

**Technical Summaries on Ionic Liquids in  
Chemical Processing**

**Prepared for the Chemical Industry Vision 2020  
Technology Partnership Workshop  
Barriers to Ionic Liquid Commercialization**

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## Introduction

Ionic liquids (ILs) – salts having a melting point below 100°C – have recently attracted considerable attention as potential alternatives to conventional (*i.e.*, molecular) organic solvents in a variety of synthetic, catalytic, and electrochemical applications. Ionic liquids are salts that typically consist of bulky organic cations and inorganic anions. These ionic solvents are composed entirely of ions, and strongly resemble ionic melts that may be produced by heating metallic salts, but are liquid at much lower temperatures. The constituents of ionic liquids are constrained by high coulombic forces, exhibiting practically no vapor pressure. This unique property gives them the capability to expand traditional laws of chemistry. For example, these liquids are highly polar, yet noncoordinating (ideal for catalytic reactions), they can be made immiscible with water and/or a number of organic solvents (providing flexibility for a number of reaction and separation schemes), and they are nonvolatile even at elevated temperatures. The physical and chemical properties (e.g. density, conductivity, viscosity, Lewis acidity, hydrophobicity, and hydrogen-bonding capability) of ionic liquids can be tuned by varying the structure of the component ions to obtain desired solvent properties. These unique traits of ionic liquids allow the possibility for more efficient reactions and separations to occur.

Significant research progress has been made in the use of ionic liquids in chemical processes. However, ionic liquids have not achieved a significant commercial status. The Chemical Industry Vision 2020 Technology Partnership, an organization that fosters collaborative R&D to accelerate innovation and technology development in the U.S. chemical and petrochemical industries, is sponsoring a “Barriers to Ionic Liquid Commercialization” workshop on September 11-12, 2003. The workshop will result in the creation and publication of a roadmap that will address key challenges for the commercial applications of ionic liquids. The purpose of this document is to provide material for a common starting point for discussions at the workshop. It presents summaries of R&D progress in the use of ionic liquids in the broad technical areas of catalysis and chemical separations and in the application areas of fuels and polymerization.

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## Ionic Liquids and Catalysis

Recently, ionic liquids have received worldwide academic and industrial attention as replacements for organic solvents in catalysis. Attractive features of ionic liquids for catalysis include: the ionic liquid can act as both catalysts and solvent; solvation, solvolysis, reaction rates, and selectivity can be increased; and side reactions can be reduced. The potential to reduce pollution in industrial processes has led to investigations of ionic liquids as alternative reaction media for a variety of applications that conventionally use organic solvents. The research groups led by Chauvin and Seddon have conducted pioneering research in this area.

Progress in the use of ionic liquids for catalysis has been detailed in several extensive reviews, including: Dupont et al. 2002; Olivier-Bourbigou & Magna 2002; Zhao et al. 2002; Sheldon 2001; Gordon 2001; Wasserscheid and Keim 2000; Holbrey and Seddon 1999; and Welton 1999.

### *Key Accomplishments*

- The IL plays an active role in the chemical reaction or catalysis, rather than used simply as a solvent (e.g., Wasserscheid 2003, Earle 2002); examples given below:
  1. Employ Lewis acid character of IL to avoid use of strong acids (e.g.,  $\text{AlCl}_3$ ) and high temperatures in synthesis – e.g., spontaneous trimerization of vanadyl acetate by vanadium(IV) acetate in  $\text{bmimPF}_6$  – effective where inorganic acids are not (Chauvin 1995)
  2. Refining
    - a. Catalytic hydrogenation (i.e., of 1,2-butadiene to but-1-ene using  $[\text{bmim}]_3\text{Co}(\text{CN})_5$  as catalyst and  $[\text{bmim}][\text{BF}_4]$  as solvent) (Suarez et al. 1997)
    - b. Manufacture of lubricating oils (O'Rear, US Patent 6,398,946)
  3. Dimerization, oligomerization, and polymerization of olefins (on-line or batch process) (e.g., Boon et al. 1986, Ranwell and Tshamano 2002, Olivier 1999)
  4. Alkylation of olefins to produce branched iso-alkenes (Chauvin et al. 1995).
  5. Bronsted-acidity of sulfonic acids for esterification (Cole et al. 2002).
  6. Reactions of aromatic rings – (e.g., Atkins et al. 2003)
    - a. Clean polymerization (Abuabdoun 1989)
    - b. Friedel Crafts alkylation (used in synthesis of detergents) using olefins rather than alkylhalides (Wasserscheid, P., Sesing, M. and Korth, W. 2002)
    - c.  $[\text{emim}]\text{Cl}-\text{AlCl}_3$  system is both a solvent and a catalyst for Friedel-Crafts acylation of aromatics (reduces consumption of  $\text{AlCl}_3$ ), up to 98% specificity to a single isomer (not necessarily the most thermodynamically stable) (Adams et al. 1998)
    - d. Reduction of aromatic rings – larger range of redox products than with conventional solvents (e.g., Ota 1987)
    - e. Carbonylation (Nemeth et al. US Patent 6288281)
    - f. Sulfonation (Earle and Katdare, Patent WO2002030878)
    - g. Nitration (Earle and Katdare, Patent WO2002030865)
    - h. Oxidation (Earle and Katdare, Patent 2002030862)
    - i. Halogenation (Earle and Katdare, Patent WO2002030852)

