**Ionic Liquids as a Medium for Ionic Chain Polymerizations: An Environmentally Responsible Approach to Macromolecular Synthesis with Controlled Architecture**

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This Short Term Innovation Research proposal set out to explore the possible advantages of using ionic liquids as a medium for ionic polymerizations. The first anionic, living polymerization in an ionic liquid medium was accomplished. Reaction conditions and process have been established to pursue the remaining proposed work in terms of controlling block copolymer composition and the effect of chiral ionic liquids on tacticity of polymerization. Observation of polymerizations in ionic liquid medium lead to the realization that ionic liquid/polymer composites have potential for use as conductive material in advanced energy conversion devices.

### List of papers submitted or published that acknowledge ARO support during this reporting period.

List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

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Number of Manuscripts: 0.00

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<td>Elizabeth Sterner</td>
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### Names of personnel receiving PHDs

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### Sub Contractors (DD882)

### Inventions (DD882)
Final Progress Report

(1) Foreword

This Short Term Innovation Research proposal set out to explore the possible advantages of using ionic liquids as a medium for ionic polymerizations. The first anionic, living polymerization in an ionic liquid medium was accomplished. Reaction conditions and process have been established to pursue the remaining proposed work in terms of controlling block copolymer composition and the effect of chiral ionic liquids on tacticity of polymerization. Observation of polymerizations in ionic liquid medium lead to the realization that ionic liquid/polymer composites have potential for use as conductive material in advanced energy conversion devices.

(2) Table of Contents

N/A (less than 10 pages)

(3) List of Appendixes, Illustrations and Tables

Figure 1. A GPC trace of polystyrene made by anionic polymerization in an ionic liquid.

Figure 2. Conductive materials with a wide range of morphology and good thermal stability can be prepared from polymer/ionic liquid composites.

Figure 3. DSC scans of PMMA, ionic liquid and an ionic liquid/PMMA composite.

(4) Statement of the Problem Studied

Ionic chain polymerization is an important methodology for synthesizing polymers with well-defined architecture. One difficulty for extending the use of ionic chain polymerization is the highly sensitive nature of the interaction between the reactive components (initiator, co-initiator, monomer). The solvent effects for ionic polymerizations are profound. The highly solvating, yet non-coordinating nature of an ionic liquid media were therefore explored as a medium to control polymer architecture.

(5) Summary of the Most Important Results

Ionic Liquids as a Medium for Ionic Polymerizations

Initial efforts of the research focused on the development of reactive component compatibility and a process for the anionic polymerization of styrene and methyl methacrylate in the ionic liquid 1-butyl-3-methylimidazolium
hexafluorophosphate \[(\text{bmim})(\text{PF}_6)_2\]. Butyllithium was used as the initiator. There is no reported case of an anionic polymerization in an ionic liquid medium in the current literature. Compared to commercially available, molecular organic solvents, implementation of commercially available ionic liquids as a medium for these ionic polymerizations were initially difficult due to 2 challenges:

(a) significant unknown contamination of commercially available ionic liquids (Sigma Aldrich and Fluka)

(b) extreme hygroscopic nature of ionic liquids compared to aprotic molecular organic solvents.

These 2 initial challenges were significant due to the stringent conditions required for ionic polymerizations. (It should be noted that these problems seemed irrelevant for free radical polymerizations). Once recognized, these challenges were overcome. In order to circumvent the issue of impurities (up to 5% v/v) in commercially available ionic liquids, the ionic liquids were simply made in the PI’s lab from pure starting materials. In order to deal with the hygroscopic nature of the ionic liquid, the ionic liquid would be dried at 120 °C for 72 hours over sieves prior to use in an experiment.

The first living anionic polymerization was accomplished in an ionic liquid medium. The polymerization product was characterized by GPC, $^1$H NMR and $^{13}$C NMR. Figure 1 below shows the GPC data of a typical polystyrene sample made by this process.

![Figure 1](image)

**Figure 1.** A GPC trace of polystyrene made by anionic polymerization in an ionic liquid.
It is interesting to note that the polydispersity of the sample was under 1.1. This result is strong evidence to support that the ionic polymerization was living.\textsuperscript{2} \textsuperscript{1}H NMR confirmed the $M_n$ of the sample. \textsuperscript{13}C NMR explored the tacticity of the polymer using an ionic liquid as the medium.\textsuperscript{3,4} Results were consistent with standard molecular solvents.

