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# **Synthesis and Characterization of Poly(Ionic Liquids) Derived from 1-ethyl-3-methyl-4-vinylimidazolium triflate**

**Darren M. Smith**

**February 2011**

Thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry

**Approved:**

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Darren M. Smith  
February, 2011

## Abstract

In the present research, 1-ethyl-3-methyl-4-vinylimidazolium trifluoromethane sulfonate (triflate) was synthesized and polymerized. For comparative purposes, 1-ethyl-3-vinylimidazolium triflate and its polymer was also prepared. Zwitterionic propane sulfonate derivatives of 1-methyl-5-vinylimidazole and 1-vinylimidazole were also synthesized and polymerized. Poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) and poly(3-ethyl-1-vinylimidazolium triflate) were characterized by means of TGA, GPC, and DSC. The TGA showed that poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) had a higher decomposition temperature range, 467-527°C, than poly(3-ethyl-1-vinylimidazolium triflate), 400-448°C. Poly(styrene) equivalent molecular weights were evaluated by GPC in DMF. Poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) had a  $M_n = 13,000$  g/mol ( $M_w = 14,500$  g/mol, PD = 1.11) and poly(3-ethyl-1-vinylimidazolium triflate) had a  $M_n = 15,700$  g/mol ( $M_w = 19,000$  g/mol, PD = 1.21). Glass transition characteristics were evaluated by DSC. Poly(3-ethyl-1-vinylimidazolium triflate) exhibited an onset  $T_g$  of 127-129°C; that for poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) was 115°C. The 1-vinylimidazolium triflate polymer was anion exchanged to create a family of polymers with anions consisting of  $(CN)_2N^-$ ,  $(CF_3SO_2)_2N^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $CF_3SO_3^-$ . This family of polymer salts was characterized by DSC and the lowest onset  $T_g$  84°C, was exhibited by the  $(CF_3SO_2)_2N^-$  salt. In the salts with fluorinated anions of similar geometry, the larger the anion,  $AsF_6^-$ , exhibited an onset  $T_g$  of 119°C. The polymer with the smaller  $PF_6^-$  anion exhibited an onset  $T_g$ , of 172°C.

A copolymer of 1-ethyl-3-methyl-4-vinylimidazolium triflate and 1-methyl-5-vinylimidazole was synthesized. This copolymer was also anion-exchanged to create a family of polymers with  $(\text{CN})_2\text{N}^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$  anions. DSC analysis of this family of copolymers revealed a similar trend in onset glass transition temperatures to that observed with the poly(1-ethyl-3-vinylimidazolium) salts.

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## **List of Abbreviations**

RTIL – Room Temperature Ionic Liquid  
PIL – poly(ionic liquid)  
4VIm – 1-ethyl-3-methyl-4-vinylimidazolium  
NVI – 3-ethyl-1-vinylimidazolium  
TFSI – Trifluoromethylsulfonyl imide  
OTf – Triflate or Trifluoromethane sulfonate  
BF<sub>4</sub> – Tetrafluoroborate  
PF<sub>6</sub> – Hexafluorophosphate  
AsF<sub>6</sub> – Hexafluoroarsenate  
DSC – Differential Scanning Calorimetry  
TMA – Thermal Mechanical Analysis  
T<sub>g</sub> – glass transition  
TGA – Thermal Gravimetric Analysis  
NMR – Nuclear Magnetic Resonance  
<sup>1</sup>H – Proton  
GPC – Gel Permeation Chromatography  
AIBN – 2,2'-azobisisobutyronitrile  
THF – Tetrahydrofuran  
HMDS – 1,1,1,3,3,3-hexamethyldisilazane  
DMF – N,N'-dimethylformamide  
LiTFSI – lithium trifluoromethylsulfonyl imide  
LiPF<sub>6</sub> – lithium hexafluorophosphate  
KAsF<sub>6</sub> – Potassium hexafluoroarsenate  
HBF<sub>4</sub> – tetrafluoroboric acid  
MWCO – molecular weight cut-off  
RAFT – Reverse Addition-Fragmentation Chain Transfer

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## Introduction

Room temperature ionic liquids (RTILs) are salts with melting points that are often below room temperature and are comprised of quaternary sulfonium, phosphonium, or ammonium (imidazolium, pyridinium, pyrrolidinium) cations in combination with anions that have low Lewis basicity, such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ , etc. The use of RTILs in advanced electrochemical devices, such as lithium ion batteries<sup>1</sup>, fuel cells<sup>2</sup>, capacitors<sup>3</sup>, solar cells<sup>4</sup>, and actuators<sup>5</sup>, is being explored. The function of such devices might be improved if the small molecular ionic liquids were replaced by film-forming ionic liquid polymers.<sup>6</sup> The current issue is that reducing the mobility of the cationic or anionic components of the ionic liquid causes the ion conductivity to be significantly diminished. It has been proposed that diminished ion conductivity can potentially be mediated by reducing the dimensionality of ion diffusion in nanostructured, precision block copolymers or polymer blends.<sup>6</sup>

## Background

An ionic liquid is defined as a salt that has a melting point below 100°C.<sup>7</sup> Molten salts are not new; ethyl ammonium nitrate, which has a melting point of 12°C, was reported in 1914.<sup>8</sup> The first solvent-free ionic liquid, *N*-ethyl pyridinium bromide/aluminum chloride, was reported by Hurley in 1951.<sup>9</sup> Since the discovery, in the early 1990's, of the hydrolytically stable, ionic liquids, 1,3-dialkylimidazolium tetrafluoroborate and hexafluorophosphate,<sup>10</sup> there has been an explosion of publications relating to the synthesis, properties, and applications of RTILs. These liquids have become quite popular due to their thermal stability,<sup>11</sup> low flammability, low volatility and utility as organic solvents.<sup>12</sup> Due to their high ion conductivity, ionic liquids, have

potential utility in many applications, ranging from actuators,<sup>5</sup> capacitors,<sup>3</sup> batteries<sup>1, 13</sup>, solar cells,<sup>4</sup> and fuel cells.<sup>2</sup> Given the mobility of the anionic and cationic components of ionic liquids, the function of these devices could possibly be improved if the conventional ionic liquids are replaced by film-forming ionic liquid/polymer gel electrolytes or poly(ionic liquids) where the mobility of the ions can be limited.<sup>14</sup> Film-forming ionic liquid/ polymer gel electrolytes can be formed by plasticization of a polymer with an ionic liquid,<sup>15</sup> or the formation of an ion gel by polymerization of nonionic monomer in an ionic liquid.<sup>16, 17</sup> Poly(ionic liquids) have been synthesized by quaternization to yield sulfonium, phosphonium, or ammonium polymers and the polymerization of ionic liquid monomers.<sup>18</sup> The strategy of plasticization has been explored in transducers,<sup>19</sup> sensors,<sup>20</sup> secondary lithium batteries, fuel cells, and other electrochemical devices.<sup>21, 22</sup> Plasticization of poly(vinylidene fluoride) and vinylidene fluoride/hexafluoropropylene copolymer membranes might be a particularly advantageous option.<sup>23, 24, 25</sup>