- Solvents for transition-metal catalysis
  1. Immobilize charged cationic transition metal catalyst in IL phase without need for special ligands (Olivier-Bourbigou and Magna 2002)
  2. IL tend to be of “neutral” form – or the anion exists as a single species – the nature of the anion governs “chemistry”: solubilities, rates of reaction, product distribution, IL are good solvents but weakly coordinating (Davis and Fox 2003)
  3. High selectivity (100%), including stereo-isomers (Wasserscheid, et al. 2002)
  4. Enhanced activity – control with concentration of active catalyst – and enhanced catalyst stability with IL because of stabilized polar transition state (Zhao et al. 2002)
  5. Reduces loss of expensive metal catalyst - [bmim][BF<sub>4</sub>] increases the rate of the Pd-catalyzed Suzuki reaction several orders of magnitude, and also extends life of Pd (Mathews et al. 2001)
  6. Acylation and alkylation reactions to derivatize sugars and complex carbohydrates (Moens and Khan 2000 – both bullets)
    - a. Vanadium(IV) acetate catalyst dissolved in IL (replaces flammable acetonitrile as solvent)
    - b. VO(salen)Cl<sub>2</sub> has additional advantage of not being removed from IL phase along with products
  7. Diels-Alder cyclisations (eliminate use of explosive perchlorate reaction media – (Zulficar and Kitazume 2000), Heck coupling reactions between aromatic halides and olefins (Kaufmann et al. 1996), hydrogenation of olefins (Rh, Ru, Co catalysts), hydrodimerization of dienes, hydroformylation (of C<sub>8</sub> olefins to C<sub>9</sub> alcohols for use in manufacturing of plasticizers) (e.g., Chauvin et al. 1988, Pagni 2003)
- In-situ catalysis directly in ionic liquid (e.g., Cornils and Herrmann 2003), rather than aqueous catalysis followed by extraction of products from solution (e.g., thermolysin-catalyzed synthesis of Z-aspartame in pure 1-butyl-3-methylimidazolium hexafluorophosphate)
  1. elimination of washing steps minimizes losses of catalyst and enhances purity of product
  2. biphasic catalysis – reaction in aqueous phase, organic products separate (Olivier 1999)
  3. triphasic catalysis – IL, organic reagents, product salt soluble in aqueous phase (Sheldon 2001)
- Support for heterogeneous synthesis (Fraga-Dubreuil and Bazureau 2001) and homogeneous catalysis (e.g., Mehnert et al. 2003)
- Chlorination reactions – Lewis acid IL
- Bromination reactions – example of the use of an “incognito IL”, 1,8-diazabicyclo[5.4.0]undec-7-ene hydrotribromide (DBU-HBr<sub>3</sub>) (Muathen 1992).
- Regio-selective solvents (mimic dipolar aprotic solvents such as DMSO) – for N- and O-alkylation (e.g., Wasserscheid et al. 2001)
- Current or Near-Term Applications of IL in industry
  1. biphasic butene dimerization that uses an IL as a support for a catalyst (Dimersol, Difasol) – commercialized by IFP (Olivier-Bourbigou and Magna 2002).
  2. Use of chloroaluminate(III) IL (acidic regime >50 mol% AlCl<sub>3</sub> – no associated waste unlike traditional use of AlCl<sub>3</sub> catalysts) – polymerization of olefins – replace industrial Cosden process (Holbrey and Seddon 1999)
  3. Production of fine chemicals and pharmaceuticals (Sheldon 2001)

## *Challenges*

- Moisture sensitivity
  - e.g., decomposition of ILs containing  $\text{AlCl}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  anions generate HF in the presence of water (Huddleston et al 2001).
- Control
  - mixtures of products
  - release of HCl during use of chloroaluminate IL (Boon et al. 1986)
- Post-catalytic separations (remove products from IL without removing catalyst).
  - Example: Non-catalytic reactivity with  $\text{AlCl}_3$  resulting in consumption of IL; in acylation of arenes, IL has to be destroyed by quenching with  $\text{H}_2\text{O}$  in order to remove products
- Cost
  - e.g., analysis for ethylbenzene production indicates an increase by factor of 5-6 with IL (Atkins et al. 2003)
- Synthesis of new task-specific ionic liquids.
- Determination of the synergistic role played by ionic liquids in enhancing catalytic processes.
- Exploration of biocompatible ionic liquids for enzyme-catalyzed reactions.

