5$$

$$\sqrt{H} \frac{R}{N} \frac{LiTf_{2}N}{R} \frac{LiTf_{2}N}{H_{2}O, RT, 1 \ h}} \sqrt{H} \frac{R}{N} \frac{R-X}{R} = \frac{R-X}{Br} = \frac{R-X}{R} =$$

Scheme 2.1. Synthesis of RTILs used in this study.

2.2.4. Typical Procedure for Synthesis of Functionalized RTILs (1a-c, 2)

1-Methylimidazole (10.00 g, 121.8 mmol) was dissolved in CH₃CN (100 mL). Chloroacetonitrile (10.12 g, 134.0 mmol) was added, and the reaction was heated at 65 $^{\circ}$ C (85 °C for 1b,c) for 16 h while stirring. After this time, the solvent was removed by rotary evaporation, and then Et₂O (200 mL) was added to the halide salt, which was then placed in a freezer at -10 °C for several hours. After this time, the Et₂O was decanted, and the halide salt dissolved in deionized H_2O (100 mL). The aqueous solution was subsequently washed with EtOAc (3 x 75 mL). LiTf₂N (38.46 g, 134.0 mmol) was then added and an oily liquid immediately separated. The reaction mixture was stirred for 1 h, after which time the product was extracted into EtOAc (100 mL) and the organic phase washed with deionized H_2O (3 x 75 mL). The organic phase was subsequently dried over anhydrous MgSO₄, stirred with activated carbon for 10 min, and filtered through a plug of basic Al₂O₃. The solvent was then removed via rotary evaporation. The remaining product was further dried in vacuo (100 mtorr) at 65 °C overnight to afford compounds **1a–c**, and **2** as clear to pale-yellow oils. Prior to the solubility experiments, the water content of **1a–c** and **2** were all found to be less than 300 ppm by Karl Fischer titration.

2.2.4.1. 1-Ethanenitrile-3-methylimidazolium bis(trifluoromethane)sulfonimide (**1a**): Yield: 18.43 g (37.6%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.88 (s, 3H), 5.56 (s, 2H), 7.78 (t, 1H), 7.88 (t, 1H), 9.23 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 36.6, 37.3, 115.1, 120.1 (q, CF₃), 123.1, 124.8, 138.4. FT-IR: 3163, 3122, 3003, 2967, 1584, 1563, 1469, 1433, 1339, 1232 cm⁻¹. HRMS (m/z): calculated as [A]⁺[A]⁺[B]⁻: 524.0609, found: 524.0611.

2.2.4.2. *1-Butanenitrile-3-methylimidazolium bis(trifluoromethane)sulfonimide* (*1b*): Yield: 31.79 g (81%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.13 (quintet, 2H), 2.57 (t, 2H), 3.83 (s, 3H), 4.23 (t, 2H), 7.71 (t, 1H), 7.77 (t, 1H), 9.12 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 13.9, 25.8, 36.1, 48.2, 115.3, 120.0 (q, CF₃), 122.7, 124.2, 137.4. FT-IR: 3159, 3121, 2967, 2251, 1577, 1567, 1467, 1454, 1430, 1350 . HRMS (m/z): calculated as [A]⁺[A]⁺[B]⁻: 580.1229, found: 580.1251.

2.2.4.3. 1-Hexanenitrile-3-methylimidazolium bis(trifluoromethane)sulfonimide (1c): Yield: 41.81 g (88.8%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.32 (quintet, 2H), 1.58 (quintet, 2H), 1.80 (quintet, 2H), 2.50 (t, 2H), 3.84 (s, 3H), 4.17 (t, 2H), 7.70 (t, 1H), 7.76 (t, 1H), 9.10 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 16.5, 24.6, 25.1, 29.1, 36.2, 49.0, 115.3 120.1 (q, CF₃), 122.8, 124.2, 137.1. FT-IR: 3158, 3120, 2947, 2872, 2246, 1714, 1574, 1463, 1429, 1347 cm⁻¹. HRMS (m/z): calculated as [A]⁺[A]⁺[B]⁻: 636.1855, found: 636.1821.

2.2.4.4. 1-Propargyl-3-methylimidazolium bis(trifluoromethane)sulfonimide (**2**): Yield: 34.66 g (82.0%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.83 (t, 1H), 3.86 (s, 3H), 5.18 (d, 2H) 7.73 (t, 1H), 7.78 (t, 1H), 9.19 (d, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 36.2, 39.1, 78.3, 115.1, 119.9 (q, CF₃), 122.5, 124.2, 137.2. FT-IR: 3275, 3158, 3125, 3034, 3029, 2987, 2138, 1932, 1849, 1798 cm⁻¹. HRMS (m/z): calculated as [A]⁺[A]⁺[B]⁻: 522.0699, found: 522.0674.

2.2.5. Physical Properties of Studied RTILs

The relevant chemical structures and physical properties of the RTILs used in this work are presented below in Fig. 2.2 and Table 2.2.



Figure 2.2. Chemical structures and name abbreviations for imidazolium-based RTILs used in this work.

RTIL	MW (g/mol)	Density (g/cm ³)	V_m (cm ³ /mol)
[NC-C ₁ mim][Tf ₂ N]	403.23	1.65	244
[NC-C ₃ mim][Tf ₂ N]	430.34	1.52	283
[NC-C ₅ mim][Tf ₂ N]	458.41	1.45	316
[HCC-C ₁ mim][Tf ₂ N]	402.24	1.54	261
[H ₃ C-C ₁ mim][Tf ₂ N]	391.31	1.52^{a}	258
[H ₃ C-C ₃ mim][Tf ₂ N]	419.37	1.44^{a}	291
[H ₃ C-C ₅ mim][Tf ₂ N]	447.42	1.38 ^a	325
^a Reference 15			

Table 2.2. Physical Properties (at 25 °C) of RTILs Used in this Work

The densities of the nitrile- and propargyl-functionalized RTILs were measured using a volumetric method described in our previous work with functionalized RTILs.[13]

2.2.6. Determination of Gas Solubilities in Studied RTILs

The ideal (single gas) solubility values of CO₂, N₂, and CH₄ for the RTILs were measured using a dual-volume, dual-transducer, pressure-decay apparatus at low pressures (~1 atm). Testing of gas mixtures is currently beyond the scope of this work and capability of our equipment. Thorough details on the construction, components, operation, and calculations associated with this equipment have been described in recent papers[13, 15].

2.3. Results and Discussion

2.3.1. Rationale behind Choice of Nitrile Functional Group

The nitrile functionality was chosen for this study due to its polar nature and large molar attraction constant relative to a methyl group (see Table 2.1). It has also been suggested, by analogy to CH_3CN , that the inclusion of a nitrile group(s) in a polymer or

solvent may be useful for improving CO_2 solubility and selectivity.[40] Lewis basic polar groups undergo acid-base interactions with the Lewis acidic (i.e., electrondeficient) carbon atom in CO_2 molecules. Furthermore, the chemical synthesis for tethering a nitrile-terminated alkyl unit to an imidazolium ring has been shown to be relatively simple. [34, 36, 37] The three nitrile-functionalized RTILs explored in this work (compounds **1a–c**) are direct analogues to the exhaustively studied 1-alkyl-3methylimidazolium (H₃C-C_nmim) RTILs.[8-10, 12, 15, 41-43] Thus, direct comparisons between the nitrile-terminated RTILs presented here and the methyl-terminated RTIL analogues reported in prior papers facilitates interpretation of experimental results and correlation of structure-property effects. For example, $[H_3C-C_1mim][Tf_2N]$ is taken to be a direct analogue for [NC-C₁mim][Tf₂N] (1a). The H₃C-C_nmim RTILs are control compounds for both alkyl length and terminal functional group (H_3C -) for the gas solubility studies. Furthermore, a terminal carbon-carbon triple bond group (i.e., an acetylene group) on the imidazolium cation was also investigated. Although the acetylene functionality is similar in electronegativity to the nitrile group, it does not have as strong a dipole moment like the carbon-nitrogen triple bond. [44] We consider this group to be a "non-polar" analogue for the nitrile functionality.

2.3.2. Ideal Gas Solubilities of CO₂, N₂ and CH₄, in Studied RTILs

The ideal (single gas) solubilities of CO₂, N₂, and CH₄ at 40 $^{\circ}$ C and 1 atm in each of the four the RTILs of interest are presented in Figs. 2.3a–2.3c.





Figure 2.3. Plots of ideal mole fractions of (a) CH₄, (b) N₂, and (c) CO₂ vs. substituent alkyl chain length (*n*) at 40 °C and 1 atm for the RTILs in this Study. ($\Delta = [NC-C_nmim][Tf_2N]$ RTILs; $\circ = [HCC-C_1mim][Tf_2N]$; $\Box = [H_3C-C_nmim][Tf_2N]$ RTILs. Error represents +/- one standard deviation. The measured error bars are within the symbol labels if they are not explicitly shown in the plots.

The Henry's constants of each gas for all of the RTILs used in this study are presented in Table 2.3. The method for calculating a Henry's constant has been detailed previously [13]. The relationship used to calculate a Henry's constant is shown below (Eqn. 7):

$$H_i = \frac{P_i}{x_i} \tag{7}$$

In the above equation, H_i is the Henry's constant (atm) for gas *i* in the RTIL, P_i is the equilibrium pressure (atm) of gas *i* above the RTIL (at 40 °C), and x_i is the equilibrium mole fraction of gas *i* in the RTIL. Examination of Eqn. 7 reveals that large and small Henry's constant values correspond to sparingly and highly soluble gases, respectively. The data in Figs. 2.3a–2.3c are plotted as mole fraction of gas vs. alkyl chain length, *n*.

Note: data for the non-functionalized imidazolium RTILs were taken from Camper and coworkers.[15] Solubilities for $[H_3C-C_3mim][Tf_2N]$ taken from the same work are predicted values.

RTIL	$H_{ m N_2}$	$H_{ m CH_4}$	$H_{\rm CO_2}$
[NC-C ₁ mim][Tf ₂ N]	1930 ± 50	1060 ± 40	58 ± 1
[NC-C ₃ mim][Tf ₂ N]	1630 ± 60	750 ± 10	47 ± 1
[NC-C ₅ mim][Tf ₂ N]	1300 ± 40	530 ± 10	40 ± 1
[HCC-C ₁ mim][Tf ₂ N]	1510 ± 40	650 ± 10	47 ± 1
[H ₃ C-C ₁ mim][Tf ₂ N]	1160 ± 80	550 ± 10	48 ± 1
[H ₃ C-C ₃ mim][Tf ₂ N]	970	420	41
[H ₃ C-C ₅ mim][Tf ₂ N]	900 ± 30	350 ± 10	40 ± 1

Table 2.3. Henry's Constants (atm) at 40 $^{\circ}$ C for N₂, CH₄, and CO₂ in the RTILs Tested in this Study

As can be seen in the plots in Fig. 2.3, the [NC-C_nmim][Tf₂N] RTILs exhibit reduced solubility of all gases compared to the "non-functionalized" [H₃C-C_nmim][Tf₂N] RTIL reference compound. However, the solubilities of N₂ and CH₄ for these compounds were reduced substantially more than CO₂. The percent decreases of CH₄ solubility in the [NC-C_nmim][Tf₂N] RTILs relative to the [H₃C-C_nmim][Tf₂N] RTILs were 47, 45, and 35% for n = 1, 3, and 5, respectively. Likewise for N₂, the solubility reductions were found to be 38, 40, and 33% for n = 1, 3, and 5, respectively. Both the alkyl- and nitrilefunctionalized RTILs displayed a strong linear correlation between alkyl length and gas mole fraction absorbed for all three gases. In the cases of CH₄ and N₂, the incorporation of the nitrile functionality seemed to shift the linear trends of the alkyl-substituted ionic liquids downward by a constant value (Figs. 2.3a and 2.3b). However, incorporation of the nitrile group had less of an impact on CO₂ solubility, particularly as alkyl spacer length was increased. For n = 1, the percent decrease in solubility was 17%, and for n = 5, there was no observable difference relative to the [H₃C-C_nmim][Tf₂N] RTILs. Incorporation of the nitrile group did not shift the linear CO₂ solubility trend of the [H₃C-C_nmim][Tf₂N] RTILs downward, as was observed for the CH₄ and N₂ solubility trends. In fact, it was found that as the alkyl spacer length increases in the [NC-C_nmim][Tf₂N] RTILs, the CO₂ solubility converges upon that of the [H₃C-C_nmim][Tf₂N] RTILs.

In contrast, incorporation of the acetylene group had no substantial effect on ideal CO_2 solubility. Instead, it was found that this functional group contributes to an appreciable reduction in CH_4 and N_2 solubility. However, the reduction was not as pronounced as that observed with the nitrile-functionalized RTILs (23% and 14% reduction for N_2 and CH_4 in [HCC-C₁mim][Tf₂N], respectively).

2.3.3. Ideal CO₂/N₂ and CO₂/CH₄ Solubility Selectivities

The ideal solubility selectivities for CO_2/N_2 and CO_2/CH_4 of all seven RTILs at 40 °C are shown in Figs. 2.4a and 2.4b, respectively. These solubility selectivities were calculated from the inverse ratio of Henry's constants for each gas pair. The data for the non-functionalized imidazolium RTILs were taken from a previous work by our group.[15] Solubilities for [H₃C-C₃mim][Tf₂N] taken from the same work are predicted values. As can be seen in Figs. 2.4a and 2.4b, substantial increases in ideal CO_2/N_2 and CO_2/CH_4 solubility selectivities relative to the analogous non-functionalized alkyl-substituted RTILs resulted from the inclusion of the nitrile group.



Figure 2.4. Plots of (a) ideal CO₂/N₂ solubility selectivity and (b) ideal CO₂/CH₄ solubility selectivity vs. substituent alkyl chain length (*n*) at 40 °C and 1 atm for the RTILs in this study. ($\Delta = [NC-C_nmim][Tf_2N] RTILs$; $\circ = [HCC-C_1mim][Tf_2N]$; $\Box = [H_3C-C_nmim][Tf_2N] RTILs$. Error represents +/- one standard deviation. The measured error bars are within the symbol labels if they are not explicitly shown in the plots.

The observed enhancements in CO_2/N_2 selectivity were calculated to be 36, 47, and 44% for n = 1, 3, and 5, respectively. Likewise, the observed CO_2/CH_4 selectivity enhancements were calculated to be 58, 57, and 52% for n = 1, 3, and 5, respectively. From Figs. 2.3a – 2.3c, it is clear that this enhancement in ideal CO_2 selectivity is a manifestation of the relative decrease in solubility of all three gases in the nitrile-functionalized RTILs. CH_4 solubility was reduced the most, followed by N_2 . CO_2 solubility was affected the least. Although the [NC-C_nmim][Tf₂N] RTILs have slightly lower CO_2 solubilities, they have a much greater rejection of CH_4 and N_2 compared to the [H₃C-C_nmim][Tf₂N] RTILs. The enhancement of CO_2/N_2 selectivity remains relatively constant over the range of alkyl lengths studied, tracking well with the relatively constant CO_2/N_2 selectivity is appreciably reduced as alkyl spacer length is extended, which follows the CO_2/CH_4 selectivity trend of the [H₃C-C_nmim][Tf₂N] RTILs.

The inclusion of the acetylene group has approximately the same enhancement effect on CO_2/N_2 solubility selectivity as the nitrile group does for the [NC- C_1 mim][Tf₂N] RTIL. As mentioned previously, the decrease in N₂ solubility in [HCC- C_1 mim][Tf₂N] is much less than that observed with [NC-C₁mim][Tf₂N]. However, this is compensated by a CO₂ solubility similar to the *n* =1 alkyl analogue, thus giving the acetylene- and nitrile-functionalized RTILs similar CO₂/N₂ selectivity performance. However, the CO₂/CH₄ selectivity of [HCC-C₁mim][Tf₂N] was found to be only marginally improved over the [H₃C-C₁mim][Tf₂N] analogue. This appears to be due to the relatively small reduction of CH₄ solubility, as mentioned previously, compared to [H₃C-C₁mim][Tf₂N]. It is also worth discussing the bulk solubility results of RTILs used in this study, which are shown in Table 2.4. It was expected that the observed enhancements in selectivity would be accompanied with a fairly substantial trade-off in bulk solubility as observed previously with the analogous *n*-alkyl-substituted RTILs.[15] However, this does not seem to be the case for the [NC-C_nmim][Tf₂N] and [HCC-C₁mim][Tf₂N] RTILs. Compared to the non-functionalized, *n*-alkyl-substutited RTILs examined in this study, the bulk solubility of the four functionalized analogues are comparable, or better in the case of [HCC-C₁mim][Tf₂N]. This attribute combined with the observed enhanced selectivity performance makes these functionalized RTILs better CO₂ separation solvents compared to their non-functionalized alkyl analogues.

		Solubility Selectivity	
RTIL	mol CO ₂ /(L RTIL)	$\frac{CO_2/N_2}{CO_2/N_2}$	CO ₂ /CH ₄
[NC-C ₁ mim][Tf ₂ N]	0.072	33	18
[NC-C ₃ mim][Tf ₂ N]	0.076	25	16
[NC-C ₅ mim][Tf ₂ N]	0.078	32	13
[HCC-C ₁ mim][Tf ₂ N]	0.083	32	14
[H ₃ C-C ₁ mim][Tf ₂ N]	0.083	24	12
[H ₃ C-C ₃ mim][Tf ₂ N]	0.085	23	10
[H ₃ C-C ₅ mim][Tf ₂ N]	0.078	22	8.7

Table 2.4. Bulk Solubility and Ideal Solubility Selectivity at 40 \degree C and 1 atm of Gases and RTILs Tested in this Study
2.3.4 Interpretation of Ideal Solubility and Ideal Solubility Selectivity with a Group Contribution Method and RST

To rationalize and understand the solubility and selectivity trends observed in this study, RST (Eqn. 2) and a group contribution method were applied to the data (Eqn. 6). Values for *a* and *b* in Eqn. (2) were determined by plotting $ln(H_{2,1})$ vs. $(\delta_1 - \delta_2)^2$ for each gas for the CH₃-C_nmim RTIL series. These values are shown in Table 2.5.

Table 2.5. Empirically Determined Values of *a* and *b* in Eqn. 2 at 40 °C

Gas	$a x 10^{3}$	$b (MPa^{-1})$
CO ₂	8.7	3.5
CH_4	7.4	4.4
N_2	2.9	5.6

The δ_1 values for the [H₃C-C_nmim][Tf₂N] RTILs were taken from the literature.[25] The values used for δ_2 are: $\delta_{CH4} = 11.6 \text{ (MPa}^{1/2}),[21] \delta_{N2} = 5.3 \text{ (MPa}^{1/2}),[21] and <math>\delta_{CO2} = 21.8 \text{ (MPa}^{1/2}).[40]$ Solubility parameters of the [NC-C_nmim][Tf₂N] and [HCC-C₁mim][Tf₂N] RTILs were determined using the values of *F* from Table 2.1 and *V*_m values in Table 2.2. Additionally, it was necessary to assign values for molar attraction constants of the cationic imidazolium ring and Tf₂N anion. These exotic polar groups and their substituents have not yet been tabulated with *F* values for use in group contribution calculations. However, an average, "lumped" value of *F* for the cation and anion (herein referred to as *F*_{TT}) was estimated from the solubility parameter data reported by another group.[25] In that work, the solubility parameters of [H₃C-C_nmim][Tf₂N] RTILs for *n* = 1, 3, 5, and 7 were determined via an intrinsic viscosity method. The value for *F*_{TT} along

with the solubility parameter values from which it was estimated are shown in Table 2.6. F_{IT} was determined from each solubility parameter using a group contribution as follows:

$$F_{IT} = V \cdot \delta_{RTIL} - n \cdot F_{CH_2} - 2 \cdot F_{CH_3} \tag{8}$$

Table 2.6. Solubility Parameters of $[H_3C-C_nmim][Tf_2N]$ RTILs and Estimated Values of F_{IT}

RTIL	δ (MPa ^{1/2})	F_{IT} (MPa ^{1/2} cm ³ mol ⁻¹)
[H ₃ C-C ₁ mim][Tf ₂ N]	27.6	6250
[H ₃ C-C ₃ mim][Tf ₂ N]	26.7	6330
[H ₃ C-C ₅ mim][Tf ₂ N]	25.6	6370
[H ₃ C-C ₇ mim][Tf ₂ N]	25.0	6380

In Eqn. 8, *V* is the RTIL molar volume, δ_{RTIL} is the ionic liquid solubility parameter (see Table 2.6), *n* is the number of -CH₂- groups, F_{CH2} is the molar attraction constant of a methylene linkage (Table 2.1), and F_{CH3} is the molar attraction constant of a methyl group (Table 2.1). The factor of 2 in front of F_{CH3} corresponds to the two methyl groups on the cation (i.e., the terminal alkyl methyl and the methyl group at the 3-position on the imidazolium ring). An average value of $F_{\text{IT}} = 6330 \text{ MPa}^{1/2} \text{ cm}^3 \text{ mol}^{-1}$ was used. It is not surprising that F_{IT} was considerably larger than typical molar attraction constants; this "compiled" *F* value accounts for several chemical groups that comprise the ring and anion, in addition to the charged nature of the cation and anion. It is worth noting that the F_{IT} values calculated are very consistent. This provides a good degree of confidence in using the average F_{IT} value for group contribution estimations of the solubility parameters of the functionalized RTILs in the present study. Estimations for the

solubility parameters of the [NC-C_nmim][Tf₂N] and [HCC-C₁mim][Tf₂N] RTILs were thus calculated using Eqn. 6, *F* values from Table 2.1, and F_{IT} calculated previously. These values are shown in Table 2.7. From these estimations, inclusion of the nitrile and acetylene functionalities appreciably increased the solubility parameter relative to the non-functionalized [H₃C-C_nmim][Tf₂N] RTIL analogues.

		Henry's Constants (atm)			Solubility Selectivity		
RTIL	δ (MPa ^{1/2})	$H_{ m N_2}$	H_{CH_4}	$H_{\rm CO_2}$	CO ₂ /N ₂	CO ₂ /CH ₄	
[NC-C ₁ mim][Tf ₂ N]	31.3	1900	1400	72	27	20	
[NC-C ₃ mim][Tf ₂ N]	28.9	1400	730	51	26	14	
[NC-C ₅ mim][Tf ₂ N]	27.6	1200	540	44	26	12	
[HCC-C ₁ mim][Tf ₂ N]	28.6	1300	680	49	27	14	

Table 2.7. Estimated Solubility Parameters, Henry's Constants and Ideal Solubility

 Selectivities at 40 °C and 1 atm for Functionalized RTILs in this Study

Using Eqn. 2 with the solubility parameters of the NC-C_nmim RTILs shown in Table 2.7, estimations were made for their Henry's constants for CO₂, CH₄, and N₂, as well as for their CO₂/N₂ and CO₂/CH₄ solubility selectivities. It was assumed that the values of *a* and *b* that were determined for the CH₃-C_nmim RTILs are approximately the same if they had been determined for an analogous set of [NC-C_nmim][Tf₂N] RTILs. The *H*(atm) estimations are also presented in Table 2.7. As can be seen in Table 2.7, the predicted trends in *H*(atm) values for all three gases are in good agreement with those experimentally measured (see Table 2.3). However, the values of H_{CH4} and H_{CO2} for [NC-C₁mim][Tf₂N] were overestimated by 33 and 23%, respectively; and the H_{N2} for CN-C₃mim was underestimated by 17%. Additionally, the RST/group contribution estimation predicted enhancements for CO₂/N₂ and CO₂/CH₄ solubility selectivity values relative to the [H₃C-C_nmim][Tf₂N] RTILs. Estimated selectivity enhancements are also

presented in Table 2.7. The CO_2/CH_4 solubility selectivity estimations are in very good agreement with measured selectivities (see Table 2.4). However, the estimated values of CO_2/N_2 selectivity are consistently underestimated. We speculate that this discrepancy arises because the above assumption for a and b is not entirely accurate. When plotting $ln(H_{2,1})$ vs. $(\delta_1 - \delta_2)^2$ for the [NC-C_nmim][Tf₂N] RTILs, it was found that the *a* values for CO_2 , CH_4 , and N_2 are approximately the same as those for the $[H_3C-C_nmim][Tf_2N]$ and $[NC-C_nmim][Tf_2N]$ RTILs. In the $[NC-C_nmim][Tf_2N]$ RTILs, however, the values of b for CH_4 and CO_2 are less, while the value of b for N_2 remains more or less unchanged. By examining Eqn. 1, we speculate that v_L (the theoretical condensed liquid molar volume of the gas) is less for CH₄ and CO₂ in the [NC-C_nmim][Tf₂N] RTILs, than in the [H₃C-C_nmim][Tf₂N] RTILs. (Note: the groupings $v_L \Phi/RT$ and $f_{pure,2}^L$ in Eqn. 1 correspond to b and a in Eqn. 2, respectively.) However, v_L for N₂ is approximately the same in both types of ILs. Reduction of the "liquid" molar volume of the gas would explain why higher CO₂ solubilities were measured compared to the predicted solubilities: physically, more gas can be absorbed. In this regard, this may also account for the 23% overestimation of H_{CH4} for [NC-C₁mim][Tf₂N].

2.3.5. Comparison with Previous Data

RST in combination with a group contribution method was used to predict the ideal CO_2/N_2 and CO_2/CH_4 solubility selectivities of the oligo(ethylene glycol)-functionalized RTILs studied previously by our group (see Fig. 2.5).[13]



Figure 2.5. General structure of oligo(ethylene glycol)-functionalized RTILs in previous work[13].

These predictions were made in the same manner as with the nitrile- and acetylenefunctionalized *n*-alkyl-imidazolium RTILs. The *F* values for ether linkages (–O–, $F = 235 \text{ MPa}^{1/2} \text{ cm}^3 \text{ mol}^{-1}$) was taken from Hoy in the Polymer Handbook.[28] The *F* values used for the -CH₃ and –CH₂– groups are shown in Table 2.1. The value for F_{IT} (6330 MPa^{1/2} cm³ mol⁻¹) was used, as discussed previously. Using these calculation parameters and methods, the predicted and measured selectivities for oligo(ethylene glycol)functionalized RTILs in Fig. 2.5 are shown in Table 2.8. Just as with the nitrile and acetylene functionalities, the CO₂/N₂ solubility selectivity is slightly underestimated, and the CO₂/CH₄ solubility selectivity prediction is in very good agreement with measured values.

		Measured Selectivity		Estimated Selectivity	
RTIL	δ (MPa ^{1/2})	CO ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /N ₂	CO ₂ /CH ₄
[P ₁ mim][Tf ₂ N]	27.4	30	13	26	12
[P ₂ mim][Tf ₂ N]	26.5	28	12	26	12
[P ₃ mim][Tf ₂ N]	26.0	33	12	24	10

Table 2.8. Predicted Solubility Parameters and Measured and Predicted Ideal Solubility Selectivities at 40 $^{\circ}$ C and 1 atm of RTILs in Previous Work[13] (Note: density of [P₂mim][Tf₂N] was re-measured to be 1.45 g/cc.)

Despite the discrepancy between the measured and predicted values, the group contribution method offers a more accurate prediction with RST than has been shown previously. In Fig. 6 of our prior work,[13] it was shown that the use of molar volume as

the sole predictor for CO₂/N₂ and CO₂/CH₄ selectivity for the PEG-functionalized RTILs is not accurate. Clearly, the measured selectivity enhancement was greatly underestimated. In that work, however, the values used for the RTIL solubility parameters were based solely on the molar volume using the Kapustinskii equation (see Eqns. 4 and 5). Undoubtedly, this solubility parameter estimation does not completely capture the chemical nature of the functionalized RTIL solvents in the previous work or this present study. To say the very least, it seems clear that a group contribution method offers an improvement for estimating RTIL solubility parameters. From our present and previous work, the molar volume argument which has been presented previously for the RTIL solubility parameter[13, 15, 20] seems insufficient when polar functionalities are included on the cation.

2.3.6. Limitations

Although a group contribution method and RST together can provide useful insight, there are specific limitations that must be understood. Clearly, the group contribution method is only as good as the tabulated F values that are available for specific chemical groups. Thus, it is important to consider the error associated with the F values reported by various researchers and what bearing the error has on any predictions one can make. Additionally, the extent to which one can use a group contribution method is limited to the number of chemical groups that have been investigated and tabulated. Fortunately, many relevant and useful chemical groups have already been investigated.[26-28]

In this work, we have proposed a value for the collective molar attraction constant of the imidazolium cation and the Tf₂N anion (F_{IT}). The value for F_{IT} is thus applicable only to imidazolium-based RTILs with the Tf_2N anion. However, there is the potential to assign *F* values to specific anions and cations in future solubility studies. We plan to extend this work to imidazolium-based RTILs with various anions with the intent of deconvoluting the chemical contribution of imidazolium and various anions. Similar studies can be done with various cations, such as substituted pyridiniums, ammoniums, and phosphoniums.

RST as applied to RTILs also has its limitations. To date, RST has only been applied to imidazolium-based RTILs.[12, 13, 15, 20] It is uncertain whether other types of cations used in RTIL design can be accurately modeled with this simple theory. Additionally, successful use of RST for RTILs has only been demonstrated at low pressures (~1 atm) and near-ambient temperatures and, therefore, may not be applicable in high pressure and/or high temperature regimes.

2.4. Conclusions

In summary, we have presented a straightforward synthesis of three imidazoliumbased RTILs incorporating an alkyl-tethered nitrile functionality and one imidazoliumbased RTIL incorporating the propargyl functionality. CO₂, CH₄, and N₂ ideal solubility data as well as CO₂/CH₄ and CO₂/N₂ ideal solubility selectivity data at 40 °C and 1 atm were measured for these RTIL gas solvents. It was found that the polar, terminal nitrile group of [NC-C_nmim][Tf₂N] RTILs contributed to enhanced CO₂/CH₄ and CO₂/N₂ solubility selectivity compared to analogous, non-functionalized, alkyl-substituted [H₃C-C_nmim][Tf₂N] RTILs. Furthermore, it was found that the inclusion of an acetylene group on the imidazolium cation provided CO₂/N₂ solubility selectivity performance similar the nitrile-functionalized RTIL of analogous alkyl length. However, CO₂/CH₄ solubility selectivity of the acetylene-functionalized RTIL did not show much improvement over the non-functionalized, alkyl-substituted, $[H_3C-C_1mim][Tf_2N]$ RTIL analogue. Bulk CO₂ solubility data of [NC-C_nmim][Tf₂N] and [HC-C₁mim][Tf₂N] RTILs was also presented. In addition to the marked improvement in CO₂ solubility selectivity, the nitrile- and propargyl-functionalized RTILs were found to have comparable bulk solubility relative to $[H_3C-C_nmim][Tf_2N]$ RTILs. Thus, a very small trade-off between bulk solubility and solubility selectivity was displayed with these functionalized RTILs. The results of this work are very similar to those reported previously in an analogous study where polar oligo(ethylene glycol) groups were tethered to the imidazolium cation.[13]

The use of a group contribution method to design, interpret, and extrapolate the performance of functionalized RTILs as gas absorbing solvents is unprecedented. The application of this well-established method allows for the prediction of solubility parameters of functionalized, imidazolium-based RTILs. Using these predicted solubility parameters with RST can subsequently provide reliable and reasonable predictions of the experimental solubility selectivity trends. In addition to aiding the interpretation of experimental data, a group contribution method can also be used in combination with RST as a guide for the systematic design of new functionalized RTIL gas solvents with targeted solubility properties. As shown in this work, the inclusion of the nitrile and acetylene functionalities increases the solubility parameter of a non-functionalized RTIL solvent by a certain degree. The result is a reduction in molar solubility of CO_2 , CH_4 , and N_2 and an enhancement in CO_2/CH_4 and CO_2/N_2 solubility selectivity.

We believe that a group contribution method has much utility as a *guide* for the design of new RTIL solvents, but not as a precise prediction of RTIL performance. It provides a screening tool for one to use when faced with various combinations of

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functional groups and subsequent RTIL gas solvents that can be used for a particular gas separation. Although simple models combining RST and a group contribution method may not provide exact predictions of physical properties such as gas solubility, they do offer a simple and straightforward method to predict the trends one may expect in RTILs with various functional groups.

Our current research in this area is focused on extension of this method to RTILs functionalized with other groups such as fluoroalkyl, siloxane, and benzyl substituents on the cation. Given the potential of RTILs, it is critical to understand how group contributions impact properties and performance.

2.5. Acknowledgments

Primary funding for this research from the U.S. Army Research Office (AB07CBT010) is gratefully acknowledged. Partial funding for this work for J.E.B. and C.J.G. from the National Science Foundation via a grant to D.L.G. (DMR-0552399) is also gratefully acknowledged. T.K.C also thanks the U.S. Dept. of Education for a GAANN Fellowship during the course of this work. The authors would also like to thank Shuji Kato for the HRMS purity analysis of our RTILs.

2.6. References

- 1. Shackley, S. and Gough, C., *Carbon capture and its storage: an integrated assessment*, 2006, Aldershot, England, Ashgate.
- 2. Basic research needs for geosciences: facilitating 21st century energy systems, 2007, Office of Basic Energy Sciences of the U.S. Dept. of Energy.
- 3. Brennecke, J.F. and Maginn, E.J., "Ionic liquids: innovative fluids for chemical processing." Aiche J. **2001**, *47*, 2384-2389.

- 4. Jessop, P.G. and Subramaniam, B., "Gas-expanded liquids." Chem. Rev. 2007, *107*, 2666-2694.
- 5. Rogers, R.D., Seddon, K.R., *Ionic liquids: industrial applications for green chemistry*. ACS symposium series; 2002, Washington, D.C.: American Chemical Society.
- 6. Rogers, R.D., Seddon, K.R., Volkov, S.V., *Green industrial applications of ionic liquids*. 2002, Boston: Kluwer Academic Publishers.
- 7. Wasserscheid, P. and Welton, T., *Ionic liquids in synthesis*, 2003, Weinheim: Wiley-VCH.
- Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F., Maginn, E.J., "Why is CO₂ so soluble in imidazolium-based ionic liquids?" J. Am. Chem. Soc. 2004, 126, 5300-5308.
- 9. Muldoon, M.J., Aki, S.N.V.K., Anderson, J.L., Dixon, J.K.,Brennecke, J.F., "Improving carbon dioxide solubility in ionic liquids." J. Phys. Chem. B **2007**, *111*, 9001-9009.
- 10. Anthony, J.L., Anderson, J.L., Maginn, E.J., Brennecke, J.F., "Anion effects on gas solubility in ionic liquids." J. Phys. Chem. B **2005**, *109*, 6366-6374.
- 11. Anthony, J.L., Maginn, E.J., Brennecke, J.F., "Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate." J. Phys. Chem. B **2002**, *106*, 7315-7320.
- 12. Camper, D., Scovazzo, P., Koval, C., Noble, R., "Gas solubilities in room-temperature ionic liquids." Ind. Eng. Chem. Res., **2004**, *43*, 3049-3054.
- Bara, J.E., Gabriel, C.J., Lessmann, S., Carlisle, T.K., Finotello, A., Gin, D.L.,Noble, R.D., "Enhanced CO₂ separation selectivity in oligo(ethylene glycol) functionalized room-temperature ionic liquids." Ind. Eng. Chem. Res. 2007, 46, 5380-5386.
- 14. Han, X. and Armstrong, D.W., "Ionic liquids in separations." Acc. Chem. Res. **2007**, *40*, 1079-1086.

- Camper, D., Bara, J., Koval, C., Noble, R., "Bulk-fluid solubility and membrane feasibility of Rmim-based room-temperature ionic liquids." Ind. Eng. Chem. Res. 2006, 45, 6279-6283.
- Anderson, J.L., Dixon, J.K., Brennecke, J.F., "Solubility of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide: Comparison to other ionic liquids." Acc. Chem. Res. **2007**, *40*, 1208-1216.
- 17. Dzyuba, S.V. and Bartsch, R.A., "Influence of structural variations in 1alkyl(aralkyl)-3-methylimidazolium hexafluorophosphates and bis(trifluorormethyl-sulfonyl)imides on physical properties of the ionic liquids." Chemphyschem 2002, *3*, 161.
- 18. MacFarlane, D.R., Golding, J., Forsyth, S., Forsyth, M., Deacon, G.B., "Low viscosity ionic liquids based on organic salts of the dicyanamide anion." Chem. Commun. **2001**, 1430-1431.
- 19. Bates, E.D., Mayton, R.D., Ntai, I., Davis, J.H., "CO₂ capture by a task-specific ionic liquid." J. Am. Chem. Soc. **2002**, *124*, 926-927.
- 20. Camper, D., Becker, C., Koval, C.,Noble, R., "Low pressure hydrocarbon solubility in room temperature ionic liquids containing imidazolium rings interpreted using regular solution theory." Ind. Eng. Chem. Res. **2005**, *44*, 1928-1933.
- 21. Prausnitz, J.M., Lichtenthaler, R.N., Azevedo, E.G.d., *Molecular thermodynamics* of fluid-phase equilibria. 3rd ed1999, Upper Saddle River, N.J.: Prentice-Hall.
- 22. Swiderski, K., McLean, A., Gordon, C.M., Vaughan, D.H., "Estimates of internal energies of vaporisation of some room temperature ionic liquids." Chem. Commun. **2004**, 2178-2179.
- Santos, L.M.N.B.F., Lopes, J.N.C., Coutinho, J.A.P., Esperanca, J.M.S.S., Gomes, L.R., Marrucho, I.M., Rebelo, L.P.N., "Ionic liquids: First direct determination of their cohesive energy." J. Am. Chem. Soc. 2007, 129, 284-285.
- 24. Kelkar, M.S. and Maginn, E.J., "Calculating the enthalpy of vaporization for ionic liquid clusters." J. Phys. Chem. B **2007**, *111*, 9424-9427.

- 25. Lee, S.H. and Lee, S.B., "The Hildebrand solubility parameters, cohesive energy densities and internal energies of 1-alkyl-3-methylimidazolium-based room temperature ionic liquids." Chem. Commun. **2005**, 3469-3471.
- 26. Hansen, C.M., *Hansen solubility parameters: a user's handbook*, 2000, Boca Raton, FL.: CRC Press.
- 27. Barton, A.F.M., *CRC handbook of solubility parameters and other cohesion parameters*, 1983, Boca Raton, FL.: CRC Press.
- 28. Brandrup, J., Immergut, E.H., Grulke, E.A., Knovel (Firm), *Polymer handbook*. 4th ed, 1999, New York: Wiley.
- 29. Arce, A., Earle, M.J., Katdare, S.P., Rodriguez, H., Seddon, K.R., "Mutually immiscible ionic liquids." Chem. Commun. **2006**, 2548-2550.
- 30. Arce, A., Earle, M.J., Katdare, S.P., Rodriguez, H.,Seddon, K.R., "Phase equilibria of mixtures of mutually immiscible ionic liquids." Fluid Phase Equilibria **2007**, *261*, 427-433.
- 31. Mikami, K., *Green reaction media in organic synthesis*, 2005, Ames, Iowa: Blackwell Pub.
- Mazille, F., Fei, Z.F., Kuang, D.B., Zhao, D.B., Zakeeruddin, S.M., Gratzel, M.,Dyson, P.J., "Influence of ionic liquids bearing functional groups in dyesensitized solar cells." Inorg. Chem. 2006, 45, 1585-1590.
- Lozinskaya, E.I., Shaplov, A.S., Kotseruba, M.V., Komarova, L.I., Lyssenko, K.A., Antipin, M.Y., Golovanov, D.G., Vygodskii, Y.S., "One-pot' synthesis of aromatic poly(1,3,4-oxadiazole)s in novel solvents-ionic liquids." J. Polym. Sci. Polym. Chem. 2006, 44, 380-394.
- 34. Zhao, D.B., Fei, Z.F., Scopelliti, R.,Dyson, P.J., "Synthesis and characterization of ionic liquids incorporating the nitrile functionality." Inorg. Chem. **2004**, *43*, 2197-2205.
- 35. Sasaki, K., Matsumura, S., Toshima, K., "A novel glycosidation of glycosyl fluoride using a designed ionic liquid and its effect on the stereoselectivity." Tetrahedron Lett. **2004**, *45*, 7043-7047.

- Fei, Z.F., Zhao, D.B., Pieraccini, D., Ang, W.H., Geldbach, T.J., Scopelliti, R., Chiappe, C.,Dyson, P.J., "Development of nitrile-functionalized ionic liquids for C-C coupling reactions: Implication of carbene and nanoparticle catalysts." Organometallics 2007, 26, 1588-1598.
- Zhang, Q.H., Li, Z.P., Zhang, J., Zhang, S.G., Zhu, L.Y., Yang, J., Zhang, X.P., Deng, Y.Q., "Physicochemical properties of nitrile-functionalized ionic liquids." J. Phys. Chem. B 2007, 111, 2864-2872.
- Vidis, A., Ohlin, C.A., Laurenczy, G., Kusters, E., Sedelmeier, G.,Dyson, P.J., "Rationalisation of solvent effects in the diels-alder reaction between cyclopentadiene and methyl acrylate in room temperature ionic liquids." Adv. Synth. Catal. 2005, 347, 266-274.
- Chiappe, C., Pieraccini, D., Zhao, D., Fei, Z., Dyson, P.J., "Remarkable anion and cation effects on Stille reaction in functionalized ionic liquids." Adv. Synth. Catal. 2006, 348, 68-74.
- 40. Lin, H.Q. and Freeman, B.D., "Materials selection guidelines for membranes that remove CO₂ from gas mixtures." J. Mol. Struct. **2005**, *739*, 57-74.
- 41. Baltus, R.E., Culbertson, B.H., Dai, S., Luo, H.M., DePaoli, D.W., "Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance." J. Phys. Chem. B **2004**, *108*, 721-727.
- 42. Kumelan, J., Kamps, I.P.S., Tuma, D., Maurer, G., "Solubility of CO₂ in the ionic liquid [hmim][Tf₂N]." J. Chem. Thermodyn. **2006**, *38*, 1396-1401.
- 43. Lee, B.C. and Outcalt, S.L., "Solubilities of gases in the ionic liquid 1-n-butyl-3methylimidazolium bis(trifluoromethylsulfonyl)imide." J. Chem. Eng. Data **2006**, *51*, 892-897.
- 44. Carey, F.A. and Sundberg, R.J., *Advanced organic chemistry*. 4th ed, 2000, New York: Kluwer Academic/Plenum Pub.