The strategy of synthesizing an ionic liquid monomer is the approach taken in the present research. In the 1970's, Salamone, *et al*, were the first to synthesize and polymerize a series of 3-alkyl-1-vinylimidazolium salts.<sup>26, 27</sup> The anion for these salts were chloride, iodide, and methylsulfate. These monomers were typically isolated as crystalline solids with melting points ranging from 193°C for 2,3-dimethyl-1-vinylimidazolium chloride to 45°C for 2-methyl-3-octyl-1-vinylimidazolium iodide. 3-n-Hexyl-1-vinylimidazolium iodide and 3-n-heptyl-1-vinylimidazolium iodide were obtained as oils that were not able to be crystallized. Salamone, *et al*,<sup>28, 29</sup> also published a series of papers relating to the synthesis and spontaneous polymerization of 4-vinyl-pyridinium salts. In this series, 1-methyl-4-vinylpyridinium sulfate,

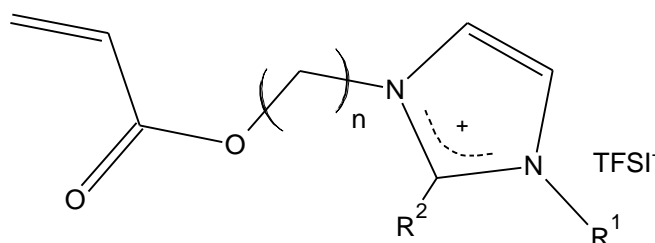
iodide, and *p*-styrene sulfonate salts were synthesized and showed melting points of 75°C, 137°C, and 134°C, respectively.

In the early 1990's, Fife, *et al.* published the synthesis,<sup>30</sup> polymerization,<sup>31</sup> and thermal properties<sup>32</sup> of a series of isolable, storage stable, 1-alkyl-4-vinylpyridinium triflates. In the series, monomers in which the alkyl group was methyl-, ethyl-, butyl-, hexyl-, and dodecyl were synthesized by the direct alkylation of 4-vinylpyridine with the corresponding alkyl triflate esters. The *N*-methyl and *N*-dodecyl- salts had melting points of 119°C and 62°C, respectively. *N*-ethyl-, butyl-, and hexyl-4-vinylpyridinium triflates were viscous liquids. These monomers were polymerized free-radically, thermally, and anionically. Neither Salamone nor Fife was cognizant of the essential ionic liquid character of these monomers and polymers.

The first intentional synthesis of an ionic liquid polymer was published by Watanabe, *et al.*,<sup>33</sup> in 1995. These workers described the dissolution of poly(*N*-butylpyridinium chloride) in *N*-butylpyridinium tetrachloroaluminate to produce rubbery polymer electrolytes. A composition containing 10 mol% of poly(*N*-butylpyridinium tetrachloroaluminate) exhibited ion conductivity greater than 10<sup>-5</sup> S/cm. Currently, the most active research group studying poly(ionic liquids) is that of Hiroyuki Ohno at Tokyo University of Agriculture and Technology. Ohno's group systematically studied the effects of the length of spacer segments between the vinyl group and the imidazolium cation, and the nature of the cation.

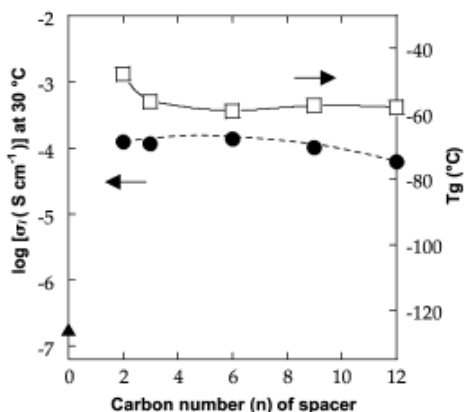
In 2004, Ohno, *et al.*, completed a study on the effect of the chain length between the imidazole cation and the polymerizable acrylate group; the structure can be seen in Figure 1 below. They found that there was little effect on the 3-ethyl-1-acryloyloxyalkylimidazolium salts when the anion is trifluoromethylsulfonylimide. When testing the monomer, the spacer size (3, 6, and 12 carbon chain) had little effect on the glass transition temperature and the ion

conductivity; however, the polymerization of the monomer drastically decreased the ion conductivity. Also, it was found that when polymerized for 3 hours, the 12 carbon chained polymer had the highest ion conductivity; however, the ion conductivity of the 12 carbon chained polymer decreased when the polymerization time was increased to 8 hours, but the ion conductivity of the 3 and 6 carbon chained polymers remained the same.<sup>34</sup>



**Figure 1.** Structure of poly(2,3-dialkyl-1-acryloyloxyhexyl imidazolium TFSI), where R1 varies from methyl, ethyl, and butyl and R2 varies from hydrogen and methyl.

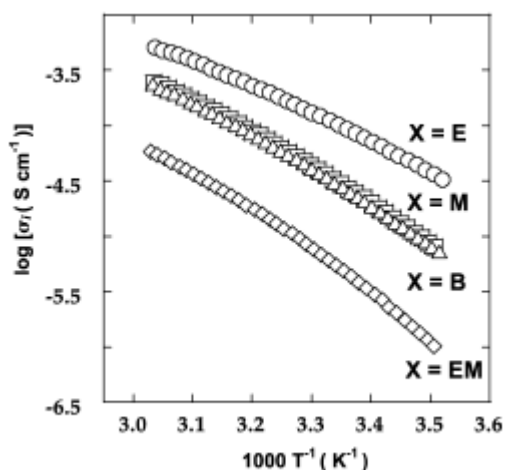
Ohno's group observed that a hydrocarbon chain length of 6, using trifluoromethylsulfonylimide (TFSI) as the anion, exhibited the highest ion conductivity of  $1.37 \times 10^{-4}$  S/cm at 30°C and had a  $T_g$  of -60°C.



**Figure 2.** Effect of HC spacer length (n) on the ion conductivity ( $\blacktriangle$ ; the data of P(EVITFSI) were also shown as reference) or  $T_g$  for ionic liquid-type polymer brushes P(EITH<sub>n</sub>A).<sup>35</sup>

Figure 2 shows the effect of spacer length,  $n$ , on the ion conductivity and glass transition temperature. The ion conductivity of poly(3-ethyl-1-vinylimidazolium trifluoromethylsulfonyl imide) is also shown for a comparison to the polymers synthesized. Ohno also compared how the alkyl groups (methyl, ethyl, butyl, and methyl-ethyl) on the imidazole would affect the ion conductivity of poly(2,3-dialkyl-1-acryloyloxyhexyl imidazolium trifluoromethyl sulfonylimide).<sup>35</sup>

The results of this study can be seen in Figure 3 and show that when R1 is ethyl and R2 is hydrogen, the polymer has the highest ionic conductivity; however it was noted that the polymer was difficult to handle due to the sticky characteristics.