## Ionic Liquids in Chemical Separations

Recent efforts by a number of investigators have focused on the application of ionic liquids in separations, typically as replacements for the organic diluents employed in traditional liquid-liquid extraction or in membrane-based separations of organic solutes, metal ions, and gases. Ionic liquids exhibit several properties that make them attractive as a potential basis for clean separation processes, among them tunability, negligible vapor pressure, good thermal stability, and a wide liquid range. Although the first air- and moisture stable ionic liquids were described in 1992 (Wilkes and Zaworotko), it was not until several years later that their potential as media in which to effect separations was first recognized. In the past several years, research publications and patent activity related to ionic-liquid-based separations have increased significantly. Key highlights of that work and remaining challenges for widespread industrial application are outlined below; additional information is available in recent reviews (e.g., Davis and Fox 2003, Marsh 2002, Brennecke and Maginn 2001).

### 1. Liquid extraction:

- a. Extraction of organics from aqueous solution
  - Ionic liquids having a miscibility gap with water have been shown to be effective solvents for a range of organic compounds (Huddleston *et al.* 1998)
  - The pH-dependent distribution of certain solutes (e.g., organic acids) can provide a route for reverse extraction (Huddleston *et al.* 1998, Visser *et al.* 2000),
- b. Metals extraction from aqueous solution
  - RTILs provide unique solvation environment for ionic species, such as metal ion-neutral ligand complexes, and have been shown to be highly effective as replacements for conventional organic diluents in the liquid-liquid extraction of metal ions. The partitioning of metal ions from aqueous solutions into ionic liquids containing extractants (e.g., crown ethers, calixarenes, or PAN) far exceeds that obtainable with any conventional solvent (Dai *et al.* 1999, Visser *et al.* 2000, Visser *et al.* 2001, Bartsch *et al.* 2002).
  - “Task-specific” Ionic Liquids (TSIL), incorporating a metal ion-ligating functional group into one of the ions of an RTIL. TSILs function as both the hydrophobic solvent and the extractant in liquid-liquid separations of metal ions. (Visser *et al.* 2001, 2002; Holbrey *et al.* 2003)

### 2. Hydrocarbon Processing

- a. Selective extraction of aromatics from hydrocarbon streams (Gmehling *et al.* DE 10154052).
- b. Sulfur removal from hydrocarbon fuels, including extraction of organosulfur compounds by selective solubilization (Wasserscheid *et al.* 2003; Schoonover 2003; Bössmann *et al.* 2001), removal of mercaptans (O’Rear *et al.* 2002), and electrochemical oxidation (Schucker and Baird 2003).
- c. Hydrocarbon separations based on interaction of metal salts (e.g., Cu, Ag) dissolved in ionic liquids (Boudreau *et al.* 2003; Munson *et al.* 2002)
- d. Extractive distillation is an apparent processing application for ionic liquids, given the possibility for selective solubility and no volatility of RTILs; discussed in patent literature

for separation of close-boiling or azeotropic mixtures (Arlt *et al.* 2002) and in multiple hydrocarbon separation processes (Munson *et al.* 2002, 2003; Boudreau *et al.* 2003).

### 3. Gas Separation

- a. Selective solubility of gases specific gases in ionic liquids has been measured, leading to the possibility for gas separations using membranes, scrubbers, etc. Carbon dioxide exhibits relatively high solubility in imidazolium-based ionic liquids; oxygen, nitrogen, hydrogen, carbon monoxide, argon have low solubility (Anthony *et al.* 2002).
  - Application: natural gas treatment through removal of acid gases (Brennecke and Maginn 2002)
- b. “Task-specific” Ionic Liquid have been demonstrated for selective gas solubilities. The structure of an imidazolium-based cation was modified by appending an amine substituent, yielding an IL with elevated carbon dioxide capture from gas mixtures (Bates *et al.* 2002)