Chapter 3

Main-chain imidazolium polymer membranes for CO₂ separations: An initial study of a new ionic liquid-inspired platform

(As seen in: Carlisle, T. K. et al, J. Membr. Sci., 2010, 359 37-43)

Summary

Three dense polymer membranes composed of *main-chain*, poly(imidazolium)s (imidazolium ionenes) with decyl ("C10") spacer groups were fabricated and shown to be selective for CO_2 -based separations. An imidazolium ionene with the bromide counterion (**Polymer 1**) exhibited good H_2/CO_2 ideal (pure component) selectivity (6.0), while H_2 permeability was slightly lower than 1 Barrer. A "Robeson Plot" was used to compare the separation performance of **Polymer 1** to other dense polymer membranes. **Polymer 2** was structurally similar to **Polymer 1** with the exception of the bulky Tf_2N anion in place of the bromide. This polymer was found to have good CO_2/CH_4 and CO_2/N_2 ideal selectivities (20 and 24, respectively), but no H_2/CO_2 separation performance with a selectivity of 1.0. A stable composite film made from an imidazolium ionene (Polymer 2) and a room-temperature ionic liquid (RTIL) was also fabricated and showed large CO₂ permeability enhancements compared to the analogous neat polymer membrane, with little or no sacrifice in CO₂/N₂ and CO₂/CH₄ ideal selectivity. The separation performance of Polymer 2 and the Polymer 2-RTIL composite films were compared to previously studied "side-chain" poly(imidazolium)s (poly(RTIL)s) and other dense polymer membranes on "Robeson Plots." Polymer 2 and the Polymer 2-RTIL

composite films exhibited CO_2 permeabilities comparable to poly(RTIL)s. This is the first known study and application of imidazolium ionenes for CO_2 light gas separation membranes.

3.1. Introduction

In the modern era of global industrialization and elevated concerns over climate change, CO₂ capture (and other light gas separations) is an ever-growing area of academic and industrial research. Over the past few decades, room-temperature ionic liquids (RTILs) have slowly carved out a niche in the CO₂ separations community [1]. Vanishingly small vapor pressure, low flammability and a high degree of chemical tunability make RTILs exceptional "designer" solvents and promising replacements for volatile organic compounds (VOCs) in gas processing applications such as natural gas "sweetening" (the removal of CO₂ from CH₄)[1-4]. However, in the interest of cost (energy and monetary) and plant scale, it may be desirable to perform CO₂ separations with a selective membrane as opposed to the use of physical solvents. In light of this there has been a recent body of works demonstrating the feasibility of using imidazolium-based, polymerizable RTIL (poly(RTIL)) membranes and poly(RTIL)-RTIL composite films for CO₂ separations [5-10]. The general structures of imidazolium-based RTILs and poly(RTIL)s are illustrated in Fig. 3.1.



R₁ = alkane, oligo(ethylene glycol), alkanenitrile



Figure 3.1. General structure of (a) imidazolium-based room-temperature ionic liquids (RTILs) and (b) polymerizable room-temperature ionic liquids (poly(RTIL)s). 'X' can be any number of anions, such as Tf_2N , BF_4 , DCA, or PF_6 .

Similar to imidazolium-based RTILs, poly(RTIL) membranes have also proven to be selective in CO_2 -based separations [5-10]. As a poly(imidazolium) platform, poly(RTIL)s offer a large degree of substituent functionality and chemical tunability, which is valuable for improving membrane performance characteristics (permeability and selectivity). However, a less obvious limitation arises from the inherent polymer architecture. The functionality of all poly(RTIL)s exists as pendant side groups tethered to a hydrocarbon backbone. This fact begged two questions: (1) can linear, main-chain poly(imidazolium) membranes (i.e. all functionality in the polymer main-chain) be fabricated and used for light gas separations? And (2) how does the gas separation performance of such an architecturally disparate polymer compare to poly(RTIL)s? Based on the large body of work involved with quaternary ammonium-based "ionenes" (mainchain polycations [11])[12], there is good evidence that a variety of imidazolium-based ionenes might also be synthesized. Very recently, a group has reported on the synthesis and structureproperty relationships of imidazolium ionene segmented block copolymers [13]. Prior to that work, there have been a handful of studies that have reported on the synthesis of imidazoliumbased ionenes, although characterization methods and data were vague in those works [14-16].

Imidazolium-based ionenes (and ionenes in general) are synthesized via $S_n 2$ step growth rather than the chain addition radical polymerization used to make many commodity polymers and poly(RTILs). Two important, innate artifacts of ionene synthesis are: 1. complete polymer modularity, rather than an inherent hyrdrocarbon backbone, and 2. the lack of an equilibrium product typical to most step growth polymerizations, such as water produced from the formation of an ester (i.e. alcohol-carboxylic acid coupling) or hydrochloric acid produced from the formation of an amide (i.e. acid chloride – amine coupling). Scheme 3.1 and Fig. 3.2 summarize these important differences.



Scheme 3.1. General step growth synthesis to produce imidazolium-based ionenes. R_1 and R_2 can be any number of functional moieties. Note the absence of an equilibrium product.



Figure 3.2. Generic structures of (a) ionenes vs. (b) poly(RTIL)s. Note the modularity of R_1 or R_2 available in the structure represented in 2a as opposed to the inherent hydrocarbon backbone in 2b. Schematic representations of (c) a poly(RTIL)-RTIL composite and (d) an ionene-RTIL composite. Note the "free" cations shown in green in (c) and (d).

The versatility and functionality of the imidazolium cation as a functional materials platform has proven incredibly valuable in designing RTILs and poly(RTIL)s for CO₂ separations and other

applications [17-19]. However, to date there have been no reports investigating the potential of imidazolium-based ionenes as a new type of polymer membrane platform.

Herein, we present initial proof-of-concept that imidazolium-based ionenes can be synthesized and fabricated into CO_2 -selective gas separation membranes. Three membranes with systematically varied properties were examined, including one which was a composite film with "free" RTIL present. The structures of these three membranes along with [C₆mim][Tf₂N] are shown in Fig. 3.3.



Figure 3.3. Structures of imidazolium-ionene polymers studied in this work and the structure of the RTIL $[C_6mim][Tf_2N]$

Ideal (single gas) permeabilities for the gases CO_2 , CH_4 , N_2 and H_2 are reported along with CO_2/CH_4 , CO_2/N_2 , and H_2/CO_2 ideal permeability selectivities. CO_2 diffusivity and solubility of in the imidazolium-ionene membranes is also reported.

3.2. Experimental

3.2.1. Materials and instrumentation

2-methylimidazole, 1,10-dibromodecane and NaH were purchased from Sigma-Aldrich (Milauwakee, WI), lithium trifluoromethanesulfonimide (LiTf₂N) was purchased from 3M (St. Paul, MN). All chemicals were obtained in the highest purity available and were used without further purification. Gases were purchased from Airgas (Randor, PA) and were of at least 99.99% purity. A Mettler-Toledo XS205 DualRange balance was used to mass all reagents and polymers. ¹H NMR data were obtained using a Varian INOVA 400 Spectrometer (400 MHz). Membrane thicknesses were measured from images obtained with a JOEL JSM-6480LV scanning electron microscope operated in high vacuum mode. Example SEM images of the studied membranes can be found in the appendix. Details on the permeability apparatus are discussed in section 2.3. A 10-50 mTorr vacuum was used whenever it is stated that a monomer or polymer was "dried under vacuum".

3.2.2. Synthesis of 1,1'-(1,10-decanediyl)bis[2-methylimidazole](Monomer 1)

Monomer 1 was synthesized according to Scheme 3.2, as shown below. To a 3-neck, 500 mL round bottom flask equipped with a reflux condenser, 6.09 g of NaH (152 mmol) (60 wt % dispersion in mineral oil) was added while maintaining Ar flow into the flask. Prior to adding the NaH, the flask and reflux condenser were evacuated and purged with Ar several times. For the duration of the reaction, the 500 mL flask was maintained under an Ar atmosphere. 265 mL of THF (dried over a column of basic alumina) was added to the flask via cannula. The NaH suspension was then stirred with a magnetic stir bar. To the suspension, 10.00 g of 2-methylimidazole (121.8 mmol) was added very slowly, as hydrogen was rapidly evolved.



Scheme 3.2. Synthesis of Monomer 1

The reaction was then heated and refluxed at 40 °C for 1 h with the 500 mL flask completely sealed and left under Ar. 16.45 g 1,10-dibromodecane (54.8 mmol) was then added and the reaction temperature was increased to 65 °C for 24 h. After cooling the reaction at room temperature for 30 minutes, the resulting suspension was filtered with a medium glass frit funnel. THF was removed from the filtrate via rotary evaporation and the crude product was then dissolved in 300 mL of MeOH. The resulting solution and mineral oil precipitate were washed 3x with 150 mL of hexanes. MeOH was removed via rotary evaporation and the product was further dried under vacuum for 24 h at room temperature to afford a pale yellow solid. Yield = 13.33 g, 80.4 %, ¹H NMR (400 MHz, DMSO) δ 7.00 (d, *J* = 1.3 Hz, 2H), 6.69 (d, *J* = 1.3 Hz, 2H), 3.82 (t, *J* = 7.2 Hz, 4H), 2.24 (s, 6H), 1.61 (m, 4H), 1.23 (s, 12H).

3.2.3. Synthesis of Polymer 1

Polymer 1 was synthesized according to Scheme 3.3a, as shown below. 5.0000 g (16.531 mmol) of **Monomer 1** was massed into a 50 mL Erlenmeyer flask. Particular care was taken to ensure no monomer was stuck to the outside of the Erlenmeyer or on the weighing surface. **Monomer 1** was then dissolved in 6 mL of MeCN and added to a 1-neck, 250 mL round bottom flask. Extra care was taken to ensure all of the MeCN solution was added to the round bottom flask. The 50 mL Erlenmeyer was then washed 3x with 2 mL MeCN, with each

wash sequentially added to the 250 mL round bottom flask. Into a separate 50 mL Erlenmeyer flask, 4.9605 g (16.531 mmol) of 1,10-dibromodecane (**Monomer 2**) was dissolved in 6 mL of MeCN, added to the 250 mL flask, and washed in the exact manner as **Monomer 1** described above. The contents of the 250 mL flask were then stirred, heated and refluxed at 85 °C for 96 h, at which point the homogenous mixture had taken on a viscous, "honey" consistency. After cooling the reaction for 1 h at room temperature, the product was extracted with an additional 25 mL of MeCN and precipitated in 300 mL of Et₂O. The Et₂O was then decanted and the polymer was collected and dried under vacuum for 24 h to afford 9.826 g (98.6 % yield) of **Polymer 1**.



Scheme 3.3. (a) Synthesis of **Polymer 1** and (b) synthesis of **Polymer 2**

3.2.4. Synthesis of Polymer 2

Polymer 2 was synthesized according to Scheme 3.3b. 9.363 g of dried **Polymer 1** was massed and dissolved in 400 mL of DI water in a 500 mL Erlenmeyer flask. 10.29 g (35.86 mmol) of LiTf₂N was massed and dissolved in 50 mL of DI water. The LiTf₂N solution was then added to a 100 mL volumetric dropping funnel. With the **Polymer 1** solution stirring, the LiTf₂N solution was slowly added at a rate of 6-12 drops per minute. Upon addition of the LiTf₂N, a white precipitate could immediately be observed. After complete addition of LiTf₂N, the water and precipitate were stirred for an additional 24 h at room temperature. The precipitate

was then filtered, collected and stirred in 400 mL DI water in a separate 500 mL Erlenmeyer flask for 3 h. The process of filtering the precipitate and stirring in 400 mL of DI water for 3 h was repeated twice more followed by filtering and drying the product under vacuum for 48 h at 50 °C. 15.07 g (94.8% yield) of **Polymer 2** powder was obtained after being thoroughly dried.

3.2.5. Membrane fabrication

It should be noted that membranes could be formed reproducibly within our lab using the methods described in Section 2.2 below.

3.2.5.1. Fabrication of **Polymer 1** membrane

A 5 wt % solution of **Polymer 1** was prepared by dissolving 5.00 g of **Polymer 1** in 95 g of warm (40-50 °C) EtOH. 10 mL of this solution was cast onto a glass plate, which had been pre-treated with RainX®, a hydrophobic coating which aids in the removal of the polymer film from the glass surface. EtOH was removed by exposing the glass plate to ambient conditions (20-23 °C, 1 atm) for 4 h followed by placing the glass onto a hot plate at 65-70 °C for 8 h until a solid, uniform film had formed. Care was taken to prevent boiling of the EtOH. The film was further dried under vacuum for 36 h at 70 °C. After allowing the film to cool for 1 h under vacuum, it was gently peeled off the glass plate and a 47 mm diameter membrane was punched using a stainless steel die. The neat **Polymer 1** membrane was optically transparent and slightly yellow colored. An example of a neat **Polymer 1** membrane is shown in Fig. 3.4a.







Figure 3.4. Examples of neat polymer membranes. (a) Polymer 1, (b) Polymer 2 and (c) Polymer $2-[C_6mim][Tf_2N]$ composite.

3.2.5.2. Fabrication of Polymer 2 membrane

1.5 g of **Polymer 2** was densely piled onto the center of a glass plate that had been treated with RainX[®]. Heat was applied to the glass plate until the entirety of the polymer had melted. One to two sheets of wax paper (depending on what membrane thickness is desired) were placed on the perimeter of the glass plate to act as a spacer. An identical glass plate (treated with RainX[®]) was placed on top of the melted polymer and pressed to gently compress and spread **Polymer 2** between the two plates. A 3 kg weight was placed on the top glass plate and mild heat (approximately 70-75 °C) was applied to the pressed polymer melt via hot plate for 24 – 36 h. When all air bubbles in the melt had been extruded out of a region large enough to punch a 47 mm diameter membrane, the press was removed from heat and allowed to cool to room temperature. Once the pressed polymer had gone from a transparent melt to a slightly opaque solid it was further cooled to 4 °C in a refrigerator for 2 h. A razor blade was then used to gently

separate the plates and remove the **Polymer 2** sheet. After closely examining the sheet for any defects (i.e. cracks or bubbles), a 47 mm diameter die was used to punch a membrane. An example of a neat **Polymer 2** membrane is shown in Fig. 3.4b.

3.2.5.3. Fabrication of a composite film comprising Polymer 2 and 20 wt% $[C_6 mim][Tf_2N]$

To a 20 mL sample vial, 1.50 g of **Polymer 2**, 375 mg of $[C_6mim][Tf_2N]$ (synthesized in accordance with previous work [20]) and 15 mL of DMSO were added and homogenized using a vortex mixer and slight heating. The DMSO solution was then cast onto a RainX®-treated glass plate and heated at 70-75 °C for 10 h via hot plate to remove DMSO. The **Polymer 2-RTIL** composite was further dried under vacuum at 75 °C for 24 h. After cooling the composite to room temperature, an opaque, homogenous solid film had formed. This film was removed from the glass plate and cut into many smaller pieces. To generate a composite film, the same methods described in section 2.2.2 were applied using the small fragments of **Polymer 2-RTIL** composite. An example of a **Polymer 2-RTIL** composite film is shown in Fig. 3.4c.

3.2.6. Single Gas Permeability Measurements and Theory

Ideal (i.e. single gas) permeability studies using CO₂, N₂, CH₄, and H₂ were performed using a time-lag apparatus. All experiments with **Polymer 2** and the **Polymer 2-RTIL** were performed at ambient temperature with an upstream pressure of 2 atm and vacuum (< 1 torr) as the initial downstream pressure. Experiments with **Polymer 1** were similar with the exception of an upstream pressure of 4 atm. A complete description of the experimental apparatus has been reported in previous works [5,21]. Each membrane was degassed for 24 h and monitored for leaks prior to starting a set of experiments. All experiments were performed in triplicate (e.g. three separate CO₂, N₂, CH₄ and H₂ experiments) on a single membrane, and the membranes were allowed to degas under vacuum overnight between runs. The complete details on running permeability experiments and acquisition of data are provided in previous works [5,21]. The transport of light gases in the membranes studied here was assumed to follow a solutiondiffusion mechanism, where permeability (*P*) is equal to the product of gas diffusivity (*D*) and solubility (*S*) in the polymer as shown in Equation 1 [22,23].

$$P = D \cdot S \qquad (1)$$

It then follows that the membrane permeability selectivity ($\alpha_{i/j}$) is the ratio of permeabilities of two permeating species (*i* and *j*), as shown in Equation 2 [22,23]. The permeability selectivity can also be represented as the product of diffusivity selectivity and solubility selectivity, as shown on the right of Equation 2 [23].

$$\alpha_{i/j} = \frac{P_i}{P_j} = \begin{pmatrix} \underline{D}_i \\ \overline{D}_j \end{pmatrix} \cdot \begin{pmatrix} \underline{S}_i \\ \overline{S}_j \end{pmatrix}$$
(2)

The permeability selectivity gives a measure of how well a membrane discriminates for one gas over another. Assuming ideal gas behavior, the steady-state, single gas fluxes (J_i) were found according to Equation 3, where T is absolute temperature of the permeate and V is the known downstream cell volume [5,21]. The quantity p_i/t in Equation 3 was found from the slope of the linear (steady-state) portion of the permeate pressure (p_i) vs. time (t) curve. The effective area (A_{eff}) is the cross-sectional area of the membrane through which gas permeation occurs. This is assumed to be the area exposed to high pressure on the upstream side of the membrane.

$$J_i = \left(\frac{p_i}{t}\right) \frac{V}{A_{eff}T} \cdot \frac{273.15 \, K}{14.696 \, psi} \left(\frac{cm^3(stp)}{cm^2 \cdot s}\right), where \, p_i[=] \, psi \qquad (3)$$

The ideal (single gas) permeability (P_i) (flux normalized for pressure drop and membrane thickness) was then calculated from the average pressure driving force ($\overline{\Delta p_i}$) and membrane thickness (l) according to Equation 4 [5,21].

$$P_{i} = \frac{J_{i}}{\Delta p_{i}/l} (Barrers) \qquad (4)$$

where, 1 Barrer = $10^{-10} \frac{cm^{3} (stp) \cdot cm}{cm^{2} \cdot s \cdot cm Hg}$

The permeate diffusivity (D_i) was calculated from the membrane thickness (l) and time lag (O) according to Equation 5 [22]. Time lag was found by extrapolating the linear, steady-state portion of the p_i vs. *t* curve back to the x-axis and obtaining the x-intercept, which is O.

$$D_i = \frac{l^2}{6\Theta} \tag{5}$$

Having calculated P_i and D_i , Equation 1 was utilized to calculate permeate solubility (S_i) in the studied polymers

3.3. Results and Discussion

3.3.1. Ideal light gas permeability and permeability selectivity

The ideal permeabilites (P_i) were calculated according to Equation 4 and the ideal permeability selectivities were found from the ratio of ideal permeability values (P_i/P_j). The single gas diffusivities (D_i) were calculated from the time lag and membrane thickness according to Equation 5. Ideal solubilities were then calculated from D_i and P_i according to Equation 1. Solubility and diffusivity data for CO₂ are summarized in Table 3.1 while permeability and permeability selectivity values for the three membranes studied are summarized in Table 3.2. The sensitivity of our time lag apparatus did not allow for reliable diffusivity and solubility measurements of H₂, CH₄ and N₂. The permeability and selectivity data in Table 3.2 are plotted along with poly(RTIL) data and a selection of other dense polymer membrane data in Figs. 3.5ac as "Robeson Plots" [24].

Table 3.1. Diffusivities (D)^a and solubilities (S)^b of CO₂ in poly(imidazolium) membranes^c.

	D _{CO2}	S_{CO_2}
Polymer 1	23 ± 6	0.45 ± 0.09
Polymer 2	500 ± 10	0.79 ± 0.05
Polymer 2-RTIL	1200 ± 100	1.2 ± 0.1

^acm²-s⁻¹, ^bcm³ (STP)-cm⁻³-atm⁻¹, ^cerror represents one standard deviation

	P _{CO2}	P _{CH4}	P_{N_2}	P_{H_2}	P_{CO_2}/P_{CH_4}	P_{CO_2}/P_{N_2}	P_{H_2}/P_{CO_2}
Polymer 1	0.13 ± 0.02	n/d	n/d	0.84 ± 0.03	-	-	6.0 ± 0.2
Polymer 2	5.3 ± 0.1	0.26 ± 0.06	0.22 ± 0.02	5.3 ± 0.2	20 ±1	24 ±2	1.0 ± 0.1
Polymer 2-RTIL	19 ± 1	1.1 ± 0.1	0.83 ±0.09	-	17 ± 1	23 ±1	-

Table 3.2. Ideal permeability $(P_i)^a$ and ideal permeability selectivity (P_i/P_j) of light gases in poly(imidazolium) membranes^b.

^aBarrers, ^berror represents one standard deviation, n/d: non-detectable





Figure 3.5. Robeson Plots of light gases in the studied membranes. Note that data are plotted on a log-log scale. The upper bound and other dense polymer membrane data (O) are adapted from Robeson [22]. (a) Ideal H₂/CO₂ permeability selectivity vs. ideal H₂ permeability of **Polymer 1** and **Polymer 2** membranes (\Box), (b) Ideal CO₂/CH₄ permeability selectivity vs. ideal CO₂ permeability of **Polymer 2** and **Polymer 2-RTIL** composite membranes (\Box), and (c) Ideal CO₂/N₂ permeability selectivity vs. ideal CO₂ permeability of **Polymer 2** and **Polymer 2-RTIL** composite membranes (\Box). Also plotted in (b) and (c) are poly(RTIL) membranes (\blacktriangle) [5-6] and poly(RTIL)-RTIL composite membranes (\diamondsuit) [8-10]. The region within the dashed ellipse in (b) and (c) represents the spectrum of poly(RTIL) performance defined thus far.

In these three figures the permeability of the more permeable gas is plotted on the x-axis while permeability selectivity is plotted on the y-axis. These types of plots are useful for showing the performance of a membrane given a particular separation. What is generally seen with dense polymer membranes is a flux-selectivity tradeoff. That is, the more permeable a membrane is, the less selective it becomes for one particular permeate. Membranes represented in the extreme lower right corner of a Robeson Plot will have remarkably high permeabilities with very little discrimination between permeating species. On the contrary, membranes plotted in the extreme upper left corner are incredibly selective for a particular separation but have vanishingly small permeabilities.

Most polymer membranes fall somewhere between these two extremes and lie below an experimentally-determined upper bound, this is illustrated in Fig. 3.5a-c. These upper bounds represent the current permeability-selectivity limits and are based on large bodies of experimental data for each separation. A membrane that is both high in selectivity and permeability is very desirable, but very difficult to achieve in practice. However, the "upper bound" serves as a performance target or benchmark for newly designed polymer membranes.

3.3.2. Polymer 1 ideal permeability and permeability selectivity

As this study details the first experiments relating to gas permeability in a poly(imidazolium) halide membrane, it was unclear what results were to be expected for **Polymer 1**. Interestingly, ideal CH_4 and N_2 fluxes could not be detected with our apparatus (indicating they are likely below 0.01 Barrers), while H_2 and CO_2 permeabilities were found to be 0.85 Barrers and 0.14 Barrers, respectively. Although we could not measure H_2/CH_4 or H_2/N_2 selectivities, this initial result does imply that **Polymer 1** should be quite selective in H_2/CH_4 or

 H_2/N_2 separations. This also appears to be the case for H_2/CO_2 , where the H_2 selectivity is 6.0. As seen in Fig. 3.5a there are only a few reported examples of polymer membranes that are more selective than **Polymer 1**, although H_2 permeability in **Polymer 1** is relatively quite low at just below 1 Barrer. Despite a measurable H_2 flux, the sensitivity of the apparatus prevented a reliable measurement of H_2 time lag and, consequently, solubility and diffusivity. It seems reasonable, however, to largely attribute the measured H_2/CO_2 selectivity of **Polymer 1** to the incredibly low CO_2 diffusivity of 23 x10⁻¹⁰ cm²/s. From Table 3.1, the CO_2 diffusivity in **Polymer 2** is over an order of magnitude larger (500 x10⁻¹⁰ cm²/s) than **Polymer 1**, while there is roughly a factor of two difference in CO_2 solubility between the two polymers. The small bromide counterion likely allows for less inter-chain free volume and closer packing of adjacent polymer chains resulting in an overall glassy polymer. The smaller diffusing specie H_2 will experience less of an impediment in such a system, compared to CO_2 .

3.3.3. Polymer 2 ideal permeability and permeability selectivity

Polymer 2 (the ion-exchanged form of **Polymer 1** with the Tf_2N anion) provided interesting permeability and selectivity results. As opposed to **Polymer 1** where CH_4 and N_2 fluxes could not be measured, their permeabilities were respectively found to be 0.25 and 0.20 Barrers in **Polymer 2**. The H₂/CO₂ selectivity dropped dramatically to 1.00, where there was no measurable difference in CO₂ and H₂ permeabilities (5.3 Barrers). As often seen with dense polymer membranes, the large jump in H₂ permeability was accompanied with a sizable decrease in selectivity. Across the board, **Polymer 2** appeared to pose a much smaller diffusion resistance to all of the gases in this study, particularly to CO₂. As discussed in section 3.1.1, the diffusivity of CO₂ in **Polymer 2** is over one order of magnitude larger than in **Polymer 1**. Replacing the bromide with the bulky Tf₂N counterion appeared to have a much less dramatic effect on CO₂ solubility. The measured values of 0.45 ± 0.09 and 0.79 ± 0.05 cm³ (STP)cm⁻³-atm⁻¹ for

Polymers 1 and 2, respectively, indicate that the bulkier, fluorinated Tf₂N counterion contributed to a slight increase in CO₂ solubility. While **Polymer 2** does not outperform any poly(RTIL)s previously tested for CO_2/N_2 or CO_2/CH_4 separations, its performance does fall in the general range of poly(RTIL) data (see Figs. 3.5b and 3.5c). The selectivity of **Polymer 2** is very comparable to most poly(RTIL)s, but the permeability lies in the lower end of the poly(RTIL) performance spectrum. The architecture of **Polymer 2** appeared to have a negative effect on CO₂ solubility. The CO₂ solubility observed in alkyl-functionalized poly(RTIL)s [5] is roughly 4 cm³ (STP)cm⁻³-atm⁻¹ compared to 0.8 cm³ (STP)cm⁻³-atm⁻¹ for **Polymer 2**. Based on previous works [5,17] we speculate that the extent of CO₂ solubility in the polymer is dominated by the accessibility of CO_2 to the imidazolium and Tf_2N ions. In **Polymer 2** the ionic functionality is very dilute, or disperse, compared to poly(RTIL)s on account of the large C-10 alkane spacer. On the contrary, the architecture of **Polymer 2** had no significant observable effect on CO_2 diffusivity compared to poly(RTIL)s. The diffusivity of CO₂ in alkyl-functionalized poly(RTIL)s [5] is roughly between 2-8 $\times 10^{-8}$ cm²/s, where we observed 5 $\times 10^{-8}$ cm²/s in Polymer 2.

3.3.4. Polymer 2- $[C_6mim][Tf_2N]$ composite ideal permeability and permeability selectivity

As discussed in section 2.2.3, the **Polymer 2-RTIL** composite film contains 20% by weight the RTIL [C_6 mim][Tf₂N]. To the best of our knowledge, this is the first example of an ionene being interfaced with an RTIL to form a stable composite material. Addition of the RTIL component to a poly(RTIL) membrane has been consistently shown to increase permeability by up to an order of magnitude with little or no sacrifice in CO_2 selectivity [8-10]. Those works also demonstrated the possibility of facile addition of a functional, non-volatile, non-polymeric component to a poly(RTIL) without noticeably compromising the mechanical integrity of the membrane. Thus, compatibility of RTILs and imidazolium ionenes is of great consequence when considering the robustness and versatility of a "next generation" poly(imidazolium) materials platform. The general structure of poly(imidazolium)-RTIL composites with a "free" cation component are illustrated in Figs. 3.2c and 3.2d. Compared to Polymer 2, the Polymer 2-**RTIL** composite film was found to have CO₂, CH₄ and N₂ permeability enhancements of roughly 360%, 430% and 380%, respectively. Yet, there was little to no observed change in CO₂/N₂ selectivity and a very slight decrease in CO₂/CH₄ selectivity. This is not a surprising result given similar observed trends in a previous study [8]. The data shown in Figs. 3.5b and 3.5c illustrate the permeability enhancement in the **Polymer 2-RTIL composite**. As discussed in a previous work [8], the RTIL acts as a non-volatile plasticizer essentially opening up the polymer matrix and lowering resistance to gas diffusion for all species. As shown in Table 3.1, the CO₂ diffusivity in the **Polymer 2-RTIL** composite is roughly a factor of two larger than in **Polymer 2**. Since CH_4 is inherently the largest and slowest diffusing specie studied, it seems likely that inclusion of the RTIL component (i.e. plasticization and expansion of the polymer matrix) would enhance CH_4 diffusivity the most. Although we could not accurately measure CH₄ diffusivity, the permeability enhancements of 360% (CO₂) and 430% (CH₄) observed for the composite film indicate that this is likely the case. The reduced CO_2/CH_4 permeability selectivity observed for the **Polymer 2-RTIL** composite (Fig. 3.5b) is then primarily attributed to a decrease in CO₂/CH₄ diffusivity selectivity. The inherent similarities between diffusing species CO₂ and N₂ likely result in the proportional permeability enhancements we observed for

the composite film (360% for CO₂ and 380% for N₂). We believe that the retention of permeability selectivity between **Polymer 2** and the **Polymer 2-RTIL** composite film (Fig. 3.5c) is primarily due to little, if any, change in CO₂/N₂ diffusivity selectivity. Incorporation of $[C_6mim][Tf_2N]$ enhanced the permeability of **Polymer 2** from the lower end of the poly(RTIL) performance spectrum to the upper end. However, the separation performance of the **Polymer 2-RTIL** composite is still less than poly(RTIL)-RTIL composite films containing similar amounts of "free" RTILs (see Figs. 3.5b and 3.5c).

3.4. Conclusions

Although initial CO_2 separation performances are moderate in comparison to the poly(RTIL)-RTIL composite platform, the feasibility and viability of unprecedented *main-chain* poly(imidazolium) membranes (imidazolium-based ionenes) for CO_2 separations has been demonstrated. In this work, the synthesis and light gas (CO_2 , N_2 , CH_4 , H_2) separation performance of three unprecedented imidazolium ionene membranes was presented. **Polymer 1**, a poly(imidazolium) bromide salt, displayed fairly high H_2/CO_2 ideal permeability selectivity (6.0), while N_2 and CH_4 fluxes were non-detectible with our apparatus. However, H_2 permeability through **Polymer 1** was considerably low at 0.84 Barrers. **Polymer 2** was structurally similar to **Polymer 1** with the exception of the Tf₂N counterion in place of the bromide. The H_2/CO_2 selectivity of this membrane reduced greatly compared to **Polymer 1** while a significant improvement in CO_2 permeability was observed. Furthermore, **Polymer 2** did not display the N_2 and CH_4 "barrier" capability observed with **Polymer 1**. The ideal CO_2/N_2 and CO_2/CH_4 permeability selectivities were found to be comparable to most poly(RTIL)s (sidechain poly(imidazolium)s). However, the CO_2 permeability of **Polymer 2** is comparable to some

of the least permeable poly(RTIL)s. Compatibility of imidazolium ionenes with RTILs was also demonstrated in this work with a homogeneous and mechanically stable Polymer 2-RTIL composite film. Blending **Polymer 2** with 20 wt% of the RTIL [C₆mim][Tf₂N] gave a significant improvement in CO₂ permeability, while CO₂/N₂ selectivity decreased little, if any, and CO_2/CH_4 selectivity decreased slightly. The overall performance of the composite film was comparable to some of best performing neat poly(RTIL) membranes, but is less permeable compared to poly(RTIL)-RTIL composite films. These initial imidazolium-ionene membranes greatly lacked functionality, with a large composition of alkyl groups present as the decyl spacer and the imidazolium 'C₂' methyl group (Scheme 3.3 (a) and (b)). There are certainly many functional groups that can be incorporated into the main-chain spacer as well as on the imidazolium ring. The modularity of the poly(imidazolium) platform (see Scheme 3.1 and Fig. 3.2b), has the potential to give rise to hundreds, if not thousands, of potential new polymer materials. The possibilities for new materials are then greatly expanded by combining poly(imidazoliums) with RTILs to generate ionene-RTIL composites. This new polymer platform serves to augment the utility of imidazolium-based materials for CO₂ separations by adding versatility in polymer processing, polymer architecture and chemical tunability. Obviously, there is an enormous amount of research opportunity available both in the design and testing of new imidazolium membranes as well as other polymer properties. Future and current work includes studying the effect of spacer length and incorporation of polar spacer functionalities on CO₂ permeability and permeability selectivity. There is also interest in developing structure-property relationships (i.e. Tg and Tm) as the set of studied imidazolium ionene membranes grows.
3.5. Acknowledgements

Primary funding from the Army Research Office (AB07CBT010 and HDTRA1-08-1-0028) is gratefully acknowledged. T.K.C thanks the U.S. Dept. of Education for a GAANN Fellowship during the course of this work. J.E.B. thanks Mauro Dal-Cin of ICPET-National Research Council Canada for providing access to electronic databases from which Figs. 3.5a-c were generated. This work was performed in part at the University of Colorado's Nanomaterials Characterization Facility.

3.6. References

- 1. Anderson, J.L., Anthony, J.L., Brennecke, J.F., Maginn, E.J, *Gas solubilities in ionic liquids*, in: P. Wasserscheid, T. Welton (Eds.), *Ionic Liquids in Synthesis*, 2nd ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008, pp. 103-129.
- Camper, D., Bara, J., Koval, C., Noble, R., "Bulk-fluid solubility and membrane feasibility of Rmim-based room-temperature ionic liquids." Ind. Eng. Chem. Res. 2006, 45, 6279-6283.
- Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L., Noble, R.D., "Guide to CO₂ separations in imidazolium-based room-temperature ionic liquids." Ind. Eng. Chem. Res. 2009, 48, 2739-2751.
- 4. Han, X., Armstrong, D.W., "Ionic liquids in separations." Acc. Chem. Res. 2007, 40, 1079-1086.
- 5. Bara, J.E., Lessmann, S., Gabriel, C.J., Hatakeyama, C.J., Noble, R.D., Gin, D.L., "Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes." Ind. Eng. Chem. Res. **2007**, *46*, 5397-5404.
- 6. J.E. Bara, E.S. Hatakeyama, C.J. Gabriel, X. Zeng, S. Lessmann, D.L. Gin, R.D. Noble, "Synthesis and light gas separations in cross-linked gemini room temperature ionic liquid polymer membranes." J. Membr. Sci. **2008**, *316*, 186-191.

- 7. Bara, J.E., Gabriel, C.J., Hatakeyama, E.S., Carlisle, T.K., Lessmann, S., Noble, R.D., Gin, D.L., "Improving CO₂ selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents." J. Membr. Sci. **2008**, *321*, 3-7.
- 8. Bara, J.E., Hatakeyama, E.S. Gin, D.L., Noble, R.D., "Improving CO₂ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid." Polym. Adv. Technol. **2008**, *19*, 1415-1420.
- Bara, J.E., Gin, D.L., Noble, R.D., "Effect of anion on gas separation performance of polymer-room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. 2008, 47, 9919-9924.
- Bara, J.E., Noble, R.D., Gin, D.L., "Effect of free cation substituent on gas separation of polymer-room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. 2009, 48, 4607-4610.
- 11. Rembaum, A., Noguchi, H., "Reactions of N,N,N',N'-tetramethyl- α , ω -diaminoalkanes with α , ω -dihaloalkanes. II. x-y reactions." Macromolecules **1972**, *5*, 261-269.
- 12. Williams, S.R., Long, T.E., "Recent advances in the synthesis and structure-property relationships of ammonium ionenes." Prog. Polym. Sci. **2009**, *34*, 762-782.
- 13. Williams, S.R., Salas-de la Cruz, D., Winey, K.I., Long, T.E., "Ionene segmented block copolymers containing imidazolium cations: structure-property relationships as a function of hard segment content." Polymer **2010**, *51*, 1252-1257.
- 14. Suzuki, K., Yamaguchi, M., Hotta, S., Tanabe, N., Yanagida, S., "A new alkyl-imidazole polymer prepared as an ionic polymer electrolyte by in situ polymerization of dye sensitized solar cells." J. Photochem. Photobiol., A **2004**, *164*, 81-85.
- 15. Liang, Z.Y., Lu, C.X., Luo, J., Dong, B., "A polymer imidazole salt as phase-transfer catalyst in halex fluorination irradiated by microwave." J. Fluorine Chem. **2007**, *128*, 608-611.
- 16. Li, F., Cheng, F., Shi, J., Cai, F., Liang, M. Chen, J., "Novel quasi-solid electrolyte for dye-sensitized solar cells." J. Power Sources **2007**, *165*, 911-915.

- 17. Tang, J., Tang, H., Sun, W., Radosz, M., Shen, Y., "Poly(ionic liquid)s as new materials for CO₂ absorption." J. Polym. Sci., Part A: Polym. Chem. **2005**, *43*, 5477-5489.
- 18. Ohno, H., "Design of ion conductive polymers based on ionic liquids." Macromol. Symp. **2007**, *249-250*, 551-556.
- Marcilla, R., Sanchez-Paniagua, M., Lopez-Ruiz, B., Lopez-Cabarcos, E., Ochoteco, E. Grande, H., Mecerreyes, D., "Synthesis and characterization of new polymeric ionic liquid microgels." J. Polym. Sci., Part A: Polym. Chem. 2006, 44, 3958-3965.
- 20. Camper, D., Bara, J.E., Gin, D.L., Noble, R.D., "Room-temperature ionic liquid-amine solutions: tunable solvents for efficient and reversible capture of CO₂." Ind. Eng. Chem. Res. **2008**, *47*, 8496-8498.
- 21. Bara, J.E., Kaminski, A.K., Noble, R.D., Gin, D.L., "Influence of nanostructure on light gas separations in cross-linked lyotropic liquid crystal membranes." J. Membr. Sci. 2007, 288, 13-19.
- 22. Kesting, R.E., Fritzsche, A.K., *Polymeric Gas Separation Membranes*, John Wiley & Sons, INC., 1993.
- 23. Winston Ho, W.S., Sirkar, K.K., Membrane Handbook, Chapman & Hall, 1992.
- 24. Robeson, L.M., "The upper bound revisited." J. Membr. Sci. 2008, 320, 390-400.

Chapter 4

Ideal CO₂/Light Gas Separation Performance of Poly(vinylimidazolium) Membranes and Poly(vinylimidazolium)-Ionic Liquid Composite Films

(Manuscript prepared to submit to Journal of Membrane Science)

Summary

Six vinyl-based, imidazolium room-temperature ionic liquid (RTIL) monomers were synthesized and photo-polymerized to form dense poly(RTIL) membranes. The effect of polymer backbone (i.e., poly(ethylene), poly(styrene), and poly(acrylate)) and functional cationic substituent (e.g., alkyl, fluoroalkyl, oligo(ethylene glycol), and disiloxane) on ideal CO₂/N₂ and CO_2/CH_4 membrane separation performance was investigated. Vinyl-based poly(RTIL)s were found to be generally less CO₂-selective compared to analogous styrene- and acrylate-based poly(RTIL)s. The CO₂ permeability of *n*-hexyl- (69 barrers) and disiloxane-substituted (130 barrers) vinyl poly(RTIL)s were found to be exceptionally larger than that of previously studied styrene and acrylate poly(RTIL)s. The CO₂ selectivity of oligo(ethylene glycol)-functionalized vinyl poly(RTIL)s was enhanced, and the CO_2 permeability was reduced compared to the *n*hexyl-substituted vinyl poly(RTIL). Nominal improvement in CO₂/CH₄ selectivity was observed upon fluorination of the *n*-hexyl vinyl poly(RTIL), with no observed change in CO₂ permeability. However, rather dramatic improvements in both CO_2 permeability and selectivity were observed upon blending 20 mol % RTIL (emim Tf₂N) into the *n*-hexyl- and disiloxanefunctionalized vinyl poly(RTIL)s to form solid-liquid composite films.