**Figure 3. Temperature dependence of the ion conductivity for various ionic liquid polymers of poly(2,3-dialkyl-1-acryloyloxyhexyl imidazolium TFSI)<sup>34</sup>**

To compensate for the sticky character, these films were also cross-linked with 0.5 mol% tetra(ethylene glycol) diacrylate and it was found that the P(EITH<sub>6</sub>A) film was still able to keep a high ion conductivity ( $1.1 \times 10^{-4}$  S/cm at 30°C).<sup>35</sup>

Ohno and his workers also went on to study the difference the cation had on the ionic conductivity of an acrylate with a 6 carbon spacer. The cations studied were pyrrolidinium, 1-

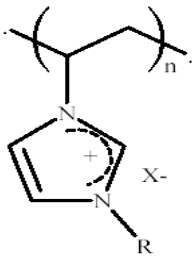


pyrrolinium, imidazolium, and piperidinium, all having bis(trifluoromethylsulfonyl)imide as the anion. Ohno found that the lowest  $T_g$ , and the highest ion conductivity belonged to 1-acryloyloxyhexyl-3-ethylimidazolium ( $-81^{\circ}\text{C}$ ,  $1.1 \times 10^{-3}$  S/cm), also the highest ion conductivity belonged to the polymer of this monomer ( $-59^{\circ}\text{C}$ ,  $1.4 \times 10^{-4}$  S/cm), which was a sticky solid; however, the polymer with the highest thermal stability was poly(1-acryloyloxyhexyl-2-methyl-3-ethylimidazolium trifluoromethylsulfonylimide) ( $389^{\circ}\text{C}$ ).<sup>36</sup>

Other groups that have been particularly active in synthesizing and characterizing poly(ionic liquids) include the group of Marcilla and Mecerreyes, from the Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastian and Youqing Shen's group at the University of Wyoming. Shen's group has synthesized poly(ionic liquids) of ammonium and imidazolium to demonstrate that the polymers were capable of selectively absorbing  $\text{CO}_2$  in a greater capacity than that of the monomeric ionic liquids.<sup>37</sup> Shen's group also worked on living (RAFT) polymerizations of ionic liquid monomers and vinylbenzyl monomers.<sup>38</sup>

Marcilla and coworkers synthesized and polymerized 3-alkyl-1-vinylimidazolium halide monomers. These imidazolium halide polymers were ion exchanged to give a family of poly(ionic liquids) wherein the anion was varied among  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{N}^-$ , and  $\text{ClO}_4^-$ . The solubility characteristics of this family of poly(ionic liquids) was reported and the essence of the results obtained by Marcilla, *et al*, are expressed in the table below.<sup>39</sup>

**Table 1: Solubility of poly(3-alkyl-1-vinylimidazolium salts) in water, methanol, acetone, and tetrahydrofuran, (Soluble ■, Not Soluble ■)**

	-R	X <sup>-</sup>	H <sub>2</sub> O	MeOH	Acetone	THF	
	C <sub>2</sub> C <sub>4</sub>	Cl <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	
	C <sub>2</sub> C <sub>4</sub>	Br <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	
	C <sub>2</sub> C <sub>4</sub>	BF <sub>4</sub> <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	
	C <sub>2</sub> C <sub>4</sub>	PF <sub>6</sub> <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	
	C <sub>2</sub> C <sub>4</sub>	CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	
	C <sub>2</sub> C <sub>4</sub>	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	
	C <sub>2</sub> C <sub>4</sub>	(CF <sub>3</sub> CF <sub>2</sub> SO <sub>2</sub> ) <sub>2</sub> N <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	
	C <sub>2</sub> C <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	■ ■	■ ■	■ ■	■ ■	

Data in the above table was extracted from Marcilla, *et al.*<sup>39</sup>

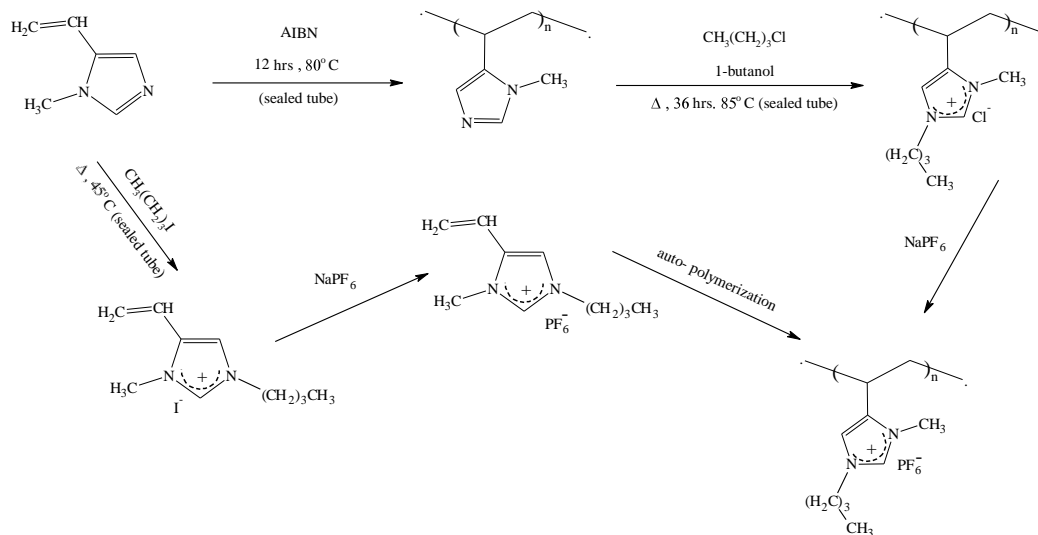
In the solubility study completed by Marcilla, *et al*, the results show that the size of the alkyl group, ethyl or butyl, has only a limited effect on the solubility of the polymer chains. The halides were the only group soluble in water and methanol (triflate salts were also soluble in methanol). As the anions became larger, the solubility of the polymers shifted to more polar aprotic solvents. Other active groups are those of Yossef Elabd from Drexel University and Ya Vygodskii from the Russian Academy of Sciences, both of which will be talked about in more depth below.

In 2009, Elabd, *et al*, synthesized 1-butyl-3-ethylmethacrylimidazolium bromide by the direct quaternization of 1-butylimidazole with 2-bromoethylmethacrylate, in a process similar to that of Ohno, *et al*. The monomer was polymerized free-radically to form homo-polymers and co-polymers with hexyl methacrylate (HMA). The polymers were then evaluated for thermal properties, ion conductivity, and glass transition. In testing by DSC, only the poly(3-butyl-1-ethylmethacrylate imidazolium tetrafluoroborate) displayed a glass transition (71.5°C). It was also found that increasing the concentration of HMA decreased the glass transition temperature. The thermal degradation was also higher with the TFSI than the BF<sub>4</sub><sup>-</sup>, 373°C verse 322°C,

respectively. Yossef also verified that the ion conductivity of the imidazolium polymer decreased by several orders of magnitude from the small molecule. The ion conductivity of the co-polymer increased as the HMA concentration increased and also, sharply increased when the co-polymer reached a 1:1 molar ratio, at 100°C.<sup>40</sup>

In 2007, Vygodskii, *et al*,<sup>41</sup> synthesized a series of poly(3-ethyl-1-vinylimidazolium salts), which varied among Br<sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>, (CN)<sub>2</sub>N<sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. The monomers were synthesized by the reaction of 1-vinylimidazole with ethyl bromide to form 3-ethyl-1-vinylimidazolium bromide. The bromide salt was then used to create the group of differing anions, from various silver and lithium salts and subsequently polymerized using 2,2'-azobisisobutyronitrile in flame sealed tubes. Vygodskii, *et al*, subjected this family of polymers to a series of thermal tests, including TGA and TMA. The difference between the TGA data from Vygodskii<sup>41</sup> and Marcilla<sup>42</sup> on the polymers is the atmosphere in which the sample was run, Vygodskii ran under air, while Marcilla ran under nitrogen. The most stable anion from Vygodskii's set was the trifluoromethylsulfonylimide, which degraded over a temperature span of 325°C to 485°C. Vygodskii, *et al*, also, for the first time, reported T<sub>g</sub>s of these poly(ionic liquids) using the technique of thermomechanical analysis. The T<sub>g</sub>s of these polymers were found to range from 19°C for the dicyanamide polymer salt to 235°C for the bromide polymer salt. In the present research, glass transition temperatures have been obtained by DSC on polymers of the same composition as those reported by Vygodskii.