### 4. Solvent regeneration (removal of solutes from ionic liquids):

- a. Contact with supercritical CO<sub>2</sub>: supercritical CO<sub>2</sub> dissolves organics, but CO<sub>2</sub> does not dissolve in IL. (Blanchard *et al.* 1999; Blanchard and Brennecke 2001; Brennecke 2002; Wu *et al.* 2003).
  - Demonstrated for product removal in continuous-flow catalytic system for hydrovinylation of styrene by Boesmann *et al.* (2001).
- b. Phase-splitting with supercritical carbon dioxide: three-phase systems can be formed in the presence of CO<sub>2</sub> (e.g., methanol in bmim<sup>+</sup>PF<sub>6</sub><sup>-</sup>, forming a methanol-rich phase that is completely free of ionic liquid). Practical implication is to simply separate solutes from ILs, even under dilute conditions. In addition to alcohols, this can also occur in water/IL mixtures, providing a possible means for treating aqueous waste from IL processes (Scurto *et al.* 2002, 2003).
- c. Pervaporation using non-porous membranes bearing a selective layer of a hydrophilic or hydrophobic polymer can remove of water, traces of starting materials, or volatile organic solutes (particularly those that are heat-sensitive) from an ionic liquid (Schäfer *et al.* 2001; Crespo & Schaefer 2003).
- d. Back-distillation, taking advantage of low vapor pressure of ionic liquid (Waffenschmidt *et al.*)

### 5. Membrane separations:

- a. Supported liquid membrane (SLM) system employing ionic liquids as carriers utilize characteristics of selective solubility and low volatility, while minimizing volume of potentially costly solvent. Examples:
  - Selective transport of three isomeric amines having similar boiling points (hexylamine, diisopropylamine (DIIPA), and triethylamine (TEA)) through a porous, hydrophilic polyvinylidene fluoride (PVDF) membrane impregnated with bmim<sup>+</sup>PF<sub>6</sub><sup>-</sup> (Branco *et al.* 2002)
  - Method for separating substances from solutions containing ionic liquids by means of a membrane (Wasserscheid *et al.* 2003)

### 6. Metals separation by electrorefining:

- a. Ionic liquid processes developed for production, refining, and recycling of metals, including aluminum processing (Wu et al) and spent nuclear fuel treatment (Bradley, et al. 2002).

7. Analytical/small-scale separations:

- b. Stationary phases for gas chromatography: Ionic liquids coated onto fused silica capillaries exhibit a dual nature, acting as low-polarity phases with nonpolar compounds and in the opposite manner (*i.e.*, highly interactive and retentive) for compounds bearing strong proton-donor groups. The chromatographic properties of these materials can be readily tuned by minor changes in the cationic or anionic constituent of the IL. (Armstrong *et al.* 1999)
- c. Electrolytes in capillary electrophoresis: RTILs have been shown to be suitable as running electrolytes in capillary electrophoresis for compounds such as polyphenols and basic proteins (Yanes *et al.* 2001, Jiang *et al.* 2003). RTILs show promise in the analytical-scale separation of the complex mixtures of natural products encountered in biological samples.

**First industrial application** – BASF use of N-methylimidazole to scavenge biphasic organic acids in manufacture of alkoxyphenylphosphines – process forms IL [Hmim]Cl (switched on and off by protonation/deprotonation). The protonated form is immiscible with organic liquids so can be separated by using a phase separator rather than filtration (Freemantle 2003a)

### ***Challenges***

A significant amount of research on ionic liquid-based separations processes has been done at the laboratory scale. Only one industrial process has been made widely known to date. Implementation of additional processes will require cost-benefit, economic (including waste) and life-cycle analyses of processes.

Several important questions remain regarding potential limitations of the applicability of many ILs, particularly in large-scale separations:

- **Loss:** Dissolution of ionic liquids in aqueous phase could present significant cost and waste-treatment challenges (Anthony et al. 2001). Loss of ionic liquids to the aqueous phase was measured during metal extraction in liquid-liquid systems. (Dietz and Dzielawa 2001 and Jensen *et al.* 2002). Progress with approaches such as supercritical phase splitting (Scurto *et al.* 2003) and water-structuring salts (Gutowski *et al.* 2003) may reduce IL losses in aqueous streams.
- **Toxicity:** There is significant uncertainty regarding the toxicity and potential environmental impact of ionic liquids. Structural similarities between certain ionic liquids and either herbicides or plant growth regulators have been noted (Jastorff *et al.* 2003). Significant efforts are ongoing, both in obtaining toxicological data – PEG-5 cocomonium methosulfate is first IL for which full toxicological data is available and to develop RTILs based on biomolecules (e.g., L-alanine ethyl ester hydrochloride) for reduced toxicity and increased biodegradability (Davis and Fox 2003).

- **Instability:** Swatloski *et al.* (2003) reported the instability of ionic liquids incorporating the widely used hexafluorophosphate anion (the decomposition of which is likely to yield HF).
- **Regenerability:** For practical process development, additional means are needed to recover nonvolatile solutes in IL, particularly salts.