4.1. Introduction

Membrane-based flue gas CO₂ removal (i.e., CO₂/N₂ separation) and natural gas sweeting (i.e., CO₂/CH₄ separation) are two areas of intensifying research [1-4]. Both separations pose an ongoing engineering challenge that have pushed researchers to develop new polymer chemistries and materials that possess both high CO₂ flux and selectivity. Industrial viability of new membrane materials is absolutely contingent on demonstrated separation performance. A relatively new and promising class of materials for membrane-based CO₂/light gas separations are room-temperature ionic liquids (RTILs). RTILs are a unique class of solvents that are molten salts at ambient conditions and possess distinctive chemical and physical properties that set them apart from traditional organic solvents. The most notable of these qualities is their vanishingly small vapor pressure [5]. RTILs, imidazolium-based RTILs in particular, have also demonstrated excellent CO₂ solubility and solubility selectivity over other light gases, such as CH₄ and N₂ [6-13]. Many researchers have exploited these two properties by employing RTILs in a membrane configuration known as a supported ionic liquid membrane, or SILM [12, 14-19]. Given the "negligible" vapor pressure of RTILs, there is no concern for liquid loss due to evaporation in SILMs. The CO₂/N₂ and CO₂/CH₄ separation performance of SILMs has, indeed, been shown to be quite impressive for a wide range of RTILs [12]; however, SILMs have a very limited range of industrial applicability. "Blowout" of the liquid RTIL component typically occurs with 1-2 atm or higher of transmembrane pressure differentia [12, 16]. Any industrially viable CO₂/N₂ or CO₂/CH₄ separation membrane must be stable to pressures much greater than any SILM can withstand.

To overcome this stability limitation inherent to SILMs, our group has previously investigated membranes based on solid, polymerized RTIL analogues, or poly(RTIL)s [20, 21]. These membranes were fabricated by photo-initiated chain-addition polymerization and/or crosslinking of styrene- and acrylate-functionalized RTIL monomers [20]. Examples of these previously studied monomers are shown in Fig. 4.1 (compounds **2** and **3**). While these membranes demonstrated good CO_2/N_2 and CO_2/CH_4 permeability selectivity and certainly did not suffer from the pressure limitations of a SILM, CO_2 permeability was found to be several orders of magnitude lower than analogous RTILs [12, 20, 21].



Figure 4.1. Structures of RTIL monomers **1a-1f** and the RTIL emim Tf_2N (**4**) investigated in this study. Structures of previously studied RTIL monomers **2a-2c** and **3a** and **3b** are also shown [20, 22].

An undesirable outcome of their stable, solid nature was a substantial decrease in gas diffusivity and permeability. A considerable effort was made to understand and improve upon acrylate- and styrene-based poly(RTIL) permeability and selectivity by functionalization of the imidazolium cation with a variety of *n*-alkyl or polar substituents [22]. For example, the permeability of a *n*hexyl-functionalized poly(RTIL) (**2b**, Fig. 4.1) was found to be considerably higher than an analogous methyl-functionalized poly(RTIL) (**2a**, Fig. 4.1) [20]. Additionally, improvements in CO₂/N₂ and CO₂/CH₄ selectivity were accomplished by incorporation of polar substituents, such as oligo(ethylene glycol) (**2c**, Fig. 4.1) [22]. However, any improvements in permeability and/or selectivity brought on by functionalization of the imidazolium cation were somewhat incremental. More dramatic improvements in poly(RTIL) CO₂ permeability were accomplished by incorporating up to 20 mol % of a non-polymerizable RTIL (i.e., a non-volatile liquid additive) in the prepolymer mixture (e.g., **4** in Fig. 4.1) [22-24]. Upon curing, these solid-liquid membranes contained 20 mol % "free RTIL" which acted as a non-volatile, selective plasticizing agent. Gas diffusivity in these hybrid materials was greatly improved with little-to-no sacrifice in CO₂/light gas selectivity [22-24]. Despite the presence of a liquid component, the Columbic ionion interactions between the free liquid RTIL and the solid polymer were found to give those poly(RTIL)-RTIL composite films a considerable degree of pressure stability as no blowout was observed [22-24].

One critical aspect of photo-polymerizable poly(RTIL) membranes that has not been thoroughly investigated is the effect of polymer structure (i.e., polymer backbone) on CO₂/light gas separation performance. As described above, previous efforts have essentially investigated imidazolium-functionalized poly(styrene) and, to a much lesser extent, imidazoliumfunctionalized poly(acrylate) membranes. However, a considerable amount of research in the areas of electrochemistry and gas chromatography have made use of vinylimidazolium-based poly(RTIL)s (i.e., **1** in Fig. 4.1) containing an imidazolium-functionalized polyethylene backbone [25-30]. Those prior papers suggest that the properties of poly(ethylene)-backbonebased poly(RTIL)s will differ quite significantly from poly(styrene) and poly(acrylate) backbone-based poly(RTIL)s with respect to CO₂ separation performance. However, it is unclear as to how vinyl-based poly(RTIL)s will differ and, more importantly, if they possess

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advantageous qualities (i.e., enhanced CO_2 permeability and/or selectivity) compared to styreneand acrylate-based poly(RTIL)s. Taking also into consideration that vinyl-imidazolium monomers are comparatively easier to synthesize and more thermally stable, we believe there is significant merit in gaining a more comprehensive understanding of the CO_2 separation performance of vinyl-based poly(RTIL) membranes.

One aim of this current study is to develop an understanding of the structure-property relationships of vinyl-based poly(RTIL)s. This was accomplished by evaluating the CO₂ separation performance of a series of functionalized vinylimidazolium polymers, some of which are chemically analogous to styrene- and acrylate-based poly(RTIL)s studied previously. We also aim to explore the permeability or selectivity improvements possible with vinyl-based poly(RTIL)-RTIL composite films that contain 20 mol % of free RTIL, similar to composite styrene-based poly(RTIL)-RTIL films previously studied.

This study also aims to investigate the CO_2/N_2 and CO_2/CH_4 separation performance of new fluoroalkyl- and disiloxane-functionalized vinylimidazolium poly(RTIL)s. Researchers have recently demonstrated improved CO_2 solubility and CO_2/CH_4 selectivity in fluoroalkyl- vs. alkylfunctionalized RTILs [14, 31]. These somewhat anomalous enhancements were attributed to the "fluorophilic" nature of CO_2 and to the unusually weak interaction of hydrocarbons (e.g., CH_4) with pendant fluorine groups [32-37]. However, there has been no report on the CO_2 permeability and permeability selectivity of analogous fluoroalkyl-functionalized poly(RTIL)s. There have also only been a handful of reports on the rather interesting disiloxane-functionalized RTIL [7, 38-41]. Although the SILM CO_2 permeability of this disiloxane-RTIL was quite good (ca. 770 barrers), CO_2/N_2 and CO_2/CH_4 permeability selectivity were somewhat reduced (ca. 19 and 10, respectively) compared to alkyl-functionalized RTILs [7]. It was pointed out that the bulky disiloxane group likely contributed to increased fractional free volume of the RTIL, which resulted in enhanced diffusivity to all studied gases [42-44]. The large amount of fractional free volume inherent to PDMS (poly(dimethylsiloxane), or silicone) is considered to be the cause of such rapid gas transport through silicone-based polymers [42-44]. Incorporation of the disiloxane group onto a poly(RTIL) tests an interesting design concept: whether poly(RTIL) membranes can be made substantially more permeable (i.e., more PDMS-like) by the incorporation of a silicone functional group on each repeat unit. As of yet, there have been no reports on the CO₂/N₂ or CO₂/CH₄ separation performance of a disiloxane-functionalized poly(RTIL). On one hand, PDMS is incredibly permeable (ca. 4500 barrers) but lacks greatly in selectivity [45]. On the other hand, poly(RTIL) membranes have been shown to be very selective for CO₂, but possess considerably low permeability (ca. 5-30 barrers) [20-22]. We believe the unique disiloxane functional group can offer valuable insight into the marriage of these two seemingly disparate, but promising polymers.

Herein, we present the room-temperature ideal CO₂ permeability and ideal CO₂/N₂ and CO₂/CH₄ permeability selectivity of six vinyl-based poly(RTIL) membranes (poly(**1a**)-poly(**1f**), Fig. 4.1) and two vinyl-based poly(RTIL)-RTIL composite films (poly(**1b**) and poly(**1f**) + 20 mol % emim Tf₂N (**4**), Fig. 4.1). The performance of poly(**1a**)-poly(**1c**) is also compared to the performance of membranes made using analogous styrene-based polymers poly(**2a**)-poly(**2c**) and analogous acrylate-based polymers poly(**3a**) and poly(**3b**).

4.2. Experimental

4.2.1. Materials and instrumentation

1H, 1H, 2H, 2H-Perfluorohexyl iodide, *N*-vinylimidazole, *N*-methylimidazole, and *p*toluenesulfonyl chloride were purchased from TCI America (Portland, OR). Iodomethane, diethylene glycol methyl ether, triethylene glycol monomethyl ether, 1-bromohexane, 2hydroxy-2-methylpropiophenone, and sodium iodide were purchased from Sigma-Aldrich (Milauwakee, WI). Chloromethylpentamethyldisiloxane was purchased from Gelest, Inc. (Morrisville, Pa). All chemicals were obtained in the highest purity available and used as is. All syntheses were performed in air unless otherwise noted. Cylinders of carbon dioxide, methane and nitrogen were purchased from Airgas (Randor, PA) and were of at least 99.99% purity. Porous poly(ether sulfone) support filters (Supor-200) were purchased from Pall Corporation (Port Washington, NY). ¹H, ¹³C, and ¹⁹F NMR spectra were acquired using a Bruker Avance-III 300 (300MHz). FT-IR spectra of monomers and polymers were acquired with a Nicolet Magna-IR 760 using a NaCl crystal substrate. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC823^e and a Julabo FT100 Intracooler.

4.2.2. Synthesis of monomers 1a-1f and RTIL 4

Monomers **1a-d** and the RTIL emim Tf₂N (**4**) (Fig. 4.1) were synthesized according to previous published literature procedures [8, 11, 20, 22]. The procedures detailing the synthesis of monomers **1e** and **1f** are contained in Sec. 4.2.2.5. and 4.2.2.6., respectively. The general synthetic route for all monomers synthesized in this study is shown in Scheme 4.1. Reported yields were calculated over the two reaction steps shown in Scheme 4.1.



Scheme 4.1. General synthesis of functionalized vinylimidazolium monomers **1a-1f** (Fig. 4.1) in this study.

4.2.2.1. 1-Vinyl-3-methylimidazolium bis(trifluoromethanesulfon)imide (**1***a*) Yield: 97 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 3.88 (s, 3H), 5.40 (dd, 1H), 5.93 (dd, 1H), 7.29 (dd, 1H), 7.81 (t, 1H), 8.14 (t, 1H), 9.39 (t, 1H). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 36.3, 108.8, 119.3, 119.9 (q, CF₃), 124.7, 129.1, 136.3. FT-IR: 3630, 3565, 3161, 3114, 2361, 2345, 1662, 1583, 1558, 1430, 1348, 1140, 1054, 955, 921, 843, 790, 741 cm⁻¹. HRMS (*m*/*z*): calculated as [A]⁺ [A]⁺[B]⁻, 498.0699; found, 498.0701.

4.2.2.2. 1-Vinyl-3-hexylimidazolium bis(trifluoromethanesulfon)imide (1b)

Yield: 97 %. ¹H NMR (300 MHz, DMSO-*d*₆): δ 0.86 (t, 3H), 1.27 (m, 6H), 1.81 (quintet, 2H), 4.18 (t, 2H), 5.42 (dd, 1H), 5.94 (dd, 1H), 7.28 (dd, 1H), 7.93 (t, 1H), 8.19 (t, 1H), 9.46 (t, 1H). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 13.7, 21.8, 25.1, 29.0, 30.5, 49.2, 108.5, 119.1, 119.5 (q, CF₃), 123.2, 125.9, 128.9. FT-IR: 3150, 2961, 2935, 1657, 1573, 1553, 1469, 1460, 1353, 1195, 1141, 1058, 954, 918, 848, 769, 763 cm⁻¹. HRMS (*m*/*z*): calculated as [A]⁺, 179.1543; found, 179.1540 4.2.2.3. 1-Vinyl-3-[2-(2-methoxy)-ethyl]imidazolium bis(trifluoromethanesulfon)imide (1c)

Yield: 95 %. ¹H NMR (300 MHz, DMSO- d_6): δ 3.21 (s, 1H), 3.42 (m, 2H), 3.56 (m, 2H), 3.80 (t, 2H), 4.39 (t, 2H), 5.42 (dd, 1H), 5.96 (dd, 1H), 7.32 (dd, 1H), 7.86 (t, 1H), 8.18 (t, 1H), 9.42 (t, 1H). ¹³C NMR (75.48 MHz, DMSO- d_6): δ 49.2, 58.0, 67.8, 69.4, 71.1, 108.7, 118.8, 119.5 (q, CF₃), 123.6, 128.8, 135.7. FT-IR: 3151, 3106, 2886, 1655, 1574, 1554, 1355, 1136, 1057, 955, 920, 844, 789, 741, 653, 617, 601, 571 cm⁻¹. HRMS (m/z): calculated as [A]⁺ [A]⁺[B]⁻, 674.1748; found, 674.1734

4.2.2.4. 1-Vinyl-3-[2-[2-(2-methoxy-ethoxy)-ethoxy]-ethyl]]imidazolium bis(trifluoromethanesulfon)imide (**1d**)

Yield: 95 %. ¹H NMR (300 MHz, DMSO- d_6): δ 3.23 (s, 3H), 3.48 (m, 8H), 3.80 (t, 2H), 4.38 (t, 2H), 5.44 (dd, 1H), 5.97 (dd, 1H), 7.32 (dd, 1H), 7.89 (t, 1H), 8.20 (t, 1H), 9.40 (t, 1H). ¹³C NMR (75.48 MHz, DMSO- d_6): δ 49.2, 58.0, 67.8, 69.5, 71.2, 108.6, 121.6, 119.5 (q, CF₃), 123.7, 128.8, 135.7. FT-IR: 3151, 2883, 1658, 1572, 1553, 1453, 1352, 1195, 1137, 1058, 956, 924, 851, 790, 762, 740 cm⁻¹. HRMS (*m*/*z*): calculated as [A]⁺, 241.1547; found, 241.1543.

4.2.2.5. 1-Vinyl-3-(3,3,4,4,5,5,6,6,6-Nonafluorohexyl)imidazolium

bis(trifluoromethanesulfon)imide (1e)

1H,1H,2H,2H-perfluorohexyl iodide (25.0 g, 66.8 mmol) and MeCN (17 mL) were added to a 1neck 250 mL round-bottomed flask equipped with a magnetic stir bar and reflux condenser. *N*vinylimidazol (18.9 g, 200 mmol) was then added and the reaction was heated to 70 $^{\circ}$ C, stirred, and refluxed for 48 h. The reaction was then cooled and the crude product was precipitated in

Et₂O (200 mL) and placed in a freezer at -4 °C for 12 h. The Et₂O was then decanted and the product was dissolved in deionized water (250 mL) (some heating was required to dissolve the iodide product) and washed with EtOAc (3 x 75 mL) and Et₂O (1 x 75 mL). The aqueous phase was then transferred to a 500-mL Erlenmeyer flask equipped with a magnetic stir bar and Lithium bis(trifluoromethanesulfon)imide (23.0 g, 80.1 mmol) was added. A precipitate was immediately observed and the reaction was stirred for 3 h at room temperature. The aqueous layer was decanted and the precipitate was dissolved into EtOAc (250 mL) and washed with deionized water (5 x 100 mL). The organic phase was then dried over anhydrous MgSO₄ and stirred with activated charcoal for 12 h to remove minor color impurities. The EtOAc layer was then filtered over plug of basic alumina and removed via rotary evaporation. The product was further in vacuo (~10 mtorr) at ambient temperature overnight. Monomer 1e was isolated as a clear, viscous oil. Yield: 24.1 g (58 %). ¹H NMR (300 MHz, DMSO- d_6): δ 3.04 (m, 2H), 4.61 (t, 2H), 5.45 (dd, 1H), 5.95 (dd, 1H), 7.33 (dd, 1H), 8.02 (t, 1H), 8.20 (t, 1H), 9.58 (t, 1H). ¹⁹F NMR $(282.40 \text{ MHz}, \text{DMSO-}d_6): \delta$ -126.0 (m, 2F), -124.3 (m, 2F), -113.7 (m, 2F), -80.9 (m, 3F), -79.0 (m, 6F). FT-IR: 3152, 3111, 3086, 2362, 2335, 1662, 1575, 1558, 1350, 950, 920, 881, 831, 792, 742, 696 cm⁻¹. HRMS (m/z): calculated as $[A]^+ [A]^+ [B]^-$, 962.0569; found, 962.0559.

4.2.2.6. 1-vinyl-3-(1,1,3,3,3-pentamethyl-disiloxanylmethyl)imidazolium

bis(trifluoromethanesulfon)imide (1f).

Chlormethylpentamethyldisiloxane (5.95 g, 30.2 mmol) along with MeCN (12 mL) were added to a 1-neck, 100-mL round-bottomed flask equipped with a magnetic stir bar and reflux condenser. *N*-vinylimidazole (8.53 g, 90.6 mmol) was then added and the reaction was heated to $60 \,^{\circ}$ C, stirred and refluxed for 48 h. The reaction mixture was then cooled, and added to Et₂O (200 mL) to precipitate the crude product, and then placed in a freezer at -4 $^{\circ}$ C for 12 h. After decanting the Et₂O, the crude product was dissolved in deionized water (150 mL) and washed with EtOAc (3 x 70 mL) and Et₂O (1 x 70 mL). The aqueous phase was then transferred to a 250-mL Erlenmeyer flask equipped with a magnetic stir bar. Lithium

bis(trifluoromethanesulfon)imide (9.55 g, 33.3 mmol) was then added, and the reaction mixture was stirred for 3 h at room temperature. A precipitate was immediately observed upon addition of the lithium salt. Most of the aqueous phase was then decanted, and the product was dissolved in Et₂O (150 mL) (solubility in Et₂O is highly unusual for RTILs) and washed with deionized water (5 x 75 mL). The organic phase was then dried over anhydrous MgSO₄ and stirred with activated charcoal for 12 h to remove minor discoloration. The Et_2O was then filtered over a plug of basic alumina and removed via rotary evaporation. The product was further dried in vacuo (~10 mtorr) at ambient temperature for an additional 12 h. Monomer 1f was isolated as a white crystalline solid with a melting point of 34-36 °C. However, we found that this monomer could also exist as a super-cooled liquid at room temperature for long periods of time. Yield: 6.78 g (41.9 %). ¹H NMR (300 MHz, DMSO- d_6): $\delta 0.03$ (m, 9H), 0.20 (m, 6H), 3.91 (s, 2H), 5.40 (dd, 1H), 5.94 (dd, 1H), 7.31 (dd, 1H), 7.71 (t, 1H), 8.20 (t, 1H), 9.31 (t, 1H). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 1.0, 1.5, 41.5, 108.15, 119.1, 119.5 (q, CF₃), 124.2, 128.8, 134.5 FT-IR: 3148, 2959, 1652, 1569, 1549, 1353, 1260, 1137, 1052, 957, 920, 845, 760, 740, 657, 617 cm⁻¹. HRMS (m/z): calculated as $[A]^+ [A]^+ [B]^-$, 790.1866; found, 790.1860

4.2.3. Poly(RTIL) membrane fabrication and characterization

Our methods for photo-polymerized poly(RTIL) membrane fabrication are described in detail elsewhere [20, 22, 46]. For completeness, they are described briefly here as well: Photo-

initiator, 2-hydroxy-2-methylpropiophenone (0.01 g, 1 wt. %), was added to 1 g of RTIL monomer in a small vial. The initiator was thoroughly blended into the monomer using a vortex mixer. Care was taken to make sure no bubbles were present in the mixture. The monomer was then slowly poured onto a piece of porous poly(ether sulfone) (PES, Supor-200), which was positioned on top of a hydrophobically-treated (RainX®) quartz glass plate. Another hydrophobically-treated quartz plate was then placed on top of the monomer solution. The two quartz plates were held together with binder clips and the supported monomer film was placed under a 365 nm UV lamp (Spectroline Model XX-15A) at an intensity of 1 mW/cm² for 3 h to complete polymerization. A razor blade was used to carefully wedge the two plates apart and the polymer film was peeled off. A 47-mm diameter stainless steel die was then used to cut out a disc from the PES-supported section to use for experimentation.

DSC studies on poly(**1a**)-poly(**1f**) revealed the presence of various, unique thermal transitions between -15 °C and 48 °C, depending on the differing chemical properties of each poly(imidazolium) derivative. DSC data for polymers poly(**1a**)-poly(**1f**) are shown in Table 4.1, below. No melt transitions were observed up to 250 °C. Number average molecular weight (M_n) could not be determined by end-group analysis from ¹H NMR spectra of polymer samples. The chemical shifts of hydrogen atoms on the initiator fragments were obfuscated by broad polymer peaks (Figs. B.1-B.6). We were also unable to obtain relative molecular weights of samples via GPC. Polymer samples were either not soluble in the GPC solvent (DMF or THF) or they stuck to the column packing. The ¹H and ¹³C NMR spectra of polymer samples can be found in Appendix B. Vinyl group conversion of all polymer samples was greater than 99% by both FT-IR and ¹H NMR spectroscopy.

4.2.3.1. Poly(1a)

¹H NMR (300 MHz, CD₃CN) δ 8.05–8.30 (br s, imidazolium C2), 6.66–7.70 (br m, imidazolium C4 and C5), 3.06–4.23 (br, -CH₃), 2.02–2.54 (br s, -CH₂CH-). ¹³C NMR (75.48 MHz, CD₃CN) δ 135.93, 127.16, 122.92, 118.67, 118.32, 37.65, 2.15, 1.87, 1.60, 1.32, 1.05, 0.77, 0.49.

4.2.3.2. Poly(1b)

¹H NMR (300 MHz, CD₃CN) δ 8.14–8.43 (br s, imidazolium C2), 6.57–7.73 (br m, imidazolium C4 and C5), 3.05–4.35 (br, -N-C*H*₂-(CH₂)₄-CH₃), 2.12–2.64 (br s, -C*H*₂C*H*-), 0.83–1.86 (br m, -CH₂-(C*H*₂)₄-C*H*₃). ¹³C NMR (75.48 MHz, CD₃CN) δ 122.88, 118.64, 118.30, 31.80, 26.72, 23.27, 14.24, 2.15, 1.87, 1.59, 1.32, 1.04, 0.77, 0.49.

4.2.3.3. Poly(1c)

¹H NMR (300 MHz, CD₃CN) δ 8.12–8.45 (br s, imidazolium C2), 6.54–7.78 (br m, imidazolium C4 and C5), 4.06–4.39 (br s, -O-C*H*₃), 3.50–3.93 (br m, -N-C*H*₂C*H*₂-O-), 3.21–3.43 (br s, -C*H*₂C*H*-). ¹³C NMR (75.48 MHz, CD₃CN) δ 118.31, 2.14, 1.87, 1.59, 1.32, 1.04, 0.77, 0.49.

4.2.3.4. Poly(1d)

¹H NMR (300 MHz, CD₃CN) δ 8.10–8.59 (br s, imidazolium C2), 6.61–7.82 (br m, imidazolium C4 and C5), 4.02–4.51 (br s, -O-C*H*₃), 3.40–3.97 (br m, -N-C*H*₂C*H*₂-O-), 3.13–3.39 (br s, -C*H*₂C*H*-). ¹³C NMR (75.48 MHz, CD₃CN) δ 122.89, 118.64, 118.34, 72.30, 70.69, 58.85, 2.15, 1.87, 1.59, 1.32, 1.04, 0.77, 0.49. 4.2.3.5. Poly(1e)

¹H NMR (300 MHz, CD₃CN) δ 8.22–8.68 (br s, imidazolium C2), 6.78–7.79 (br m, imidazolium C4 and C5), 3.35–4.70 (br, -*CH*₂*CH*₂-C₄F₉), 2.21–3.04 (br m, -*CH*₂*CH*-). ¹³C NMR (75.48 MHz, CD₃CN) δ 207.96, 118.36, 30.72, 30.46, 30.20, 29.95, 29.69, 2.15, 1.87, 1.59, 1.32, 1.04, 0.77, 0.49.

4.2.3.6. Poly(1f)

¹H NMR (300 MHz, CD₃CN) δ 8.13–8.44 (br s, imidazolium C2), 6.81–7.57 (br m, imidazolium C4 and C5), 3.29–4.27 (br, -N-CH₂-Si-), 2.10–2.61 (br s, -CH₂CH-), 0.01–0.45 (br m, -Si(CH₃)₂-O-Si(CH₃)₃). ¹³C NMR (75.48 MHz, CD₃CN) δ 87.63, 83.36, 79.10, 74.84, 61.89, 2.15, 1.88, 1.60, 1.32, 1.04, 0.76, 0.49.

4.2.4. Single gas permeability, diffusivity and solubility measurements and theory

Ideal (i.e., single gas) permeabilities and diffusivities were measured using a constant volume-variable pressure, or time-lag, apparatus. A full description of this experimental setup is described elsewhere [20]. All experiments were performed at room temperature with an upstream pressure of 2 atm (0.8 atm for SILMs) and vacuum (< 10 mtorr) as the initial downstream pressure. The permeability of each gas was measured at random three separate times on a single membrane, (i.e., three separate CO_2 , H_2 , N_2 , and CH_4 experiments). Complete details on performing these experiments and data analysis can be found in previous papers [20, 47]. Light gas transport through the studied polymer composite films was assumed to follow a

solution-diffusion mechanism, whereby the separation of a species *i* from a mixture of gasses is based on relative differences in kinetic transport (i.e., diffusivity, D_i) and thermodynamic affinity (i.e., solubility, S_i) in the membrane [45]. The permeability of a species *i* (P_i) through dense materials is related to solubility (S_i) and diffusivity (D_i) of *i* by the relationship shown in Eq. (1) [45].

$$P_{i} \equiv S_{i} \times D_{i} \quad (1)$$

Where, $P_{i} = \frac{J_{i}}{\Delta p_{i}} l \quad (2)$
$$P[=]barrer, 1 \ barrer = 10^{-10} \frac{cm^{3}(STP) \cdot cm}{cm^{2} \cdot s \cdot cm \ Hg}$$

In Eq. (2), J_i is the species *i* steady state volume flux (STP), *l* is the membrane thickness, and Δp_i is the average transmembrane partial pressure drop. The quantity J_i was determined by Eq. (3) where, p_i is the downstream pressure (psia), *t* is the experimental time, *V* is the downstream volume, A_{eff} is the effective membrane surface area, and *T* is the absolute temperature.

$$J_i = \left(\frac{dp_i}{dt}\right) \frac{V}{A_{eff}T} \cdot \frac{273.15K}{14.696 \, psi} \left(\frac{cm^3(STP)}{cm^2s}\right) \quad (3)$$

The quantity (dp_i/dt) in Eq. (3) was determined from the slope of the linear (i.e. steady state) portion of the p_i vs *t* curve. The permeability selectivity in materials that follow a solution diffusion mechanism is defined as [45]:

Permeability Selectivity
$$(\alpha_{i/j}) = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j}$$
 (4)

The selectivity is typically determined as the ratio of the permeability of the more permeable species to the permeability of the less permeable species. As shown in Eq. (4), permeability selectivity can be written as the product of diffusivity and solubility selectivity. The time-lag apparatus allows for single gas diffusivity (D_i) measurements according to Eq. (5), where, l is the membrane thickness, and (θ) is the "time-lag" [48].

$$D_i = \frac{l^2}{6\theta} \quad (5)$$

The time-lag was determined by extrapolation of the linear, steady state, portion of the p_i vs t curve to the t-axis, where the intercept is equal to θ . The slope of this line is equal to the quantity (p_i/t) in Eq. (3). Once D_i and P_i were determined, single gas solubilities (S_i) were calculated from Eqs. (1) and (5).

4.3. Results and Discussion

The measured ideal CO₂ permeability and ideal CO₂/N₂ and CO₂/CH₄ permeability selectivity of the studied vinyl-based poly(RTIL)s is summarized in Table 4.1. CO₂ diffusivity, solubility, diffusivity selectivity, and solubility selectivity data for these polymers is reported in Table 4.1 as well. The composite film ideal permeability and permeability selectivity values of poly(**1b**) + 20 mol % **4** and poly(**1f**) + 20 mol % **4** are reported in Table 4.2. The CO₂ permeability and selectivity of all membranes studied here as well as previously studied styreneand acrylate-based membranes are plotted in Fig. 4.2 as "Robeson Plots" [49]

					CO ₂ /N ₂ Selectivity		CO ₂ /0	CO ₂ /CH ₄ Selectivity		
Polymer	T _g (^o C)	P(CO ₂)	D(CO ₂)	S(CO ₂)	Р	S	D	Р	S	D
Poly(1a)	48	4.8 ± 0.3	1.1 ± 0.1	3.3 ± 0.2	29	26	N/A	40.	10.	3.9
Poly(1b)	40	69 ± 5	14 ± 1	3.8 ± 0.2	17	29	0.60	9.9	6.8	1.4
Poly(1c)	-10	14 ± 1	3.4 ± 0.4	3.2 ± 0.2	32	30.	1.1	32	9.5	3.3
Poly(1d)	-15	26 ± 2	5.2 ± 0.5	3.9 ± 0.3	34	23	1.4	25	7.7	3.3
Poly(1e)	52	69 ± 5	13 ± 1	3.9 ± 0.3	11	20.	0.60	14	7.0	2.0
Poly(1f)	-10	130 ± 10	29 ± 2	3.5 ± 0.3	14	23	0.63	8.7	5.8	1.5
Poly(2a) ^f	-	9.2 ± 0.5	1.7 ± 0.1	4.0 ± 0.1	32	N/A	N/A	39	19	2.0
Poly(2b) ^f	-	32 ± 1	7.7 ± 0.4	3.9 ± 0.1	28	39	0.70	17	6.9	2.5
Poly(2c) ^g	-	22 ± 1	N/A	N/A	44	N/A	N/A	29	N/A	N/A
Poly(3a) ^f	-	7.0 ± 0.4	1.5 ± 0.1	3.6 ± 0.1	31	N/A	N/A	37	21	1.6
Poly(3b) ^f	-	22 ± 1	3.6 ± 0.4	4.5 ± 0.4	30.	N/A	N/A	22	7.7	2.9

Table 4.1. Ideal room temperature CO_2 permeability, diffusivity, and selectivity of studied membranes as well as those studied previously.^{a,b,c,d,e}

^aPermeability [=] barrer, 1 barrer = 10^{-10} cm³(stp)cm cm⁻²s⁻¹cmHg⁻¹

^bDiffusivity [=] cm²s⁻¹

^cSolubility [=] cm³(stp)cm⁻³atm⁻¹

^dN/A signifies that our apparatus could not accurately measure the quantity

^eError represents one standard deviation acquired from three replicates

^fRef. [20]

^gRef [22]

Polymer	P(CO ₂)	$P(CO_2)/P(N_2)$	$P(CO_2)/P(CH_4)$
Poly(1b)	69 ± 5	17	9.9
Poly(1b) + 20 mol % 4	105 ± 9	21	12
Poly(1f)	130 ± 10	14	8.7
Poly(1f) + 20 mol % 4	190 ± 10	19	11
4 (SILM of emim Tf_2N)	1000 ± 100	31	16

Table 4.2. Ideal CO₂ permeability and permeability selectivity of studied composite films.^{a,b}

^aPermeability [=] barrer, 1 barrer = 10^{-10} cm³(stp)cm cm⁻²s⁻¹cmHg⁻¹

^bError represents one standard deviation acquired from three replicates





Figure 4.2. CO₂ separation performance of studied vinyl (\square) poly(RTIL)s plotted on (a) CO₂/N₂ and (b) CO₂/CH₄ Robeson Plots. The performance of previously studied styrene (\square), and acrylate (\blacksquare) poly(RTIL)s are also shown [20, 22]. Performance of composite vinyl poly(RTIL) films (\blacklozenge) with 20 mol % of 4 and the SILM performance of 4 (\bigcirc) are plotted as well. All data were acquired at room temperature. Poly(RTIL) or RTIL structure is identified next to each data point (Fig. 4.1). Experimental error is within the data points. Robeson's upper bounds were adapted from a prior work [49].

Based on the acquired data shown in Tables 4.1 and 4.2 and Fig. 4.2, we found that vinylbased poly(RTIL)s possessed CO₂ permeabilities that were either substantially less or substantially greater than analogous styrene- and acrylate-based poly(RTIL)s. Whether or not we observed a relative reduction or enhancement seemed to depend strongly on the vinyl poly(RTIL) substituent. For example, the CO₂ permeability of the methyl-functionalized vinyl polymer (poly(**1a**)) was 4.8 barrers compared to 9.2 barrers for the analogous methylfunctionalized styrene polymer (poly(**2a**)). In that case, the styrene poly(RTIL) CO₂ permeability was approximately double that of the analogous vinyl poly(RTIL). Likewise, the methylfunctionalized acrylate poly(RTIL) (poly(**3a**)) had a permeability of 7.0 barrers, or about 1.5 times greater than the analogous vinyl-based poly(**1a**). We noticed that the primary factor differentiating CO₂ permeability in poly(**1a**) from poly(**2a**) and poly(**3a**) was diffusivity. For example, the diffusivity of poly(**1a**), was 1.1 x 10^{-8} cm² s⁻¹ compared to 1.7 x 10^{-8} and 1.5 x 10^{-8} cm² s⁻¹ for poly(**2a**) and poly(**3b**), respectively. These data seem to suggest that poly(**1a**) possesses a much glassier, or rigid polymer matrix compared to the analogous acrylate- and styrene-based poly(RTIL)s. It seems likely that the relatively small methylimidazolium pendant group in poly(**1a**) would interrupt linear chain packing substantially less than the comparatively bulkier pendant groups in poly(**2a**) and poly(**3a**), respectively [44]. It may be that the dense ion content of this polymer contributes to the formation of a very rigid polymers matrix that inhibits permeate diffusion. The permeability of the *n*-hexyl-functionalized vinyl polymer (poly(**1b**)) was 69 barrers compared to 32 barrers for the analogous styrene polymer (poly(**2b**)). In this case, The CO₂ permeability of poly(**1b**) was nearly double the permeability of poly(**2b**) (the styrene analogue) and approximately 3 times larger than the analogous butyl-functionalized acrylate polymer (poly(**3b**)).

We also noticed that the critical factor differentiating CO₂ permeability of poly(**1b**) from poly(**2b**) and poly(**3b**) was diffusivity. For instance, the CO₂ diffusivity of poly(**1b**), was 14 x 10^{-8} cm²s⁻¹ compared to 7.7 x 10^{-8} cm²s⁻¹ and 3.6 x 10^{-8} cm²s⁻¹ for poly(**2b**) and poly(**3b**) respectively. Contrary to what was observed for poly(**1a**), these data suggest that the *n*-hexyl vinyl polymer (poly(**1b**)) matrix was significantly less rigid than those of poly(**2b**) and poly(**3b**). In other words, the *n*-hexyl substituent in poly(**1b**) seemed to reduce linear chain packing much more effectively than the *n*-hexyl and *n*-butyl substituents in poly(**2b**) and poly(**3b**). The CO₂ permeability of *n*-hexyl-functionalized poly(**1b**) was also about 14 times larger than methylfunctionalized poly(**1a**). We also noticed that the T_g of poly(**1b**) was slightly reduced compared to that of poly(**1a**) (Table 1). Such a dramatic increase in CO₂ permeability was not observed

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between poly(**2a**) and poly(**2b**), or between poly(**3a**) and poly(**3b**), as shown in Table 4.1 and Fig. 4.2. For example, the CO₂ permeability of poly(**2b**) (*n*-hexyl-functionalized) was only about 3.5 times larger than poly(**2a**) (methyl-functionalized). The large difference in CO₂ diffusivity between poly(**1a**) and poly(**1b**) (Table 4.1) suggests that the morphological effect of increased substituent length on the polymer matrix was very substantial. Whereas in poly(**2b**) and poly(**3b**), the effect of increased substituent length was somewhat dwarfed by the presence of the already bulky styrene-imidazolium and ethyl-acrylate-imidazolium groups. Others have noted that the effect of flexible, pendant side groups is more substantial when the polymer backbone is inherently very rigid [44] (e.g., as with poly(**1a**)).

The styrene- and acrylate-based poly(RTIL)s were generally found to be more CO₂selective than the analogous vinyl poly(RTIL)s studied here. For instance, the ideal CO₂/N₂ permeability selectivity of poly(**2b**) was shown to be 28, while the selectivity of poly(**1b**) measured here was only 17. Likewise, the ideal CO₂/CH₄ permeability selectivity of poly(**2b**) was 17 compared to 9.9 for poly(**1b**). In comparing solubility selectivity of poly(**1b**), poly(**2b**), and poly(**3b**) in Table 4.1, we notice very little difference between the three membranes. The styrene and acrylate polymers (poly(**2b**) and poly(**3b**)) are, however, significantly more diffusivity-selective compared to poly(**1b**). This implies that the bulkier side groups present in poly(**2b**) and poly(**3b**) contribute to enhanced size-selective ability compared to poly(**1b**). Poly(**1a**), on the other hand, has significantly higher CO₂/CH₄ diffusivity selectivity (3.9) compared to poly(**2a**) (2.0) and poly(**3a**) (1.6). This is likely due to the efficient chain packing and highly rigid nature of poly(**1a**) discussed above.

The CO₂ permeability selectivity of the vinyl poly(RTIL)s was certainly improved by incorporation of an oligo(ethylene glycol) substituent (**1c** and **1d** in Fig. 4.1). The CO₂/N₂

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permeability of poly(1c) was 32 compared to 17 for poly(1b), for example. A similar observation was made previously with styrene-based polymers [22] (e.g., comparing the CO₂ selectivity of poly(2c) and poly(2b) in Table 4.1 and Fig. 4.2). The polar alkylether groups in PEG, or PEO, are believed to interact with the quadrapole moment of CO_2 , resulting in improved CO_2 selectivities compared to a simple hydrocarbon substituent of similar length [50]. Incorporation of the oligo(ethylene oxide) appendages were also found to drastically reduce T_g compared to the alkyl-functionalized vinyl polymers (Table 1), indicating that poly(1c) and poly(1d) are inherently rubbery materials. The CO_2 permeability of poly(1c) was slightly less than that of poly(2c) (14 barrers compared to 22 barrers), perhaps because the bulkier repeat unit side group on poly(2c) interrupts chain packing more effectively, allowing for lower diffusion resistance. However, we found that the permeability of poly(1c) could be improved nearly 90% by extending the length of the oligo(ethylene glycol) group in poly(1d). The CO₂ permeability was enhanced from 14 barrers in poly(1c) to 26 barrers in poly(1d), respectively, with little change in CO_2 selectivity. Although there does not seem to be any clear advantage to using styrene- rather than vinyl-based oligo-ether poly(RTIL)s for CO₂/CH₄ separation, the styrene membrane poly(2c) certainly possessed superior selectivity performance for CO_2/N_2 separation.

The fluoroalkyl-functionalized vinyl poly(RTIL) (poly(**1e**)) possesses the same CO₂ permeability (69 barrers) as the analogous alkyl-functionalized poly(RTIL) (i.e., poly(**1b**)). This seems reasonable when considering how structurally similar the two polymers are to one another. We did, however, find the CO₂/CH₄ permeability selectivity to be enhanced by approximately 40% in poly(**1e**) relative to poly(**1b**). This too is not highly unexpected since similar observations have been made previously with fluorinated RTILs [14] and other fluorinated liquids [33-35]. Except for hydrocarbons (i.e., CH₄, C₂H₄, C₂H₆, etc.), gas solubility typically increases with the degree of fluorination [35, 36]. The observed reduction in CO_2/N_2 solubility and permeability selectivity between poly(**1b**) and poly(**1e**) suggests that N₂ solubility was increased upon fluorination. Researches have recently observed a similar trend for the CO_2/N_2 permeability selectivity of fluorinated RTILs [14]. The CO_2/CH_4 solubility selectivity remained relatively unchanged between poly(**1b**) and poly(**1e**) (Table 4.1). However, the CO_2/CH_4 diffusivity selectivity of poly(**1e**) seems to be enhanced by the fluorinated appendage in poly(**1e**). The observed enhancement in CO_2/CH_4 selectivity was nonetheless a marginal improvement compared to the alkyl-functionalized vinyl poly(**1b**). However, these results do merit future studies investigating poly(RTIL)s with higher degrees of fluorination, or perhaps blends with highly fluorinated RTILs.