In exploratory research at RIT by Jun Wang,<sup>43</sup> it was found that direct alkylation of 1-methyl-5-vinylimidazole with n-butyliodide produced a quantitative yield of 1-butyl-3-methyl-4-vinylimidazolium iodide. However, the use of n-butylchloride produced a viscous oil that spontaneously polymerized.



**Figure 4.** Synthetic pathways to poly(1-butyl-3-methyl-4-vinylimidazolium salts)

Wang also performed the polymer analogous reaction, on poly(1-methyl-5-vinylimidazole) by alkylation with n-butylchloride and n-butyliodide. The polymer obtained in the polymer analogous reaction was not fully quaternized. Since 1-butyl-3-methyl-4-vinylimidazolium iodide was resistant to free-radical polymerization, Wang performed an ion exchange of the iodide salt with lithium hexafluorophosphate. This yielded 1-butyl-3-methyl-4-vinylimidazolium hexafluorophosphate, which was not able to be crystallized and had a monomeric  $T_g$  of  $-12^\circ\text{C}$ . The problem with the ion exchange of the monomer in this way is that it has a similar reaction to that of the chloride, where the monomer spontaneously polymerizes once the ion exchange is complete.

The present research built on the work of Wang to synthesize 1-alkyl-3-methyl-4-vinylimidazolium salts that can be polymerized in a controlled fashion.

## Experimental

### *Materials*

Unless otherwise noted, all chemicals were used as received, without further purification.

1,1,1,3,3,3-hexamethyl disilazane (99.9%), 1-vinylimidazole (NVIm, 99+%, see purification below), 1,3-propane sultone, 2,2'-azobisisobutyronitrile (AIBN, 98%, recrystallized from methanol), 4-imidazoleacrylic acid (99%), ammonium dihydrogenphosphate (98+%, ACS reagent), calcium hydride (coarse granules, -20mm, 95%), ethyl trifluoromethane sulfonate (99%), lithium hexafluorophosphate (LiPF<sub>6</sub>, 98%), lithium trifluoromethanesulfonimide (LiTFSI, 99.95%), picric acid (99+%), tetrafluoroboric acid (48 wt% solution in water) were purchased from Sigma-Aldrich.

1,1,1,3,3,3-hexamethyl disilazane (98%), 4-tertbutyl catechol (4-TBC, 99%), ammonium chloride (99.5%, analysis ACS), ammonium sulfate (reagent ACS), iodomethane (stabilized, 99%), isopropanol (IPA, analysis), methyl alcohol (reagent ACS, 99.8%), potassium carbonate (reagent grade ACS, anhydrous), sodium bicarbonate (p.a.), sodium dicyanamide (97% pure), styrene (stabilized, 99%, see purification below) were purchased from Acros Organic.

Ethyl acetate (EA, AR ACS), hydrochloric acid (AR ACS), dichloromethane (AR ACS) were obtained from Mallinckrodt Chemicals.

Sodium hydroxide (pellets), silica gel (40-140 Mesh), magnesium sulfate (Anhydrous Powder) were obtained from J.T. Baker.

*N,N'*-Dimethylformamide (Spectrograde), benzene (GR ACS), acetonitrile (GR ACS), hexanes (GR ACS) were obtained from EMD.

Methanol (GR ACS), hexanes (GR ACS), Spectra/Por Membranes (MWCO 6-8,000) were purchased from VWR Inc.

2,2'-[Carbonothioylbis(thio)]bis[2-methyl-propanoic acid] (min 97%) was purchased from Strem Chemicals.

### *Instrumentation*

Proton NMR data was gathered using a Bruker 300Hz spectrometer with samples dissolved in chloroform-d (Aldrich, 99.8 atom % D, 0.05% v/v TMS) unless otherwise noted.

Thermal gravimetric analysis was carried out under nitrogen atmosphere with a TA Instruments TGA Q500. The temperature was increased from 25-600°C at 20°C/min under a nitrogen atmosphere, and then held at 600°C for 10 minutes under an air atmosphere.

Glass transition data was gathered using a TA Instruments DSC Q100 with attached refrigerated cooling system under a nitrogen atmosphere. All samples were prepared, in an inert atmosphere, by placing the sample in an open aluminum pan and heated to 100°C for 15 minutes on a hot plate, then capped and sealed. Samples were ramped to 200°C then cooled to -50°C at a rate of 20°C/min. The temperature was held for 1 minute at the end of each heating and cooling cycle. All  $T_g$  values are reported as  $T_g$  onset temperatures, which allowed for more consistent results. An example of the 7-step analysis process is described below.

Step 1 – Heat from 22°C to 200°C at 20°C/min

Step 2 – Hold 1 minute

Step 3 – Cool from 200°C to -50°C at 20°C/min

Step 4 – Hold 1 minute

Step 5 – Heat from -50°C to 200°C at 20°C/min

Step 6 – Hold 1 minute

Step 7 – Cool from 200°C to -50°C at 20°C/min

Molecular weights and polydispersities were determined using an Agilent 1100 series gel permeation chromatograph with two Agilent Zorbax PSM 60-S columns (in series). The sample was eluted @ 35°C, using *N,N'*-dimethylformamide as the solvent. Molecular weight values reported are styrene equivalent molecular weights based on hydrodynamic radius.

## **Purification**

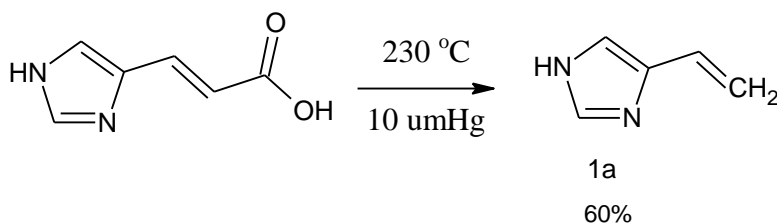
Styrene (100 mL, 0.873 mol) was charged to a 250 mL separatory funnel. The styrene was then washed with four 50 mL aliquots of 10% sodium hydroxide solution, followed by four 25 mL aliquots of distilled water. The organic layer was then dried over potassium carbonate and run over a dry packed silica gel column (15 cm x 2 cm). The resulting styrene was stored over calcium hydride at 10°C, overnight.