Research efforts in several areas are needed to accelerate the industrial implementation of ionic-liquid-based separations. These include:

Thermophysical properties measurements useful for development of correlations to implement in process simulators are needed to reduce uncertainty in industrial application (Mantz and Trulove 2003; Nunes *et al.* 2003). Among the bulk-fluid properties to be measured include density, interfacial tension, heat capacity, stability at elevated temperature, viscosity, diffusion coefficients, refractive index, conductivity, effect of contaminants, solubilities in water and other solvents, vapor-liquid equilibria, properties of mixtures of ionic liquids.

1. Conduct further measurements – need to collect data beyond 1-alkyl-3-alkylimidazolium hexafluorophosphates
2. Develop correlations based on structure to be able to predict properties of new ILs
3. It is difficult to develop predictive models as equations of state require information on critical properties of ionic liquids
4. Public web-based database useful (much industrial research is proprietary, and neither successes nor failures are publicized).

Property prediction: predict thermophysical and chemical properties and identify structure-property relationships. In the absence of such ability, selection of an appropriate IL for a particular separation can become a matter of trial and error, a clearly undesirable situation when nearly  $10^{18}$  candidates are available for consideration. Recently, several investigators have sought to develop quantitative relationships (QSPR: quantitative structure-property relationships) between one of the most fundamental of IL characteristics, melting point, and various structural features of alkylpyridinium and quaternary ammonium salts (Katrisky 2002; Eike *et al.* 2003). In addition, significant efforts are underway in quantum chemical and molecular dynamics computations (e.g., Diedenhofen *et al.* 2003; Turner *et al.* 2003; Morrow and Maginn 2003; Margulis *et al.* 2002; Hanke *et al.* 2003) of ionic liquids, providing long-term promise for property prediction.

Production and Analysis – The application of ionic liquids in separations requires a means of reproducibly preparing these solvents in high purity and a facile method of assessing that purity. ILs cannot be analyzed by GC or HPLC directly. Development of rapid and efficient techniques for the analysis of ionic liquids are thus required if ILs are to assume a place as a convenient alternative to conventional organic solvents in chemical separations (Holbrey and Rogers 2002, Davis and Fox 2003).

## Ionic Liquids and Fuels

The potential for the use of ionic liquids in the energy sector is present across the board, from nuclear applications to the petroleum industry. Ionic liquids may be used to solve some of the outstanding issues in industry, from recovery of useful hydrocarbon fuels from refractory sources to the recycling and minimization of waste. Many of these concepts have been demonstrated on the laboratory scale, but scale up to industrial proportions has not yet been broadly accomplished or reported. The reasons for this are many. One is that the petroleum industry has already implemented measures to minimize waste in production and processing, driven by the economics of handling huge volumes of feedstock and waste. Hence, environmental issues that may drive implementation of technologies based on ionic liquids in other chemical industries, such as pharmaceuticals and the production of fine chemicals, pose a greater challenge in the energy sector. Additionally, concerns about cost and toxicity are magnified when applied to the very large feedstock and waste streams in petroleum processing, and lead to a conservative approach to implementation of new processes. The energy sector, however, has a history of supporting research and development into new approaches to industry problems. This support is likely to continue as the investigations into applications of ionic liquids deal with considerations such as high viscosities, moisture sensitivity, contamination and degradation/regeneration. Increased patent activity on fuels-related topics indicate

As with all of the ionic liquid subject areas, there are many recent extensive reviews and dedicated journal issues that describe fuels-related applications (e.g., *Green Chemistry* Special Issue 2, 2002; *Ionic Liquids: Industrial Applications to Green Chemistry* ACS Symposium Series 818, 2002; *Green Industrial Applications of Ionic Liquids*, NATO Science Series II, 2003; and Holbrey and Seddon 1999)

### ***Key Accomplishments***

- Laboratory studies show ILs have potential for application in a number of energy-related areas:
  1. Liquefaction, gasification and chemical modification of solid fuels (coal, oil shale, kerogen), biomass at temperatures below 400°C. (e.g., Patell 1993, Keol et al. 2001)
    - a. Reduction of viscosity, molecular weight of components in heavy oil (Johnson 2002)
    - b. Coals can be dissolved in chloroaluminate(III) IL, reacted (acylated) for liquifaction and desulfurization (Boesmann et al. 2001)
    - c. Acidification of petroleum wells (Fu and Card, US Patent 6,350,721)
  2. Sweetening of sour gas (replacement for amine scrubbing)
    - a. Absorption of H<sub>2</sub>S and CO<sub>2</sub> (Brennecke & Maginn US patent 6,579,343)
    - b. Mercaptan removal (O'Rear et al. Patent WO2002034863)
  3. Optimization for high-octane fuel additives – Use of nickel catalyst solvated in IL in formation of 2,3-dimethylbutenes from propene (e.g., Chauvin and Olivier-Bourbigou 1995)
  4. Environmental removal of contaminants from waste streams.
    - a. Adsorption of CO<sub>2</sub> and other compounds from gas streams (Brennecke and Maginn 2003)