At 130 barrers, the disiloxane-functionalized membrane (poly(**1f**)) is, by far the most light gas permeable poly(RTIL) synthesized and measured by our lab. To our knowledge, poly(**1f**) is also the most permeable neat poly(RTIL) membrane reported to date. However, poly(**1f**) is clearly one of the least selective poly(RTIL)s with CO₂/N₂ and CO₂/CH₄ permeability selectivity values of 14 and 8.7, respectively. Incorporation of the disiloxane appendage certainly imparts a certain degree of PDMS-like character to the poly(RTIL), which has been observed by others for neutral styrene polymers [44]. For instance, the diffusivity of poly(**1f**) is 29 x 10⁻⁸ cm² s⁻¹, which is nearly 4 times larger than the most permeable styrene-based poly(RTIL) membrane (i.e., poly(**2b**)) and about twice as large as that of poly(**1b**), the *n*-hexyl substituted vinyl polymer. The T_g of poly(**1f**) (-10 °C) was also substantially less than the two studied alkylfunctionalized polymers, poly(**1a**) and poly(**1b**). The T_g and diffusivity data of poly(**1f**) (Table 1) suggests that this polymer is inherently rubbery and likely possesses higher fractional free volume compared to poly(**1a**) or poly(**1b**). Two well-known traits of silicone-based polymers are their considerably large fractional free volume and extremely low glass transition temperatures [42-44]. These properties give silicone rubbers characteristically high gas diffusivity and characteristically low permeability selectivity [42-44]. The relatively low values measured here for CO_2/N_2 and CO_2/CH_4 solubility and diffusivity selectivity, as well as reduced T_g , indicates that the disiloxane functional group in poly(**1f**) contributes to an enhancement in fractional free volume. Highly permeable, marginally selective poly(RTIL)s, such as poly(**1b**) and poly(**1f**) may not be without certain advantages, however.

Poly(1b) (n-hexyl-substituted) and poly(1f) (disiloxane-substituted) stand apart from the other studied vinyl poly(RTIL)s, and certainly from previously studied styrene and acrylate poly(RTIL)s, because of their considerably high CO₂ permeability. It can be argued that any merits in using these poly(RTIL)s for CO₂/N₂ and CO₂/CH₄ separation are diminished by their considerably low permeability selectivity for these gas separation pairs. However, with such inherently good CO_2 permeabilities, poly(1b) and poly(1f) are, perhaps, ideal candidates to blend with "free RTIL." Recall that previous papers in the literature demonstrated improved permeability with little or no loss in permeability selectivity by incorporating 20 mol % free RTIL into poly(RTIL) membranes [23, 24, 46]. However, in those studies, the parent poly(RTIL) selectivity was greater than the RTIL (emim Tf_2N , 4), which has ideal CO_2/N_2 and CO_2/CH_4 permeability selectivity of 31 and 16, respectively. In the case of poly(1b) and poly(1f), the inherent permeability selectivity was found to be significantly lower than emim Tf2N (4) (Table 4.2 and Fig. 4.2). However, we found that incorporation of 20 mol % 4 contributes to enhanced CO₂ permeability and CO₂ permeability selectivity in composite films of poly(**1b**) and poly(**1f**) (see Table 4.2 and Fig. 4.2). For example, the CO₂ permeability of poly(1b) was increases from 69 to 105 barrers, while CO_2/N_2 permeability selectivity was increased from 17 to 21. Likewise,

the permeability of poly(1f) was found to increase from 130 to 190 barrers, while CO_2/N_2 selectivity increases from 14 to 19. This seemingly anomalous behavior completely contradicts the well-known tradeoff between polymer membrane flux and selectivity. Significant improvement in membrane permeability is generally coupled with a loss in selectivity and vice versa. In previous papers it was shown that incorporation of 20 mol % free RTIL would, at best, maintain a constant value for CO_2 selectivity [23, 24, 46]. In most cases, both CO_2/N_2 and CO_2/CH_4 selectivity were shown to drop slightly [23, 24]. The coupled improvement observed for the free RTIL-blended composite films of poly(1b) and poly(1f) indicates that poly(RTIL) selectivity can be improved by incorporation of a more CO₂-selective RTIL. Since the ultimate goal is to develop poly(RTIL)-RTIL films that approach or exceed the "upper bound,"[49] perhaps it is more appropriate to focus on designing new poly(RTIL) materials that possess enhanced permeability, rather than selectivity. On the other hand, the primary focus of RTIL design, or selection, should be toward maximizing CO₂/light gas selectivity. Maximizing membrane performance can then be realized upon blending these solid and liquid materials into stable composite structures. Compared to styrene- and acrylate-based poly(RTIL)s, vinyl-based poly(RTIL)s seem to be better candidates for the design of new, more permeable polymeric membranes. The disiloxane moiety seems particularly promising as a candidate to further investigate improved poly(RTIL) permeability performance.

4.4. Conclusions

Six vinyl-based poly(RTIL) membranes were synthesized and evaluated for their ideal CO_2/N_2 and CO_2/CH_4 separation performance. The structure-property relationships of these vinyl poly(RTIL)s were evaluated by tethering *n*-alkyl, oligo(ethylene glycol), fluoroalkyl, and

disiloxane substituents to the vinyl monomer cation. Compared to analogous styrene- and acrylate-based poly(RTIL)s with different polymer backbones, the CO₂ permeability of the vinyl-based poly(RTIL)s was found to be either substantially less or considerably larger. The difference depended greatly upon the length of the *n*-alkyl substituent on the poly(RTIL) repeat units, where the longer *n*-hexyl group was found to contribute to substantially higher CO_2 permeability. The vinyl-based poly(RTIL)s were also found to be generally less CO₂-selective for both gas separation pairs studied. Incorporation of the oligo(ethylene glycol) functional group was found to improve vinyl poly(RTIL) CO₂ selectivity. However, the CO₂ selectivity of the oligo(ethylene glycol)-substituted vinyl poly(RTIL) was slightly less compared to the analogous styrene poly(RTIL). The CO₂ permeability was enhanced, although somewhat incrementally, by increasing the length of the oligo(ethylene glycol) substituent. We also found that analogous alkyl- and fluoroalkyl-substituted vinyl poly(RTIL)s had the same CO_2 permeability (69 barrers). However, the fluoroalkyl group was found to contribute to enhanced CO₂/CH₄ permeability selectivity compared to the analogous alkyl-substituted vinyl poly(RTIL). The disiloxanefunctionalized vinyl poly(RTIL) afforded the highest measured CO₂ permeability (130 barrers) but possessed rather low CO₂/N₂ and CO₂/CH₄ selectivity. At 69 and 130 barrers, the *n*-hexyland disiloxane-substituted vinyl poly(RTIL)s were the two most permeable, albeit least selective, poly(RTIL) membranes known in the literature. Prior work demonstrated a maximum permeability of 32 barrers possible in a neat, *n*-hexyl-functionalized styrene poly(RTIL) [20]. Despite a measured enhancement in CO_2 permeability, the neat *n*-hexyl- and disiloxanefunctionalized vinyl poly(RTIL)s do not possess particularly desirable CO₂ selectivities. However, when blended with 20 mol % "free RTIL" relative to the monomer, these two membranes demonstrated enhanced CO_2 permeability and selectivity. The free RTIL component

contributes to enhanced selectivity because it is inherently more selective than the two parent poly(RTIL)s.

As demonstrated here and in previous studies [23, 24, 46], the most promising route toward industrially viable poly(RTIL) membrane materials is via the formation of stable poly(RTIL)-RTIL composite structures. That is, materials that have free RTIL liquid-like diffusivity and selectivity, but solid-like mechanical integrity and stability. Composite structures containing vast amounts of "free RTIL" may not be optimal from the standpoint of membrane stability. Maximizing poly(RTIL) CO₂ permeability by varying polymer architecture or chemistry will ultimately require the use of less "free RTIL" to push composite structure permeability toward, or beyond the Robeson Plot "upper bound." In this regard, vinyl-based poly(RTIL)s, particularly *n*-hexyl- and disiloxane-functionalized polymers, appear to be good initial candidates for maximizing parent polymer CO_2 permeability. Designing new poly(RTIL) materials that possess higher light gas permeability will likely result in substantial tradeoffs in CO₂ selectivity. However, as demonstrated in this work, the added liquid RTIL component can increase CO₂ selectivity as well as permeability. An underlying key to the stability of any poly(RTIL)-RTIL composite film is the inherently strong ion-ion attractive interactions between the solid and liquid charged components. Our work and the recent work of others up to this point have focused on creating poly(olefin)-based ionic polymers by the polymerization of unsaturated ionic RTIL monomers. However, poly(olefin) polymer backbones do not possess inherently desirable CO2 separation properties [51]. Poly(ethylene oxide) (PEO) and silicon rubbers (PDMS), on the other hand, contain oxygenated polymer backbones that possess excellent transport characteristics in their own right[3, 42, 52]. Our research groups are currently undertaking two new approaches towards the design and synthesis of new, highly permeable

poly(RTIL)s, based on imidazolium-functionalized PEO and PDMS polymers to ultimately blend with CO₂-selective RTILs.

4.5 Acknowledgements

The authors gratefully acknowledge primary financial support for the work performed at CU Boulder , which was provided by the Advanced Research Projects Agency-Energy (Grant DE-AR0000098). Additional financial support for this research was provided by the National Science Foundation via an SBIR Phase 1 subcontract grant through Membrane Technology and Research (Grant IIP1047356).

4.6. References

- 1. Powell, C.E. and Qiao, G.G., "Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases." J. Membr. Sci. **2006**, *279*, 1-49.
- 2. Jones, C.W. and Maginn, E.J., "Materials and processes for carbon capture and sequestration." ChemSusChem **2010**, *3*, 863-864.
- 3. Lin, H., Van Wagner, E., Raharjo, R., Freeman, B.D., Roman, I., "High-performance polymer membranes for natural-gas sweetening." Adv. Mater. **2006**, *18*, 39-44.
- 4. Sridhar, S., Smitha, B., Aminabhavi, T.M., "Separation of carbon dioxide from natural gas mixtures through polymeric membranes—a review." Separ. Purif. Rev. **2007**, *36*, 113-174.
- 5. Earle, M.J., Esperanca, J.M.S.S., Gilea, M.A., Canongia Lopes, J.N., Rebelo, L.P.N., Magee, J.W., Seddon, K.R., Widegren, J.A., "The distillation and volatility of ionic liquids." Nature **2006**, *439*, 831-834.

- 6. Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F., Maginn, E.J., "Why is CO₂ so soluble in imidazolium-based ionic liquids?" J. Am. Chem. Soc. **2004**, *126*, 5300-5308.
- Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L., Noble, R.D., "Guide to CO₂ separations in imidazolium-based room-temperature ionic liquids." Ind. Eng. Chem. Res. 2009, 48, 2739-2751.
- 8. Bara, J.E., Gabriel, C.J., Lessmann, S., Carlisle, T.K., Finotello, A., Gin, D.L., Noble, R.D., "Enhanced CO₂ separation selectivity in oligo(ethylene glycol) functionalized room-temperature ionic liquids." Ind. Eng. Chem. Res. **2007**, *46*, 5380-5386.
- 9. Carlisle, T.K., Bara, J.E., Gabriel, C.J., Noble, R.D., Gin, D.L., "Interpretation of CO₂ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach." Ind. Eng. Chem. Res. **2008**, *47*, 7005-7012.
- 10. Camper, D., Bara, J., Koval, C., Noble, R., "Bulk-fluid solubility and membrane feasibility of rmim-based room-temperature ionic liquids." Ind. Eng. Chem. Res. **2006**, *45*, 6279-6283.
- 11. Finotello, A., Bara, J.E., Camper, D., Noble, R.D., "Room-temperature ionic liquids: Temperature dependence of gas solubility selectivity." Ind. Eng. Chem. Res. **2007**, *47*, 3453-3459.
- 12. Scovazzo, P., "Determination of the upper limits, benchmarks, and critical properties for gas separations using stabilized room temperature ionic liquid membranes (silms) for the purpose of guiding future research." J. Membr. Sci. **2009**, *343*, 199-211.
- 13. Mahurin, S.M., Lee, J.S., Baker, G.A., Luo, H., Dai, S., "Performance of nitrilecontaining anions in task-specific ionic liquids for improved CO₂/N₂ separation." J. Membr. Sci. **2010**, *353*, 177-183.
- 14. Bara, J.E., Gabriel, C.J., Carlisle, T.K., Camper, D.E., Finotello, A., Gin, D.L., Noble, R.D., "Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes." Chem. Eng. J. **2009**, *147*, 43-50.
- 15. Hanioka, S., Maruyama, T., Sotani, T., Teramoto, M., Matsuyama, H., Nakashima, K., Hanaki, M., Kubota, F., Goto, M., "CO₂ separation facilitated by task-specific ionic liquids using a supported liquid membrane." J. Membr. Sci. **2008**, *314*, 1-4.

- 16. Morgan, D., Ferguson, L., Scovazzo, P., "Diffusivities of gases in room-temperature ionic liquids: Data and correlations obtained using a lag-time technique." Ind. Eng. Chem. Res. **2005**, *44*, 4815-4823.
- 17. Myers, C., Pennline, H., Luebke, D., Ilconich, J., Dixon, J.K., Maginn, E.J., Brennecke, J.F., "High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes." J. Membr. Sci. **2008**, *322*, 28-31.
- 18. Raeissi, S. and Peters, C.J., "A potential ionic liquid for CO₂-separating gas membranes: Selection and gas solubility studies." Green Chem. **2009**, *11*, 185-192.
- Scovazzo, P., Kieft, J., Finan, D.A., Koval, C., DuBois, D., Noble, R., "Gas separations using non-hexafluorophosphate [pf₆]⁻ anion supported ionic liquid membranes." J. Membr. Sci. 2004, 238, 57-63.
- 20. Bara, J.E., Lessmann, S., Gabriel, C.J., Hatakeyama, E.S., Noble, R.D., Gin, D.L., "Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes." Ind. Eng. Chem. Res. **2007**, *46*, 5397-5404.
- Bara, J.E., Hatakeyama, E.S., Gabriel, C.J., Zeng, X., Lessmann, S., Gin, D.L., Noble, R.D., "Synthesis and light gas separations in cross-linked gemini room temperature ionic liquid polymer membranes." J. Membr. Sci. 2008, *316*, 186-191.
- 22. Bara, J.E., Gabriel, C.J., Hatakeyama, E.S., Carlisle, T.K., Lessmann, S., Noble, R.D., Gin, D.L., "Improving CO₂ selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents." J. Membr. Sci. **2008**, *321*, 3-7.
- Bara, J.E., Gin, D.L., Noble, R.D., "Effect of anion on gas separation performance of polymer-room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. 2008, 47, 9919-9924.
- 24. Bara, J.E., Noble, R.D., Gin, D.L., "Effect of "free" cation substituent on gas separation performance of polymer–room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. **2009**, *48*, 4607-4610.
- 25. Anderson, J.L. and Armstrong, D.W., "Immobilized ionic liquids as highselectivity/high-temperature/high-stability gas chromatography stationary phases." Anal. Chem. **2005**, *77*, 6453-6462.

- 26. Hsieh, Y.-N., Horng, R., Ho, W.-Y., Huang, P.-C., Hsu, C.-Y., Whang, T.-J., Kuei, C.-H., "Characterizations for vinylimidazolium based ionic liquid polymer stationary phases for capillary gas chromatography." Chromatographia **2008**, *67*, 413-420.
- 27. Jin, X., Tao, J., Yang, Y., "Synthesis and characterization of poly(1-vinyl-3propylimidazolium) iodide for quasi-solid polymer electrolyte in dye-sensitized solar cells." J. Appl. Polym. Sci. **2010**, *118*, 1455-1461.
- 28. Ohno, H., "Design of ion conductive polymers based on ionic liquids." Macromol. Symp. **2007**, *249-250*, 551-556.
- 29. Salamone, J.C.I., S. C.; Taylor, P.; Snider, B., "Synthesis and homopolymerization studies of vinylimidazolium salts." Polymer **1973**, *14*, 639-644.
- 30. Washiro, S., Yoshizawa, M., Nakajima, H., Ohno, H., "Highly ion conductive flexible films composed of network polymers based on polymerizable ionic liquids." Polymer **2004**, *45*, 1577-1582.
- 31. Muldoon, M.J., Aki, S.N.V.K., Anderson, J.L., Dixon, J.K., Brennecke, J.F., "Improving carbon dioxide solubility in ionic liquids." J. Phys. Chem. B **2007**, *111*, 9001-9009.
- Morgado, P., Tomás, R., Zhao, H., dos Ramos, M.C., Blas, F.J., McCabe, C., Filipe, E.J.M., "Solution behavior of perfluoroalkanes and perfluoroalkylalkane surfactants in noctane." J. Phys. Chem. C 2007, 111, 15962-15968.
- Pasternak, R.A., Christensen, M.V., Heller, J., "Diffusion and permeation of oxygen, nitrogen, carbon dioxide, and nitrogen dioxide through polytetrafluoroethylene." Macromolecules **1970**, *3*, 366-371.
- 34. Prabhakar, R. and Freeman, B., "Application of hydrocarbon-fluorocarbon interactions in membrane-based gas separations." Desalination **2002**, *144*, 79-83.
- 35. Prabhakar, R.S., Freeman, B.D., Roman, I., "Gas and vapor sorption and permeation in poly(2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole-co-tetrafluoroethylene)." Macromolecules **2004**, *37*, 7688-7697.
- 36. Scott, R.L., "The anomalous behavior of fluorocarbon solutions." J. Phys. Chem. **1958**, 62, 136-145.

- 37. Song, W., Rossky, P.J., Maroncelli, M., "Modeling alkane+perfluoroalkane interactions using all-atom potentials: Failure of the usual combining rules." J. Chem. Phys. **2003**, *119*, 9145-9162.
- 38. Chung, S.H., Lopato, R., Greenbaum, S.G., Shirota, H., Castner, E.W., Wishart, J.F., "Nuclear magnetic resonance study of the dynamics of imidazolium ionic liquids with -CH₂Si(CH₃)₃ vs -CH₂C(CH₃)₃ substituents." J. Phys. Chem. B **2007**, *111*, 4885-4893.
- 39. Niedermeyer, H., Ab Rani, M.A., Lickiss, P.D., Hallett, J.P., Welton, T., White, A.J.P., Hunt, P.A., "Understanding siloxane functionalised ionic liquids." Phys. Chem. Chem. Phys. **2010**, *12*, 2018-2029.
- 40. Shirota, H. and Castner, E.W., "Why are viscosities lower for ionic liquids with -CH₂Si(CH₃)₃ vs -CH₂C(CH₃)₃ substitutions on the imidazolium cations?" J. Phys. Chem. B **2005**, *109*, 21576-21585.
- 41. Shirota, H., Wishart, J.F., Castner, E.W., "Intermolecular interactions and dynamics of room temperature ionic liquids that have silyl- and siloxy-substituted imidazolium cations." J. Phys. Chem. B **2007**, *111*, 4819-4829.
- 42. Merkel, T.C., Bondar, V.I., Nagai, K., Freeman, B.D., Pinnau, I., "Gas sorption, diffusion, and permeation in poly(dimethylsiloxane)." J. Polym. Sci. Polym. Phys. **2000**, *38*, 415-434.
- 43. Stern, S.A., Shah, V.M., Hardy, B.J., "Structure-permeability relationships in silicone polymers." J. Polym. Sci. Polym. Phys. **1987**, *25*, 1263-1298.
- 44. Platé, N. and Yampol'skii, Y., in *Polymeric gas separation membranes*, Paul, D.R. and Yampol'skii, Y.P., Editors. 1994, CRC Press, Inc.: Boca Raton, FL. p. 155.
- 45. Zolandz, R.R. and Fleming, G.K., *Membane handbook* 1992, New York, NY: Chapman & Hall.
- 46. Bara, J.E., Hatakeyama, E.S., Gin, D.L., Noble, R.D., "Improving CO₂ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid." Polym. Adv. Technol. **2008**, *19*, 1415-1420.

- 47. Carlisle, T.K., Bara, J.E., Lafrate, A.L., Gin, D.L., Noble, R.D., "Main-chain imidazolium polymer membranes for CO₂ separations: An initial study of a new ionic liquid-inspired platform." J. Membr. Sci. **2010**, *359*, 37-43.
- 48. Jenkins, R.C.L., Nelson, P.M., Spirer, L., "Calculation of the transient diffusion of a gas through a solid membrane into a finite outflow volume." Trans. Faraday. Soc. **1970**, *66*, 1391-1401.
- 49. Robeson, L.M., "The upper bound revisited." J. Membr. Sci. 2008, 320, 390-400.
- 50. Lin, H. and Freeman, B.D., "Gas solubility, diffusivity and permeability in poly(ethylene oxide)." J. Membr. Sci. **2004**, *239*, 105-117.
- 51. Brandrup, J.I., E. H.; Grulke, E. A., *Polymer handbook*. 4th ed 1999, New York, NY: John Wiley & Sons.
- 52. Lin, H., Freeman, B.D., Kalakkunnath, S., Kalika, D.S., "Effect of copolymer composition, temperature, and carbon dioxide fugacity on pure- and mixed-gas permeability in poly(ethylene glycol)-based materials: Free volume interpretation." J. Membr. Sci. **2007**, *291*, 131-139.
Chapter 5

CO₂/Light Gas Separation Performance of Cross-linked Poly(vinylimidazolium) Gel Membranes as a Function of Ionic Liquid Loading and Cross-linker Content

(Manuscript prepared for submission to Journal of Membrane Science)

Summary

A series of cross-linked poly(vinylimidazolium)-RTIL gel membranes were synthesized and evaluated for room-temperature, ideal CO₂/N₂, CO₂/CH₄, and CO₂/H₂ separation performance. The membranes were formed by photo-polymerization of oligo(ethylene glycol)functionalized cross-linking (i.e., di-functional) and non-cross-linking (i.e., mono-functional) vinylimidazolium RTIL monomers with non-polymerizable, "free RTIL." The effect of free RTIL (emim Tf_2N) loading on CO_2 separation performance was evaluated by varying RTIL loading at three levels (45, 65, and 75 wt. %). The effect of cross-linker content on CO₂ separation performance was also evaluated by varying the copolymer composition of crosslinked membranes from 5-100 mol % di-functional monomer. The substituent on the monofunctional RTIL monomer was also varied to investigate the effect of substituent structure and chemistry on CO_2 separation performance. CO_2 permeability was dramatically increased with higher loading of free RTIL. Increased RTIL loading had no effect on CO₂/N₂ or CO₂/CH₄ permeability selectivity, but significantly improved CO_2/H_2 permeability selectivity. Reducing the cross-linking monomer concentration generally improved CO₂ permeability. However, anomalous permeability and selectivity behavior was observed below critical concentrations of

cross-linker. The effect of mono-functional monomer substituent on CO_2 separation performance was minimal compared to the effects of RTIL loading and copolymer composition.

5.1. Introduction

Effective and economical removal of CO_2 from process streams containing other light gases such as N₂, CH₄, or H₂ is of vital importance and represents an ongoing chemical engineering challenge[1-5]. Specifically, the separation of CO₂ from N₂, CO₂ from CH₄, and CO₂ from H₂ are three distinct separation challenges faced by the electrical energy, natural gas, and syngas production sectors, respectively. In the production of electrical energy, potential climate change issues attributed to anthropogenic CO₂ have recently highlighted the importance of CO_2 separation from flue gas (i.e., CO_2/N_2 separation)[1, 2]. This separation will become more important as world population expands and coal- and natural gas-fired electric power plants are increasingly utilized as sources of cheap electricity. In the natural gas industry, "sweetening" (i.e., CO_2/CH_4 separation) is a crucial process needed to obtain CH_4 from natural gas wells with a degree of purity acceptable for piping, transport, and combustion[4, 5].CH₄ is also an incredibly important feedstock for the production of H₂ via steam methane reforming (SMR) and the water gas shift (WGS) reaction [3, 6, 7]. The Production of H₂ in this manner is vital for the synthesis of other major chemicals, such as NH_3 and urea, as well as for clean energy applications (i.e., H_2 fuel cells or combustion). Since CO_2 is produced as an impurity in the SMR-WGS process, it must be separated and removed from the desired H₂ product to generate sufficiently low levels for efficient H₂ production [3, 7]. Ideally, the CO₂ should be removed while leaving the H₂ at high pressure and ready for transport or combustion. The development of

separation technologies that can effectively and economically remove CO_2 from these light gases will be imperative to meeting the increasing regulations placed on CO_2 emissions.

There are three current industrial practices for the CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 separations described above. Pressure swing adsorption using solid porous media is a relatively new technology, but it has not yet found wide-spread use for CO_2 separation [8, 9]. Aqueous amine scrubbing is often used for natural gas sweetening and is under consideration for CO_2/N_2 separation[10, 11]. In this process, CO_2 is removed by absorption and subsequent reaction with the dissolved organic amine. The aqueous solvent is regenerated by heating the solution to elevated temperatures to liberate the carbamate-bound CO_2 . Selexol and Rectisol are two other scrubbing technologies that use solvents to remove CO_2 [6]. Selexol uses a proprietary glycol solution, while Rectisol uses refrigerated methanol. Both processes have found wide-spread use in syngas production. In general, all of the current separation practices described above suffer from high capital and/or operating costs. The use of VOCs (volatile organic compounds) in these scrubbing processes also contributes to considerable issues, notably operating cost and environmental impact.

Polymer membrane-based gas separations have the potential to overcome many of the disadvantages associated with traditional CO_2 separation technologies. Membrane processes have the advantages of scalability, small plant footprint, and ease of operation. However, in order for polymer membranes to be competitive with traditional separation methods they must possess both high CO_2 flux *and* high CO_2 selectivity [12, 13]. The range of polymer materials and separation performances for H_2/CO_2 , CO_2/CH_4 , and CO_2/N_2 separations are considerably large[14]. Most polycondensation polymers, such as polycarbonates and polyimides, have been exhaustively studied for CO_2/CH_4 and CO_2/N_2 separations [4, 15]. CO_2 -selective polymer

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membranes for CO_2/H_2 separations (i.e., "reverse selective") are quite rare due to the typically high diffusion rate of H_2 vs. CO_2 [12, 16, 17]. Only a few examples of polymeric CO_2 -selective membranes for CO_2/H_2 separations exist in the literature, and include poly(ethylene glycol) (PEG) and its co-polymers[16, 17], which have exceptional CO_2 /light gas selectivities and CO_2 permeabilities[18, 19].

Room-temperature ionic liquids (RTILs) are a relatively new class of materials that have exhibited excellent promise for membrane-based CO_2 separations. Molten salts at ambient conditions in the absence of a molecular co-solvent are ubiquitously termed RTILs. Perhaps the most attractive and unique characteristics of RTILs are their extremely small vapor pressure and fluid, charged nature. Additionally, an increasing number of RTILs have demonstrated inherently high CO_2 solubility and solubility selectivity for the three separations described here [20-27]. One of the most widely studied groups of RTILs is based on the imidazolium cation, which has the general structure shown in Fig. 5.1.



R = alkane, oligo(ethylene glycol), alkanenitrile, diol

Figure 5.1: General structures of (a) an imidazolium-based RTIL; and (b)-(d) imidazolium-based polymerizable RTILs

Favorable CO_2 solubility selectivity combined with "non-volatility" has led many researchers to investigate the performance of RTILs in a membrane configuration known as a supported ionic liquid membrane (SILM) [28-34]. Fabrication of a SILM is accomplished by saturating a non-

selective, highly porous polymer support (e.g., poly(ether sulfone)) with a RTIL. Capillary forces alone are predominantly responsible for retention of the liquid RTIL component within the support. Despite very attractive CO₂ permeabilities and CO₂/N₂ and CO₂/CH₄ selectivities (which often exceed Robeson's "upper bound"), SILM-based separations are limited to low trans-membrane pressure differentials. "Blow out" of the fluid RTIL component typically occurs at ≥ 1 atm of pressure drop.

Recent approaches to overcome the pressure stability issue inherent to SILMs have involved the functionalization and subsequent polymerization of RTIL monomers [35-37]. The general structures of several imidazolium-based RTIL monomers are shown in Fig. 5.1. While polymerization of RTIL monomers affords stable, solid membranes with excellent selectivity, the gas permeability (i.e., gas diffusivity) of these solid RTIL analogues was significantly lower than that of SILMs, in which the active separation material is fluid in nature. More recently, researchers have been able to improve poly(RTIL) gas permeability by incorporating up to 20 mole % "free" RTIL into poly(RTIL)-RTIL composite films [38-40]. Those works clearly demonstrated the advantages of a composite membrane structure formed between an ionic polymer and a RTIL. In these materials, significant improvement in CO_2 permeability was observed with little-to-no loss in CO₂ selectivity in these solid-liquid composite materials. The liquid RTIL component acted essentially as a CO₂-selective plasticizing agent, imparting more liquid-like diffusivity to the polymer membrane. Perhaps the most significant conclusion from these works was that the ionic interaction between the polymer and the RTIL enhanced the stability of the liquid component, since no liquid "blow out" was observed [38]. Others have also pointed out the potential value of using ionic polymers with ionic liquids [41]. Despite these improvements, the CO_2 permeability of the studied solid-liquid membranes is still nearly an

order of magnitude lower than the analogous SILMs. An ideal poly(RTIL)-RTIL membrane should have the mechanical (i.e., pressure) stability of a solid polymer and the gas separation characteristics (i.e., permeability and selectivity) of a liquid as in a SILM.

One method to obtaining a material that could approach such an ideal membrane is to form a cross-linked poly(RTIL) gel containing a large amount of free RTIL, analogous to PEGbased hydrogels [42]. A cross-linked ionic polymer component would act as a very robust solid matrix, or binder, to impart both the high mechanical stability and the Columbic interactions needed to retain the liquid RTIL component. There have been many studies investigating such cross-linked, polymer-based, solid-liquid, composite materials for electrochemical applications [43-49]. For example, a membrane was fabricated by photo-polymerization of a di-functional (cross-linking) RTIL monomer in the presence of 50 mol% "free RTIL" [45]. These membranes demonstrated promising "liquid-like" ion conductivity behavior. Although the value and utility of cross-linked poly(RTIL)-RTIL films has been established in the electrochemistry field for some time, a limited number of studies currently exists that have explored the CO₂ separation performance of similar cross-linked poly(RTIL) gel membranes [50-53]. Researchers have recently investigated the CO₂ separation performance of non-ionic and non-covalently crosslinked P(VDF-HFP) with up to 66 wt. % [50] and 80 wt. % [51] liquid RTIL. Others have demonstrated excellent CO₂ separation performance with imidazolium-functionalized tri-block copolymer membranes that contained 85 wt. % free RTIL [52]. However, to our knowledge only one group has investigated the use of photo-polymerizable, chemically cross-linked, poly(RTIL)-RTIL gel membranes for CO_2 separations [53]. That recent work investigated the effect of RTIL loading (up to 65 wt. %) on CO₂ permeability and CO₂/N₂ selectivity of a copolymer composed of di-functional (i.e. cross-linker) and mono-functional RTIL monomers [53]. However, no

investigation has been performed to probe the effect of copolymer composition of these photopolymerizable poly(RTIL)/RTIL gelled networks on CO₂/N₂, CO₂/CH₄, or CO₂/H₂ separation performance. A substantial body of evidence exists in the hydrogel and copolymer network literature [42, 54-64] that strongly suggests that cross-linked poly(RTIL)-RTIL gel membrane properties and CO₂ separation performance will depend greatly on the copolymer composition, monomer structure, and RTIL content. To further evaluate cross-linked poly(RTIL)-RTIL gels as commercially-viable gas separation membrane materials, we believe it is imperative to gain an initial understanding of the structure-property relationships between copolymer composition and RTIL loading on CO₂ separation performance.

Herein, we systematically investigate the effects of varying the liquid RTIL loading level and the amount of cross-linking monomer in a prototype cross-linked gel membrane composed of monomer **1**, monomer **2** (**a**, **b**, or **c**), and RTIL **3** (Fig. 5.2) on the ideal, room temperature separation of CO_2 from CH₄, N₂, and H₂.



emim Tf₂N 3

Figure 5.2: Structures of RTIL-based monomers 1, 2a-c, and RTIL 3 used in this study

In doing this study we found that a stable membrane can be made containing up to 75 wt. % RTIL and that both CO₂ permeability and selectivity performance approaches those of the SILM with increasing RTIL content. We also observed an increase in diffusivity of the target gases with decreasing cross-linker (1) concentration. However, in every system (at a constant RTIL loading), decreasing the cross-linker content below a certain value was found to unexpectedly reverse the trends in gas permeability and/or selectivity as a function of composition. This observation is clearly non-intuitive based on structure-property trends of homogeneous polymer networks. We speculate that this phenomenon is a reflection of the microscopically heterogeneous nature of these cross-linked membrane systems (i.e., the observed trends implicate the formation of non-homogeneous network structures).

5.2. Experimental

5.2.1. Materials and instrumentation

N-Vinylimidazole, *N*-methylimidazole, and *p*-toluenesulfonyl chloride were purchased from TCI America (Portland, OR). Tetra(ethylene glycol), triethylene glycol monomethyl ether, 2-Methoxyethanol, 1-bromohexane, 2-hydroxy-2-methylpropiophenone, and sodium iodide were purchased from Sigma-Aldrich (Milauwakee, WI). Lithium trifluoromethanesulfonimide (LiTf₂N) was purchased from 3M (St. Paul, MN). All reagents and solvents were obtained in the highest purity available and used without additional purification. Cylinders of CO₂, CH₄, N₂, and H₂ were purchased from Airgas (Randor, PA) and were of at least 99.99% purity. Supor-200 (porous poly(ether sulfone)) filters were purchased from Pall Corporation (Port Washington, NY). ¹H and ¹³C NMR spectra were acquired using a Bruker Avance-III 300 (300MHz). FT-IR spectra of **1** and **2a-c** were obtained with a model 960M0027 Matteson Satelite spectrometer with samples supported on Ge crystal substrates. FT-IR spectra of pre- and post-polymerized samples were obtained with a Nicolet Magna-IR 760 with samples on a porous UHMW PE support substrates (Solupor E075-9H01A, donated by DSM Solutech, Netherlands). DMA experiments were performed using a TA Instruments Q800 DMA. Glass transition temperature (T_g) was determined from polymer samples with approximate dimensions $12 \times 5 \times 1$ mm. Sample temperature was ramped at 3 °C/min from -80 to 50 °C with a frequency of 1 Hz and a strain of 0.05% in tension. The T_g was assigned as the temperature at the tan δ curve maximum. The rubbery modulus values were determined at a temperature 25°C above the T_g and the T_g width was measured as the full width at half height (FWHH) of the tan δ peak.

5.2.2. Synthesis of monomers 1 & 2 and RTIL 3

Monomers **1** and **2a-c** were synthesized according to Scheme 5.1. RTIL **3** was synthesized according to known literature procedures [65].



Scheme 5.1: Synthesis of monomers 1 and 2a-c.

5.2.3. Synthesis of monomers 1, 2a and 2b

The methods described below detail the synthesis of monomer **1** and are directly applicable to the synthesis of monomers 2a - 2c. Tetra(ethylene glycol) (40.01 g, 206 mmol) was dissolved in THF (137 mL) and added to a single-neck, 500 mL round-bottomed flask equipped with a magnetic stir bar and placed in an ice bath. Sodium hydroxide (28.84 g, 721 mmol) was then dissolved in deionized water (137 mL) and added to the 500mL flask while stirring the THF solution. P-toluenesulfonyl chloride (p-TsCl) (86.4 g, 453 mmol) was dissolved in THF (135 mL) and added to a volumetric dropping funnel, which was then equipped to the neck of the 500 mL flask. The *p*-TsCl was added dropwise for approximately 3 h, after which time the dropping funnel was removed and replaced with a glass stopper. The reaction was then allowed to warm up to room temperature and stir for an additional 24 h. The reaction was then quenched with 1.2 M HCl, (685 mL) and the product (a clear, slightly yellow oil) was extracted into EtOAc (350 mL) and washed with deionized water (2 x 500 mL), saturated NaHCO₃ (2 x 500 mL), and deionized water (2 x 500 mL). The organic phase was then dried over anhydrous $MgSO_4$ and filtered. EtOAc was removed via rotary evaporation followed by vacuum (< 20 mtorr) for 24 h at room temperature to afford (ii) (Scheme 5.1) as a clear, viscous oil (88.7 g, 176 mmol). Compound ii (17.5 g, 34.7 mmol) was dissolved in acetone (130 mL) and added to a 250 mL Erlenmeyer flask equipped with a magnetic stir bar. With the solution stirring, NaI (11.45 g, 76.3 mmol) was added and a white precipitate (sodium tosylate) was observed almost immediately. The reaction was allowed to stir for 24 h at room temperature before filtering to remove the solid precipitate. Acetone was then removed from the filtrate via rotary evaporation and the product was extracted into Et_2O (200 mL) to facilitate precipitation of excess NaI. The Et_2O was then filtered over a plug of silica and removed via rotary evaporation followed by

vacuum (< 20 mtorr) for 24 h at room temperature to afford (v) as clear, yellow liquid (13.6 g, 32.9 mmol)). Compound v (13.6 g, 32.9 mmol) was dissolved in CH₃CN (52 mL) and added to a 250 mL single-neck, round-bottomed flask equipped with a magnetic stir bar and reflux condenser. N-vinylimidazole (7.74 g, 82.3 mmol) was added to the flask and the reaction was heated to reflux (approximately 85 ⁰C) and stirred for 48 h. The reaction was then cooled and the product was precipitated in Et₂O (275 mL) and placed in the freezer (-4 °C) for 12 h. The Et₂O was then decanted, and the product was extracted into deionized water (200 mL) and washed with EtOAc (4 x 60 mL) and Et_2O (1 x 60 mL). The aqueous phase was then transferred to a 500 mL erlenmyer flask equipped with a magnetic stir bar and, LiTf₂N (20.8 g, 72.4 mmol) was added. An oil precipitate was observed immediately, and the reaction was allowed to stir for 3 h at room temperature. The aqueous phase was then decanted and the product was extracted into EtOAc (250 mL) and washed with deionized water (100 mL) until addition of AgNO₃ to an aliquot of the aqueous phase did not result in precipitate formation (i.e., no presence of halide). The organic phase was then dried over anhydrous MgSO₄ and stirred with activated charcoal for 12 h before filtering over a small plug of basic alumina. EtOAc was then removed via rotary evaporation followed by vacuum (< 20 mtorr) for 24 h at room temperature to afford monomer 1 a clear, viscous oil (27.3 g, 91.2% yield).

5.2.3.1. Monomer 1

Yield: 91.2%. ¹H NMR (300 MHz, DMSO- d_6): δ 2.50 (quintet, 2H), 3.50 (m, 8H), 3.79 (t, 4H), 4.37 (t, 4H), 5.44 (dd, 2H), 5.95 (dd, 2H), 7.31 (dd, 2H), 7.86 (t, 2H), 8.19 (t, 2H), 9.40 (t, 2H). ¹³C NMR (75.48 MHz, DMSO- d_6): δ 49.1, 67.8, 69.4, 69.5, 108.7, 118.8, 119.4 (q, CF₃), 123.6, 128.7, 135.6. FT-IR: 1658, 1572, 1553, 1450, 953, 923, 839, 791, 763, 741 cm⁻¹. HRMS (*m/z*): calculated as [A]²⁺[B]⁻, 628.1329; found, 628.1319.

5.2.3.2. Monomer 2a

Yield: 97.1%. ¹H NMR (300 MHz, DMSO- d_6): δ 3.28 (s, 3H), 3.71 (t, 2H), 4.39 (t, 2H), 5.43 (dd, 1H), 5.96 (dd, 1H), 7.32 (dd, 1H), 7.88 (t, 1H), 8.20 (t, 1H), 9.44 (t, 1H). ¹³C NMR (75.48 MHz, DMSO- d_6): δ 49.1, 58.1, 69.3, 108.7, 118.86, 119.5 (q, CF₃), 123.6, 128.8, 135.7. FT-IR: 1659, 1572, 1553, 1478, 1453, 1013, 955, 920, 837, 791 cm⁻¹. HRMS (*m*/*z*): calculated as [A]⁺, 153.1023; found, 153.1016.

5.2.3.3. Monomer 2b

Yield: 94.8%. ¹H NMR (300 MHz, DMSO-*d*₆): δ 3.23 (s, 3H), 3.48 (m, 8H), 3.80 (t, 2H), 4.38 (t, 2H), 5.44 (dd, 1H), 5.97 (dd, 1H), 7.32 (dd, 1H), 7.89 (t, 1H), 8.20 (t, 1H), 9.40 (t, 1H). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 49.2, 58.0, 67.8, 69.5, 71.2, 108.6, 121.6, 119.5 (q, CF₃), 123.7, 128.8, 135.7. FT-IR: 1658, 1572, 1553, 1453, 956, 924, 851, 790, 762, 740 cm⁻¹. HRMS (*m/z*): calculated as [A]⁺, 241.1547; found, 241.1543.