*N*-vinylimidazole (35 mL, 0.387 mol) was added to a 100 mL single neck round bottom flask equipped with a short-path distillation head with a three-neck distillation cow receiver. The system pressure was lowered to 2.8 mmHg and held in place using a Man-o-watch. The system was placed in an oil bath at 94°C. The oil bath was slowly heated to 115°C and the distillation was carried out until no more clear liquid was distilled. The product was stored at 10°C. Yield = 34.0 g, 93.4%. B.P. = 54°C, 2.8 mmHg



### Synthesis of 4(5)-vinylimidazole

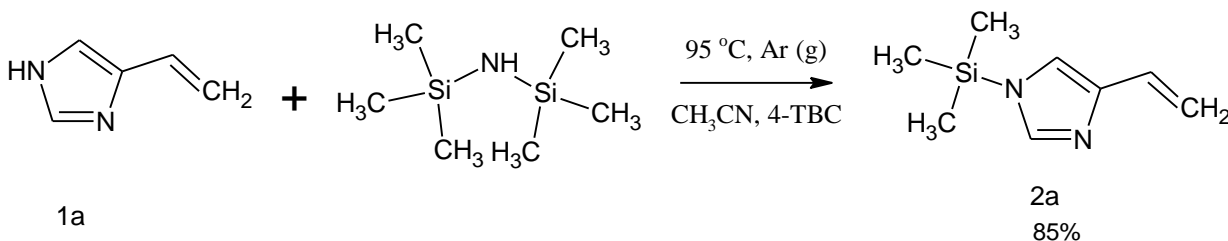
4(5)-vinylimidazole was synthesized by a procedure analogous to that of Overberger,<sup>44</sup> by means of the decarboxylation of urocanic acid. In a typical procedure, urocanic acid (5.00 g, 36.2 mmol) was charged to a 100 mL single-neck round bottom flask with attached elbow. The flask was then connected to a 50 mL three-neck round bottom flask by the elbow. The three-neck round bottom flask was immersed in an ice water bath for the duration of the experiment and also connected to a 50 mL two-neck round bottom flask; this flask was placed in a liquid-nitrogen bath during the experiment. From the two-neck round bottom flask the reaction system was connected to the vacuum line. The single-neck flask was heated in an oil bath at 230°C under vacuum (10μmHg) for 3 hours, leaving a dark black sludge in the reaction vessel and yellow oil of crude 4(5)-vinylimidazole in the three-neck flask. The reaction vessel was allowed to come to room temperature and removed from the vacuum. The 4(5)-vinylimidazole was then cooled overnight at 10°C to obtain a yellow crystalline material. Yield = 2.03 g, 60%.



**Scheme 1. Synthesis of 4(5)-vinylimidazole.**

### 1-trimethylsilyl-4-vinylimidazole

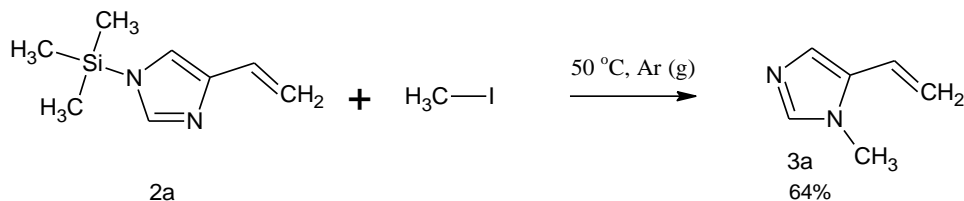
The synthesis of 1-trimethylsilyl-4-vinylimidazole was carried out in a procedure analogous to that of Kawakami and Overberger.<sup>45</sup> Thus, crude 4(5)-vinylimidazole, 1a, (5.00 g, 53.1 mmol), 1,1,1,3,3,3-hexamethyldisilazane (8.57 g, 53.1 mmol), benzene (20 mL, 225 mmol), ammonium sulfate (catalytic amount), and 4-tertbutyl catechol (catalytic amount) were charged to a 50 mL three-neck round bottom flask. The three-neck flask was equipped with a Teflon® adapter with thermometer, 14/20 ground-glass stopper, reflux condenser with gas inlet valve, and a magnetic stir bar. The reaction mixture was blanketed with argon, heated, and stirred in an oil bath at 95°C for 20 hours. The reaction mixture was then allowed to come to room temperature and the solvent was removed by rotary evaporation. The remaining clear oil was then vacuum-distilled for purification. The resulting oil was stored at 10°C overnight where the oil formed a white solid. Yield = 7.47 g, 85%. B.P. = 50°C, 0.13 mmHg.



**Scheme 2. Synthesis of 1-trimethylsilyl-4-vinylimidazole**

### 1-methyl-5-vinylimidazole

The synthesis of 1-methyl-5-vinylimidazole was carried out by a procedure analogous to that of Kawakami and Overberger.<sup>45</sup> Thus, pure, 1-trimethylsilyl-4-vinylimidazole, 2a (7.47 g, 44.9 mmol) was charged to a 50mL three-neck round bottom flask. The three-neck flask was equipped with an addition funnel, reflux condenser with gas inlet valve, Teflon® adapter with thermometer, and magnetic stir bar. Under an argon blanket and stirring, iodomethane (6.06 g, 42.7 mmol, 0.95 eq) was charged to the addition funnel and added drop-wise to the 1-trimethylsilyl-4-vinylimidazole over 30 minutes. After the addition, the reaction mixture was heated in an oil bath at 50°C for 20 hours. A white/yellow solid formed, which was dissolved in dichloromethane (30 mL, 0.469 mol). The mixture was then added to a dilute hydrochloric acid solution (2 drops of conc. HCl to 200 mL of distilled water) and stirred vigorously. The aqueous and dichloromethane layers were then charged to a 500 mL separatory funnel and 100 mL of a saturated sodium bicarbonate solution was added. The mixture was shaken vigorously and the dichloromethane layer removed. The aqueous layer was then washed with three aliquots of 100 mL of dichloromethane. The organic layer was dried over magnesium sulfate. The solution was then filtered and the solvent reduced by rotary evaporation, resulting in a clear oil of 1-methyl-5-vinylimidazole. Picric acid was added to the product and was stored at 10°C until distillation. Crude yield = 2.52 g, 64%



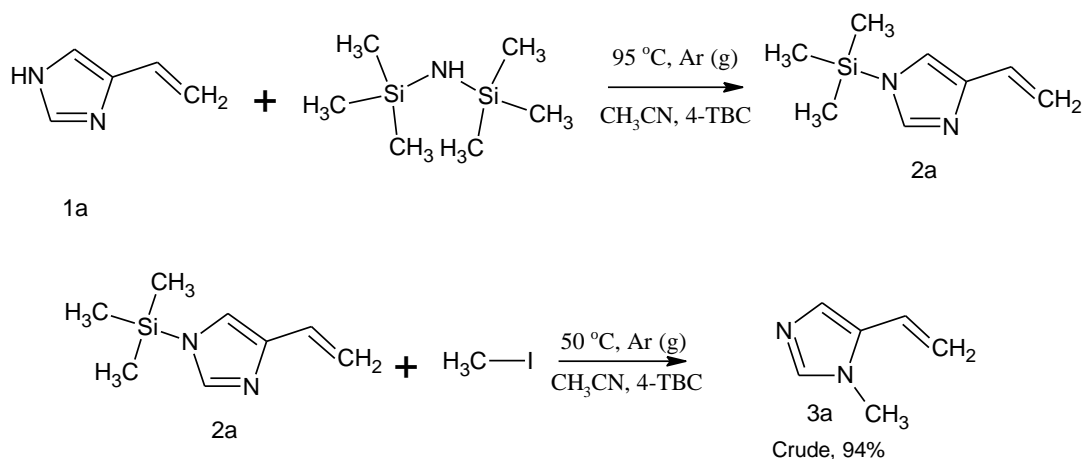
Scheme 3. Synthesis of 1-methyl-5-vinylimidazole

### **1-methyl-5-vinylimidazole (1-pot synthesis)**

The synthesis was attempted using crude material without intermediate purification steps. The 1-pot process was run in acetonitrile instead of benzene; also a sub-stoichiometric (1:0.95 equivalent of 1-trimethylsilyl-4-vinylimidazole to methyl iodide) amount of methyl iodide was used. These steps differ from those of Kawakami and Overberger<sup>45</sup> and Wang and Smith.<sup>43</sup> Although Kawakami and Overberger used a 0.5 molar excess of methyl iodide, they did not report and loss of product due to the creation of 1,3-dimethyl-4-vinylimidazolium iodide, where Wang and Smith did report this loss. The loss of product due to the dimethylation of the imidazole ring is believed to occur when excess methyl iodide nucleophilically displacing the trimethylsilyl group on the nitrogen in the 1 position opening up the possibility of methylation. The use of sub-stoichiometric amounts of methyl iodide did not allow for this to happen, as the methyl iodide is nucleophilically attacked by the non-blocked nitrogen before there can be any removal of the trimethylsilyl group.