- b. Sulfuric acid production and cleaning of flue gas (Fehrmann et al. 2003)
  - c. Remediation of produced water (Ridenour and McFarlane 2003)
- 5. Desulfurization –
  - a. IL investigated for removal of sulfur compounds (~500 ppm) in diesel fuel type components (e.g., dodecane) but not with fuel itself – forms separate phases – low temperature and pressure process that could replace hydrotreating. However, found to lose effectiveness with real diesel fuel because of the wide variety of compounds. (Boesmann, et al. 2001; Zhang and Zhang 2002).
  - b. Multiple patents and applications on sulfur removal from hydrocarbon fuels (e.g. O'Rear et al., Schoonover, Wasserscheid et al., Schucker and Baird)
- 6. Petrochemical –
  - a. Multiple patents and applications on high-volume hydrocarbon separations (e.g., paraffins from olefins, (Munson et al., Boudreau et al., Gmehling et al.)
- 7. Nuclear fuel cycle (Pitner et al. 2003)
  - a. Replacement of conventional solvents in reprocessing (e.g., Dissolution of spent nuclear fuel in IL - 1-butyl-pyridinium nitrate) (Oldham et al. 2002, Fields et al. US Patent 6,379,634)
  - b. Use of crown ethers to extract  $\text{Cs}^+$  and  $\text{Sr}^{+2}$  from aqueous solution to IL
  - c. Enhancement of recycling methods (e.g, treatment of molten salts, US Patent 6,468,495)

### **Challenges**

- Cost of ILs must be reduced before considered for use in energy sector – includes schemes for reuse-recovery. Small fractional losses are costly at high throughput.
  - a. Development of competitive commercial supplies required for a limited number of IL.
  - b. Fluorinated anions likely to remain too expensive for commercial use (Davis and Fox 2003)
- Toxicity studies need to be performed, especially when IL are to be used to remediate waste streams (also includes bioactivity, biodegradation, bioaccumulation, safety, health, environmental impact). (Jastorff et al. 2003, Nelson 2002, Sheldon 2001)
  - Full toxicological data available for one ionic liquid, and others being produced with low expected toxicity (Davis and Fox 2003)
- Demonstration of effectiveness in multi-component systems (e.g., separations in diesel fuel versus 2 or 3 component systems).
- Demonstration of economic operation with continued cycling in process; evaluation of IL losses, poisoning, degradation of performance and regeneration performance.
- Moisture sensitivity
- High viscosity and effects on fluid flow and mass transfer (e.g., of 1-butyl-3-butylamineimidazolium tetrafluoroborate used in  $\text{CO}_2$  absorption study (Bates et al. 2002) – typically desire low viscosity/high diffusivity
- Investigate stability at high temperatures/cycled temperatures over extended periods of time, under adverse conditions –
  - a. Extraction of oxidized organic compounds from fuels may require elevated temperatures (Koel et al. 2003)
  - b. Radiochemical stability (Baston et al. 2002)

## **Polymerization in Ionic Liquids**

One of society's biggest challenges in coming years is the minimization of industrial pollution. Worldwide usage of volatile organic compounds (VOCs) as industrial solvents currently exceeds \$5 billion annually, indicating the tremendous volumes employed. One of the largest segments of the chemical industry is the polymer industry, with over 30 million tons of polymers produced annually. A major component of industrial waste in this industry is used solvent, and strategies for eliminating solvent vapors will have huge importance in cleaning up industrial production of polymers. While aqueous reaction media are widely used (emulsion and suspension polymerization), not all polymerizations are amenable to these conditions, and solution polymerization using VOCs is still widely practiced. Ionic liquids (ILs) have great potential as a nonvolatile organic medium for polymerization and polymer processing due to the near-zero vapor pressures of these materials. In addition to the "green chemistry" aspect of ILs, they also offer the potential for new polymerization processes with unique kinetics as documented below.

### ***Key Accomplishments***

#### **1. Homopolymerization**

The first reported successful polymerizations using ionic liquids as solvents occurred in the early 1990s. Much of the early work in this field was concerned with creating electrically-active materials by incorporating chloroaluminate-based ILs as dopants. This work established that polymerization could be carried out successfully in IL solvents to synthesize materials including polyethylene (Carlin and Wilkes, 1990), polyaniline (Tang and Osteryoung, 1991), and polyphenylene (Kobryanskii and Arnautov, 1993; Goldenberg and Osteryoung, 1994). Since the activity in the early 1990s, there has been only one subsequent paper (Stenzel et al., 2003) on polymerizations in these chloroaluminate ionic liquids, perhaps because of their high moisture sensitivity and tendency to decompose and form HCl.