5.2.3.4. Monomer 2c

Yield: 96.6%. ¹H NMR (300 MHz, DMSO- d_6): δ 0.86 (t, 3H), 1.27 (m, 6H), 1.81 (quintet, 2H), 4.18 (t, 2H), 5.42 (dd, 1H), 5.94 (dd, 1H), 7.28 (dd, 1H), 7.93 (t, 1H), 8.19 (t, 1H), 9.46 (t, 1H). ¹³C NMR (75.48 MHz, DMSO- d_6): δ 13.7, 21.8, 25.1, 29.0, 30.5, 49.2, 108.5, 119.1, 119.5 (q, CF₃), 123.2, 125.9, 128.9. FT-IR: 1657, 1573, 1553, 1469, 1460, 954, 918, 848, 769, 763 cm⁻¹. HRMS (m/z): calculated as [A]⁺, 179.1543; found, 179.1540

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5.2.4. Polymerization and fabrication of cross-linked poly(RTIL)/RTIL films

To a 10-mL vial, the desired amounts of **1**, **2** (**a**,**b**, or **c**) and **3** were added to give a total of 1.2 g. For example, to fabricate the membrane listed in Table 5.1, entry 2 (below), it would be necessary to measure out 0.577 g of **1**, 0.083 g of **2b**, and 0.540 g of **3**. Photo-initiator (2-hydroxy-2-methylpropiophenone) (0.012 g, 1 wt. %) was added, and the contents were thoroughly mixed. A 47-mm porous support (Pall Supor-200) was placed on a hydrophobically-treated (RainX®) quartz glass plate, and the pre-polymerized mixture was poured onto the center of the support. A second, hydrophobically treated quartz glass plate was used to gently sandwich the membrane and spread the monomer/RTIL mixture over the entirety of the support surface. The membrane was placed under a UV lamp (Spectroline Model XX-15A) with an intensity of 1 mW/cm² for 3 h, then flipped and irradiated for an additional hour. Excess polymer gel was removed from the outer edges of the supported film with a Kimwipe. FT-IR spectroscopy of the cross-linked composite films indicated that vinyl group conversion ranged from 70 to 85%. Average membrane thickness was measured with a digital micrometer.

5.2.5. Single gas permeability, diffusivity and solubility measurements and theory

Ideal (i.e., single gas) permeability and diffusivity values were measured using a constant volume-variable pressure, or time-lag, apparatus. A full description of this experimental setup is described elsewhere [35, 66]. All experiments were performed at room temperature with an upstream pressure of 2 atm and vacuum (< 10 mtorr) as the initial downstream pressure. SILMs were tested with a transmembrane pressure drop of 0.8 to 1 atm. Permeability of each gas was measured at random three separate times on a single membrane, (i.e. three separate CO_2 , H_2 , N_2 ,

and CH₄ experiments). Complete details on performing these experiments and data analysis can be found in previous papers in the literature[35, 66]. Transport through the cross-linked gels tested was assumed to follow a solution-diffusion mechanism,[12, 13] whereby the separation of a species *i* from a mixture of gasses is based on relative differences in kinetic transport (i.e., diffusivity, D_i) and thermodynamic affinity (i.e., solubility, S_i) in the membrane. The permeability of a species *i* (P_i) through dense materials is related to solubility (S_i) and diffusivity (D_i) of gas species, *i* by the relationship shown in Eq. (1) [12, 13]:

 $P_i \equiv S_i \times D_i \quad (1)$

where, $P_i = \frac{J_i}{\Delta p_i} l$ (2)

 $P[=]barrer, 1 \ barrer = 10^{-10} \frac{cm^3(STP) \cdot cm}{cm^2 \cdot s \cdot cm \ Hg}$

In Eq. (2), J_i is the steady state volume flux (STP) of species *i*, *l* is the membrane thickness, and Δp_i is the average transmembrane partial pressure drop. The quantity J_i was determined by Eq. (3) where, p_i is the downstream pressure (psia), *t* is the experimental time, *V* is the downstream volume, A_{eff} is the effective membrane surface area, and *T* is the absolute temperature.

$$J_i = \left(\frac{dp_i}{dt}\right) \frac{V}{A_{eff}T} \cdot \frac{273.15K}{14.696 \, psi} \left(\frac{cm^3(STP)}{cm^2s}\right) \quad (3)$$

The quantity (dp_i/dt) in Eq. (3) was determined from the slope of the linear (i.e. steady state) portion of the p_i vs *t* curve. The permeability selectivity in materials that follow a solution diffusion mechanism is defined as [12, 13]:

Permeability Selectivity
$$(\alpha_{i/j}) = \frac{P_i}{P_j} = \frac{S_i}{S_j} \times \frac{D_i}{D_j}$$
 (4)

The selectivity is typically determined as the ratio of the permeability of the more permeable species to the permeability of the less permeable species. As shown in Eq. (4), permeability selectivity can be written as the product of diffusivity and solubility selectivity. The time-lag apparatus allows for single gas diffusivity (D_i) measurements according to Eq. (5), where, l is the membrane thickness, and (θ) is the "time-lag" [29, 67].

$$D_i = \frac{l^2}{6\theta} \quad (5)$$

The time-lag was determined by extrapolation of the linear, steady state, portion of the p_i vs t curve to the t-axis, where the intercept is equal to θ . The slope of this line is equal to the quantity (p_i/t) in Eq. (3). Once D_i and P_i were determined, single gas solubilities (S_i) were calculated from Eqs. (1) and (5).

5.3. Results and discussion

5.3.1. Choice of studied di- and mono-functional monomers and RTIL

Our systematic choice of the two types of monomers studied here was motivated by the general trends measured both experimentally and theoretically for a wide number of cross-linked copolymer networks [61, 63, 68, 69]. For example, it is well known that length, or molecular weight, of cross-linking monomer can have an adverse effect on homogeneous network formation. Shorter cross-linking monomers tend to result in low network double bond conversion

and facilitate the formation of "wasted cross-links," i.e. loops or cycles [61, 63, 68, 69]. We also took into consideration that oligo(ethylene glycol) functionality on the polymer tends to enhance CO₂ permeability and selectivity [20, 36, 70]. Monomer **1** (Fig. 5.2) was the outcome of an attempt to avoid some of the well-known drawbacks of using a short cross-linker and simultaneously incorporate ethylene oxide units into the structure. The synthesis of **1** is fairly straightforward, but analogous monomers with greater than three oligo(ethylene oxide) groups are substantially more difficult to synthesize and isolate. In an attempt to keep copolymer composition as consistent as possible, monomer **2b** was synthesized as a "non-cross-linking analogue" to 1 and incorporated into polymer structure as we systematically reduced 1. Monomers 2a and 2c were synthesized and evaluated as control experiments to analyze the effect of mono-functional monomer substituent on separation performance. The vinyl polymerizable group was chosen for several reasons. It is substantially easier to synthesize compared to styreneor acrylate-functionalized RTIL monomers. Our group has also found vinyl RTILs, especially cross-linking monomers, to be considerably more shelf/temperature stable than the styrene- or acrylate-based monomers. Vinyl monomers also have the "highest functional density", that is all extraneous or non-ionic functionality is kept to a minimum; for example, the molecular weight of the vinyl group is 27.04 g/mol compared to 117.17 and 99.1 g/mol for styrene and ethyl acrylate polymerizable groups, respectively. We chose to perform this study with $[\text{emim}][\text{Tf}_2\text{N}]$ (3) because of its ease of synthesis and purification, favorable CO₂ SILM performance, its ubiquity among the RTIL gas separation community, and because it contains the same anion as 1 and 2a-C.

The effect of RTIL loading and copolymer composition on CO₂ separation performance was studied by varying the content of RTIL **3**, the amount of cross-linking monomer from 5-100

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mol % of total monomer, and by varying the substituent on the mono-functional monomer (2a-

c). The range of composite films examined in this work is summarized in Table 5.1.

Table 5.1 Summary of compositions of the studied cross-linked films. In this study, membrane compositions are given by the identifier X-Y-Z, where X is the mol % of 1 out of total monomer, Y is the type of mono-functional monomer (if any, i.e., 2a-c), and Z is the wt. % of 3 out of the total mass of 1, 2, and 3.

		Mc				
	Membrane	1	2a	2b	2c	3 (wt %)
1.	100-45	100	-	-	-	45
2.	80- 2b -45	80	-	20	-	45
3.	60- 2b -45	60	-	40	-	45
4.	40- 2b -45	40	-	60	-	45
5.	20- 2b -45	20	-	80	-	45
6.	10- 2b -45	10	-	90	-	45
7.	5- 2b -45	5	-	95	-	45
8.	100-65	100	-	-	-	65
9.	80- 2b -65	80	-	20	-	65
10.	60- 2b -65	60	-	40	-	65
11.	40- 2b -65	40	-	60	-	65
12.	20- 2b -65	20	-	80	-	65
13.	15- 2b -65	15	-	85	-	65
14.	100-75	100	-	-	-	75
15.	80- 2b -75	80	-	20	-	75
16.	60- 2b -75	60	-	40	-	75
17.	40- 2b -75	40	-	60	-	75
18.	20- 2a -45	20	80	-	-	45
19.	20- 2a -65	20	80	-	-	65
20.	20- 2c -45	20	-	-	80	45
21.	20- 2c -65	20	-	-	80	65

Throughout this study, we refer to membranes by the identifier X-Y-Z, where X is the mol % of 1 out of total monomer present, Y denotes the type of monofunctional monomer, if any (i.e., 2a, 2b or 2c), and Z denotes the amount of free RTIL 3 by wt. % out of total weight of all species in the membrane. For example, a membrane composed of 40 mol % 1 with monomer 2b and contains 65 wt. % of 3 would be identified by 40-2b-65. It is important to note that below a

minimal amount of **1**, the RTIL mixtures do not form a solid, tractable membrane after UVinitiated polymerization. This minimal amount was found to be highly dependent on the loading level of RTIL **3**. Samples 5-**2b**-45 15-**2b**-65, and 40-**2b**-75 (Table 5.1) represent the approximate limits at 45, 65, and 75 wt %, respectively. The ideal (i.e., single gas) permeabilities of CO₂, N₂, CH₄, and H₂ were calculated according to Eqs. (2) and (3). Ideal CO₂/N₂, CO₂/CH₄, and CO₂/H₂ selectivities were then calculated according to Eq. (4). Ideal CO₂ permeability and selectivity data for 100-45, 100-65, and 100-75 are plotted and summarized in Figs 5.4 and 5.5, respectively, as "Robeson Plots" [14]. Robeson Plots of membranes 1-7 and membranes 14-17 (Table 5.1) can be found in Appendix C.





Figure 5.3. Ideal CO₂ permeability and selectivity of 100-45, 100-65 and 100-75 (see Table 5.1) graphed in (a) CO₂/N₂, (b) CO₂/CH₄ and (c) CO₂/H₂ Robeson Plots. The values next to the corresponding data points denote the composition of the membrane. The SILM performance of RTIL **3** (\bullet) is also plotted. Experimental error is within the data points and represents +/- one standard deviation. The upper bound shown in (c) was drawn according to a model prediction developed in a previous paper [71]. The prediction was made by setting the value of *f* to 0, which is consistent with rubbery polymers that do not possess non-equilibrium excess free volume [17, 71].





Figure 5.4. Ideal CO₂ permeability and selectivity of 100-65, 80-**2b**-65, 60-**2b**-65, 40-**2b**-65, 80-**2b**-65, 20-**2b**-65, and 15-**2b**-65 (see Table 5.1) graphed in (a) CO₂/N₂, (b) CO₂/CH₄ and (c) CO₂/H₂ Robeson Plots. The values above or below the corresponding data points denote the mol % of **1** out of total monomer in the membrane. The SILM performance of RTIL **3** (\bullet) is also plotted. Experimental error is within the data points and represents one standard deviation. The upper bound shown in (c) was drawn according to a model prediction developed in a previous paper [71]. The prediction was made by setting the value of *f* to 0, which is consistent with rubbery polymers that do not possess non-equilibrium excess free volume [17, 71].

The solid black line on these log-log plots represents the current upper limit to the so called "flux-selectivity tradeoff." Robeson's upper limits were determined by statistical evaluation of large sets of polymer membrane separation data and were adapted for the CO_2/N_2 and CO_2/CH_4 plots here (Figs. 5.3 and 5.4) [14]. The upper bound is a very useful bench mark by which to gauge the separation performance of new membrane materials. The upper bound shown in the CO_2/H_2 plots was drawn according to a model prediction developed in a previous paper [71]. The prediction was made by setting the value of *f* to 0, which is consistent with rubbery polymers that do not possess non-equilibrium excess free volume [17, 71]. Unlike in the upper bound slopes

shown in the CO_2/N_2 and CO_2/CH_4 Robeson plots, the slope of the CO_2/H_2 upper bound is positive. This is a consequence of the reduced size-sieving nature of polymers as they become more rubbery and permeable, which causes CO_2/H_2 diffusivity selectivity to approach unity. The ideal CO_2 permeability and selectivity data of all studied membranes are also tabulated in Table C.1 in Appendix C.

Diffusivity and solubility data are summarized in Table 5.2 for CO_2 and CH_4 in membranes 1 and 8 – 14 (Table 5.1). The complete set of tabulated data for CO_2 and CH_4 diffusivity, diffusivity selectivity, solubility, and solubility selectivity can be found in Table C.2 in Appendix C. The diffusivity of N₂ and H₂ were difficult to accurately measure with our apparatus and are not reported in this study.

Table 5.2. CO_2 and CH_4 diffusivity and solubility as well as CO_2/CH_4 diffusivity and solubility selectivity of selected membranes, RTIL **3**, and a homopolymer of **2b**.^{a,b,c,d}

Membrane	Mol % (1)	D(CO ₂) x 10 ⁷	D(CH ₄) x 10 ⁷	D(CO ₂)/D(CH ₄)	S(CO ₂)	S(CH ₄)	S(CO ₂)/S(CH ₄)
100-45	100	2.3 ± 0.3	0.94 ± 0.09	2.4	4.3 ± 0.2	0.48 ± 0.05	9.0
100-65	100	5.4 ± 0.5	2.0 ± 0.1	2.7	4.9 ± 0.3	0.67 ± 0.02	7.3
100-75	100	9.0 ± 0.6	4.3 ± 0.3	2.1	4.4 ± 0.2	0.45 ± 0.05	9.8
^d Neat 3	-	13 ± 1	4.5 ± 0.4	2.6	6.6 ± 0.4	1.2 ± 0.1	5.7
80- 2b -65	80	5.7 ± 0.7	2.3 ± 0.1	2.5	5.3 ± 0.6	0.64 ± 0.02	8.3
60- 2b -65	60	7.2 ± 0.8	3.6 ± 0.3	2.0	4.5 ± 0.3	0.48 ± 0.04	9.4
40- 2b -65	40	7.3 ± 0.7	3.1 ± 0.2	2.4	4.9 ± 0.2	0.57 ± .03	8.6
20- 2b -65	20	7.0 ± 0.5	3.6 ± 0.2	1.9	4.2 ± 0.2	0.45 ± 0.04	9.3
15- 2b -65	15	5.3 ± 0.5	1.0 ± 0.1	5.3	7.0 ± 0.3	2.7 ± 0.08	2.6
^d 0- 2b -65	0	5.6 ± 0.5	1.7 ± 0.5	3.4	6.1 ± 0.3	1.2 ± 0.1	4.9

^aDiffusivity in cm²s⁻¹

^bSolubility in cm³(stp)cm⁻³atm⁻¹

^cError represents +/- one standard deviation

^dSILMs that were tested at 1 atm transmembrane pressure drop

5.3.2. Effect of RTIL 3 content on CO₂ separation performance

Adjusting the content of RTIL **3** in the 100 mol % cross-linker (**1**) membranes had a dramatic effect on ideal CO₂ permeability and in the case of CO₂/H₂, a marked effect on ideal selectivity. Furthermore, the permeability of all the gel membranes studied here is much improved compared to the neat polymer membranes consisting only of monomers **1** or **2b** precursors (i.e., poly(**1**) and poly(**2b**)). The data shown in Fig 5.3 have also been plotted with neat polymer performance in Fig. C.5. As the content of free RTIL **3** was increased from 45 to 65 wt. %, the CO₂ permeability increased from 130 to 350 barrers (Fig. 5.3a-c). By subsequently increasing the content of **3** to 75 wt. %, the CO₂ permeability was further increased to 520 barrers. With such large observed enhancements in permeability, it was expected to also observe a decrease in selectivity from the 45 wt. % to 75 wt. % membranes. As clearly seen in both Figs. 5.3a and 3b, no decrease was observed for CO₂/N₂ and CO₂/CH₄ selectivity (Figs. 5.3a and 5.3b, respectively). A similar observation has been made previously in papers investigating lower RTIL membrane compositions [38-40]. Surprisingly, an increase in CO₂/H₂ selectivity was observed (Fig. 5.3c) with enhanced CO₂ permeability.

Upon inspection of CO₂ diffusivity and CO₂ solubility data for test membranes 100-45, 100-65, and 100-75, it is clear that improvement in diffusivity was the dominating factor for the observed permeability enhancement in these membranes. For example, the measured CO₂ diffusivities for samples 100-45, 100-65, and 100-75 were 2.3 x 10^{-7} , 5.4 x 10^{-7} and 9.0 x 10^{-7} cm²s⁻¹, respectively (Table 5.2). The CO₂ permeability of membrane 100-75 was four times larger than the membrane 100-45, which is the same enhancement measured for CO₂ diffusivity between the same two membranes. CO₂ solubility, on the other hand, remained relatively constant and was measured to be 4.3, 4.9, and 4.4 cm³(stp) cm⁻³atm⁻¹ for membranes 100-45,

100-65, and 100-75, respectively. Clearly, by increasing the amount of free RTIL **3** incorporated, the membranes gained more "liquid-like" diffusivity, which applied to all studied gases. Notice that the CH₄ diffusivity of sample 100-75 was approximately 4.6 times larger compared to 100-45, similar to the observed enhancement in CO_2 diffusivity. However, polymer morphology may also play a more subtle role in the observed permeabilities. It is well known that cross-link density increases with the concentration of di-functional (i.e., cross-linking) monomer **1** [18, 42, 69, 72]. With respect to the system studied here, for example, it is reasonable to assume that the cross-link density decreases from samples 100-45 to 100-75 as more free RTIL (i.e., diluent) effectively reduces the cross-linking monomer concentration. At present, it is unclear how this network property affects RTIL (i.e., **3**) or gas diffusivity. Previous papers have investigated the effects of cross-link density on membrane properties and gas transport, but all of those studies were on pure polymer systems [18, 73, 74].

The effect of free RTIL **3** content on CO₂ permeability selectivity was less straightforward than the effect on CO₂ permeability, particularly for the CO₂/H₂ separation pair. Whereas N₂ and CH₄ are both larger than CO₂ (kinetic diameters of 3.64, 3.8, and 3.3 Å, respectively [12]), H₂ is substantially smaller (2.6 Å [12]). Consequently, the CO₂/H₂ diffusivity selectivity will be less than unity in the absence of a CO₂-facilitating agent. However, as RTIL content was increased, an increase in CO₂/H₂ permeability selectivity was clearly observed (Fig. 5.3c). This suggests that possibly two cooperative phenomena are occurring. The first is that the CO₂/H₂ diffusivity selectivity is enhanced due to the increasing presence of the liquid component (**3**) and "opening" of the three-dimensional polymer network. In other words, the membranes become less size-selective, allowing the larger molecule (i.e., CO₂) to diffuse more freely. The second is that the membranes become dominantly more CO₂/H₂ solubility selective with increasing free RTIL content. As can be seen in Fig. 5.3c, the permeability selectivity of 100-75 is nearly identical to that of the neat liquid. It has been demonstrated in previous papers that the favorable CO₂ permeability selectivity of SILMs is dominated by differences in solute solubility, rather than differences in diffusivity [28-31]. CO₂/H₂ solubility selectivity, in particular, has been shown to be significantly large for imidazolium-based RTILs (e.g., >>10) [27, 65]. This would certainly indicate that the CO_2/H_2 solubility selectivity of **3** would overwhelmingly dominate the overall separation performance in membrane 100-75. The notion that the membrane selectivity performance approaches that of the neat liquid upon increasing RTIL content seems to resonate with the two other separation pairs in this study. However, in the case of CO_2/N_2 and CO_2/CH_4 , the diffusivity selectivity effect is competitive, rather than cooperative as in the case of CO_2/H_2 . That is to say, a reduction in "size selectivity" with increasing content of RTIL 3 allows the larger gases (N_2 and CH_4 in this case) to diffuse more freely. However, this competitive effect appears to be compensated by the increasing solubility-selective nature of the membranes. For example, in Fig. 5.3a, we observed that the CO_2/N_2 permeability selectivity remained nearly unchanged from membranes 100-45 to 100-75 and approached that of the neat RTIL. However, the permeability selectivity of 100-75 was slightly larger (by 19%) than that of the neat RTIL (37 compared to 31). In Fig. 5.3b, we observed only a slight reduction in CO_2/CH_4 permeability selectivity as free RTIL content was increased. Similar to the case of CO₂/N₂, the permeability selectivity of the 75 wt% membrane was larger (25%) than the neat RTIL (20 compared to 16). We suspect that the presence of ethylene oxide units in 1 act to enhance the CO₂ solubility selectivity compared to the neat alkyl-functionalized RTIL. Inspection of data presented in Table 5.2 suggests that this may be the case. The solubility selectivity values of membranes 100-45,

100-65, and 100-75 was 9.0, 7.3 and 9.8, respectively, compared to 5.7 for the SILM of neat RTIL **3**.

5.3.3. Effect of cross-link content on CO₂ separation performance

To investigate the effect of reduced cross-linking monomer (1), membranes that contained 20, 40, 60, 80, 85, 90, and 95 mol % of **2b** and the balance of **1** were examined. The effect of reduced cross-linking monomer concentration was investigated at all three loading levels of **3** (i.e., at 45, 65, and 75 wt. %). The ideal CO₂ permeability and permeability selectivity of the 65 wt. % RTIL membranes (entries 8-13, Table 5.1) are summarized in Fig. 5.4a-c. The trends and analysis made here for these apply directly to the observations made for the membranes shown in entries 1-7 (45 wt. % RTIL) and 14-17 (75 wt. % RTIL), which are also summarized in Robeson Plots in the Supplemental Information. Reducing the content of **1** generally resulted in a CO₂ permeability enhancement (Fig. 5.4a-c). Although, these enhancements were found to be much more incremental than those observed for increasing free RTIL content. Reducing the amount of cross-linking monomer **1** in the membranes was also found to generally have little, if any, effect on ideal CO₂ permeability selectivity. However, below a certain concentration of **1**, a reversal of the general, intuitive, trends stated above were observed.

5.3.3.1. Effect of cross-link content on ideal CO₂ permeability

As can be seen in Fig. 5.4a-c, as the mol % of **1** was reduced from 100 mol % to 40 mol %, the CO_2 permeability was significantly enhanced. For example, the ideal CO_2 permeability of membrane 40-**2b**-65 was measured to be 470 barrers, while the permeability of membrane 100-

65 was 350 barrers. The enhancement between sequential membranes (e.g., 80-2**b**-65 and 60-2**b**-65) was much more incremental. For example, the ideal CO₂ permeability of membrane 80-2**b**-65 was 390 barrers compared to 430 barrers for 60-2**b**-65. As expected, reducing the amount of added cross-linking monomer **1** improved permeate diffusivity. The CO₂ and CH₄ diffusivity values of 80-2**b**-65 were 5.4 x 10⁻⁷ and 2.0 x 10⁻⁷ cm²s⁻¹, respectively. For sample 40-2**b**-65, on the other hand, the CO₂ and CH₄ diffusivity values were found to be 7.3 x 10⁻⁷ and 3.1 x 10⁻⁷ cm² s⁻¹, respectively. As discussed previously with increasing free RTIL **3** content, the observed permeability enhancements with reduced concentrations of **1** were due largely in part to enhancement of CO₂ diffusivity, rather than solubility. From Table 5.2, it can be seen that both CO₂ and CH₄ solubility changed little, if any, with decreasing cross-linking content.

Two anomalous behaviors, however, were observed upon further reduction in cross-link content. First, an unexpected drop in gas permeability was measured for membranes 40-**2b**-65 and 20-**2b**-65, as seen in Fig. 5.4a-c. The permeability went from 470 barrers for 40-**2b**-65 to 390 barrers for 20-**2b**-65. Second, the permeability greatly increased from membranes 20-**2b**-65 to 15-**2b**-65 at a measured 490 barrers. Upon reducing the amount of of cross-linking monomer, one would normally expect a lowering of polymer glass transition temperature (T_g), an increase in fractional free volume and, consequently, improved diffusivity for all permeate gases [75]. The unexpected reversal in permeability was observed in the series of membranes containing 45 wt. % and 75 wt. % of free RTIL **3** as well. When the membranes contained 45 wt. % **3**, the reversal in permeability was observed with reduced cross-linking monomer when the membrane contained 75 wt. % free RTIL **3** (Fig. C.1). At the lowest tested concentrations of cross-linking monomer **1** we observed a sharp rise in CO₂ permeability for all three series of

membranes (i.e., 45, 65, and 75 wt. % 3). To better illustrate these anomalies, the CO₂ permeability of the membranes shown in entries 1-17 (Table 5.1) have been plotted vs. mol % of cross linking monomer 1 in the pre-polymer mixture (Fig. 5.5a-c). Previously, we defined mol % of 1 above as moles of 1 divided by moles of 1 and 2; here we define the mol % as 1 divided by the total moles of monomer plus moles of diluent, i.e., RTIL 3. This was done to allow for ease of comparison to similar plots in prior polymer gel papers that document similar phenomena as a function of varying cross-linking monomer content [55, 68, 69, 76].





Figure 5.5. CO₂ permeability of membranes 1-17 (see Table 5.1) vs mol % of cross-linking monomer **1** in the entire pre-polymer mixture with (a) 45 wt % (\square), (b) 65 wt % (\square) and (c) 75 wt% (\square) RTIL **3**. Mol % here is defined as moles of **1** divided by total moles of **1**, **2** and **3**. The molar compositions listed in Table 5.1 are defined as moles of **1** (or **2**) dived by total moles of **1** and **2**. The lines connecting data points in a-c are only meant to guide the eye. Error bars shown represent +/- one standard deviation.

Although the observed permeability trends shown in Fig. 5.4a-c are unusual, they are not entirely unexpected. A handful of studies in the literature have documented such seemingly anomalous behavior with cross-linked copolymer networks similar to those investigated here [55, 68, 69, 74, 77]. The superposition of the "cross-linking effect" and the "copolymer effect," for example, has been shown to result in unexpected trends of T_g (or another polymer property) with cross-linking monomer concentration [55, 68, 69, 74, 76, 78]. The "cross-linking effect" refers to the increase in T_g due to a loss in long-range segmental motion as polymer chains become more restricted with increased cross-links between chains. The "copolymer effect" refers to the change in T_g with changing copolymer composition of the linear chain segments. For example, in the absence of any cross-linking, the T_g of 80-**2b**-45 would likely differ from 5-**2b**-45 by virtue of compositional differences alone (i.e., 80 % of **1** vs. 5 % of **1**). It has been shown that the copolymer and cross-linking effects are independent and additive on the total change in T_g [55, 76, 78]. This effect has been expressed mathematically as shown by Eq. (6) [55]:

$$\Delta T_g = \Delta_p T_g + \Delta_c T_g \quad (6)$$

where, ΔT_g is the overall change in T_g , $\Delta_\rho T_g$ is the change in T_g due to increasing cross-link density and $\Delta_c T_g$ is the change in T_g due to the change in copolymer composition [55]. As Eq. (6) implies, depending on the magnitudes of $\Delta_\rho T_g$ and $\Delta_c T_g$ as well as the sign of $\Delta_c T_g$, ΔT_g may not necessarily be positive in all cases. In other words, the two effects could very well be opposing [55, 69]. We suspect that the cross-linking and copolymer effects influence CO₂ permeability in copolymer RTIL gel membranes in the same way that they affect glass transition temperature. Upon inspection of Fig. 5.5a-c, it was noticed that the anomalous behaviors occurred around the same concentrations of cross-linking monomer **1**. The sudden drop in permeability with *increasing* concentration of **1** occurred at approximately 4 mol %, 5 mol %, and 9 mol % of **1**, respectively. Likewise, a sudden increase in permeability was found to occur at approximately 9 mol % **1** as seen in Figs. 5.5a and 5.5b, and at approximately 11 mol % **1** in Fig. 5.5c. Based on previous papers on the sometimes opposing cross-linker and copolymer effects in cross-linking systems [55, 68, 69], the above observations seem to suggest that the cross-linking effect dominates the permeability behavior at the lower concentrations of cross-linker. Small increases in cross-linker content at low concentrations can result in an otherwise unexpected rapid change (i.e., increase) of cross-link density, glass transition temperature [55, 68, 69], and in this case, CO_2 permeability.

To investigate this effect further, a Soxhlet extraction was performed on 100-65, 80-2b-65, 60-2b-65, 40-2b-65, 20-2b-65, and 15-2b-65 (membrane entries 8-13, Table 5.1) to determine the soluble-fraction (sol-fraction) (i.e., free, non-cross-linked) of the polymerized networks (see Appendix C for methods and Table C.3 for results). The sol-fraction of 15-2b-65 was found to be approximately 0.93 by mass, or in other words, an excess of about 28%. If all monomer were incorporated into the polymer gel network, we would expect about a 0.65 sol-fraction – the mass due to the presence of free RTIL **3** only. The higher than expected sol-fraction strongly suggests that very little macrogelation, or inter-polymer cross-linking, occurs upon polymerization of 15-2b-65. The sol-fraction of membrane 20-2b-65, however, was found to be 0.80 by mass, or an excess of about 15%. This suggests that 20-2b-65 is significantly more cross-linked than 15-2b-65 and lends qualitative evidence that the "cross-linking effect" was perhaps dominantly responsible for the reduction in CO_2 permeability observed between

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membranes 15-2b-65 and 20-2b-65. These extraction results also suggest that a substantial amount of "wasted cross-links" formed during polymerization. These are inhomogeneities (e.g., the formation of primary or secondary loops or cycles with pendant vinyl groups) [42, 56, 57, 59, 61, 69], which tend to lead to microgelation, rather than macrogelation and uniform network formation [42, 56, 57, 59, 61, 69]. We found by FT-IR analysis that the degree of vinyl group conversion of membranes 100-65, 80-2b-65, 60-2b-65, 40-2b-65, 20-2b-65, and 15-2b-65 was nearly constant, regardless of cross-linker content (between 71 and 75% (Table C.3)). The fact that there remained a significant degree of unsaturation also suggests that the formed polymer networks are considerably inhomogeneous [59]. Microgel formation can lead to "trapping" of radicals and pendant double bonds in regions of high polymer density and viscosity (i.e., microgels); this has been shown to be the case, particularly in the dilute cross-linker concentration regime and with shorter cross-linking monomer length, similar to 1 studied here [59, 60, 72]. Soxhlet extraction of membranes 100-65, 80-2b-65, 60-2b-65, and 40-2b-65 revealed nearly identical sol. mass fractions of about 0.71, or an excess of 6-7%. This indicated that these membranes had developed fully formed polymer networks; although, not necessarily homogeneous as mentioned above. It is likely that the observed small excess sol fractions are due to unreacted monomer "pools," which tend to form in heterogeneous polymer gel networks [59, 72, 79]. In the case of our unique copolymer gel networks, these "pools" would be a mixture of unreacted monomer and free RTIL 3.

To better understand the anomalous permeability behavior of the studied cross-linked RTIL gels, T_g and storage modulus (G') of the membranes in entries 8-13 (Table 5.1) were measured using dynamic mechanical analysis (DMA). These data are plotted in Fig. 5.6. The cross-link density of these membranes was not calculated, but it is proportional to G' [54, 63,

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69]. Thus, G' provides a relative and qualitative measure of cross link density, or average molecular weight between cross-linking elements, M_c (e.g., G' $\propto M_c^{-1}$) [54, 63, 69].



Figure 5.6. (a) Glass transition temperature, T_g (°C), and (b) storage modulus, G'(Pa), of membranes 100-65, 80-2b-65, 60-2b-65, 40-2b-65, 80-2b-65, 20-2b-65, and 15-2b-65 (Table 5.1). The values next to the corresponding data points denote the membrane composition (see

Table 5.1). Error given represents +/- one standard deviation. Error is within the data point if no error bars are shown.

The storage modulus in sample 40-**2b**-65 is clearly much higher than in 20-**2b**-65 (Fig. 5.6b), implying that the 40 mol % cross-linker membrane was substantially more cross-linked. We also noticed that the value for T_g remained unchanged between membranes 20-**2b**-65 and 40-**2b**-65 (Fig. 5.6a). This certainly suggests that opposing cross-linking and co-polymer effects are occurring at low concentrations of **1**. However, based on the measured CO₂ permeability of membrane 20-**2b**-65, we expected the T_g of this sample to be higher, (i.e., similar to the T_g of 80-**2b**-65). Recall that the sol-fraction of sample 20-**2b**-65 was 0.80 by mass, or about 15 % more than expected. This indicates the presence of unreacted monomers **1** and **2b**, which likely reside in "pools" or "channels" along with RTIL **3** [59, 72, 79]. Since these monomers are substantially more viscous than RTIL **3**, they would significantly increase diffusional resistance in these RTIL channels. It is well known that gas diffusivity and permeability is a strong function of RTIL viscosity [23, 28, 29, 31, 80]. We suspect the anomalous drop in CO₂ permeability at low concentration of cross-linker **1** is due to the combined effects of increased cross-link density and the presence of viscous, unreacted monomers.

We suspect that the "copolymer effect" gives rise to the unexpected increase in permeability observed from samples 10-2b-45 to 20-2b-45, 20-2b-65 to 40-2b-65, and 60-2b-75 to 100-75 as seen in Fig. 5.5a, 5.5b and 5.5c, respectively. This presupposes that the T_g is inherently lower or, in this case, CO₂ permeability is inherently higher in the homopolymer (noncross-linked) of **1** compared to the homopolymer of **2b**. From a chain-packing or free-volume standpoint, it is arguable that one would find this to be the case [81, 82]. If cross-linker **1** were considered to be monofunctional (i.e., only one vinyl group is reactive), the pendant side groups on a homopolymer of **1** would be considerably bulkier compared to those on a homopolymer of **2b**. Researchers have shown that incorporation of bulky side groups to the polymer backbone tends to enhance gas permeability (i.e., reduce T_g) [81, 82]. No observed change in T_g between membranes 20-**2b**-65 and 40-**2b**-65 (Fig. 5.6a), despite clear increase in cross-link density (Fig. 5.6b), also provides further evidence for the "co-polymer effect."

As cross-linker (1) concentration was increased beyond membranes 20-2b-45 and 40-2b-65, we observed a steady decrease in CO_2 permeability (Fig. 5.5a and 5.5b, respectively). This trend suggests that the number of effective cross-links in the resulting polymer networks was increased with increasing concentration of 1. As mentioned previously, the double bond conversions of membranes 100-65, 80-2b-65, 60-2b-65, 40-2b-65, 20-2b-65, and 15-2b-65 were approximately the same (e.g., 71-74%) as determined by FT-IR spectroscopy. In other words, the relative number of double bonds incorporated into the polymer network was nearly the same regardless of cross-linker 1 content. As the amount of added 1 in the copolymer system was increased, however, the average monomer functionality approaches the value of 2 (i.e., all difunctional monomer). This clearly indicates that an increasing number of pendant double bonds participates in network-forming (i.e., cross-linking) reactions as 1 was systematically increased. Similar observations have been well documented by others for cross-linked copolymer networks [60, 62, 69, 72]. The steady increase observed for Tg (Fig. 5.6a) and storage modulus (Fig. 5.6b) clearly implicates the "cross-linking effect" as being more dominant with increased concentration of 1. Furthermore, by comparison of Fig. 5.6a with Fig. 5.5b, it is quite evident that the steady increase in T_g brought about the observed decline in CO₂ permeability for membranes 40-2b-65 to 100-65. We suspect a similar trend also lead to the steady decline in CO₂ permeability observed for membrane 20-2b-45 to 100-45 (Fig. 5.5a). In Fig. 5.5c.,

however, only an increase was observed in CO₂ permeability beyond sample 60-**2b**-75. Notice that the mol % of cross-linker **1** in Figs. 5.5a and 5.5b was approximately 9 mol % before the "cross-linking effect" causes a steady decline in permeability. In actuality, the maximum permeability before the onset of the "cross-linking effect" could very well exist between 9 and 13 mol %, or between 20-**2b**-45 and 40-**2b**-45 (Fig. 5.5a) and between 40-**2b**-65 and 60-**2b**-65 (Fig. 5.5b). The fact that the mol % of **1** in Fig. 5.5c never exceeds 13 mol % (due to 75 wt. % free RTIL **3**) suggests that the above stated range of 9-13 mol % is likely where this turnover of the two competing effects occurs.

5.3.3.2. Effect of cross-link content on Ideal CO₂ permeability selectivity

As seen in Fig. 5.4a-c, a rather dramatic reduction in ideal CO₂ selectivity occurred when a minimal amount of cross-linking monomer **1** was used, e.g., in membrane 15-**2b**-65. For example, the CO₂/N₂ selectivity of membrane 40-**2b**-65 was 37 compared to 26 for membrane 15-**2b**-65 (Fig. 5.4a). Similar selectivity reductions can be seen for CO₂/CH₄ and CO₂/H₂ (Figs. 5.4b and 5.4c, respectively). To better understand this effect, we have plotted ideal CO₂ permeability vs. mol % of cross-linking monomer in the pre-polymer mixture in Fig. 5.7a-c. It is important to note that very similar behavior was observed for the membranes that contained 45 wt. % and 75 wt. % of free RTIL **3**. However, for the sake of brevity we limit the focus of discussion here to the membranes shown in Table 5.1 entries 8-13, i.e. 65 wt. % free RTIL **3**. Additional figures can be found in Appendix C.




Figure 5.7. Ideal (a) CO_2/N_2 , (b) CO_2/CH_4 and (c) CO_2/H_2 permeability selectivity of 100-65, 80-2b-65, 60-2b-65, 40-2b-65, 80-2b-65, 20-2b-65, and 15-2b-65 (see Table 5.1) vs mol % of cross-linking monomer 1 in the pre-polymer mixture for. Mol % here is defined as moles of 1 divided by total moles of 1, 2 and 3. The molar compositions listed in Table 5.1 are defined as moles of 1 (or 2) dived by total moles of 1 and 2. The SILM performance of a membrane containing no cross-linkner (0-2b-65) (\blacktriangle) is also plotted. The lines connecting data points in figures a-c are only meant to guide the eye. The values next to the corresponding data points denote the membrane composition (see Table 5.1). Error given represents +/- one standard deviation.

The values for CO_2/N_2 and CO_2/CH_4 selectivity remained relatively constant as the content of cross-linker **1** was reduced from samples 100-65 to 40-**2b**-65 (Figs. 5.7a and 5.7b). CO_2/H_2 selectivity, on the other hand, was found to increase as the amount of **1** was reduced from 18 mol % to about 9 mol % (Fig. 5.7c). We suspect that the observed increase is a result of enhanced CO_2 diffusivity and, subsequently, CO_2/H_2 diffusivity selectivity. A clear increase in CO_2 diffusivity can be seen from membrane 100-65 (5.4 x 10^{-7} cm²s⁻¹) to membrane 40-**2b**-65 (7.3 x 10^{-7} cm²s⁻¹) (Table 5.2). This would imply that the polymer matrix becomes less size-selective upon reduced cross-linking (i.e., becomes more rubbery). In Section 3.1., we discussed a similar observation for CO_2/H_2 permeability selectivity as free RTIL content was increased. In that case,

the steady increase in selectivity was likely due to two cooperative effects: an "opening" of the polymer matrix (i.e., via reduced cross-linking) as the initial concentration of cross-linking monomer **1** became more dilute and an increase in the solubility selective nature as the content of free RTIL **3** was increased. The second of these two effects is likely not applicable here since the content of **3** remained constant. The first of these two effects, however, would seem to apply to the trend observed in Fig. 5.7c.

The significant reduction in CO₂ permeability selectivity below ca. 9 mol % **1** observed for all gas separation pairs does not follow a specific trend. It is reasonable to assume that the CO₂ selectivity becomes more "RTIL-like" since both CO₂/N₂ and CO₂/CH₄ selectivity of membrane 15-**2b**-65 are nearly identical to that of the pure RTIL **3** (Figs. 5.4a and 5.4b). This is not the case with CO₂/H₂ selectivity (Fig. 5.4c.), where we expect to observe an increase if membrane selectivity is indeed more "RTIL-like." The CO₂/CH₄ diffusivity and solubility selectivity for neat RTIL **3** was 2.6 and 5.7, respectively, but that of membrane 15-**2b**-65 was 5.3 and 2.6, respectively. Thus, the dominant selectivity mechanisms are switched for these two membranes, indicating sample 15-**2b**-65 is not inherently "RTIL-like." The dominant factor of selectivity for membranes 100-65 to 20-**2b**-65 was also based on solubility, rather than diffusivity, similar to RTIL **3**.

Clearly the reduction in CO_2/CH_4 and CO_2/N_2 permeability selectivity is due to the significant drop in solubility selectivity of membrane 15-**2b**-65 (Table 5.2). The reduction in CO_2/H_2 permeability selectivity (Figs. 5.7c and 5.4c), on the other hand, is likely due to the increased diffusivity selectivity of membrane 15-**2b**-65 (Table 5.2). The reduction in CO_2 diffusivity and increase in CO_2/CH_4 diffusivity selectivity (Table 5.2) implies that the membranes become more size-selective at the lowest concentrations of cross-linking monomer **1**.

This, of course, would result in favored diffusion of small molecule penetrants (i.e., H_2) compared to larger ones (i.e., CO_2). The data in Table 5.2 would also imply that a reduction in CO_2/H_2 solubility selectivity simultaneously occurs as well.