Crude 1a (5.00 g, 53.1 mmol), 1,1,1,3,3,3-hexamethyldisilazane (8.57 g, 53.1 mmol), acetonitrile (20 mL, 0.383 mol), ammonium sulfate (catalytic amount), and 4-tertbutyl catechol (catalytic amount) were charged to a 100 mL three-neck round bottom flask, equipped with a reflux condenser with gas inlet valve, Teflon® adapter with thermometer, 14/20 ground-glass stopper, and magnetic stir bar. Under an argon blanket, the reaction mixture was allowed to stir and the vessel was immersed in an oil bath at 95°C for 20 hours. The reaction vessel was then allowed to come to room temperature and the stopper was replaced with an addition funnel containing iodomethane (7.10 g, 50.0 mmol, 0.94 eq) and acetonitrile (15 mL, 0.287 mol). The diluted iodomethane was

added drop-wise over 30 minutes, under an argon blanket and stirring. Once addition was completed, the addition funnel was replaced by the 14/20 ground-glass stopper and the reaction vessel was immersed in an oil bath at 50°C for 20 hours. The reaction vessel was cooled to room temperature and the reaction mixture was added to 100 mL of dilute hydrochloric acid (1 drop of 8M hydrochloric acid in 100 mL of distilled water) and stirred vigorously. The mixture was then transferred to a 500 mL separatory funnel and 100 mL of saturated sodium bicarbonate solution was added and shaken vigorously. The aqueous layer was then extracted three times with 100 mL aliquots of dichloromethane and the organic layer was dried over magnesium sulfate. The organic layer was filtered and the solvent was removed *via* rotary evaporation to yield a colorless oil, to which picric acid was added prior to storage at 10°C and subsequent purification. Crude yield = 5.08 g, 94%



**Scheme 4. Single pot synthesis of 1-methyl-5-vinylimidazole**

### **Vacuum distillation of 1-methyl-5-vinylimidazole**

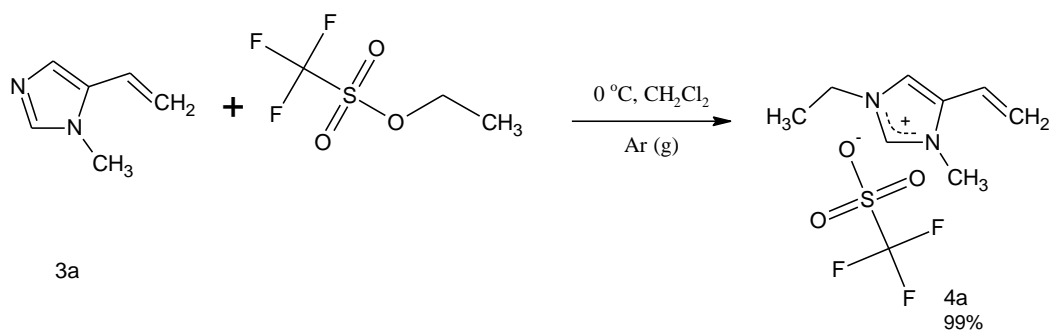
Crude 3a (9.42 g, 87.2 mmol) was charged to a 35 mL single-neck pear-shaped flask, equipped with a cutter-head distillation apparatus (subsequent distillations used a vacuum-jacketed short path distillation apparatus with better results). The vacuum was pulled down to 50  $\mu$ mHg and the pear-shaped flask was immersed in an oil bath at 70°C. The temperature of the oil bath was slowly increased to 180°C until no more of the 3a was being distilled over. The product was stored at 0°C. Yield = 5.26 g, 62.6%. B.P. = 58°C, 0.050 mmHg

### **1-ethyl-3-methyl-4-vinylimidazolium trifluoromethane sulfonate**

The synthesis of 1-ethyl-3-methyl-4-vinylimidazolium trifluoromethane sulfonate is analogous to the work of Fife, *et al.*,<sup>30</sup> completed on 4-vinylpyridine. Fife and coworkers used alkyl triflates to alkylate 4-vinylpyridine in a dried methylene chloride solution to obtain *N*-alkyl-4-vinylpyridinium triflates. The alkyl substituents Fife and coworkers utilized were methyl, ethyl, hexyl, and dodecyl and achieved ~80% or higher yield on all syntheses, showing the robustness of this pathway.

Freshly distilled 3a (1.09 g, 10.1 mmol) and dichloromethane (50 mL) were charged to a 250 mL three-neck round bottom flask, equipped with gas inlet valve, Teflon® adapter with thermometer, addition funnel, and magnetic stir bar. The solution was cooled to 0°C, by immersion into an ice-water bath, and stirred under an argon blanket. To the addition funnel, ethyl trifluoromethane sulfonate (2.16 g, 12.1 mmol, 1.2 eq) and dichloromethane (50 mL) were added. This solution was added to the reaction vessel drop-wise over a 30 minute period. The reaction vessel was kept at 0°C and allowed to stir for 2 hours. The addition funnel was replaced by a short-path distillation apparatus and the solvent was removed by vacuum, while water was used to keep the temperature of the reaction vessel around 0°C, yielding a white solid of 1-ethyl-3-methyl-4-vinylimidazolium trifluoromethane sulfonate. Yield = 2.88 g, 99% Subsequent runs used ethyl acetate as the solvent and a 1:1 eq ratio of imidazole monomer to ethyl trifluoromethane sulfonate, allowing for immediate polymerization without the need for purification. <sup>1</sup>H NMR (in CDCl<sub>3</sub>) 1.47 (3H, t, N-CH<sub>2</sub>CH<sub>3</sub>), 3.81 (3H, s, N-CH<sub>3</sub>), 4.18 (2H, q, N-CH<sub>2</sub>CH<sub>3</sub>), 5.54 (1H, d, <sup>3</sup>J 11.31Hz, *cis*-vinyl H), 5.88 (1H, d, <sup>3</sup>J 17.46Hz,

*trans*-vinyl H), 6.54 (1H, q,  $^3J_{cis}$  11.31,  $^3J_{trans}$  17.46, vinyl *H*-C), 7.75 (1H, s, C-4*H*), 8.92 (1H, s, C-2*H*).