Starting around 2000, several groups began working on using ionic liquids in polymerization, focusing on two different areas: green manufacturing methodologies to reduce environmental emissions, and creating novel molecular architectures more easily than in traditional solvents. Being a new field, work on "conventional" free radical polymerizations in ionic liquids is relatively limited. Much of the work that does exist has utilized imidazolium- and pyridinium-based ILs (primarily due to the availability of these ILs), with several successful reports. Noda and Watanabe (Noda and Watanabe, 2000) polymerized 2-hydroxyethyl methacrylate by a free radical polymerization, and attempted several other vinyl-type polymerizations in ILs. Csihony and co-workers (Csihony et al., 2002) reported ring opening methasis polymerization of norbornene in a biphasic medium consisting of IL and toluene. The IL phase contained a ruthenium catalyst and the toluene dissolved the formed polymer. Good yields were reported and the catalyst and IL could be recycled several times.

Although the study of free radical polymerization is many decades old and the initiators and monomers employed are among the most studied, some remarkable effects have already been observed when ionic liquids are used to replace standard solvents. One especially notable observation is that free radical polymerization reactions conducted in ionic liquids are faster than in molecular solvents and tend to yield polymers with higher molecular weights (Harrisson et al,

2001; Benton and Brazel, 2002; Hong et al., 2002). The exact impact on the mechanism of the polymerization caused by the replacement of traditional solvents with ionic liquids is not fully understood, but includes reduced termination rates (due partly to higher viscosity solvents), increased propagation rate constants (Harrisson et al, 2001), and low chain transfer constants (Benton and Brazel, 2002). Mays and co-workers (Hong et al., 2002) recently reported the synthesis and isolation of polystyrene and poly(methyl methacrylate) in an ionic liquid using a thermal free radical initiator. They found that PMMA formed in 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], had higher molecular weights (often 10-fold higher) than those formed in traditional VOC solvents. They also found the relative rates of polymerization to be much higher in ILs than in VOCs and attributed the rate difference, as noted above, to diffusion-controlled termination taking longer in the highly viscous ILs. Haddleton and co-workers (Harrisson et al, 2003) very recently measured rate constants for propagation,  $k_p$ , and termination,  $k_t$ , for the methylmethacrylate/[bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] system. They observed a doubling of  $k_p$  and an order of magnitude decrease in  $k_t$  for polymerizations conducted at high concentrations of IL as compared to bulk polymerization of MMA. They attributed the increase in propagation rate to the increased polarity of the medium, while the decrease in the termination rate constant was attributed to the high viscosity of the IL medium (impact on  $k_t$  diminished as temperature was increased and the viscosity of the system decreased). This suggests kinetic advantages are to be realized by using high polarity IL media of high viscosity. Free radical polymerization of various monomers can thus be carried out in ILs with practical advantages (high MW, high rate of polymerization) and purified using aqueous ethanol or methanol (green process).

## 2. Living Radical Homopolymerization

The first free radical 'living' polymerization in an ionic liquid was reported in 2000. Haddleton and co-workers (Carmichael, et al., 2000) polymerized methyl methacrylate with a copper catalyst using a non-hygroscopic IL, [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]. This was an attempt to find novel reaction conditions which would eliminate the need to remove copper catalyst from the produced polymers, a common problem in many living radical (atom transfer or ATRP) polymerizations. Their results were encouraging, as the polymerizations were successful and narrow molecular weight distribution polymers formed were catalyst-free, eliminating the need for a catalyst recovery step. Living ATRP polymerizations have also been conducted by Matyjaszewski's group (Sarbu and Matyjaszewski, 2001) and others (Biedron and Kubisa, 2001). Depending upon the IL used, polymerizations have relatively low initiator efficiency (accounting for high molecular weights), and the polymerization of methyl methacrylate can be controlled allowing for polymers with conversions that grow linearly with respect to time and have low polydispersities (Sarbu and Matyjaszewski, 2001). Ma and co-workers (Ma et al. 2003) reported reverse ATRP of MMA in [bmim<sup>+</sup>][PF<sub>6</sub><sup>-</sup>]. The resulting polymers had very low polydispersity and the IL and catalyst could easily be reused after removal of the polymer and residual monomer. Quite recently, Haddleton and Davis reported the first successful RAFT (reversible addition-fragmentation transfer) polymerizations in ILs (Perrier et al., 2003).