To gain more insight into the unusual selectivity trend we observed with reduced crosslinker content, a control membrane containing no cross-linker was fabricated and tested (as a SILM, since a solid was not formed). To allow for comparison of the results summarized in Table 5.2 and Fig. 5.7, this control membrane contained 2b and 65 wt % free RTIL 3 (i.e., 0-2b-65). The performance of control membrane 0-2b-65 represents the extreme limit for CO_2 permeability and selectivity as the amount of cross-linking monomer **1** is reduced. Membrane 0-**2b**-65 is composed of linear homopolymer dissolved in RTIL **3**, since no solid was formed. The ideal CO_2/N_2 , CO_2/CH_4 , and CO_2/H_2 permeability selectivities of membrane 0-2b-65 were found to be 30, 16, and 9.7, respectively. We noticed that the selectivity performance of 0-2b-65 lies between that of membranes 20-2b-65 and 15-2b-65 (Figs. 5.7a-c). The values for CO₂ and CH₄ diffusivity were also quite similar between samples 0-2b-65 and 15-2b-65 (Table 5.2). Thus, we suspect that membranes 15-2b-65 and 0-2b-65 are structurally and morphologically similar (i.e., linear polymer dissolved in liquid). Diffusivity and selectivity data (Table 5.2) also suggests that the morphology of sample 15-2b-65 is quite different from membranes 20-2b-65 to 100-65, where higher concentrations of 1 were used. Based on prior studies [59, 72, 79], it is likely that at higher cross-linker concentrations (e.g. $> -5 \mod \%$), the membrane structure is composed of heterogeneous regions of dense, polymer microgels and highly fluid RTIL/monomer channels, which would act as conduits for gas diffusion. If this were the case, one would expect much lower transport resistance in the RTIL domains compared to dense microgel regions. This would imply that heterogeneous RTIL-gel membranes would have CO₂ separation performance

characteristics more similar to the pure free RTIL, rather than to the polymer, at higher concentrations of **1**. The solubility and diffusivity selectivity data for membranes 100-65 to 20-**2b**-65 in Table 5.2 strongly suggests that separation performance of these membranes is, in fact, more "RTIL-like" than 15-**2b**-65 and 0-**2b**-65. Recall that the wt. % of sol in 20-**2b**-65 and 15-**2b**-65 was 80 % and 93 %, respectively, which indicated little occurrence of macrogelation in 20-**2b**-65 and almost none in 15-**2b**-65. Perhaps at these lower concentrations of **1**, the disconnect between the two regimes became less distinct to the point where RTIL "pools" no longer exist, but rather polymer and RTIL are mutually intermixed with one another. The similarity in performance between membranes 0-**2b**-65 (which has no cross-linker) and 15-**2b**-65 suggests that this is likely the case.

The reason as to why the membranes became more dominantly diffusivity-selective at low concentrations of cross-linking monomer **1** still remains somewhat unclear. We hypothesize that the membranes are more liquid- than solid-like in nature, and the presence of the polymer component acted to drastically increase liquid (i.e. RTIL **3**) viscosity. This may explain why we observed a reduction in CO_2 diffusivity and an increase in CO_2/CH_4 diffusivity selectivity for membranes 15-**2b**-65 and 0-**2b**-65 compared to 40-**2b**-65. In membranes 15-**2b**-65 and 0-**2b**-65, we suspect that much longer and more uniformly dispersed poly(ethylene) units (i.e., linear polymer backbone) exist in the membrane. This may have led to the dramatic rise in CH₄ solubility and subsequent loss in CO_2/CH_4 solubility selectivity observed for these two membranes (Table 5.2).

5.3.4. Effect of monofunctional monomer substituent on CO_2 permeability and selectivity

To investigate the effect of the mono-functional monomer substituent on cross-linked membrane performance, monomers 2a and 2c were synthesized and copolymerized with crosslinking monomer 1 to afford four membranes. The CO₂ diffusivity, solubility, permeability and permeability selectivity of these membranes is summarized in Table 5.3, along with the performance of analogous films composed of just 2b (80 mol %) and 1 (20 mol %).

Table 5.3. CO₂ diffusivity, solubility, permeability and permeability selectivity of selected membranes in this study.^{a,b,c,d}

Membrane	Mol % 1	Wt. % 3	D(CO ₂) x 10 ⁷	S(CO ₂)	P(CO ₂)	P(CO ₂)/P(CH ₄)	$P(CO_2)/P(N_2)$	P(CO ₂)/P(H ₂)
20- 2a -45	20	45	2.8 ± 0.2	4.9 ± 0.3	180 ± 10	22	35	6.6
20- 2b -45	20	45	4.0 ± 0.3	4.7 ± 0.3	250 ± 10	22	35	6.7
20- 2c -45	20	45	4.2 ± 0.3	4.3 ± 0.2	240 ± 10	17	31	7.1
20- 2a -65	20	65	6.9 ± 0.6	4.1 ± 0.2	370 ± 20	19	34	9.8
20- 2b -65	20	65	7.0 ± 0.5	4.2 ± 0.2	390 ± 20	19	36	10
20- 2c -65	20	65	8.2 ± 0.6	3.9 ± 0.2	420 ± 20	18	32	9.6

^aDiffusivity in cm²s⁻¹

^bSolubility in cm³(stp) cm⁻³atm⁻¹

^cPermeability in barrer

^dError represents +/- one standard deviation

The effect of monomer substituent was investigated at two loading levels of RTIL **3**, 45 wt. % and 65 wt. %. At the lower loading of RTIL **3** (45 wt. %), there was no significant difference in CO₂ permeability between samples 20-**2b**-45 (250 barrers) and 20-**2c**-45 (240 barrers). A slightly lower CO₂ permeability of 180 barrers, however, was observed for membrane 20-45-**2a** compared to 20-**2b**-45. This would suggest that the shorter substituent on monomer **2a** allows for more efficient packing of polymer chains at this concentration of **3** compared to the membrane with **2b**. The lower diffusivity of membrane 20-**2a**-45 ($2.8 \times 10^{-7} \text{ vs } 4.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) also suggests this is the case. At higher RTIL **3** loading, however, the length of the substituent on the mono-functional monomer appears to have a lesser influence on permeability and diffusivity. For example, the CO₂ permeability of membrane 20-**2a**-65 was 370 barrers compared to 390 barrers for 20-**2b**-65. Likewise, the chemical nature of the substituent (i.e., polar vs. apolar) seems to make only a minimal difference at the higher loading of free RTIL **3**. As seen in Table 5.3, the permeability of membrane 20-**2c**-65 is 420 barrers.

The length of the monomer substituent has no observable effect on CO₂ permeability selectivity at the lower loading level of **3**, as seen by comparison of membranes 20-**2a**-45 to 20-**2b**-45 in Table 5.3. A noticeable, although marginal, difference in selectivity, for CO₂/N₂ and CO₂/CH₄ in particular, was observed for membrane 20-**2c**-45. CO₂/CH₄ and CO₂/N₂ permeability selectivity for this membrane was 17 and 31, respectively, compared to 22 and 35 for 20-**2b**-45. We suspect that the enhanced CO₂ selectivity of membranes 20-**2b**-45 and 20-**2a**-45 is due to the presence of polar ethylene oxide units, which are known to improve CO₂ solubility [20, 70]. At the higher loadings of RTIL **3** (65 wt. %), the length of the monomer substituent has no effect on CO₂/CH₄ permeability selectivity and little, if any, effect on CO₂/N₂ permeability selectivity. For example, the CO₂/N₂ permeability selectivity for membranes 20-**2a**-65 and 20-**2b**-65 was found to be 34 and 36, respectively. As seen with the lower loading level of **3**, membrane 20-**2b**-45 (Table 5.3).

5.4. Conclusions

A series of cross-linked, poly(vinylimidazolium)-RTIL gel membranes were synthesized. These membranes contained three distinct components: di-functional (i.e. cross-linking) RTIL monomer, mono-functional RTIL monomer (if copolymerized), and free, non-polymerizable RTIL (emim Tf₂N). The effect of free RTIL loading on ideal CO₂ permeability and ideal CO₂/N₂, CO₂/CH₄, and CO₂/H₂ permeability selectivity was investigated by evaluating membranes fabricated with di-functional monomer and 45, 65, or 75 wt. % free RTIL. The effect of cross-link content on copolymer membrane separation performance was also investigated by varying copolymer composition from 5-100 mol % di-functional monomer at all three levels of RTIL loading. The substituent on the mono-functional monomer (i.e., non-cross-linking) was varied in length and structure to investigate the effect of this component on cross-linked copolymer gel membrane CO₂ separation performance.

 CO_2 permeability dramatically increased and ideal CO_2/N_2 and CO_2/CH_4 permeability selectivity remained nearly constant with higher loading of free RTIL. However, ideal CO_2/H_2 permeability selectivity was significantly improved as the content of free RTIL in the membranes was increased. The membrane containing 75 wt. % free RTIL certainly possessed the most impressive CO_2 permeability (520 barrers). While ideal CO_2/N_2 and CO_2/CH_4 permability selectivities for this membrane were good (37 and 20, respectively), ideal CO_2/H_2 permeability selectivity was quite remarkable (12). There are very limited examples of membranes possessing CO_2 permeabilities exceeding 100 barrers and CO_2/H_2 selectivities over 10 [16, 17, 51].

Decreasing the amount of cross-linking monomer generally resulted in enhanced diffusivity for all studied gases. The ideal CO_2/N_2 and CO_2/CH_4 permeability selectivity remained nearly constant, while CO_2/H_2 selectivity was slightly improved with decreasing

concentration of cross-linking monomer. However, each system (45, 65, or 75 wt. % RTIL) displayed somewhat anomalous permeability and selectivity behavior below critical concentrations of cross-linking monomer. For example, CO₂ permeability was found to *decrease* when the concentration of di-functional monomer went below a certain amount. We suspect that these unexpected trends were due to a significant degree of residual unsaturation, inhomogeneous network formation, and competition between the "cross-linking" and "co-polymer" effects on CO₂ permeability. Ideal CO₂ permeability was found to dramatically increase at the lowest concentrations of di-functional monomer. However, ideal CO₂ permeability selectivity for all gas pairs was greatly reduced at the lowest studied concentrations of di-functional monomer. We attributed these observations to a radical morphological change in copolymer network structure when minimal di-functional monomer was used.

Copolymer membrane separation performance was affected very minimally by varying the length or chemical composition of the mono-functional monomer substituent. Shortening the length of the substituent resulted in a slight reduction in ideal CO_2 permeability and no observable effect on ideal CO_2 selectivity. Replacing the substituent with an apolar, *n*-hexyl appendage affected CO_2 permeability very little, but slightly reduced ideal CO_2 selectivity. This indicated that the presence of ether-oxygen groups in the mono-functional monomer contributes to enhanced, "PEO-like" CO_2 selectivity. However, it is unclear as to how the mono-functional monomer structure impacts network formation during polymerization.

The studied cross-linked poly(RTIL)-RTIL gels have certainly demonstrated much promise as a configuration that both "stabilizes" the liquid RTIL *and* possesses "liquid-like" CO₂ separation performance. We have recognized that performance of these membranes can be improved by the "simple choice" of a more CO_2 -selective RTIL, and we are currently investigating several RTIL candidates that substantially improve membrane performance. As described in this work, these membranes are considerably straightforward to fabricate; this fact belies the complex nature of network formation and resulting membrane properties. While it is certainly important to investigate the RTIL aspect (i.e., gels of different RTILs), it is perhaps more critical to gain a fundamental understanding of these cross-linked poly(RTIL)-RTIL membranes with respect to network formation and gel properties. Only then can researchers truly tailor these materials for enhanced CO_2 separation performance and, more critically, optimization of liquid stability at higher pressures. Clearly the CO_2 separation performances presented here, however impressive, are meaningless if liquid stability is compromised at elevated pressures. The industrial viability of these materials will depend not only on demonstrated long-term pressure stability, but also on the ability to form thin (e.g. $\leq 1 \mu m$) poly(RTIL)-RTIL gel films. Progress toward both of these ends will require a comprehensive understanding of material-property relationships.

5.5. Acknowledgements

The authors gratefully acknowledge primary financial support for the work performed at CU Boulder , which was provided by the Advanced Research Projects Agency-Energy (Grant DE-AR0000098). Additional financial support for this research was provided by the National Science Foundation via an SBIR Phase 1 subcontract grant through Membrane Technology and Research (Grant IIP1047356).

5.6. References

- 1. *Basic research needs for geosciences: Facilitating 21st century energy systems*, 2007, Office of Basic Energy Sciences of the U.S. Dept. of Energy.
- 2. Jones, C.W. and Maginn, E.J., "Materials and processes for carbon capture and sequestration." ChemSusChem **2010**, *3*, 863-864.
- 3. Descamps, C., Bouallou, C., Kanniche, M., "Efficiency of an integrated gasification combined cycle (IGCC) power plant including CO₂ removal." Energy **2008**, *33*, 874-881.
- 4. Sridhar, S., Smitha, B., Aminabhavi, T.M., "Separation of carbon dioxide from natural gas mixtures through polymeric membranes—a review." Separ. Purif. Rev. **2007**, *36*, 113-174.
- 5. *Review of emerging resources: U.S. Shale gas and shale plays.* 2011 [cited 2011 August]; Available from: <u>http://www.eia.gov</u>.
- 6. Kohl, A.L. and Nielsen, R.B., *Gas purification (5th edition)*, Elsevier.
- 7. Barelli, L., Bidini, G., Gallorini, F., Servili, S., "Hydrogen production through sorptionenhanced steam methane reforming and membrane technology: A review." Energy **2008**, *33*, 554-570.
- Ko, D., Siriwardane, R., Biegler, L.T., "Optimization of a pressure-swing adsorption process using zeolite 13x for CO₂ sequestration." Ind. Eng. Chem. Res. 2003, 42, 339-348.
- 9. Ho, M.T., Allinson, G.W., Wiley, D.E., "Reducing the cost of CO₂ capture from flue gases using pressure swing adsorption." Ind. Eng. Chem. Res. **2008**, *47*, 4883-4890.
- 10. Oyenekan, B.A. and Rochelle, G.T., "Energy performance of stripper configurations for CO₂ capture by aqueous amines." Ind. Eng. Chem. Res. **2005**, *45*, 2457-2464.
- 11. Rochelle, G.T., "Amine scrubbing for CO₂ capture." Science **2009**, *325*, 1652-1654.

- 12. Zolandz, R.R. and Fleming, G.K., *Membane handbook* 1992, New York, NY: Chapman & Hall.
- 13. Baker, R.W., *Membrane technology and applications*. 2nd ed 2004, West Sussex, England: John Wiley & Sons, Ltd.
- 14. Robeson, L.M., "The upper bound revisited." J. Membr. Sci. 2008, 320, 390-400.
- 15. Powell, C.E. and Qiao, G.G., "Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases." J. Membr. Sci. **2006**, *279*, 1-49.
- 16. Patel, N.P., Miller, A.C., Spontak, R.J., "Highly CO₂-permeable and selective polymer nanocomposite membranes." Adv. Mater. **2003**, *15*, 729-733.
- 17. Lin, H., Van Wagner, E., Freeman, B.D., Toy, L.G., Gupta, R.P., "Plasticizationenhanced hydrogen purification using polymeric membranes." Science **2006**, *311*, 639-642.
- Lin, H., Kai, T., Freeman, B.D., Kalakkunnath, S., Kalika, D.S., "The effect of crosslinking on gas permeability in cross-linked poly(ethylene glycol diacrylate)." Macromolecules 2005, *38*, 8381-8393.
- 19. Lin, H., Van Wagner, E., Raharjo, R., Freeman, B.D., Roman, I., "High-performance polymer membranes for natural-gas sweetening." Adv. Mater. **2006**, *18*, 39-44.
- 20. Bara, J.E., Gabriel, C.J., Lessmann, S., Carlisle, T.K., Finotello, A., Gin, D.L., Noble, R.D., "Enhanced CO₂ separation selectivity in oligo(ethylene glycol) functionalized room-temperature ionic liquids." Ind. Eng. Chem. Res. **2007**, *46*, 5380-5386.
- 21. Muldoon, M.J., Aki, S.N.V.K., Anderson, J.L., Dixon, J.K., Brennecke, J.F., "Improving carbon dioxide solubility in ionic liquids." J. Phys. Chem. B **2007**, *111*, 9001-9009.
- 22. Carlisle, T.K., Bara, J.E., Gabriel, C.J., Noble, R.D., Gin, D.L., "Interpretation of CO₂ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach." Ind. Eng. Chem. Res. **2008**, *47*, 7005-7012.

- 23. Bara, J.E., Gabriel, C.J., Carlisle, T.K., Camper, D.E., Finotello, A., Gin, D.L., Noble, R.D., "Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes." Chem. Eng. J. **2009**, *147*, 43-50.
- 24. Raeissi, S. and Peters, C.J., "A potential ionic liquid for CO₂-separating gas membranes: Selection and gas solubility studies." Green Chem. **2009**, *11*, 185-192.
- 25. Mahurin, S.M., Lee, J.S., Baker, G.A., Luo, H., Dai, S., "Performance of nitrilecontaining anions in task-specific ionic liquids for improved CO₂/N₂ separation." J. Membr. Sci. **2010**, *353*, 177-183.
- 26. Camper, D., Bara, J., Koval, C., Noble, R., "Bulk-fluid solubility and membrane feasibility of rmim-based room-temperature ionic liquids." Ind. Eng. Chem. Res. **2006**, *45*, 6279-6283.
- 27. Yokozeki, A. and Shiflett, M.B., "Hydrogen purification using room-temperature ionic liquids." Applied Energy **2007**, *84*, 351-361.
- Scovazzo, P., Kieft, J., Finan, D.A., Koval, C., DuBois, D., Noble, R., "Gas separations using non-hexafluorophosphate [pf₆]⁻ anion supported ionic liquid membranes." J. Membr. Sci. 2004, 238, 57-63.
- 29. Morgan, D., Ferguson, L., Scovazzo, P., "Diffusivities of gases in room-temperature ionic liquids: Data and correlations obtained using a lag-time technique." Ind. Eng. Chem. Res. **2005**, *44*, 4815-4823.
- Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L., Noble, R.D., "Guide to CO₂ separations in imidazolium-based room-temperature ionic liquids." Ind. Eng. Chem. Res. 2009, 48, 2739-2751.
- 31. Scovazzo, P., "Determination of the upper limits, benchmarks, and critical properties for gas separations using stabilized room temperature ionic liquid membranes (silms) for the purpose of guiding future research." J. Membr. Sci. **2009**, *343*, 199-211.
- 32. Riisagera, A., Fehrmanna, R., Haumann, M., Wasserscheid, P., "Supported ionic liquids: Versatile reaction and separation media." Top. Catal. **2006**, *40*, 91-102.

- 33. Hanioka, S., Maruyama, T., Sotani, T., Teramoto, M., Matsuyama, H., Nakashima, K., Hanaki, M., Kubota, F., Goto, M., "CO₂ separation facilitated by task-specific ionic liquids using a supported liquid membrane." J. Membr. Sci. **2008**, *314*, 1-4.
- 34. Myers, C., Pennline, H., Luebke, D., Ilconich, J., Dixon, J.K., Maginn, E.J., Brennecke, J.F., "High temperature separation of carbon dioxide/hydrogen mixtures using facilitated supported ionic liquid membranes." J. Membr. Sci. **2008**, *322*, 28-31.
- 35. Bara, J.E., Lessmann, S., Gabriel, C.J., Hatakeyama, E.S., Noble, R.D., Gin, D.L., "Synthesis and performance of polymerizable room-temperature ionic liquids as gas separation membranes." Ind. Eng. Chem. Res. **2007**, *46*, 5397-5404.
- 36. Bara, J.E., Gabriel, C.J., Hatakeyama, E.S., Carlisle, T.K., Lessmann, S., Noble, R.D., Gin, D.L., "Improving CO₂ selectivity in polymerized room-temperature ionic liquid gas separation membranes through incorporation of polar substituents." J. Membr. Sci. **2008**, *321*, 3-7.
- Bara, J.E., Hatakeyama, E.S., Gabriel, C.J., Zeng, X., Lessmann, S., Gin, D.L., Noble, R.D., "Synthesis and light gas separations in cross-linked gemini room temperature ionic liquid polymer membranes." J. Membr. Sci. 2008, *316*, 186-191.
- 38. Bara, J.E., Hatakeyama, E.S., Gin, D.L., Noble, R.D., "Improving CO₂ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid." Polym. Adv. Technol. **2008**, *19*, 1415-1420.
- Bara, J.E., Gin, D.L., Noble, R.D., "Effect of anion on gas separation performance of polymer-room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. 2008, 47, 9919-9924.
- 40. Bara, J.E., Noble, R.D., Gin, D.L., "Effect of "free" cation substituent on gas separation performance of polymer–room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. **2009**, *48*, 4607-4610.
- 41. Lodge, T.P., "A unique platform for materials design." Science 2008, 321, 50-51.
- 42. Peppas, N.A. and Mikos, A.G., in *Hydrogels in medicine and pharmacy*, Peppas, N.A., Editor 1986, CRC Press, Inc.: Boca Raton, FL. p. 1.

- 43. Ohno, H., Yoshizawa, M., Ogihara, W., "Development of new class of ion conductive polymers based on ionic liquids." Electrochim. Acta **2004**, *50*, 255-261.
- 44. Washiro, S., Yoshizawa, M., Nakajima, H., Ohno, H., "Highly ion conductive flexible films composed of network polymers based on polymerizable ionic liquids." Polymer **2004**, *45*, 1577-1582.
- 45. Nakajima, H. and Ohno, H., "Preparation of thermally stable polymer electrolytes from imidazolium-type ionic liquid derivatives." Polymer **2005**, *46*, 11499-11504.
- 46. Susan, M.A.B.H., Kaneko, T., Noda, A., Watanabe, M., "Ion gels prepared by in situ radical polymerization of vinyl monomers in an ionic liquid and their characterization as polymer electrolytes." J. Am. Chem. Soc. **2005**, *127*, 4976-4983.
- 47. Ohno, H., "Design of ion conductive polymers based on ionic liquids." Macromol. Symp. **2007**, *249-250*, 551-556.
- 48. Mizumo, T., Watanabe, T., Matsumi, N., Ohno, H., "Preparation of ion conductive inorganic–organic composite systems by in situ sol–gel reaction of polymerizable ionic liquids." Polym. Adv. Technol. **2008**, *19*, 1445-1450.
- 49. Jin, X., Tao, J., Yang, Y., "Synthesis and characterization of poly(1-vinyl-3propylimidazolium) iodide for quasi-solid polymer electrolyte in dye-sensitized solar cells." J. Appl. Polym. Sci. **2010**, *118*, 1455-1461.
- 50. Uk Hong, S., Park, D., Ko, Y., Baek, I., "Polymer-ionic liquid gels for enhanced gas transport." Chem. Commun. **2009**, 7227-7229.
- 51. Jansen, J.C., Friess, K., Clarizia, G., Schauer, J., Izák, P., "High ionic liquid content polymeric gel membranes: Preparation and performance." Macromolecules **2011**, *44*, 39-45.
- 52. Gu, Y. and Lodge, T.P., "Synthesis and gas separation performance of triblock copolymer ion gels with a polymerized ionic liquid mid-block." Macromolecules **2011**, *44*, 1732-1736.
- 53. Li, P., Pramoda, K.P., Chung, T.-S., "CO₂ separation from flue gas using polyvinyl-(room temperature ionic liquid)–room temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. **2011**, *50*, 9344-9353.

- 54. Peppas, N.A. and Barr-Howell, B.D., in *Hydrogels in medicine and pharmacy*, Peppas, N.A., Editor 1986, CRC Press, Inc.: Boca Raton, FL. p. 27.
- 55. Loshaek, S., "Crosslinked polymers. Ii. Glass temperatures of copolymers of methyl methacrylate and glycol dimethacrylates." J. Polym. Sci. **1955**, *15*, 391-404.
- 56. Dušek, K. and Ilavský, M., "Cyclization in crosslinking polymerization. I. Chain polymerization of a bis unsaturated monomer (monodisperse case)." J. polym. Sci. Polym. Symp. **1975**, *53*, 57-73.
- 57. Dušek, K. and Ilavský, M., "Cyclization in crosslinking polymerization. Ii. Chain polymerization of a bis unsaturated monomer (polydisperse case)." J. Polym. Sci. Polym. Symp. **1975**, *53*, 75-88.
- 58. Boots, H.M.J., Kloosterboer, J.G., Van Hei, G.M.M.D., Pandey, R.B., "Inhomogeneity during the bulk polymerisation of divinyl compounds: Differential scanning calorimetry experiments and percolation theory." Brit. Polym. J. **1985**, *17*, 219-223.
- 59. Anseth, K.S. and Bowman, C.N., "Kinetic gelation predictions of species aggregation in tetrafunctional monomer polymerizations." J. Polym. Sci. Polym. Phys. **1995**, *33*, 1769-1780.
- 60. Kannurpatti, A.R., Anderson, K.J., Anseth, J.W., Bowman, C.N., "Use of "living" radical polymerizations to study the structural evolution and properties of highly crosslinked polymer networks." J. Polym. Sci. Polym. Phys. **1997**, *35*, 2297-2307.
- 61. Ward, J.H., Furman, K., Peppas, N.A., "Effect of monomer type and dangling end size on polymer network synthesis." J. Appl. Polym. Sci. **2003**, *89*, 3506-3519.
- 62. Elliott, J.E., Macdonald, M., Nie, J., Bowman, C.N., "Structure and swelling of poly(acrylic acid) hydrogels: Effect of ph, ionic strength, and dilution on the crosslinked polymer structure." Polymer **2004**, *45*, 1503-1510.
- 63. Lin-Gibson, S., Jones, R.L., Washburn, N.R., Horkay, F., "Structure-property relationships of photopolymerizable poly(ethylene glycol) dimethacrylate hydrogels." Macromolecules **2005**, *38*, 2897-2902.
- 64. Chesnokov, S.A., Zakharina, M.Y., Shaplov, A.S., Lozinskaya, E.I., Malyshkina, I.A., Abakumov, G.A., Vidal, F., Vygodskii, Y.S., "Photopolymerization of poly(ethylene

glycol) dimethacrylates: The influence of ionic liquids on the formulation and the properties of the resultant polymer materials." J. Polym. Sci. Polym. Chem. **2010**, *48*, 2388-2409.

- 65. Finotello, A., Bara, J.E., Camper, D., Noble, R.D., "Room-temperature ionic liquids: Temperature dependence of gas solubility selectivity." Ind. Eng. Chem. Res. **2007**, *47*, 3453-3459.
- 66. Carlisle, T.K., Bara, J.E., Lafrate, A.L., Gin, D.L., Noble, R.D., "Main-chain imidazolium polymer membranes for CO₂ separations: An initial study of a new ionic liquid-inspired platform." J. Membr. Sci. **2010**, *359*, 37-43.
- 67. Jenkins, R.C.L., Nelson, P.M., Spirer, L., "Calculation of the transient diffusion of a gas through a solid membrane into a finite outflow volume." Trans. Faraday. Soc. **1970**, *66*, 1391-1401.
- 68. Ortega, A.M., Kasprzak, S.E., Yakacki, C.M., Diani, J., Greenberg, A.R., Gall, K., "Structure–property relationships in photopolymerizable polymer networks: Effect of composition on the crosslinked structure and resulting thermomechanical properties of a (meth)acrylate-based system." J. Appl. Polym. Sci. **2008**, *110*, 1559-1572.
- 69. Kannurpatti, A.R., Anseth, J.W., Bowman, C.N., "A study of the evolution of mechanical properties and structural heterogeneity of polymer networks formed by photopolymerizations of multifunctional (meth)acrylates." Polymer **1998**, *39*, 2507-2513.
- 70. Lin, H. and Freeman, B.D., "Gas solubility, diffusivity and permeability in poly(ethylene oxide)." J. Membr. Sci. **2004**, *239*, 105-117.
- 71. Freeman, B.D., "Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes." Macromolecules **1999**, *32*, 375-380.
- 72. Kannurpatti, A.R. and Bowman, C.N., "Structural evolution of dimethacrylate networks studied by dielectric spectroscopy." Macromolecules **1998**, *31*, 3311-3316.
- 73. Lieberman, E.R. and Gilbert, S.G., "Gas permeation of collagen films as affected by cross-linkage, moisture, and plasticizer content." J. Polym. Sci. Polym. Symp. **1973**, *41*, 33-43.

- 74. Kalakkunnath, S., Kalika, D.S., Lin, H., Freeman, B.D., "Segmental relaxation characteristics of cross-linked poly(ethylene oxide) copolymer networks." Macromolecules **2005**, *38*, 9679-9687.
- 75. Lin, H., Freeman, B.D., Kalakkunnath, S., Kalika, D.S., "Effect of copolymer composition, temperature, and carbon dioxide fugacity on pure- and mixed-gas permeability in poly(ethylene glycol)-based materials: Free volume interpretation." J. Membr. Sci. **2007**, *291*, 131-139.
- 76. Greenberg, A.R. and Kusy, R.P., "Influence of crosslinking on the glass transition of poly(acrylic acid)." J. Appl. Polym. Sci. **1980**, *25*, 1785-1788.
- 77. Bowman, C.N. and Anseth, K.S., "Microstructural evolution in polymerizations of tetrafunctional monomers." Macromol. Symp. **1995**, *93*, 269-276.
- 78. Chomff, A.J., in *Polymer networks: Structure and mechanical properties*, Chomff, A.J. and Newman, S., Editors. 1971, Plenum Press: New York, NY. p. 145.
- 79. Simon, G.P., Allen, P.E.M., Bennett, D.J., Williams, D.R.G., Williams, E.H., "Nature of residual unsaturation during cure of dimethacrylates examined by cppemas carbon-13 nmr and simulation using a kinetic gelation model." Macromolecules **1989**, *22*, 3555-3561.
- 80. Anderson, J.L., Ding, R., Ellern, A., Armstrong, D.W., "Structure and properties of high stability geminal dicationic ionic liquids." J. Am. Chem. Soc. **2004**, *127*, 593-604.
- 81. Platé, N. and Yampol'skii, Y., in *Polymeric gas separation membranes*, Paul, D.R. and Yampol'skii, Y.P., Editors. 1994, CRC Press, Inc.: Boca Raton, FL. p. 155.
- 82. Pinnau, I., Morisato, A., He, Z., "Influence of side-chain length on the gas permeation properties of poly(2-alkylacetylenes)." Macromolecules **2004**, *37*, 2823-2828.

Chapter 6

Conclusions and Recommendations

6.1 Summary of thesis work

In Chapter 2 it was demonstrated that group contribution theory and regular solution theory can be used in combination to interpret the CO₂ solubility and CO₂/light gas solubility selectivity performance of imidazolium-based RTILs. More importantly, it was demonstrated that this simple model can be used to predict RTIL solubility parameter and, subsequently, CO₂ solubility and selectivity of newly synthesized RTILs; one need only to obtain the RTIL density. It was shown that CO_2 solubility is reduced while CO_2 selectivity is enhanced when RTIL solubility parameter is increased. Increasing the solubility parameter can be achieved by appending the cation with functional groups that possess large molar attraction constants, such as nitriles, alkynes, or ethers. This design concept was explored and validated further in a recent review [1]. As there are certainly millions upon millions of possible RTIL structures, this model will no doubt assist in substantially narrowing the field of "promising" RTIL candidates. However, it seems clear that radical changes in RTIL solubility parameter (i.e. CO₂ selectivity) are difficult to achieve via addition of an increasing number of functional groups on the cation or anion. Adding more functionality will result in an increase in molar volume, which effectively "dilutes" the effect of further functionalization. The optimal approach toward developing highly CO₂-selective RTILs may be to functionalize RTILs that have inherently small molar volumes (e.g., RTILs with small anions: BF₄, dca, OTf, tcm, etc).

An important consequence of appending polar substituents (i.e., high molar attraction constants) to the cation is generally enhanced RTIL-RTIL interactions and increased RTIL viscosity [2]. It is well-known that RTIL gas diffusivity and permeability are strong functions of RTIL viscosity [2-5]. Highly viscous RTILs generally have poor CO₂ permeabilities and reduced CO_2/H_2 diffusivity selectivities, due to their enhanced size-selective nature. As bulk liquids, functionalized RTILs may be synthesized that possess excellent CO₂ selectivity, but their permeability may suffer significantly due to their viscous nature. This highlights a very important tradeoff inherent to the design of higher solubility parameter, more CO₂-selective, RTILs. In addition to minimizing RTIL molar volume as described above, it also recommended to focus the design of new RTILs that possess minimal bulk viscosities. RTILs that will prove optimal for membrane-based separations will likely possess large solubility parameters (e.g., > 27 MPa^{1/2}) and low viscosities (e.g., < 20 cP). In the near term, imidazolium-based RTILs with nitrile-functionalized anions appear to be promising candidates for use in composite and gel configurations (Ch. 3-5) [6, 7]. However, there will no doubt be other significant tradeoffs in material properties to consider that have not been discussed here, such as hydrophobicity and thermal and chemical stability. Perhaps many of these tradeoffs can be balanced by blending RTILs that possess disparate material properties.

The synthesis and performance of new, main-chain poly(imidazolium) membranes was presented in Chapter 3. These polymers were fabricated by the Sn2 step growth polymerization of bisimidazole and dialkylhalide monomers followed by subsequent anion exchange to the Tf₂N anion. Main-chain poly(imidazolium)s are a unique class of linear, step-growth polymerization polymers since the reaction mechanism does not involve the condensation of a small molecule bi-product, such as HCl or H₂O, which typically hinder continued polymerization [8]. However, the Sn2 mechanism is certainly slower compared to the reaction of an acid chloride with an alcohol or an amine (i.e., as in the step-growth polymerization of poly(ester)s or poly(amide)s) [8, 9]. It was demonstrated that CO₂ separation with these membranes was moderate in terms of CO_2 permeability and CO_2 /light gas selectivity. However, the CO_2 permeability of these preliminary materials was improved by incorporation of "free RTIL." It was also shown that the CO_2 separation performance of these polymers was quite moderate in comparison to previously studied photo-polymerizable, chain-addition poly(RTIL)s. However, there is much room for improvement upon main-chain poly(imidazolium) performance. Replacement of the *n*-decyl spacer group with an oligo(ethylene glycol) spacer could certainly improve linear chain flexibility (i.e., permeability) and CO_2 /light gas selectivity, for example [10]. The greatest value in main-chain imidazolium polymers is, perhaps, their unique ability to homogenously blend with liquid RTILs. New polymeric materials that possess this quality are of great value, since the performance of composite structures has been shown to be very promising (Ch. 4 and 5) [11-13]. Main-chain poly(imidazolium)s may also offer unique material properties that are not available in poly(olefin)-based, chain-addition poly(RTIL)s. This initial study serves as a demonstration and new platform upon which future studies of main-chain poly(imidazolium)s should certainly be based.

The synthesis and CO_2 /light gas membrane separation performance for a series of photopolymerized, vinyl-based poly(RTIL)s was presented in Chapter 4. This study investigated the effect of poly(RTIL) polymer backbone (e.g., poly(ethylene) vs. poly(styrene) and poly(acrylate)) on CO_2 permeability and selectivity. This study also investigated the structurepermeability relationships of vinyl-based poly(RTIL)s by varying the imidazolium monomer substituent from *n*-alkyl to oligo(ethylene glycol), fluoroalkyl, and disiloxane. It was

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demonstrated that vinyl-based poly(RTIL)s are generally less selective than analogous styreneand acrylate-based poly(RTIL)s. However, depending on monomer substituent, the vinyl-based poly(RTIL)s were shown to be substantially more permeable. This was the case for *n*-hexyl- and disiloxane-functionalized poly(RTIL)s. Although these relatively permeable vinyl poly(RTIL)s do not possess favorable CO_2/N_2 or CO_2/CH_4 permeability selectivity, it was shown that inclusion of 20 mol % "free RTIL" improves CO₂ permeability and CO₂ selectivity. It is incredibly rare to observe an improvement in polymer membrane permeability coupled with an improvement in permeability selectivity (or vice versa). It was demonstrated that this type of enhancement is possible if the parent polymer is less selective than the inherent CO₂ selectivity of the neat liquid RTIL. The results of this work have established a new approach toward poly(RTIL) design and performance. The development of future poly(RTIL)s should be focused on increasing neat polymer permeability, rather than selectivity. Since the difference in current vinyl poly(RTIL) and SILM permeability is nearly an order of magnitude (i.e., 100 barrers vs. 1000 barrers), a large amount of free RTIL will be needed to improve permeability to a level that can be considered competitive. This will likely result in mechanical stability issues due to the presence of high liquid volumes. The difference in vinyl poly(RTIL) and SILM CO₂ selectivity, on the other hand, is only a factor of about 1.5-3. Developing more permeable "parent poly(RTIL)s" will require less free RTIL to improve membrane permeability to a point that can be considered competitive (i.e., approaches or exceeds the "upper bound" [14]). Since the difference in CO₂ selectivity between poly(RTIL)s and SILMs is substantially less than the difference in permeability, minimal amounts of free RTIL (e.g. < 50 wt %) can possibly result in large improvements in selectivity. Based on the work presented in Chapter 4, vinyl-based poly(RTIL)s are good candidates to further improve parent polymer permeability. The

disiloxane-functionalized poly(RTIL) is especially promising. However, there are certainly other polymer moieties, such as PEO and PDMS, which possess inherently higher CO_2 permeability and/or selectivity. There may be much value in functionalizing these polymers with RTIL units (e.g. imidazolium) to allow compatibility and stability with free liquid RTIL.

The synthesis and CO_2 separation performance of cross-linked poly(RTIL)-RTIL gel membranes was presented in Chapter 5. The "free RTIL" component in these membranes was stabilized by the cross-linked, copolymer network formed during photo-copolymerization of difunctional and mono-functional RTIL monomers. The effect of free RTIL content was investigated by varying the loading at three levels (45, 65, and 75 wt % RTIL). The membrane permeability was drastically improved by increasing the liquid RTIL loading. However, little change in CO₂/N₂ and CO₂/CH₄ permeability selectivity was observed. The measured CO₂/H₂ selectivity, on the other hand, was found to substantially improve with increasing liquid loading. The permeability of the studied membranes was generally increased by reducing the amount of di-functional (i.e. cross-linking) monomer. However, below certain concentrations (which depended on free RTIL content) of di-functional monomer the permeability was found to decrease. This anomalous behavior was likely due to heterogeneous network formation and competition between the "copolymer effect" and "cross-linking effect" on CO₂ permeability. The measured CO₂ selectivity remained relatively unchanged with reduced di-functional monomer concentration, although CO_2/H_2 selectivity was found to increase slightly. However, at the lowest concentrations of cross-linking monomer, a drastic reduction in CO₂ selectivity was observed. This was attributed to a radical change in membrane morphology as the membranes went from highly cross-linked to linear a linear polymer matrix mixed with free RTIL.

The studied cross-linked poly(RTIL)-RTIL gels have certainly demonstrated much promise as a configuration that both "stabilizes" the liquid RTIL and possesses "liquid-like" CO₂ separation performance. We have recognized that performance of these membranes can be improved by the "simple choice" of a more CO₂-selective RTIL, and we are currently investigating several RTIL candidates that substantially improve membrane performance. As described in this work, these membranes are considerably straightforward to fabricate; this fact belies the complex nature of network formation and resulting membrane properties. While it is certainly important to investigate the RTIL aspect (i.e., gels of different RTILs), it is perhaps more critical to gain a fundamental understanding of these cross-linked poly(RTIL)-RTIL membranes with respect to network formation and gel properties. Only then can researchers truly tailor these materials for enhanced CO_2 separation performance and, more critically, optimization of liquid stability at higher pressures. Clearly the CO₂ separation performances presented here, however impressive, are meaningless if liquid stability is compromised at elevated pressures. The industrial viability of these materials will depend not only on demonstrated long-term pressure stability, but also on the ability to form thin (e.g. $\leq 1 \ \mu m$) poly(RTIL)-RTIL gel films. Progress toward both of these ends will require a comprehensive understanding of material-property relationships.

6.2 Recommendations for future work

6.2.1. Cross-linked poly(RTIL)-RTIL gel membrane performance with highly CO₂-selective RTILs

Chapter 2 of this work as well as recent studies [7], strongly suggest that the CO₂-selectivity of poly(RTIL)-RTIL gel membranes can be significantly improved by incorporating a more

selective "free" RTIL liquid component. It is recommended to investigate the CO₂ separation performance of poly(RTIL)-RTIL gels for a series of promising RTILs. Based on these studies a summary of highly CO₂-selective RTIL candidates is shown in Fig. 6.3. The RTILs that contain nitrile-functionalized anions are of particular interest since they possess inherently low viscosities. One important aspect of this study should be to determine the correlation between RTIL viscosity and CO₂ separation performance, particularly CO₂ permeability.



Figure 6.1. RTILs to investigate for enhanced CO₂ selectivity in cross-linked, poly(RTIL)-RTIL gel membranes.

6.2.2. New poly(RTIL) architectures for enhanced CO_2 permeability and/or selectivity

Two polymers that have inherently desirable qualities for CO_2 separation performance are poly(ethyle oxide) (PEO) [10, 15-17] and poly(dimethylsiloxane) (PDMS) [18-20]. PEO has been shown to be very selective for CO_2 /light gas separations and possess very good CO_2 permeability (ca. 100-700 barrers) [10, 15-17]. PDMS, on the other hand is well known for its substantially high permeability for all gases, and inherently low CO_2 /light gas selectivity. The CO_2 permeability and CO_2/CH_4 permeability selectivity for PDMS is about 4500 barrers and 3.7, respectively [21]. The already impressive performance of these materials can be greatly enhanced by blending them with a CO_2 -selective RTIL. However, both polymers, particularly PDMS, are not known to form stable (i.e., homogeneous) composite structures. Furthermore, PEO and PDMS on their own do not possess ionic moieties that will strongly interact with a free liquid RTIL component and effectively "stabilize" the RTIL within the polymer matrix. It is therefore highly recommended to focus future research efforts on synthesizing ionically-functionalized (e.g., imidazolium-functionalized) PEO and PDMS polymers.