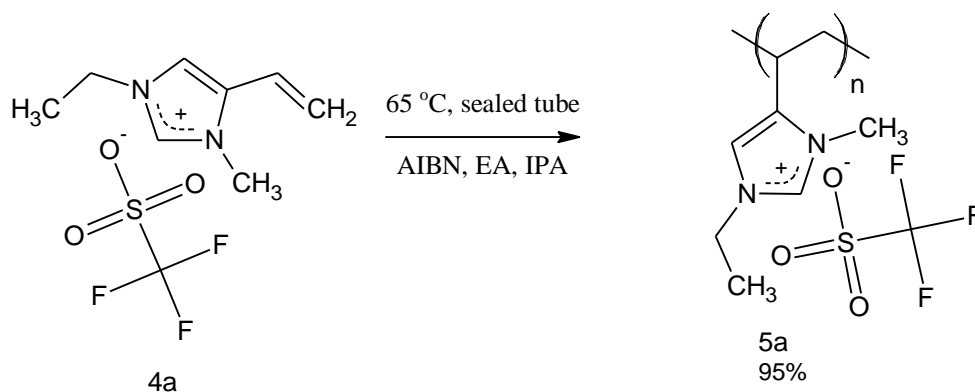


**Scheme 5. Synthesis of 1-ethyl-3-methyl-4-vinylimidazolium trifluoromethane sulfonate**



### Polymerization of 1-ethyl-3-methyl-4-vinylimidazolium trifluoromethane sulfonate

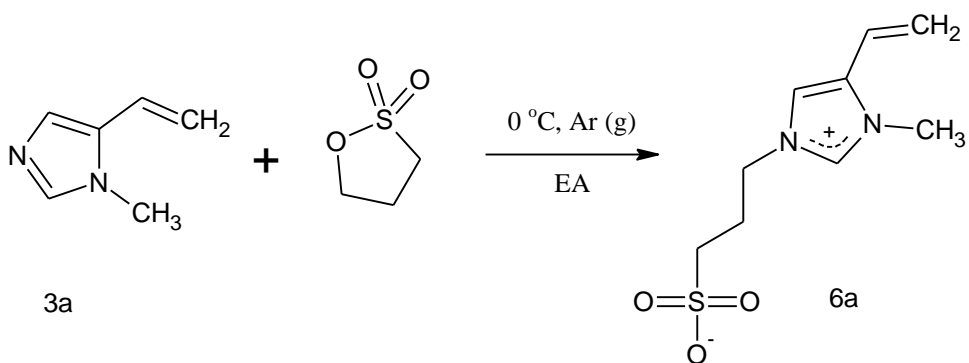
4a (2.88 g, 10.1 mmol) was dissolved in ethyl acetate (10 mL) and isopropanol (2 mL) and transferred to a polymerization tube at 0°C, under an argon blanket. A solution was made of AIBN (0.03 g, 0.183 mmol) by dissolution in ethyl acetate (10 mL). The AIBN solution (1 mL) was added to the polymerization tube and mixed thoroughly. The solution was then degassed by three freeze-thaw cycles by freezing the contents in liquid nitrogen (-192°C). The tube was then flame sealed and immersed in a water bath at 65°C for 20 hours. A polymer gel formed as a result of the polymerization process. The resulting polymer was uncapped in an inert atmosphere and the remaining liquid was decanted. The gel was dissolved in methanol and precipitated in methyl-*tert*-butyl ether. The precipitate was dried on a hot plate at 90°C for 1 hour. Yield = 1.44 g, 49.8%,  $M_n = 13,088$  g/mol,  $M_w = 14,485$  g/mol, PD = 1.11. Subsequent polymerizations were run in 10wt% ethyl acetate where the polymer precipitated readily as a white fluffy solid and with better yield. Yield = 2.70 g, 95%.



**Scheme 6. Polymerization of 1-ethyl-3-methyl-4-vinylimidazolium triflate**

### **1-methyl-5-vinylimidazolium-3-propanesulfonate**

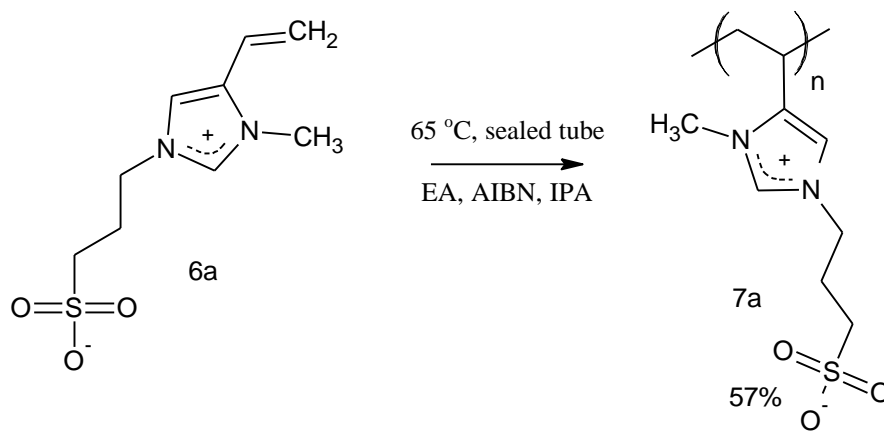
To a 250 mL three-neck round bottom flask; equipped with stopper, magnetic stir bar, Teflon® adapter with thermometer, and gas inlet valve; charge 3a (0.75 g, 6.94 mmol) and ethyl acetate (36 mL, 0.366 mol), cool reaction vessel to 0°C under an argon blanket. Added 1,3-propanesultone (0.85 g, 6.94 mmol, requires warming to 40°C) drop-wise over 24 minutes and then stirred for 100 minutes. After 60 minutes an exotherm was noticed by a rise in temperature of the solution from 0°C to 5°C.



**Scheme 7. Synthesis of 1-methyl-5-vinylimidazolium-3-propanesulfonate**

### Polymerization of 1-methyl-5-vinylimidazolium-3-propanesulfonate

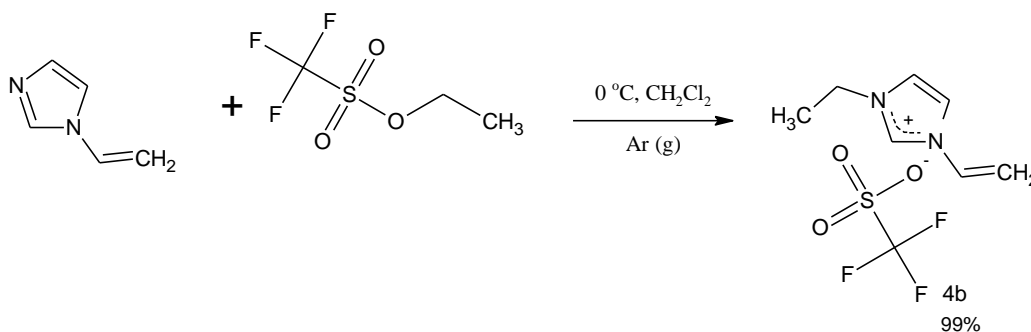
To the solution, AIBN (15  $\mu$ L, 0.1M in ethyl acetate) was added and the solution was transferred to a polymerization tube. The tube was degassed by three freeze-thaw cycles and flame sealed. The tube was then placed in a water bath and heated at 65°C for 15 hrs. The tube was opened and the solution was centrifuged/decanted/rinsed with ethyl acetate three times to yield a white fluffy polymer. Yield = 0.91 g, 56.8% conversion