## 3. Statistical Copolymerization

Little work has been reported on copolymerization in ionic liquids. Very recently, atom transfer radical polymerization of n-hexylmaleimide and styrene was studied in an ionic liquid and a greater tendency for forming an alternating copolymer was found in the IL (Zhao et al., 2002). Mays' group reported on the conventional free radical statistical copolymerization of styrene and

methyl methacrylate (Zhang et al., 2003). It was found that the use of an IL as solvent during the copolymerization resulted in reactivity ratios that were significantly different from those obtained in conventional free radical copolymerizations in bulk or in conventional solvents. The reasons for these results are not clear, however possible contributing factors include variations in the solubilities of reagents, variations in the bulk phase properties such as viscosity and solute diffusion, and changes in the overall solvent nature of the different ILs investigated, for example in terms of hydrogen bond donating and accepting ability, aromaticity, etc. Regardless of the reasons, these results demonstrate that copolymerization in ILs has the potential to create copolymers having new monomer sequences, not readily achievable using conventional solvents. At the same time, other inherent advantages of ILs, such as their Green potential and high rates of polymerization and high molecular weight, are retained.

Zhao and co-workers (Zhao et al., 2003) reported living radical copolymerization of N-substituted maleimides with styrene in  $[\text{bmim}^+][\text{PF}_6^-]$ . Well-defined molecular weights and low polydispersities were obtained, and the use of the IL medium resulted in an increased tendency for alternation in the copolymerization. Novel polymer electrolytes were recently reported via copolymerization of ionic liquid monomers (Yoshizawa et al., 2002). The resulting materials were used to form ion conducting matrices. Alternating copolymerization of styrene and carbon monoxide in an IL was reported (Hardacre et al., 2002). The reusability of the catalyst-IL system was discussed.

#### 4. Block Copolymerization

Another significant step in using ionic liquids in free radical polymerizations is the ability to more easily produce block copolymers. The group of Mays (Zhang et al., 2002) recently synthesized poly(MMA-*b*-styrene) in high yields (50% isolated) using conventional radical initiators, conventional polymerization conditions, and simple sequential monomer addition. This synthesis took advantage of the reduced termination rates observed in certain polymerizations in ILs to produce the block copolymer by sequential monomer addition. Some residual homopolymer of the first monomer was present in the crude product, however for many applications such homopolymer impurities could be tolerated. Thus, it has now been shown that “conventional radical polymerization in ILs has the potential to yield tailored polymer architectures with potential applications in nanotechnology. Furthermore, the use of a simplified approach, not requiring exhaustive purification of reagents or removal of catalysts, may provide significant savings in the production of block copolymers with defined structures, especially when compared with cationic and anionic polymerizations.

ATRP was used to synthesize acrylate-based block copolymers in an IL (Biedron and Kubisa, 2002). The clean synthesis of narrow polydispersity materials in high yields was reported, as expected for ATRP. Thus, the use of more rigorous ATRP conditions leads to improvements in yield, polydispersity and molecular weight control.

#### 5. Polymer-ionic liquid composites

A series of composites composed of ILs and polymers were prepared by in-situ polymerization by Snedden and co-workers (Snedden et al., 2003). The characteristics of both the composites and isolated polymers were investigated.

## *Challenges*

### 1. Optimization of IL for a Particular Polymerization

Despite the impressive progress described above, clear understanding of how to optimize an IL for a particular polymerization is still lacking, since many factors must be optimized including polymer isolation, IL recycling, toxicity, etc. The poor solubility of many polymers in the more common currently used ILs is a factor that complicates polymer isolation and purification.

### 2. Lower Cost, Less Toxic, More Available ILs

Much of the work to date on polymerization in ILs has been done using the imidazolium hexafluorophosphate ILs. These materials are toxic and expensive. There is clearly a strong need for cheaper, less toxic and readily available ILs.

### 3. Further investigation of the core variables controlling polymerization reactions in IL media

Molecular level understanding of how ILs impact the various kinetic parameters during polymerization and copolymerization is sorely lacking and must be addressed by systematic studies.

### 4. Nitroxide Mediated Polymerizations Employing ILs

To our knowledge, there have been no reports on nitroxide-mediated radical polymerization in ILs. It would be interesting to see if ILs can be useful as “accelerants” in these polymerizations, since, despite the great promise of this method for synthesis of tailored polymer architectures, the use of these methods is limited commercially due to the high temperatures and long polymerization times required.

### 5. Industrial Applications

Industrial implementation of ILs is attractive for pollution prevention and the kinetic advantages outlined above. The ability to recycle IL and, in some cases, catalyst is an advantage of IL-based systems. In addition, the potential to cheaply prepare high performance block copolymers by simple sequential monomer addition using inexpensive conventional free radical initiators is very attractive. However, prior to industrial implementation Challenges 1-3 outlined just above must be met.

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