Synthesis of epoxide-funcitonalized imidazolium RITL monomers is the most obvious route toward PEO-based poly(RTIL)s. These monomers can be subsequently polymerized via well-known, cationic or anionic chain-addition mechanisms. A very attractive polymerization mechanism would involve the use of photo-acids to initiate cationic polymerization. This method would eliminate the need for air/water-free techniques and having to handle highly reactive and dangerous lewis acid initiators.

Functionalization of PDMS with RTIL moieties may difficult. There is one report describing the synthesis of imidazolium-functionalized silicone macromers [22], and no known reports on ionically-functionalized PDMS. However, that initial report does demonstrate that structures like that shown in Fig. 6.1 are possible. Furthermore, there are a vast number of affordable, reactive silicones available on the market. Functionalization of an acrylate-terminated silicone oil would be optimal, as it would allow for facile, radical photo- or thermal-curing and membrane formation.



Figure 6.2. Possible structure of an imidazolium-functionalized PDMS.

It is also highly recommended to investigate the synthesis of bisepoxide RTIL monomers, which can be cured with multifunctional amines to form cross-linked, step-growth polymer networks. It would be advantageous, of course, to incorporate free RTIL into these systems for enhanced membrane transport characteristics. This is a well-known and highly robust polymerization system that has been used industrially and residentially for a considerable time now. The curing (i.e., polymerization) of epoxide-amine resins is not sensitive to oxygen or water. Curable bis(epoxide) RTIL monomers would then have a huge advantage compared to radically- or ionically-initiated polymerization systems, which are highly oxygen and water sensitive, respectively. The structures of possible bis(epoxide) imidazolium monomers are shown in Fig. 6.2. Curable bis(epoxide)-RTIL resins may offer an incredibly robust method to form composite structures that may not be attainable with the polymer systems presented in this thesis work.



Figure 6.3. Possible structures for amine-curable bis(epoxide) RTIL monomers

6.2.3. Study of the effect of readily tunable membrane components on cross-linked poly(RTIL)-RTIL gel network structure, properties, pressure stability, CO₂ permeability, and CO₂ permeability selectivity.

As described in Chapter 5, cross-linking monomer molecular weight (i.e., size) and concentration can have wildly varying effects on polymer network formation and resulting gel properties. Future studies investigating the various fundamental aspects of poly(RTIL)-RTIL network formation are highly recommended. It may be synthetically challenging to synthesize di-functional RTIL monomers of increasing molecular weight. However, there are many commercially available PEG-diacrylate cross-linking monomers that can be used instead. It is then highly advisable to use acrylate-based RTIL mono-functional co-monomers, rather than vinyl-based co-monomers. This eliminates any undesirable co-polymerization effects that could occur based on reactivity differences between the two monomers. The four most easily controlled aspects of poly(RTIL)-RTIL gel formation are cross-linker molecular weight, crosslinker concentration, initiator concentration, and free RTIL loading. A study that investigates these effects on the following properties will be of great value for future optimization of poly(RTIL)-RTIL gel performance: glass transition temperature (Tg), elastic modulus (G'), heterogeneity (width of Tan(δ) peak), double bond conversion, CO₂ diffusivity, CO₂ permeability selectivity, membrane pressure stability, and RTIL diffusion (via solid state NMR). Gaining an understanding of network properties and their relation to membrane pressure stability is, perhaps, of utmost concern for the studied gel membranes. Demonstrated, long term pressure stability, particularly for CO_2/H_2 separations, will be needed to bring these materials closer to industrial viability.

6.2.4. Temperature and pressure effects on CO₂ permeability and CO₂ permeability-selectivity of cross-linked poly(RTIL)-RTIL gels

It has been demonstrated that CO_2 /light gas solubility selectivity of imidazolium based RTILs generally improves with decreasing temperature [23]. It is not known, however, what the effect of reduced temperature will have on the CO_2 permeability and permeability selectivity of cross-linked poly(RTIL)-RTIL gel membranes. It is expected that RTIL viscosity will increase with reduced temperature, which will very likely reduce gas permeate diffusivity. It is unclear how the competing effects of increased CO_2 solubility and decreased CO_2 diffusivity will contribute to overall CO_2 permeability and CO_2 permeability selectivity. Furthermore, the membranes studied in Chapter 5 may very well be susceptible plasticization at elevated CO_2 pressures, particularly at lower temperatures. Increased pressure may, in fact, offset the effect of reduced diffusivity at lowered temperatures [17]. A comprehensive study investigating both temperature and pressure effects will be of great value. This is particularly important in the interest in separating of CO_2 from H₂, where higher pressures (~500-800 psig) are typical to syngas streams and current separation techniques involve lowered temperatures. A reasonable range of pressures to study would be between 2 and 35 atm. Temperatures should studied between -20 and 20 °C.

6.2.5. Thin film development for new poly(RTIL)-RTIL composite materials

It is genuinely important to demonstrate competitive CO_2 permeability and permeability selectivity of newly developed poly(RTIL)-RTIL composite materials (i.e., performance approaches or exceeds upper bound[14]). However, new polymer membrane materials will likely not be considered industrially viable until the formation of thin, defect-free films is demonstrated. Permeance (gas permeation units, GPU), rather than permeability, is the true metric by which industrially viable membranes are measured. The gas permeance of a membrane scales with membrane thickness: the thinner the membrane, the higher the permeance. Permeance can easily be calculated by dividing the permeability in barrers by the membrane thickness in micrometers. For example, a membrane with a permeability of 100 barrers will have a permeance of 50 GPU, if the membrane is 2 μ m thick. To be considered "equivalent" with current membrane technologies, poly(RTIL)-RTIL materials need to possess a CO_2 permeance of at least 100 GPU. This implies that membrane thickness for some of the more permeable materials studied in this thesis must be on the order of 1-5 µm. To be highly competitive with current technologies, poly(RTIL)-RTIL membrane thicknesses will likely need to be sub-1 µm.

It is highly recommended to immediately begin a concerted effort toward developing defect-free, thin-film deposition techniques for promising poly(RTIL)-RTIL composite materials. As discussed above, it is important to demonstrate thin film formation, but with even 1 % of surface area defects (e.g., pin-holes), CO₂/light gase selectivity will be greatly diminished [24, 25].Thus, films must not only be thin, but highly defect-free [24, 25]. For the linear, soluble polymers presented in Ch. 3 and 4, current industrial thin film techniques would apply quite well [24, 25]. However, the cross-linked poly(RTIL)-RTIL membranes presented in Ch. 5 may be quite difficult to process. A casting technique is not a viable option since these are cross-linked, insoluble networks. The only available option is to perform the polymerization step on a thin monomer/RTIL film. This is technologically challenging due to issues with oxygen inhibition during the polymerization of a thin monomer film. The formation of a thin monomer film will also be difficult, since the liquid monomer will tend to penetrate any porous substrate. "Wetcasting" techniques [25] may help overcome this issue, as many RTILs studied here are hydrophobic.

A different approach toward the cross-linking of poly(RTIL)-RTIL membranes may be necessary to allow for thin film processing. Forming a linear copolymer that contains a limited number of curable pendant groups may be one alternative approach. The linear poly(RTIL) could then be blended with "free RTIL" and co-dissolved in a casting solvent. Once a thin film is formed, a final photo- or thermally-intiated cure step could cross-link the polymer network via

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the reactive pendant groups. This technique would require a RTIL co-monomer that contains two reactive groups: one which is used to form linear polymer, and one that is used to form the final cross-links. Chemical groups which are polymerizable by orthogonal reaction techniques, such as radical chain-addition and cationic chain-addition, can be appended to the same imidazolium RTIL monomer. Vinyl and epoxide groups are two chemically orthogonal polymerizable units that could be suited for this application.

6.3 References

- Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L., Noble, R.D., "Guide to CO₂ separations in imidazolium-based room-temperature ionic liquids." Ind. Eng. Chem. Res. **2009**, *48*, 2739-2751.
- 2. Scovazzo, P., "Determination of the upper limits, benchmarks, and critical properties for gas separations using stabilized room temperature ionic liquid membranes (silms) for the purpose of guiding future research." J. Membr. Sci. **2009**, *343*, 199-211.
- 3. Bara, J.E., Gabriel, C.J., Carlisle, T.K., Camper, D.E., Finotello, A., Gin, D.L., Noble, R.D., "Gas separations in fluoroalkyl-functionalized room-temperature ionic liquids using supported liquid membranes." Chem. Eng. J. **2009**, *147*, 43-50.
- 4. Morgan, D., Ferguson, L., Scovazzo, P., "Diffusivities of gases in room-temperature ionic liquids: Data and correlations obtained using a lag-time technique." Ind. Eng. Chem. Res. **2005**, *44*, 4815-4823.
- Scovazzo, P., Kieft, J., Finan, D.A., Koval, C., DuBois, D., Noble, R., "Gas separations using non-hexafluorophosphate [pf₆]⁻ anion supported ionic liquid membranes." J. Membr. Sci. 2004, 238, 57-63.
- 6. Carlisle, T.K., Bara, J.E., Gabriel, C.J., Noble, R.D., Gin, D.L., "Interpretation of CO₂ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach." Ind. Eng. Chem. Res. **2008**, *47*, 7005-7012.

- Mahurin, S.M., Lee, J.S., Baker, G.A., Luo, H., Dai, S., "Performance of nitrilecontaining anions in task-specific ionic liquids for improved CO₂/N₂ separation." J. Membr. Sci. 2010, 353, 177-183.
- 8. Odian, G., *Principles of polymerization*. 4th ed 2004, Hoboken, NJ: John Wiley and Sons, Inc.
- 9. Bruice, P.Y., *Organic chemistry*. 4th ed 2004, Upper Saddle River, NJ: Pearson Education, Inc.
- 10. Lin, H. and Freeman, B.D., "Gas solubility, diffusivity and permeability in poly(ethylene oxide)." J. Membr. Sci. **2004**, *239*, 105-117.
- Bara, J.E., Gin, D.L., Noble, R.D., "Effect of anion on gas separation performance of polymer-room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. 2008, 47, 9919-9924.
- 12. Bara, J.E., Hatakeyama, E.S., Gin, D.L., Noble, R.D., "Improving CO₂ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid." Polym. Adv. Technol. **2008**, *19*, 1415-1420.
- 13. Bara, J.E., Noble, R.D., Gin, D.L., "Effect of "free" cation substituent on gas separation performance of polymer–room-temperature ionic liquid composite membranes." Ind. Eng. Chem. Res. **2009**, *48*, 4607-4610.
- 14. Robeson, L.M., "The upper bound revisited." J. Membr. Sci. 2008, 320, 390-400.
- 15. Lin, H. and Freeman, B.D., "Gas permeation and diffusion in cross-linked poly(ethylene glycol diacrylate)." Macromolecules **2006**, *39*, 3568-3580.
- Lin, H., Kai, T., Freeman, B.D., Kalakkunnath, S., Kalika, D.S., "The effect of crosslinking on gas permeability in cross-linked poly(ethylene glycol diacrylate)." Macromolecules 2005, *38*, 8381-8393.
- 17. Lin, H., Van Wagner, E., Freeman, B.D., Toy, L.G., Gupta, R.P., "Plasticizationenhanced hydrogen purification using polymeric membranes." Science **2006**, *311*, 639-642.

- Merkel, T.C., Bondar, V.I., Nagai, K., Freeman, B.D., Pinnau, I., "Gas sorption, diffusion, and permeation in poly(dimethylsiloxane)." J. Polym. Sci. Polym. Phys. 2000, 38, 415-434.
- 19. Stern, S.A., Shah, V.M., Hardy, B.J., "Structure-permeability relationships in silicone polymers." J. Polym. Sci. Polym. Phys. **1987**, *25*, 1263-1298.
- 20. Platé, N. and Yampol'skii, Y., in *Polymeric gas separation membranes*, Paul, D.R. and Yampol'skii, Y.P., Editors. 1994, CRC Press, Inc.: Boca Raton, FL. p. 155.
- 21. Zolandz, R.R. and Fleming, G.K., *Membane handbook* 1992, New York, NY: Chapman & Hall.
- 22. Sun, X., Wu, C., Xing, J., "Ionic liquid-bonded polysiloxane as stationary phase for capillary gas chromatography." J. Sep. Sci. **2010**, *33*, 3159-3167.
- 23. Finotello, A., Bara, J.E., Camper, D., Noble, R.D., "Room-temperature ionic liquids: Temperature dependence of gas solubility selectivity." Ind. Eng. Chem. Res. **2007**, *47*, 3453-3459.
- 24. Baker, R.W., *Membrane technology and applications*. 2nd ed 2004, West Sussex, England: John Wiley & Sons, Ltd.
- 25. Koros, W.J.P., I., in *Polymeric gas separation membranes* 1994, CRC Press: Boca Raton, FL. p. 209.

Chapter 7

Bibliography

(In alphabetical order)

- Anderson, J.L., Anthony, J.L., Brennecke, J.F., Maginn, E.J. "Gas Solubilities in Ionic Liquids." In *Ionic Liquids in Synthesis (2nd Edition)*, 1, 103-129: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- Anderson, J.L.Armstrong, D.W. "Immobilized Ionic Liquids as High-Selectivity/High-Temperature/High-Stability Gas Chromatography Stationary Phases." Anal. Chem. 77, 19 (2005): 6453-6462.
- Anderson, J.L., Ding, R., Ellern, A., Armstrong, D.W. "Structure and Properties of High Stability Geminal Dicationic Ionic Liquids." *J. Am. Chem. Soc.* 127, 2 (2004): 593-604.
- Anderson, J.L., Dixon, J.K., Brennecke, J.F. "Solubility of CO₂, CH₄, C₂H₆, C₂H₄, O₂, and N₂ in 1-Hexyl-3-Methylpyridinium Bis(Trifluoromethylsulfonyl)Imide: Comparison to Other Ionic Liquids." Acc. Chem. Res. 40 (2007): 1208-1216.
- Anseth, K.S.Bowman, C.N. "Kinetic Gelation Predictions of Species Aggregation in Tetrafunctional Monomer Polymerizations." J. Polym. Sci. Polym. Phys. 33, 12 (1995): 1769-1780.
- Anthony, J.L., Anderson, J.L., Maginn, E.J., Brennecke, J.F. "Anion Effects on Gas Solubility in Ionic Liquids." J. Phys. Chem. B 109 (2005): 6366-6374.
- Anthony, J.L., Maginn, E.J., Brennecke, J.F. "Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-N-Butyl-3-Methylimidazolium Hexafluorophosphate." J. Phys. Chem. B 106 (2002): 7315-7320.

- Arce, A., Earle, M.J., Katdare, S.P., Rodriguez, H., Seddon, K.R. "Mutually Immiscible Ionic Liquids." *Chem. Commun.* (2006): 2548-2550.
- Arce, A., Earle, M.J., Katdare, S.P., Rodriguez, H., Seddon, K.R. "Phase Equilibria of Mixtures of Mutually Immiscible Ionic Liquids." *Fluid Phase Equilib.* 261 (2007): 427-433.
- Baker, R.W. *Membrane Technology and Applications*. 2nd ed. West Sussex, England: John Wiley & Sons, Ltd, 2004.
- Baltus, R.E., Culbertson, B.H., Dai, S., Luo, H., DePaoli, D.W. "Low-Pressure Solubility of Carbon Dioxide in Room-Temperature Ionic Liquids Measured with a Quartz Crystal Microbalance." J. Phys. Chem. B 108 (2004): 721-727.
- Bara, J.E., Camper, D.E., Gin, D.L., Noble, R.D. "Room-Temperature Ionic Liquids and Composite Materials: Platform Technologies for CO₂ Capture." Acc. Chem. Res. 43, 1 (2009): 152-159.
- Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L., Noble, R.D.
 "Guide to CO₂ Separations in Imidazolium-Based Room-Temperature Ionic Liquids." *Ind. Eng. Chem. Res.* 48, 6 (2009): 2739-2751.
- Bara, J.E., Gabriel, C.J., Carlisle, T.K., Camper, D.E., Finotello, A., Gin, D.L., Noble, R.D. "Gas Separations in Fluoroalkyl-Functionalized Room-Temperature Ionic Liquids Using Supported Liquid Membranes." *Chem. Eng. J.* 147, 1 (2009): 43-50.
- Bara, J.E., Gabriel, C.J., Hatakeyama, E.S., Carlisle, T.K., Lessmann, S., Noble, R.D., Gin, D.L.
 "Improving CO₂ Selectivity in Polymerized Room-Temperature Ionic Liquid Gas Separation Membranes through Incorporation of Polar Substituents." *J. Membr. Sci.* 321, 1 (2008): 3-7.

- Bara, J.E., Gabriel, C.J., Lessmann, S., Carlisle, T.K., Finotello, A., Gin, D.L., Noble, R.D.
 "Enhanced CO₂ Separation Selectivity in Oligo(Ethylene Glycol) Functionalized Room-Temperature Ionic Liquids." *Ind. Eng. Chem. Res.* 46, 16 (2007): 5380-5386.
- Bara, J.E., Hatakeyama, E.S., Gabriel, C.J., Zeng, X., Lessmann, S., Gin, D.L., Noble, R.D.
 "Synthesis and Light Gas Separations in Cross-Linked Gemini Room Temperature Ionic Liquid Polymer Membranes." *J. Membr. Sci.* 316, 1-2 (2008): 186-191.
- Bara, J.E., Hatakeyama, E.S., Gin, D.L., Noble, R.D. "Improving CO₂ Permeability in Polymerized Room-Temperature Ionic Liquid Gas Separation Membranes through the Formation of a Solid Composite with a Room-Temperature Ionic Liquid." *Polym. Adv. Technol.* 19, 10 (2008): 1415-1420.
- Bara, J.E., Kaminski, A.K., Noble, R.D., Gin, D.L. "Influence of Nanostructure on Light Gas Separations in Cross-Linked Lyotropic Liquid Crystal Membranes." J. Membr. Sci. 288 (2007): 13-19.
- Bara, J.E., Lessmann, S., Gabriel, C.J., Hatakeyama, E.S., Noble, R.D., Gin, D.L. "Synthesis and Performance of Polymerizable Room-Temperature Ionic Liquids as Gas Separation Membranes." *Ind. Eng. Chem. Res.* 46, 16 (2007): 5397-5404.
- Bara, J.E., Noble, R.D., Gin, D.L. "Effect of "Free" Cation Substituent on Gas Separation Performance of Polymer-Room-Temperature Ionic Liquid Composite Membranes." *Ind. Eng. Chem. Res.* 48 (2009): 4607-4610.
- Bara, J.E.G., Douglas L.; Noble, Richard D. "Effect of Anion on Gas Separation Performance of Polymer-Room-Temperature Ionic Liquid Composite Membranes." *Ind. Eng. Chem. Res.* 47, . (2008): 9919-9924.
- Barelli, L., Bidini, G., Gallorini, F., Servili, S. "Hydrogen Production through Sorption-Enhanced Steam Methane Reforming and Membrane Technology: A Review." *Energy* 33, 4 (2008): 554-570.
- Barton, A.F.M. Crc Handbook of Solubility Parameters and Other Cohesion Parameters. Boca Raton, FL: CRC Press, 1983.
- Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems. Office of Basic Energy Sciences of the U.S. Dept. of Energy, 2007.
- Bates, E.D., Mayton, R.D., Ntai, I., Davis, J.H., Jr. "CO₂ Capture by a Task-Specific Ionic Liquid." J. Am. Chem. Soc. 124 (2002): 926-927.
- Bauwens-Crowet, C.Bauwens, J.C. "Annealing of Polycarbonate Below the Glass Transition: Quantitative Interpretation of the Effect on Yield Stress and Differential Scanning Calorimetry Measurements." *Polymer* 23, 11 (1982): 1599-1604.
- Boots, H.M.J., Kloosterboer, J.G., Van Hei, G.M.M.D., Pandey, R.B. "Inhomogeneity During the Bulk Polymerisation of Divinyl Compounds: Differential Scanning Calorimetry Experiments and Percolation Theory." *Brit. Polym. J.* 17, 2 (1985): 219-223.
- Bowman, C.N.Anseth, K.S. "Microstructural Evolution in Polymerizations of Tetrafunctional Monomers." *Macromol. Symp.* 93, 1 (1995): 269-276.
- Brandrup, J., Immergut, E.H., Grulke, E.A. *Polymer Handbook*. 4th ed. New York, NY: John Wiley & Sons, 1999.
- Brennecke, J.F.Maginn, E.J. "Ionic Liquids: Innovative Fluids for Chemical Processing." *AIChE J*. 47, 11 (2001): 2384-2389.
- Bruice, P.Y. Organic Chemistry. 4th ed. Upper Saddle River, NJ: Pearson Education, Inc., 2004.
- Cadena, C., Anthony, J.L., Shah, J.K., Morrow, T.I., Brennecke, J.F., Maginn, E.J. "Why Is CO₂ So Soluble in Imidazolium-Based Ionic Liquids?" *J. Am. Chem. Soc.* 126, 16 (2004): 5300-5308.

- Camper, D., Bara, J., Koval, C., Noble, R. "Bulk-Fluid Solubility and Membrane Feasibility of Rmim-Based Room-Temperature Ionic Liquids." *Ind. Eng. Chem. Res.* 45, 18 (2006): 6279-6283.
- Camper, D., Bara, J.E., Gin, D.L., Noble, R.D. "Room-Temperature Ionic Liquid-Amine Solutions: Tunable Solvents for Efficient and Reversible Capture of CO₂." *Ind. Eng. Chem. Res.* 47 (2008): 8496-8498.
- Camper, D., Bara, J.E., Gin, D.L., Noble, R.D. "Room-Temperature Ionic Liquid–Amine Solutions: Tunable Solvents for Efficient and Reversible Capture of CO₂." *Ind. Eng. Chem. Res.* 47, 21 (2008): 8496-8498.
- Camper, D., Becker, C., Koval, C., Noble, R. "Low Pressure Hydrocarbon Solubility in Room Temperature Ionic Liquids Containing Imidazolium Rings Interpreted Using Regular Solution Theory." *Ind. Eng. Chem. Res.* 44 (2005): 1928-1933.
- Camper, D., Scovazzo, P., Koval, C., Noble, R. "Gas Solubilities in Room-Temperature Ionic Liquids." *Ind. Eng. Chem. Res.* 43 (2004): 3049-3054.
- Carey, F.A.Sundberg, R.J. Advanced Organic Chemistry. 4th ed. New York, NY: Klewer Academic/Plenum, 2000.
- Carlisle, T.K., Bara, J.E., Gabriel, C.J., Noble, R.D., Gin, D.L. "Interpretation of CO₂ Solubility and Selectivity in Nitrile-Functionalized Room-Temperature Ionic Liquids Using a Group Contribution Approach." *Ind. Eng. Chem. Res.* 47, 18 (2008): 7005-7012.
- Carlisle, T.K., Bara, J.E., Lafrate, A.L., Gin, D.L., Noble, R.D. "Main-Chain Imidazolium Polymer Membranes for CO₂ Separations: An Initial Study of a New Ionic Liquid-Inspired Platform." *J. Membr. Sci.* 359, 1-2 (2010): 37-43.

- Chesnokov, S.A., Zakharina, M.Y., Shaplov, A.S., Lozinskaya, E.I., Malyshkina, I.A., Abakumov, G.A., Vidal, F., Vygodskii, Y.S. "Photopolymerization of Poly(Ethylene Glycol) Dimethacrylates: The Influence of Ionic Liquids on the Formulation and the Properties of the Resultant Polymer Materials." *J. Polym. Sci. Polym. Chem.* 48, 11 (2010): 2388-2409.
- Chiappe, C., Pieraccini, D., Zhao, D., Fei, Z., Dyson, P.J. "Remarkable Anion and Cation Effects on Stille Reaction in Functionalized Ionic Liquids." *Adv. Synth. Catal.* 348 (2006): 68-74.
- Chomff, A.J. *Polymer Networks: Structure and Mechanical Properties*. New York, NY: Plenum Press, 1971.
- Chung, S.H., Lopato, R., Greenbaum, S.G., Shirota, H., Castner, E.W., Wishart, J.F. "Nuclear Magnetic Resonance Study of the Dynamics of Imidazolium Ionic Liquids with -CH₂Si(CH₃)₃ Vs -CH₂C(CH₃)₃ Substituents." *J. Phys. Chem. B* 111, 18 (2007): 4885-4893.
- Climate Change 2007: Synthesis Report. Contribution of Working Groups I, Ii and Iii to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland, 2007.
- Daynes, H.A. "The Process of Diffusion through a Rubber Membrane." *Proc. R. Soc. London, A* 97, 685 (1920): 286-307.
- Descamps, C., Bouallou, C., Kanniche, M. "Efficiency of an Integrated Gasification Combined Cycle (IGCC) Power Plant Including CO₂ Removal." *Energy* 33, 6 (2008): 874-881.
- Dorner, R.W., Hardy, D.R., Williams, F.W., Willauer, H.D. "Heterogeneous Catalytic CO₂ Conversion to Value-Added Hydrocarbons." *Energy & Environmental Science* 3, 7 (2010): 884-890.

- Dušek, K.Ilavský, M. "Cyclization in Crosslinking Polymerization. I. Chain Polymerization of a Bis Unsaturated Monomer (Monodisperse Case)." J. Polym. Sci. Polym. Symp. 53, 1 (1975): 57-73.
- Dušek, K.Ilavský, M. "Cyclization in Crosslinking Polymerization. Ii. Chain Polymerization of a Bis Unsaturated Monomer (Polydisperse Case)." J. Polym. Sci. Polym. Symp. 53, 1 (1975): 75-88.
- Dzyuba, S.V.Bartsch, R.A. "Influence of Structural Variations in 1-Alkyl(Aralkyl)-3-Methylimidazolium Hexafluorophosphates and Bis(Trifluoromethyl-Sulfonyl)Imides on Physical Properties of the Ionic Liquids." *ChemPhysChem* 3 (2002): 161-166.
- Earle, M., Wasserscheid, P., Schulz, P., Olivier-Bourbigou, H., Favre, F., Vaultier, M., Kirschning, A., Singh, V., Riisager, A., Fehrmann, R., Kuhlmann, S. "Organic Synthesis." In *Ionic Liquids in Synthesis*, 265-568: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- Earle, M.J., Esperanca, J.M.S.S., Gilea, M.A., Canongia Lopes, J.N., Rebelo, L.P.N., Magee, J.W., Seddon, K.R., Widegren, J.A. "The Distillation and Volatility of Ionic Liquids." *Nature* 439, 7078 (2006): 831-834.
- Elliott, J.E., Macdonald, M., Nie, J., Bowman, C.N. "Structure and Swelling of Poly(Acrylic Acid) Hydrogels: Effect of Ph, Ionic Strength, and Dilution on the Crosslinked Polymer Structure." *Polymer* 45, 5 (2004): 1503-1510.
- Fei, Z., Zhao, D., Pieraccini, D., Ang, W.H., Geldbach, T.J., Scopelliti, R., Chiappe, C., Dyson, P.J. "Development of Nitrile-Functionalized Ionic Liquids for C-C Coupling Reactions: Implication of Carbene and Nanoparticle Catalysts." *Organometallics* 26 (2007): 1588-1598.
- Finotello, A., Bara, J.E., Camper, D., Noble, R.D. "Room-Temperature Ionic Liquids: Temperature Dependence of Gas Solubility Selectivity." *Ind. Eng. Chem. Res.* 47, 10 (2007): 3453-3459.

Flory, P.J. Principles of Polymer Chemistry. Ithaca, NY: Cornell University Press, 1953.

- Freeman, B.D. "Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes." *Macromolecules* 32, 2 (1999): 375-380.
- Goodell, J. *Big Coal: The Dirty Secret Behind America's Energy Future*. New York, NY: Houghton Mifflin, Company, 2006.
- Goodwin, A.A., Beevers, M.S., Clarson, S.J., Semlyen, J.A. "Studies of Cyclic and Linear Polydimethylsiloxanes: 32. Dielectric Relaxation Investigations." *Polymer* 37, 13 (1996): 2603-2607.
- Gordon, C.M., Muldoon, M.J., Wagner, M., Hilgers, C., Davis, J.H., Wasserscheid, P. "Synthesis and Purification." In *Ionic Liquids in Synthesis*, 7-55: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- Greenberg, A.R.Kusy, R.P. "Influence of Crosslinking on the Glass Transition of Poly(Acrylic Acid)." J. Appl. Polym. Sci. 25, 8 (1980): 1785-1788.
- Gu, Y.Lodge, T.P. "Synthesis and Gas Separation Performance of Triblock Copolymer Ion Gels with a Polymerized Ionic Liquid Mid-Block." *Macromolecules* 44, 7 (2011): 1732-1736.
- Haddleton, D.M., Welton, T., Carmichael, A.J. "Polymer Synthesis in Ionic Liquids." In *Ionic Liquids in Synthesis*, 619-640: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.

Han, X.Armstrong, D.W. "Ionic Liquids in Separations." Acc. Chem. Res. 40 (2007): 1079-1086.

- Hanioka, S., Maruyama, T., Sotani, T., Teramoto, M., Matsuyama, H., Nakashima, K., Hanaki, M., Kubota, F., Goto, M. "CO₂ Separation Facilitated by Task-Specific Ionic Liquids Using a Supported Liquid Membrane." J. Membr. Sci. 314, 1-2 (2008): 1-4.
- Hansen, C.M. Hansen Solubility Parameters: A User's Handbook. Boca Raton, FL: CRC Press, 2000.
- Hardacre, C., Hunt, P.A., Maginn, E.J., Lynden-Bell, R.M., Richter, J., Leuchter, A., Palmer, G., Dölle, A., Wahlbeck, P.G., Carper, W.R. "Molecular Structure and Dynamics." In *Ionic Liquids in Synthesis*, 175-264: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- Havran, V., Duduković, M.P., Lo, C.S. "Conversion of Methane and Carbon Dioxide to Higher Value Products." *Ind. Eng. Chem. Res.* 50, 12 (2011): 7089-7100.
- Ho, M.T., Allinson, G.W., Wiley, D.E. "Reducing the Cost of CO₂ Capture from Flue Gases Using Pressure Swing Adsorption." *Ind. Eng. Chem. Res.* 47, 14 (2008): 4883-4890.
- Holbrey, J.D., Rogers, R.D., Mantz, R.A., Trulove, P.C., Cocalia, V.A., Visser, A.E., Anderson, J.L., Anthony, J.L., Brennecke, J.F., Maginn, E.J., Welton, T., Mantz, R.A.
 "Physicochemical Properties." In *Ionic Liquids in Synthesis*, 57-174: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- Hook, R.J. "An Investigation of Some Sterically Hindered Amines as Potential Carbon Dioxide Scrubbing Compounds." *Ind. Eng. Chem. Res.* 36, 5 (1997): 1779-1790.
- Hsieh, Y.-N., Horng, R., Ho, W.-Y., Huang, P.-C., Hsu, C.-Y., Whang, T.-J., Kuei, C.-H.
 "Characterizations for Vinylimidazolium Based Ionic Liquid Polymer Stationary Phases for Capillary Gas Chromatography." *Chromatographia* 67, 5 (2008): 413-420.
- Hudiono, Y.C., Carlisle, T.K., LaFrate, A.L., Gin, D.L., Noble, R.D. "Novel Mixed Matrix Membranes Based on Polymerizable Room-Temperature Ionic Liquids and Sapo-34 Particles to Improve CO₂ Separation." *J. Membr. Sci.* 370, 1-2 (2011): 141-148.

- Jansen, J.C., Friess, K., Clarizia, G., Schauer, J., Izák, P. "High Ionic Liquid Content Polymeric Gel Membranes: Preparation and Performance." *Macromolecules* 44, 1 (2011): 39-45.
- Jenkins, R.C.L., Nelson, P.M., Spirer, L. "Calculation of the Transient Diffusion of a Gas through a Solid Membrane into a Finite Outflow Volume." *Trans. Faraday Soc.* 66 (1970): 1391-1401.
- Jessop, P.G.Subramaniam, B. "Gas-Expanded Liquids." Chem. Rev. 107 (2007): 2666-2694.
- Jin, X., Tao, J., Yang, Y. "Synthesis and Characterization of Poly(1-Vinyl-3-Propylimidazolium) Iodide for Quasi-Solid Polymer Electrolyte in Dye-Sensitized Solar Cells." J. Appl. Polym. Sci. 118, 3 (2010): 1455-1461.
- Jones, C.W.Maginn, E.J. "Materials and Processes for Carbon Capture and Sequestration." *ChemSusChem* 3, 8 (2010): 863-864.
- Jordan, S.M., Koros, W.J., Fleming, G.K. "The Effects of CO₂ Exposure on Pure and Mixed Gas Permeation Behavior: Comparison of Glassy Polycarbonate and Silicone Rubber." J. Membr. Sci. 30, 2 (1987): 191-212.
- Kalakkunnath, S., Kalika, D.S., Lin, H., Freeman, B.D. "Segmental Relaxation Characteristics of Cross-Linked Poly(Ethylene Oxide) Copolymer Networks." *Macromolecules* 38, 23 (2005): 9679-9687.
- Kannurpatti, A.R., Anderson, K.J., Anseth, J.W., Bowman, C.N. "Use of "Living" Radical Polymerizations to Study the Structural Evolution and Properties of Highly Crosslinked Polymer Networks." J. Polym. Sci. Polym. Phys. 35, 14 (1997): 2297-2307.
- Kannurpatti, A.R., Anseth, J.W., Bowman, C.N. "A Study of the Evolution of Mechanical Properties and Structural Heterogeneity of Polymer Networks Formed by

Photopolymerizations of Multifunctional (Meth)Acrylates." *Polymer* 39, 12 (1998): 2507-2513.

- Kannurpatti, A.R.Bowman, C.N. "Structural Evolution of Dimethacrylate Networks Studied by Dielectric Spectroscopy." *Macromolecules* 31, 10 (1998): 3311-3316.
- Kelkar, M.S.Maginn, E.J. "Calculating the Enthalpy of Vaporization for Ionic Liquid Clusters." *J. Phys. Chem. B* 111 (2007): 9424-9427.
- Kesting, R.E.Fritzsche, A.K. *Polymeric Gas Separation Membranes*: John Wiley and Sons, Inc., 1993.
- Klembt, S., Dreyer, S., Eckstein, M., Kragl, U. "Biocatalytic Reactions in Ionic Liquids." In *Ionic Liquids in Synthesis*, 641-661: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- Kloosterboer, J. "Network Formation by Chain Crosslinking Photopolymerization and Its Applications in Electronics." In *Electronic Applications*, 84, 1-61: Springer Berlin / Heidelberg, 1988.
- Ko, D., Siriwardane, R., Biegler, L.T. "Optimization of a Pressure-Swing Adsorption Process Using Zeolite 13x for CO₂ Sequestration." *Ind. Eng. Chem. Res.* 42, 2 (2003): 339-348.
- Kohl, A.L.Nielsen, R.B. "Gas Purification (5th Edition)." Elsevier.
- Koros, W.J.Pinnau, I. "Polymeric Gas Separation Membranes." edited by Paul, D.R.Yampol'skii, Y.P., 209. Boca Raton, FL: CRC Press, 1994.
- Kumelan, J., Perez-Salado, K.A., Tuma, D., Maurer, G. "Solubility of CO₂ in the Ionic Liquid [Hmim][Tf₂n]." *J. Chem. Thermodyn.* 38 (2006): 1396-1401.

- Kusuma, V.A., Freeman, B.D., Borns, M.A., Kalika, D.S. "Influence of Chemical Structure of Short Chain Pendant Groups on Gas Transport Properties of Cross-Linked Poly(Ethylene Oxide) Copolymers." J. Membr. Sci. 327, 1-2 (2009): 195-207.
- Lee, B.-C.Outcalt, S.L. "Solubilities of Gases in the Ionic Liquid 1-N-Butyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide." J. Chem. Eng. Data 51 (2006): 892-897.
- Lee, S.H.Lee, S.B. "The Hildebrand Solubility Parameters, Cohesive Energy Densities and Internal Energies of 1-Alkyl-3-Methylimidazolium-Based Room Temperature Ionic Liquids." *Chem. Commun.* (2005): 3469-3471.
- Li, F., Cheng, F., Shi, J., Cai, F., Liang, M., Chen, J. "Novel Quasi-Solid Electrolyte for Dye-Sensitized Solar Cells." *J. Power Sources* 165 (2007): 911-915.
- Li, P., Pramoda, K.P., Chung, T.-S. "CO₂ Separation from Flue Gas Using Polyvinyl-(Room Temperature Ionic Liquid)–Room Temperature Ionic Liquid Composite Membranes." *Ind. Eng. Chem. Res.* 50, 15 (2011): 9344-9353.
- Liang, Z.Y., Lue, C.X., Luo, J., Dong, L.B. "A Polymer Imidazole Salt as Phase-Transfer Catalyst in Halex Fluorination Irradiated by Microwave." J. Fluorine Chem. 128 (2007): 608-611.
- Lieberman, E.R.Gilbert, S.G. "Gas Permeation of Collagen Films as Affected by Cross-Linkage, Moisture, and Plasticizer Content." *J. Polym. Sci. Polym. Symp.* 41, 1 (1973): 33-43.
- Lin-Gibson, S., Jones, R.L., Washburn, N.R., Horkay, F. "Structure–Property Relationships of Photopolymerizable Poly(Ethylene Glycol) Dimethacrylate Hydrogels." *Macromolecules* 38, 7 (2005): 2897-2902.
- Lin, H.Freeman, B.D. "Gas Solubility, Diffusivity and Permeability in Poly(Ethylene Oxide)." *J. Membr. Sci.* 239, 1 (2004): 105-117.

- Lin, H.Freeman, B.D. "Gas and Vapor Solubility in Cross-Linked Poly(Ethylene Glycol Diacrylate)." *Macromolecules* 38, 20 (2005): 8394-8407.
- Lin, H.Freeman, B.D. "Materials Selection Guidelines for Membranes That Remove CO₂ from Gas Mixtures." *J. Mol. Struct.* 739 (2005): 57-74.
- Lin, H.Freeman, B.D. "Gas Permeation and Diffusion in Cross-Linked Poly(Ethylene Glycol Diacrylate)." *Macromolecules* 39, 10 (2006): 3568-3580.
- Lin, H., Freeman, B.D., Kalakkunnath, S., Kalika, D.S. "Effect of Copolymer Composition, Temperature, and Carbon Dioxide Fugacity on Pure- and Mixed-Gas Permeability in Poly(Ethylene Glycol)-Based Materials: Free Volume Interpretation." *J. Membr. Sci.* 291, 1-2 (2007): 131-139.
- Lin, H., Kai, T., Freeman, B.D., Kalakkunnath, S., Kalika, D.S. "The Effect of Cross-Linking on Gas Permeability in Cross-Linked Poly(Ethylene Glycol Diacrylate)." *Macromolecules* 38, 20 (2005): 8381-8393.
- Lin, H., Van Wagner, E., Freeman, B.D., Toy, L.G., Gupta, R.P. "Plasticization-Enhanced Hydrogen Purification Using Polymeric Membranes." *Science* 311, 5761 (2006): 639-642.
- Lin, H., Van Wagner, E., Raharjo, R., Freeman, B.D., Roman, I. "High-Performance Polymer Membranes for Natural-Gas Sweetening." *Adv. Mater.* 18, 1 (2006): 39-44.
- Lin, H., Wagner, E.V., Swinnea, J.S., Freeman, B.D., Pas, S.J., Hill, A.J., Kalakkunnath, S., Kalika, D.S. "Transport and Structural Characteristics of Crosslinked Poly(Ethylene Oxide) Rubbers." J. Membr. Sci. 276, 1-2 (2006): 145-161.

Lodge, T.P. "A Unique Platform for Materials Design." Science 321, 5885 (2008): 50-51.

- Loshaek, S. "Crosslinked Polymers. Ii. Glass Temperatures of Copolymers of Methyl Methacrylate and Glycol Dimethacrylates." *J. Polym. Sci.* 15, 80 (1955): 391-404.
- Lozinskaya, E.I., Shaplov, A.S., Kotseruba, M.V., Komarova, L.I., Lyssenko, K.A., Antipin, M.Y., Golovanov, D.G., Vygodskii, Y.S. ""One-Pot" Synthesis of Aromatic Poly(1,3,4-Oxadiazole)S in Novel Solvents-Ionic Liquids." J. Polym. Sci. Polym. Chem. 44 (2006): 380-394.
- Maase, M. "Industrial Applications of Ionic Liquids." In *Ionic Liquids in Synthesis*, 663-687: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- MacFarlane, D.R., Forsyth, S.A., Golding, J., Deacon, G.B. "Ionic Liquids Based on Imidazolium, Ammonium and Pyrrolidinium Salts of the Dicyanamide Anion." *Green. Chem.* 4, 5 (2002): 444-448.
- MacFarlane, D.R., Golding, J., Forsyth, S., Forsyth, M., Deacon, G.B. "Low Viscosity Ionic Liquids Based on Organic Salts of the Dicyanamide Anion." *Chem. Commun.* (2001): 1430-1431.
- Mahurin, S.M., Lee, J.S., Baker, G.A., Luo, H., Dai, S. "Performance of Nitrile-Containing Anions in Task-Specific Ionic Liquids for Improved CO₂/N₂ Separation." *J. Membr. Sci.* 353, 1-2 (2010): 177-183.