In addition to the “front end” challenges of using ionic liquids as a polymerization medium for ionic polymerizations, purification of the polymer proved to be a challenge compared to standard molecular organic solvents. Due to the extremely low vapor pressure of ionic liquids, standard vacuum drying of the polymer to remove solvent at elevated temperatures is not effective. Instead, many washings with a polar solvent like methanol were required to extract the ionic liquid. The methanol could then be removed by standard vacuum techniques at elevated temperatures.

**Ionic Liquids as a Composite Additive for Advanced Energy Conversion**

A striking observation while working with methyl methacrylate as the monomer phase in an ionic liquid medium was that the solution polymerization remained homogeneous at all molar ratios of ionic liquid to monomer. A wide range of morphologies from sol to gel to wax to rigid glass could be prepared as the ratio of methacrylate to ionic liquid increased.

![Gel Wax Glass](image)

**Figure 2.** Conductive materials with a wide range of morphology and good thermal stability can be prepared from polymer/ionic liquid composites.

This observation, coupled with the difficulty of purification (removal of ionic liquid) of the polymer encountered in the previous section suggests that ionic liquid/polymer composites may be useful in conductive polymer applications.

As a result, characterization of the thermal properties and conductivities of these composites are being investigated. Thermal properties depended strongly on the ratio of ionic liquid to polymer. For example, Figure 3 shows the $T_g$ is a strong function of ionic liquid content. Preliminary conductivity measurements suggest that the room temperature conductivity of the glassy composite is on the order of $10^{-3}$ S/cm$^2$. 
Current polymer electrolyte composites used for these applications typically comprise polyethers with ethylene carbonate solvents containing lithium salts. These systems lack the durability and mechanical strength needed under many practical application conditions. Additionally, these systems often fail due to leakage of the electrolyte, posing both health and safety risks. These new ionic liquid/polymer composites can have their mechanical properties fine tuned as a function of crosslink density and ionic liquid to polymer ratio. Composites made in the PIs lab have not leaked ionic liquid from the polymer in over 9 months.

**Future Efforts**

The work funded by this STIR has created 2 areas of research in the PI’s lab. The first is the continued exploration of ionic liquids as a medium for ionic polymerizations. The second area investigates the possible exploitation of ionic liquid/polymer composites for advanced energy conversion.

**Ionic Liquids as a Medium for Ionic Polymerizations**

Initial research efforts in this proposed area of study was dedicated to the fundamental development of performing a living, anionic polymerization in an ionic liquid medium. With this accomplished, the PI plans to truly explore some of the novel aspects of the proposed research in the original STIR proposal. These efforts include the opportunity of controlling block copolymer architecture by variation of the ionic liquid medium. Another area of great interest is to synthesize a chiral ionic liquid and determine if this influences the tacticity of the final polymer product.

**Ionic Liquids as a Composite Additive for Advanced Energy Conversion**
There are two clear opportunities for exploiting the properties of ionic liquid/polymer composites: lithium polymer batteries and dye sensitized solar cells. In terms of using these composites for these types of devices, the balance of mechanical strength and ionic conductivity must be understood. Therefore, two areas of fundamental research are being explored. The effect of polymer crosslink density and the properties of the ionic liquid anion are being studied. From the research conducted on ionic polymerizations in ionic liquid medium, a series of 5 ionic liquids have been prepared where the anion differs in terms of polarizability, thermodynamic acidity and viscosity. Money from the PI’s start up funds have been used to purchase an AC Impedance instrument and an environmental control chamber to measure these variables on composite conductivity.

(6) Listing of Publications

(a) Peer Reviewed Journals
   N/A

(b) Non-peer reviewed journals
   N/A

(c) Meetings
   Research funded from this proposal will result in 2 oral presentations at the Nebraska Academy of Science Meeting on 4/21/06 in Lincoln, Nebraska. Abstracts were submitted and accepted.

(d) Manuscripts submitted
   Due to the short term nature of the STIR, a complete manuscript has not been submitted to date. However, we fully intend to submit a paper to Macromolecules by 7/06 based on research funded by this grant.

(e) Technical reports submitted to ARO
   N/A

(7) Participating scientific personnel earning advanced degrees while employed on this project

As Creighton University is a PUI, there were no personnel working towards a Ph. D. on this research. However, there are 2 graduate school bound students who were employed on this research (that are still active on this project) that are working towards ACS Certified Chemistry BS degrees:

John Hamilton and Elizabeth Sterner
It should be noted that Elizabeth Sterner won a Clare Booth Luce Scholarship for her participation on this project. This prestigious scholarship is awarded to women involved in scientific research that are dedicated to pursuing an academic career in the basic sciences. The award pays a student’s full tuition, room and board for a full academic year.

(8) Report of Inventions

N/A

(9) Bibliography


(10) Appendixes

N/A