Majumdar, S.Sirkar, K.K. Membrane Handbook. New York, NY: Chapman and Hall, 1992.

Marcilla, R., Sanchez-Paniagua, M., Lopez-Ruiz, B., Lopez-Cabarcos, E., Ochoteco, E., Grande, H., Mecerreyes, D. "Synthesis and Characterization of New Polymeric Ionic Liquid Microgels." J. Polym. Sci. Polym. Chem. 44 (2006): 3958-3965.

- Mazille, F., Fei, Z., Kuang, D., Zhao, D., Zakeeruddin, S.M., Graetzel, M., Dyson, P.J.
 "Influence of Ionic Liquids Bearing Functional Groups in Dye-Sensitized Solar Cells." *Inorg. Chem.* 45 (2006): 1585-1590.
- Merkel, T.C., Bondar, V.I., Nagai, K., Freeman, B.D., Pinnau, I. "Gas Sorption, Diffusion, and Permeation in Poly(Dimethylsiloxane)." J. Polym. Sci. Polym. Phys. 38, 3 (2000): 415-434.
- Mikami, K. Green Reaction Media in Organic Synthesis. Ames, IA: Blackwell, 2005.
- Mizumo, T., Watanabe, T., Matsumi, N., Ohno, H. "Preparation of Ion Conductive Inorganic– Organic Composite Systems by in Situ Sol–Gel Reaction of Polymerizable Ionic Liquids." *Polym. Adv. Technol.* 19, 10 (2008): 1445-1450.
- Morgado, P., Tomás, R., Zhao, H., dos Ramos, M.C., Blas, F.J., McCabe, C., Filipe, E.J.M. "Solution Behavior of Perfluoroalkanes and Perfluoroalkylalkane Surfactants in N-Octane." J. Phys. Chem. C 111, 43 (2007): 15962-15968.
- Morgan, D., Ferguson, L., Scovazzo, P. "Diffusivities of Gases in Room-Temperature Ionic Liquids: Data and Correlations Obtained Using a Lag-Time Technique." *Ind. Eng. Chem. Res.* 44, 13 (2005): 4815-4823.
- Muldoon, M.J., Aki, S.N.V.K., Anderson, J.L., Dixon, J.K., Brennecke, J.F. "Improving Carbon Dioxide Solubility in Ionic Liquids." *J. Phys. Chem. B* 111, 30 (2007): 9001-9009.
- Myers, C., Pennline, H., Luebke, D., Ilconich, J., Dixon, J.K., Maginn, E.J., Brennecke, J.F. "High Temperature Separation of Carbon Dioxide/Hydrogen Mixtures Using Facilitated Supported Ionic Liquid Membranes." *J. Membr. Sci.* 322, 1 (2008): 28-31.
- Nakajima, H.Ohno, H. "Preparation of Thermally Stable Polymer Electrolytes from Imidazolium-Type Ionic Liquid Derivatives." *Polymer* 46, 25 (2005): 11499-11504.

- Niedermeyer, H., Ab Rani, M.A., Lickiss, P.D., Hallett, J.P., Welton, T., White, A.J.P., Hunt, P.A. "Understanding Siloxane Functionalised Ionic Liquids." *Phys. Chem. Chem. Phys.* 12, 8 (2010): 2018-2029.
- Odian, G. Principles of Polymerization. Hoboken, NJ: John Wiley and Sons, Inc., 2004.
- Ohno, H. "Design of Ion Conductive Polymers Based on Ionic Liquids." *Macromol. Symp.* 249-250, 1 (2007): 551-556.
- Ohno, H., Yoshizawa, M., Ogihara, W. "Development of New Class of Ion Conductive Polymers Based on Ionic Liquids." *Electrochim. Acta* 50, 2-3 (2004): 255-261.
- Ortega, A.M., Kasprzak, S.E., Yakacki, C.M., Diani, J., Greenberg, A.R., Gall, K. "Structure– Property Relationships in Photopolymerizable Polymer Networks: Effect of Composition on the Crosslinked Structure and Resulting Thermomechanical Properties of a (Meth)Acrylate-Based System." J. Appl. Polym. Sci. 110, 3 (2008): 1559-1572.
- Oyenekan, B.A.Rochelle, G.T. "Energy Performance of Stripper Configurations for CO₂ Capture by Aqueous Amines." *Ind. Eng. Chem. Res.* 45, 8 (2005): 2457-2464.
- Pasternak, R.A., Christensen, M.V., Heller, J. "Diffusion and Permeation of Oxygen, Nitrogen, Carbon Dioxide, and Nitrogen Dioxide through Polytetrafluoroethylene." *Macromolecules* 3, 3 (1970): 366-371.
- Patel, N.P., Miller, A.C., Spontak, R.J. "Highly CO₂-Permeable and Selective Polymer Nanocomposite Membranes." *Adv. Mater.* 15, 9 (2003): 729-733.
- Peppas, N.A.Barr-Howell, B.D. Vol. 1. 3 vols. Hydrogels in Medicine and Pharmacy, Edited by Peppas, N.A. Boca Raton, FL: CRC Press, Inc., 1986.

- Peppas, N.A.Mikos, A.G. Vol. 1. 3 vols. Hydrogels in Medicine and Pharmacy, Edited by Peppas, N.A. Boca Raton, FL: CRC Press, Inc., 1986.
- Petropoulos, J.H. Polymeric Gas Separation Membranes, Edited by Paul, D.R.Yampol'skii, Y.P. Boca Raton, FL: CRC Press, Inc., 1994.
- Pinnau, I., Morisato, A., He, Z. "Influence of Side-Chain Length on the Gas Permeation Properties of Poly(2-Alkylacetylenes)." *Macromolecules* 37, 8 (2004): 2823-2828.
- Platé, N.Yampol'skii, Y. "Polymeric Gas Separation Membranes." edited by Paul, D.R.Yampol'skii, Y.P., 155. Boca Raton, FL: CRC Press, Inc., 1994.
- Powell, C.E.Qiao, G.G. "Polymeric CO₂/N₂ Gas Separation Membranes for the Capture of Carbon Dioxide from Power Plant Flue Gases." *J. Membr. Sci.* 279, 1-2 (2006): 1-49.
- Prabhakar, R.Freeman, B. "Application of Hydrocarbon--Fluorocarbon Interactions in Membrane-Based Gas Separations." *Desalination* 144, 1-3 (2002): 79-83.
- Prabhakar, R.S., Freeman, B.D., Roman, I. "Gas and Vapor Sorption and Permeation in Poly(2,2,4-Trifluoro-5-Trifluoromethoxy-1,3-Dioxole-Co-Tetrafluoroethylene)." *Macromolecules* 37, 20 (2004): 7688-7697.
- Prausnitz, J.M., Lichtenthaler, R.N., Azevedo, E.G.d. *Molecular Thermodynamics of Fluid-Phase Equilibria*. 3rd ed. Upper Saddle River, NJ: Prentice-Hall PTR, 1999.
- Raeissi, S.Peters, C.J. "A Potential Ionic Liquid for CO₂-Separating Gas Membranes: Selection and Gas Solubility Studies." *Green. Chem.* 11, 2 (2009): 185-192.
- Rao, A.B.Rubin, E.S. "A Technical, Economic, and Environmental Assessment of Amine-Based CO₂ Capture Technology for Power Plant Greenhouse Gas Control." *Env. Sci. Technol.* 36, 20 (2002): 4467-4475.

- Rembaum, A.Noguchi, H. "Reactions of N,N,N',N'-Tetramethyl-A,Ω-Diaminoalkanes with A,Ω-Dihaloalkanes. Ii. X-Y Reactions." *Macromolecules* 5 (1972): 261-9.
- "Review of Emerging Resources: U.S. Shale Gas and Shale Plays", <u>http://www.eia.gov</u> (accessed August 2011).
- Riisagera, A., Fehrmanna, R., Haumannb, M., Wasserscheidb, P. "Supported Ionic Liquids: Versatile Reaction and Separation Media." *Top. Catal.* 40, 1 (2006): 91-102.

Robeson, L.M. "The Upper Bound Revisited." J. Membr. Sci. 320, 1-2 (2008): 390-400.

Rochelle, G.T. "Amine Scrubbing for CO₂ Capture." Science 325, 5948 (2009): 1652-1654.

- Rogers, R.D.Seddon, K.R. *Ionic Liquids: Industrial Applications for Green Chemistry*. Washington, DC: American Chemical Society, 2002.
- Rogers, R.D., Seddon, K.R., Volkov, K.R. *Green Industrial Applications of Ionic Liquids*. Dordrecht, The Netherlands: Kluwer Academic, 2002.
- Salamone, J.C.I., S. C.; Taylor, P.; Snider, B. "Synthesis and Homopolymerization Studies of Vinylimidazolium Salts." *Polymer* 14 (1973): 639-644.
- Santos, L.M.N.B.F., Lopes, J.N.C., Coutinho, J.A.P., Esperanca, J.M.S.S., Gomes, L.R., Marrucho, I.M., Rebelo, L.P.N. "Ionic Liquids: First Direct Determination of Their Cohesive Energy." J. Am. Chem. Soc. 129 (2007): 284-285.
- Sasaki, K., Matsumura, S., Toshima, K. "A Novel Glycosidation of Glycosyl Fluoride Using a Designed Ionic Liquid and Its Effect on the Stereoselectivity." *Tetrahedron Lett.* 45, d. (2004): 7043-7047.

- Scott, R.L. "The Anomalous Behavior of Fluorocarbon Solutions." J. Phys. Chem. 62, 2 (1958): 136-145.
- Scovazzo, P. "Determination of the Upper Limits, Benchmarks, and Critical Properties for Gas Separations Using Stabilized Room Temperature Ionic Liquid Membranes (Silms) for the Purpose of Guiding Future Research." J. Membr. Sci. 343, 1-2 (2009): 199-211.
- Scovazzo, P., Kieft, J., Finan, D.A., Koval, C., DuBois, D., Noble, R. "Gas Separations Using Non-Hexafluorophosphate [Pf₆]⁻ Anion Supported Ionic Liquid Membranes." J. Membr. Sci. 238, 1-2 (2004): 57-63.
- Shackley, S.G., C. *Carbon Capture and Its Storage: An Integrated Assessment*. Aldershot, UK: Ashgate, 2006.
- Shirota, H.Castner, E.W. "Why Are Viscosities Lower for Ionic Liquids with –CH₂Si(CH₃)₃ Vs –CH₂C(CH₃)₃ Substitutions on the Imidazolium Cations?" *J. Phys. Chem. B* 109, 46 (2005): 21576-21585.
- Shirota, H., Wishart, J.F., Castner, E.W. "Intermolecular Interactions and Dynamics of Room Temperature Ionic Liquids That Have Silyl- and Siloxy-Substituted Imidazolium Cations." J. Phys. Chem. B 111, 18 (2007): 4819-4829.
- Simon, G.P., Allen, P.E.M., Bennett, D.J., Williams, D.R.G., Williams, E.H. "Nature of Residual Unsaturation During Cure of Dimethacrylates Examined by Cppemas Carbon-13 Nmr and Simulation Using a Kinetic Gelation Model." *Macromolecules* 22, 9 (1989): 3555-3561.
- Snedden, P., Cooper, A.I., Scott, K., Winterton, N. "Cross-Linked Polymer–Ionic Liquid Composite Materials." *Macromolecules* 36, 12 (2003): 4549-4556.

- Song, W., Rossky, P.J., Maroncelli, M. "Modeling Alkane+Perfluoroalkane Interactions Using All-Atom Potentials: Failure of the Usual Combining Rules." J. Chem. Phys. 119, 17 (2003): 9145-9162.
- Sridhar, S., Smitha, B., Aminabhavi, T.M. "Separation of Carbon Dioxide from Natural Gas Mixtures through Polymeric Membranes—a Review." Separ. Purif. Rev. 36, 2 (2007): 113-174.
- Stern, S.A., Shah, V.M., Hardy, B.J. "Structure-Permeability Relationships in Silicone Polymers." J. Polym. Sci. Polym. Phys. 25, 6 (1987): 1263-1298.
- Sun, X., Wu, C., Xing, J. "Ionic Liquid-Bonded Polysiloxane as Stationary Phase for Capillary Gas Chromatography." J. Sep. Sci. 33, 20 (2010): 3159-3167.
- Susan, M.A.B.H., Kaneko, T., Noda, A., Watanabe, M. "Ion Gels Prepared by in Situ Radical Polymerization of Vinyl Monomers in an Ionic Liquid and Their Characterization as Polymer Electrolytes." J. Am. Chem. Soc. 127, 13 (2005): 4976-4983.
- Suzuki, K., Yamaguchi, M., Hotta, S., Tanabe, N., Yanagida, S. "A New Alkyl-Imidazole Polymer Prepared as an Ionic Polymer Electrolyte by in Situ Polymerization of Dye Sensitized Solar Cells." *J. Photochem. Photobiol.*, A 164 (2004): 81-85.
- Swiderski, K., McLean, A., Gordon, C.M., Vaughan, D.H. "Estimates of Internal Energies of Vaporisation of Some Room Temperature Ionic Liquids." *Chem. Commun.* (2004): 2178-2179.
- Tang, J., Tang, H., Sun, W., Radosz, M., Shen, Y. "Poly(Ionic Liquid)S as New Materials for CO₂ Absorption." *J. Polym. Sci. Polym. Chem.* 43 (2005): 5477-5489.
- Uk Hong, S., Park, D., Ko, Y., Baek, I. "Polymer-Ionic Liquid Gels for Enhanced Gas Transport." *Chem. Commun.*, 46 (2009): 7227-7229.

- Vidis, A., Ohlin, C.A., Laurenczy, G., Kuesters, E., Sedelmeier, G., Dyson, P.J. "Rationalisation of Solvent Effects in the Diels-Alder Reaction between Cyclopentadiene and Methyl Acrylate in Room Temperature Ionic Liquids." *Adv. Synth. Catal.* 347 (2005): 266-274.
- Ward, J.H., Furman, K., Peppas, N.A. "Effect of Monomer Type and Dangling End Size on Polymer Network Synthesis." J. Appl. Polym. Sci. 89, 13 (2003): 3506-3519.
- Washiro, S., Yoshizawa, M., Nakajima, H., Ohno, H. "Highly Ion Conductive Flexible Films Composed of Network Polymers Based on Polymerizable Ionic Liquids." *Polymer* 45, 5 (2004): 1577-1582.
- Wilkes, J.S., Wasserscheid, P., Welton, T. "Introduction." In *Ionic Liquids in Synthesis*, 1-6: Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- Williams, S.R.Long, T.E. "Recent Advances in the Synthesis and Structure-Property Relationships of Ammonium Ionenes." *Prog. Polym. Sci.* 34 (2009): 762-782.
- Williams, S.R., Salas-de la Cruz, D., Winey, K.I., Long, T.E. "Ionene Segmented Block Copolymers Containing Imidazolium Cations: Structure-Property Relationships as a Function of Hard Segment Content." *Polymer* 51, 6 (2010): 1252-1257.
- Wong, S.Bioletti, R. *Carbon Dioxide Separation Technologies*. Edmonton, AB: Alberta Research Council Report; Alberta Research Council, 2002.
- Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R.B., Bland, A.E., Wright, I. "Progress in Carbon Dioxide Separation and Capture: A Review." J. Env. Sci. 20, 1 (2008): 14-27.
- Yokozeki, A.Shiflett, M.B. "Hydrogen Purification Using Room-Temperature Ionic Liquids." *Applied Energy* 84, 3 (2007): 351-361.

- Zhang, Q., Li, Z., Zhang, J., Zhang, S., Zhu, L., Yang, J., Zhang, X., Deng, Y. "Physicochemical Properties of Nitrile-Functionalized Ionic Liquids." J. Phys. Chem. B 111 (2007): 2864-2872.
- Zhao, D., Fei, Z., Scopelliti, R., Dyson, P.J. "Synthesis and Characterization of Ionic Liquids Incorporating the Nitrile Functionality." *Inorg. Chem.* 43 (2004): 2197-2205.

Zolandz, R.R.Fleming, G.K. Membane Handbook. New York, NY: Chapman & Hall, 1992.

Appendix A

Scanning Electron Microscope (SEM) Images of the Three Polymer Membranes Studied in Chapter 3

A side-on view of freeze-fractured membranes studied in this work are shown in Figs. A.1-A.3. The membrane thicknesses were estimated using the scale bar provided by the SEM image capture software. These images serve as examples. Several images were used to obtain accurate thickness estimates.



Figure A.1.Electrion micrograph of Polymer 1



Figure A.2. Electrion micrograph of Polymer 2



Figure A.3. Electrion micrograph of Polymer 2-RTIL composite

Appendix B

¹H and ¹³C NMR Spectra of Poly(**1a**) through Poly(**1f**) in Chapter 4





Figure B.1. ¹H NMR sprectrum (a) and ¹³C NMR spectrum (b) of poly(1a) in CD₃CN





Figure B.2. ¹H NMR sprectrum (a) and ¹³C NMR spectrum (b) of poly(**1b**) in CD₃CN





Figure B.3. ¹H NMR sprectrum (a) and ¹³C NMR spectrum (b) of poly(1c) in CD₃CN





Figure B.4. ¹H NMR sprectrum (a) and ¹³C NMR spectrum (b) of poly(1d) in CD₃CN





Figure B.5. ¹H NMR sprectrum (a) and ¹³C NMR spectrum (b) of poly(**1e**) in CD₃CN





Figure B.6. ¹H NMR sprectrum (a) and ¹³C NMR spectrum (b) of poly(**1f**) in CD₃CN

Appendix C

Supplementary Figures, Tables, and Methods for Chapter 5

C.1. Supplementary Figures





Figure C.1. Ideal CO₂ permeability and selectivity of 100-75, 80-**2b**-75, 60-**2b**-75, 40-**2b**-75, (Table 1) graphed in (a) CO₂/N₂, (b) CO₂/CH₄, and (c) CO₂/H₂ Robeson Plots. The values above or below the corresponding data points denote the mol % of **1** out of total monomer in the membrane. The SILM performance of RTIL **3** (\bullet) is also plotted. Experimental error is within the data points and represents +/- one standard deviation. The upper bound shown in (c) was drawn according to a model prediction developed in a previous paper [71]. The prediction was made by setting the value of *f* to 0, which is consistent with rubbery polymers that do not possess non-equilibrium excess free volume [17, 71].





Figure C.2. Ideal CO₂ permeability and selectivity of 100-45, 80-**2b**-45, 60-**2b**-45, 40-**2b**-45, 20-**2b**-45, 10-**2b**-45, 5-**2b**-45 (Table 1) graphed in (a) CO₂/N₂, (b) CO₂/CH₄, and (c) CO₂/H₂ Robeson Plots. The values above or below the corresponding data points denote the mol % of **1** out of total monomer in the membrane. The SILM performance of RTIL **3** (\bigcirc) is also plotted. Experimental error is within the data points and represents +/- one standard deviation. The upper bound shown in (c) was drawn according to a model prediction developed in a previous paper [71]. The prediction was made by setting the value of *f* to 0, which is consistent with rubbery polymers that do not possess non-equilibrium excess free volume [17, 71].





Figure C.3. Ideal (a) CO_2/N_2 , (b) CO_2/CH_4 , and (c) CO_2/H_2 permeability selectivity of 100-75, 80-2b-75, 60-2b-75, 40-2b-75 (see Table 1) vs mol % of cross-linking monomer 1 in the prepolymer mixture for. Mol % here is defined as moles of 1 divided by total moles of 1, 2 and 3. The molar compositions listed in Table 1 are defined as moles of 1 (or 2) dived by total moles of 1 and 2. The lines connecting data points in figures a-c are only meant to guide the eye. The values next to the corresponding data points denote the membrane composition (see Table 1). Error given represents +/- one standard deviation.





Figure C.4. Ideal (a) CO_2/N_2 , (b) CO_2/CH_4 , and (c) CO_2/H_2 permeability selectivity of 100-45, 80-2b-45, 60-2b-45, 40-2b-45, 20-2b-45, 10-2b-45, 5-2b-45 (see Table 1) vs mol % of cross-linking monomer 1 in the pre-polymer mixture for. Mol % here is defined as moles of 1 divided by total moles of 1, 2 and 3. The molar compositions listed in Table 1 are defined as moles of 1 (or 2) dived by total moles of 1 and 2. The lines connecting data points in figures a-c are only meant to guide the eye. The values next to the corresponding data points denote the membrane composition (see Table 1). Error given represents +/- one standard deviation.





Figure C.5. Ideal CO₂ permeability and selectivity of 100-45, 100-65, 100-75, neat poly(**2b**), and neat poly(**1**) graphed in (a) CO₂/N₂, (b) CO₂/CH₄, and (c) CO₂/H₂ Robeson Plots. The values next to the corresponding data points denote the composition of the membrane. The SILM performance of RTIL **3**(\bullet) is also plotted. Experimental error is within the data points and represents +/- one standard deviation. The upper bound shown in (c) was drawn according to a model prediction developed in a previous paper [71]. The prediction was made by setting the value of *f* to 0, which is consistent with rubbery polymers that do not possess non-equilibrium excess free volume [17, 71].
C.2. Supplementary Tables

Table C.1. Idea	al CO ₂ permeability (barrer) and	d ideal CO ₂ permeability se	lectivity for studied
membranes			

	Membrane	P(CC) ₂)	$P(CO_2)/P(N_2)$	P(CO ₂)/P(CH ₄)	P(CO ₂)/P(H ₂)
1.	100-45	130	±10	36	22	6.7
2.	80- 2b -45	140	±10	35	22	6.7
3.	60- 2b -45	190	±10	37	22	7
4.	40- 2b -45	180	±10	34	21	6.9
5.	20- 2b -45	250	±10	35	21	7.5
6.	10- 2b -45	210	±10	34	20	7.7
7.	5- 2b -45	290	±10	27	14	7.3
8.	100-65	350	±20	34	20	9.3
9.	80- 2b -65	400	±20	34	20	9.7
10.	60- 2b -65	430	±20	37	20	11
11.	40- 2b -65	470	±20	37	20	11
12.	20- 2b -65	390	±20	36	19	10.
13.	15- 2b -65	490	±20	27	14	9.1
14.	100-75	520	±30	37	20	12
15.	80- 2b -75	440	±20	36	19	11
16.	60- 2b -75	410	±20	35	18	11
17.	40- 2b -75	490	±20	32	18	11
18.	20- 2a -45	180	±10	35	22	6.6
19.	20- 2a -65	370	±20	34	19	9.8
20.	20- 2c -45	240	±10	31	17	7.1
21.	20- 2c -65	420	±20	32	18	9.6

	Membrane	Mol % (1)	D(CO ₂) x 10 ⁷	$D(CH_4) \times 10^7$	D(CO ₂)/D(CH ₄)	S(CO ₂)	S(CH ₄)	S(CO ₂)/S(CH ₄)
1.	100-45	100	2.3 ± 0.3	0.94 ± 0.09	2.4	4.3 ± 0.2	0.48 ± 0.05	9.0
2.	80- 2b -45	80	2.5 ± 0.2	1.0 ± 0.1	2.5	4.3 ± 0.2	0.48 ± 0.05	8.9
3.	60- 2b -45	60	2.9 ± 0.3	1.1 ± 0.1	2.7	4.8 ± 0.4	0.57 ± 0.06	8.4
4.	40- 2b -45	40	3.2 ± 0.3	1.3 ± 0.1	2.4	4.3 ± 0.2	0.49 ± 0.05	8.9
5.	20- 2b -45	20	4.0 ± 0.3	1.5 ± 0.2	2.6	4.7 ± 0.4	0.58 ± 0.06	8.0
6.	10- 2b -45	10	3.1 ± 0.3	1.3 ± 0.2	2.3	5.1 ± 0.4	0.58 ± 0.06	8.7
7.	5- 2b -45	5	4.6 ± 0.3	0.88 ± 0.09	5.2	4.8 ± 0.05	1.8 ± 0.2	2.7
8.	100-65	100	5.4 ± 0.5	2.0 ± 0.1	2.7	4.9 ± 0.3	0.67 ± 0.02	7.3
9.	80- 2b -65	80	5.7 ± 0.7	2.3 ± 0.1	2.5	5.3 ± 0.6	0.64 ± 0.02	8.3
10.	60- 2b -65	60	7.2 ± 0.8	3.6 ± 0.3	2.0	4.5 ± 0.3	0.48 ± 0.04	9.4
11.	40- 2b -65	40	7.3 ± 0.7	3.1 ± 0.2	2.4	4.9 ± 0.2	0.57 ± .03	8.6
12.	20- 2b -65	20	7.0 ± 0.5	3.6 ± 0.2	1.9	4.2 ± 0.2	0.45 ± 0.04	9.3
13.	15- 2b -65	15	5.3 ± 0.5	1.0 ± 0.1	5.3	7.0 ± 0.3	2.7 ± 0.08	2.6
14.	100-75	100	9.0 ± 0.6	4.3 ± 0.3	2.1	4.4 ± 0.3	0.45 ± 0.05	9.8
15.	80- 2b -75	80	8.6 ± 0.8	3.5 ± 0.4	2.5	3.9 ± 0.3	0.51 ± 0.05	7.6
16.	60- 2b -75	60	7.5 ± 0.7	3.3 ± 0.3	2.3	4.2 ± 0.4	0.53 ± 0.05	7.9
17.	40- 2b -75	40	5.3 ± 0.4	2.3 ± 0.2	2.3	7.1 ± 0.5	0.93 ± 0.09	7.6
18.	20- 2a -45	20	2.8 ± 0.2	1.2 ± 0.2	2.5	4.9 ± 0.3	0.56 ± 0.06	8.8
19.	20- 2a -65	20	6.9 ± 0.6	3.1 ± 0.3	2.2	4.1 ± 0.2	0.47 ± 0.05	8.8
20.	20- 2c -45	20	4.2 ± 0.3	1.9 ± 0.2	2.2	4.3 ± 0.2	0.53 ± 0.05	8.1
21.	20- 2c -65	20	8.2 ± 0.6	4.0 ± 0.3	2.1	3.9 ± 0.2	0.46 ± 0.05	8.5

Table C.2. CO_2 and CH_4 diffusivity (cm² s⁻¹) and solubility (cm³(STP) cm⁻³ atm⁻¹) as well as CO_2/CH_4 diffusivity and solubility selectivity of studied membranes

Table C.3. Mass soluble-fraction as determined by Soxhlet extraction and vinyl group double bond conversion as determined by FT-IR spectroscopy for membranes 8-13.

		Mass Sol-	Vinyl Group
	Membrane	fraction	Conversion
8.	100-65	0.71	0.71
9.	80- 2b -65	0.71	0.72
10.	60- 2b -65	0.71	0.74
11.	40- 2b -65	0.73	0.75
12.	20- 2b -65	0.80	0.74
13.	15- 2b -65	0.93	0.74

C.3. Methods for determination of soluble mass fraction of cross-linked membranes

A detailed schematic of the experimental apparatus used to perform the extraction is shown in Scheme C.1. The masses of all membranes were measured and recorded prior to extraction. MeOH (300 mL) was then added to a 500-mL 1-neck, round-bottomed flask equipped with a magnetic stir bar. Membranes were then placed in a coarse, glass Soxhlet thimble, and then placed into the Soxhlet extractor. The extractor was then adapted to the 500-mL flask as shown in Scheme C.1. A reflux condenser was then adapted to the top of the Soxhlet extractor, and the base of the extractor and the vapor tube were adequately wrapped with insulating material (absorbent cotton). The MeOH was then stirred and heated sufficiently so that the Soxhlet extractor would fill up and flush at approximately 5-10 min intervals. The extraction was allowed to proceed for 36 h at which time the membranes were removed and allowed to dry at ambient conditions for 1 h. The membranes were then further dried in vacuo for 24 h at room temperature and their mass was recorded. To calculate sol-fraction, the dry support mass (Supor-200) was subtracted from the initial and final membrane masses. The dry support mass was found by measuring and averaging the mass of three separate Supor-200 support filters. Solfraction was calculated according to Eq. (S1):

$$Sol - fraction = 1 - \frac{Final\ mass - dry\ support\ mass}{Initial\ mass - dry\ support\ mass}$$
 (S1)



Scheme C.1. Soxhlet extraction setup used to remove membrane sol-fractions

Appendix D

Improving CO₂ Permeability Selectivity in Cross-linked Poly(RTIL)-RTIL Membranes by Incorporating Highly Selective RTILs: Preliminary Data

D.1. Summary of Methods and Preliminary Results

In Chapter 5 it was demonstrated that cross-linked poly(RTIL)-RTIL gels possess excellent CO_2 permeability and CO_2 /light gas permeability selectivity. However, the best performing membranes of that study did not exceed the current upper bounds for CO₂/N₂ and CO_2/CH_4 separations (Figs. 5.3a and 5.3b). One conclusion that came out of that study was that the liquid RTIL-selectivity has a fairly substantial impact on overall membrane selectivity when the membrane contains large amounts of "Free RTIL." The RTIL used in Chapter 5 (emim Tf₂N) is certainly not the most CO₂-selective RTIL available, although it is considerably easy to synthesize and isolate. As discussed in Chapter 6, there are numerous RTILs that have demonstrated enhanced CO₂ selectivity as a bulk liquid. RTILs that possess nitrile-functionalized anions, in particular, have shown very high CO₂ selectivites and relatively low bulk viscosities (Fig. 6.1). These are two highly desirable properties for membrane-based separations, as discussed in Chapter 6. Based on the known CO₂ solubility selectivities of many of these "highly selective" RTILs, there is a good possibility that poly(RTIL)-RTIL gel membranes can be formulated to exceed the current upper bound for CO₂/N₂ separation, as well as greatly improve CO₂/H₂ separation. To test this possibility, a preliminary study has been performed with the RTIL 1-ethyl-3-methylimidazolium dicyanamide (emim dca). No examination of CO₂/CH₄

separation was performed, since the CO_2/CH_4 solubility of emim dca is very similar to emim Tf_2N .

A membrane containing 75 wt. % emim dca (Fig. 6.1) and 25 wt. % cross-linking monomer (**1**, Fig. 5.2) was fabricated and tested for CO_2/N_2 and CO_2/H_2 separation performance. Experimental conditions for membrane fabrication and testing were identical to those described in Section 5.2. The synthesis of emim dca was performed according to known literature procedures [1]. Since emim dca is inherently hygroscopic, much care was taken to ensure that the formed membranes did not sit out in open air for more than a minute or two. The results of this membrane are shown in Fig. D.1. The separation performance of the membrane 100-75 (Table 6.1) from Chapter 6 is plotted as well for comparison. The measured values for CO_2 diffusivity and solubility for the two gel membranes plotted in Fig. D.1 are shown in Table D.1.





Figure D.1: Ideal CO₂ permeability and selectivity of 100-75 (Table 5.1), where the "free RTIL" is emim Tf₂N (\square) and emim dca (\square) graphed in (a) CO₂/N₂ and (b) CO₂/H₂ Robeson Plots. The SILM performance of RTIL **3** (\bigcirc) (emim Tf₂N, Ch. 5) is also plotted. Experimental error is within the data points and represents +/- one standard deviation.

Table D.1. CO_2 diffusivity (D(CO₂)) and solubility (S(CO₂)) of poly(RTIL)-RTIL gel membranes containing emim dca and emim Tf₂N.^{a,b}

poly(RTIL)-RTIL	D(CO ₂)	S(CO ₂)
75 wt. % dca	17 ± 2	2.0 ± 0.2
75 wt. % Tf ₂ N	9±1	4.4 ± 0.5

^aDiffusivity in cm²s⁻¹ x 10⁷

^bSolubility in cm³(stp)cm⁻³atm⁻¹

A large improvement in CO_2/N_2 and CO_2/H_2 permeability selectivity was observed for the dca-containing membrane (Fig. D.1). With a measured CO_2/N_2 permeability selectivity of 59, the dca membrane clearly exceeds the current upper bound (Fig. D.1a). Compared to the Tf₂Ncontaining membrane, the CO_2/N_2 and CO_2/H_2 permeability selectivities of the dca membrane were improved by 60% and 33%, respectively. Only a slight reduction in CO_2 permeability (16%) was observed for the dca membrane compared to the Tf₂N membrane. From Table D.1 we noticed that the CO₂ diffusivity of the dca membrane is nearly double that of the Tf₂N membrane. This is likely a consequence of lowered viscosity in emim dca compared to emim Tf₂N [1, 2]. The CO₂ solubility of the dca membrane was quite a bit lower than that of the Tf₂N membrane (Table D.1). This highly suggests that the dca-containing gel is significantly more solubility-selective than the Tf₂N-containin membrane [3, 4]. The reduction in CO₂ permeability for the dca membrane is likely due to the observed drop in CO₂ selectivity.

It is important to point out that the membrane containing 75 wt. % emim dca also contains a significant amount of Tf_2N anion from the cross-linking monomer. Thus, the dca membrane studied here contains a mixture of emim dca and emim Tf_2N by virtue of the free nature of anions in the polymer gel system. By mol. %, the dca-membrane contains 70% dca and 30% Tf_2N anions. It is reasonable to assume that this mixed-anion membrane will perform differently than a cross-linked membrane that contains only dca anions. Likewise, the performance may very well depend on the ratio of dca to Tf_2N anion. To investigate the "mixed anion" effect on gel membrane separation performance, further studies will have to be performed.

This preliminary report clearly demonstrates the value in using highly CO₂-selective RTILs in cross-linked poly(RTIL)-RTIL formulations. Furthermore, it validates the future studies that are recommended in 6.2.1. In the near-term, large improvements in poly(RTIL)-RTIL gel performance will likely be achieved by "simple" choice of RTIL. It will be important to understand the permeability-property relationships of these new formulations, particularly in terms of RTIL viscosity. The effect of free RTIL chemistry on network formation and properties should also be carefully considered [5].

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D.2. References

- 1. MacFarlane, D.R., Forsyth, S.A., Golding, J., Deacon, G.B., "Ionic liquids based on imidazolium, ammonium and pyrrolidinium salts of the dicyanamide anion." Green Chem. **2002**, *4*, 444-448.
- 2. Scovazzo, P., "Determination of the upper limits, benchmarks, and critical properties for gas separations using stabilized room temperature ionic liquid membranes (silms) for the purpose of guiding future research." J. Membr. Sci. **2009**, *343*, 199-211.
- Bara, J.E., Carlisle, T.K., Gabriel, C.J., Camper, D., Finotello, A., Gin, D.L., Noble, R.D., "Guide to CO₂ separations in imidazolium-based room-temperature ionic liquids." Ind. Eng. Chem. Res. 2009, 48, 2739-2751.
- 4. Carlisle, T.K., Bara, J.E., Gabriel, C.J., Noble, R.D., Gin, D.L., "Interpretation of CO₂ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach." Ind. Eng. Chem. Res. **2008**, *47*, 7005-7012.
- Chesnokov, S.A., Zakharina, M.Y., Shaplov, A.S., Lozinskaya, E.I., Malyshkina, I.A., Abakumov, G.A., Vidal, F., Vygodskii, Y.S., "Photopolymerization of poly(ethylene glycol) dimethacrylates: The influence of ionic liquids on the formulation and the properties of the resultant polymer materials." J. Polym. Sci. Polym. Chem. 2010, 48, 2388-2409.

Appendix E

Synthesis and Characterization of First-Generation Epoxide-Functionalized RTIL monomers

E.1. Summary

In 6.6.2. it was recommended to investigate the synthesis and CO₂ separation performance imidazolium-functionalized PEO materials. The motivation for this work comes from the fact that PEO-based polymers have inherently good CO₂ permeability and CO₂/light gas selectivity compared to poly(olefin)-based materials [1-3]. One proposed synthetic route towards imidazolium-functionalized PEO is presented in Scheme E.1. However, this approach first requires the development of a successful synthetic route toward epoxide-functionalized imidazolium RTIL monomers. The general structure of such epoxide-RTIL monomers is shown in Fig. E.1. It was also recommended in 6.6.2. to investigate the synthesis of amine-curable bisepoxide RTIL monomers for cross-linked poly(RTIL)-RTIL gel membrane applications. Structures of these proposed monomers are shown in Fig. 6.3. The synthetic route toward monoand bis-epoxide monomers should be very similar.



Scheme E.1. Synthetic route toward imidazolium-functionalized PEO materials



Figure E.1. Structures of proposed mono-epoxide (1) and bis-epoxide (2) imidazolium RTIL monomers

Methods toward synthesizing 1st-generation epoxide RTIL monomers are presented here that have been developed in conjunction with this thesis work. The structure and purity of epoxide-functionalized imidazolium monomers are also verified with ¹H and ¹³C NMR spectroscopy, HRMS, and elemental analysis. The synthetic route toward monomers **1** and **2** are summarized in Scheme E.2.



Scheme E.2. Synthetic route toward monomers 1 and 2 (Fig. D.1)

E.2. Experimental

E.2.1. Materials

4-bromobutene was purchased from TCI America (Portland, OR). Metachloroperoxybenzoic acid (76% w/w) was purchased from Sigma-Aldrich (Milauwakee, WI). All reagents were obtained in the highest purity available and used without further purification.

E.2.2. Synthesis of Monomer 1

The reaction steps 1 and 2 as well as steps 4 through 6 (Scheme E.2.) were performed according to published literature procedures [4-7]. The Following procedure details the methods used to isolate monomer **1**. These procedures are directly applicable to the synthesis of monomer 2. Note, the stoichiometric ratio of peroxyacid to alkenyl group is two to one in reaction steps 3 and 7 (Scheme E.2).

M-CPBA (10.9 g (76 % w/w), 48 mmol) was added to a 100-mL, single neck, roundbottomed flask equipped with a magnetic stir bar. Compound **ii** (10g, 24 mmol) was dissolved in CH₃CN (24 mL) and added to the 100-mL flask. A glass stopper was used to seal the flask and the reaction was stirred at room temperature for 35 h. A white precipitate was observed within 3 h of initiating the reaction. The acetonitrile was then removed via rotary evaporation at 22 °C. The reaction was then quenched with Et₂O (150 mL), and the RTIL product precipitated as a clear oil. The RTIL product was stirred vigorously in Et₂O for 8 h, and the Et₂O phase was decanted. Additional Et₂O was added (200 mL), and the product was vigorously stirred for an additional 8 h. The Et₂O was decanted and the Et₂O was hstep performed described above was repeated twice more. After the last wash, the Et₂O was decanted and the RTIL product was dried in vacuo at room temperature for 24 h. Monomer **1** was isolated as a clear, slightly yellow oil.

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Yield: 7.17g (68.9%). Elemental Analysis: Carbon 27.72%, found 27.36%; Nitrogen 9.70%, found 9.08%; Hydrogen 3.02%, found 3.08% . HRMS: $\Delta = +1.2$ ppm. ¹H and ¹³C NMR spectra of monomer **1** are shown in Fig. E.2. ¹H NMR spectrum of monomer **2** is shown in Fig. E.3.



Figure E.2. ¹H NMR (a) and ¹³C NMR (b) spectra (300 MHz, in D_6 -DMSO) of epoxide monomer **1**.



Figure E.3. ¹H NMR spectrum (300 MHz, in D_6 -DMSO) of epoxide monomer 2.

E.3. References

- 1. Lin, H. and Freeman, B.D., "Gas solubility, diffusivity and permeability in poly(ethylene oxide)." J. Membr. Sci. **2004**, *239*, 105-117.
- 2. Lin, H., Van Wagner, E., Freeman, B.D., Toy, L.G., Gupta, R.P., "Plasticizationenhanced hydrogen purification using polymeric membranes." Science **2006**, *311*, 639-642.
- 3. Lin, H., Van Wagner, E., Raharjo, R., Freeman, B.D., Roman, I., "High-performance polymer membranes for natural-gas sweetening." Adv. Mater. **2006**, *18*, 39-44.
- 4. Bara, J.E., Gabriel, C.J., Lessmann, S., Carlisle, T.K., Finotello, A., Gin, D.L., Noble, R.D., "Enhanced CO₂ separation selectivity in oligo(ethylene glycol) functionalized room-temperature ionic liquids." Ind. Eng. Chem. Res. **2007**, *46*, 5380-5386.
- 5. Camper, D., Bara, J., Koval, C., Noble, R., "Bulk-fluid solubility and membrane feasibility of rmim-based room-temperature ionic liquids." Ind. Eng. Chem. Res. **2006**, *45*, 6279-6283.

- 6. Carlisle, T.K., Bara, J.E., Gabriel, C.J., Noble, R.D., Gin, D.L., "Interpretation of CO₂ solubility and selectivity in nitrile-functionalized room-temperature ionic liquids using a group contribution approach." Ind. Eng. Chem. Res. **2008**, *47*, 7005-7012.
- 7. Finotello, A., Bara, J.E., Camper, D., Noble, R.D., "Room-temperature ionic liquids: Temperature dependence of gas solubility selectivity." Ind. Eng. Chem. Res. **2007**, *47*, 3453-3459.