**Scheme 8. Polymerization of 1-methyl-5-vinylimidazolium-3-propanesulfonate**

### **3-ethyl-1-vinylimidazolium trifluoromethane sulfonate**

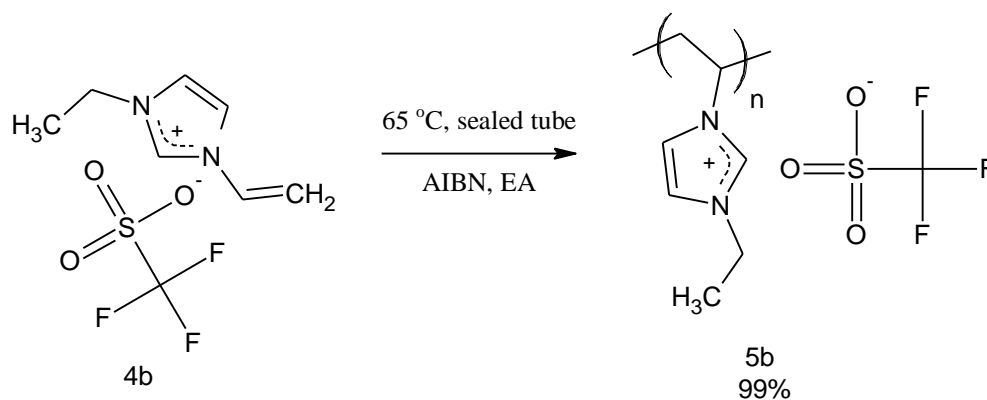
3-ethyl-1-vinylimidazolium trifluoromethane sulfonate was synthesized in a reaction analogous to that of 4a. Freshly distilled *N*-vinylimidazole (1.73 g, 18.4 mmol) and ethyl trifluoromethane sulfonate (3.93 g, 22.1 mmol, 1.2 eq) were used. The reaction vessel was kept at 0°C and allowed to stir for 1.5 hours. A white solid was left after vacuum distillation of solvent. Yield = 5.00 g, 99% Subsequent runs used ethyl acetate as the solvent and a 1:1 eq ratio of imidazole monomer to ethyl trifluoromethane sulfonate, allowing for immediate polymerization without the need for purification.



**Scheme 9. Synthesis of 3-ethyl-1-vinylimidazolium trifluoromethane sulfonate**

### Polymerization of 3-ethyl-1-vinylimidazolium trifluoromethane sulfonate

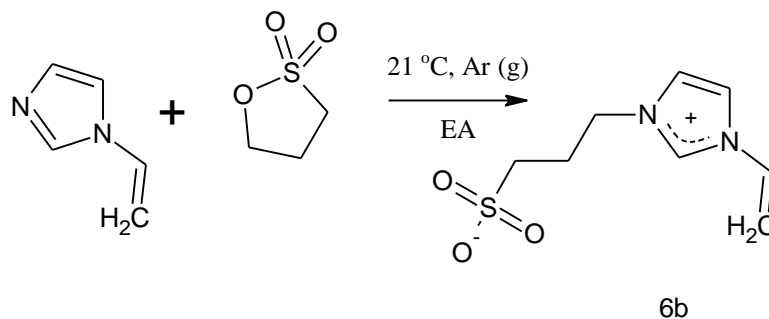
Poly(3-ethyl-1-vinylimidazolium trifluoromethane sulfonate) was synthesized by an analogous reaction to that of 5a, except that isopropanol was not used as a co-solvent. Subsequent polymerizations were run in 10wt% ethyl acetate were the polymer precipitated readily with better yield. Yield = 4.90 g, 99%,  $M_n = 15,706$  g/mol,  $M_w = 18,968$  g/mol, PD = 1.21.



**Scheme 10. Polymerization of 3-ethyl-1-vinylimidazolium triflate**

### **1-vinylimidazolium-3-propanesulfonate**

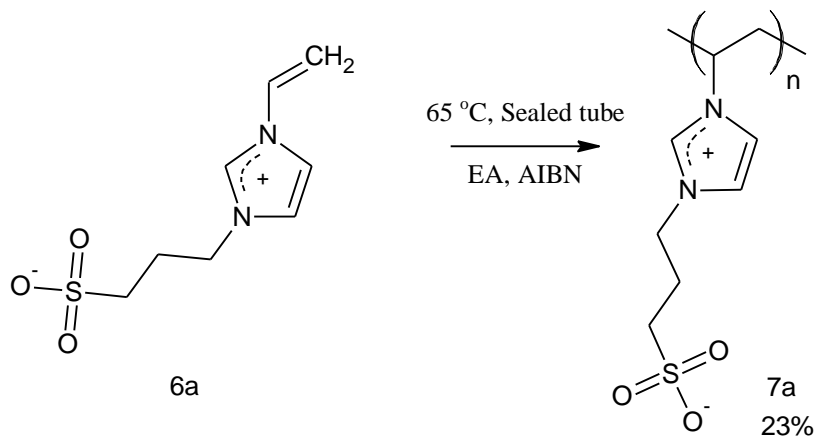
Reaction was run the same as the synthesis of 1-methyl-5-vinylimidazolium-3-propanesulfonate, with the following exceptions. *N*-vinylimidazole (0.87 g, 9.26 mmol), 1,3-propanesultone (1.13 g, 9.26 mmol), and ethyl acetate (20 mL, 0.204 mol). The reaction was run at 21°C and mixed for 30 minutes.



**Scheme 11. Synthesis of 1-vinylimidazolium-3-propanesulfonate**

### Polymerization of 1-vinylimidazolium-3-propanesulfonate

The reaction was run analogous to the reaction of the 1-methyl-5-vinylimidazolium-3-propanesulfonate, with changes as follows. AIBN was added to the solution and mixed for 2 minutes. A large amount of yellow residue remained at the bottom of the polymerization tube. Yield = 0.45 g, 23% conversion.



Scheme 12. Polymerization of 1-vinylimidazolium-3-propanesulfonate

### **Anion exchange of poly(3-ethyl-1-vinylimidazolium salts)**

A solution with a concentration of 0.05 g/mL of 5b in methanol was used for the anion exchange.

#### **Poly(3-ethyl-1-vinylimidazolium tetrafluoroborate)**

10 mL (1.80 mmol) of the above solution was added to a centrifuge tube, to which 5 mL of 48% tetrafluoroboric acid (79.5 mmol) in water was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and rinsed several times with methanol to remove excess  $\text{HBF}_4$ , in order to prevent the decomposition of the polymer; the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.35 g, 90.0%,  $T_g$  onset: heating = 97.73°C, cooling = 114.22-121.25°C

#### **Poly(3-ethyl-1-vinylimidazolium hexafluorophosphate)**

10 mL (1.80 mmol) of the above solution was added to a centrifuge tube, to which a 30 mL methanol solution containing  $\text{LiPF}_6$  (2.08 g, 13.7 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.65 g, 132.7%,  $T_g$  onset: heating = 162.80-172.85°C, cooling = 138.10°C



### **Poly(3-ethyl-1-vinylimidazolium hexafluoroarsenate)**

5 mL (0.945 mmol) of the above solution was added to a centrifuge tube, to which a 5 mL methanol/water (50/50) solution containing KAsF<sub>6</sub> (0.43 g, 1.89 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.18 g 59.8%, T<sub>g</sub> onset: heating = 119.22-122.92°C, cooling = none observed

### **Poly(3-ethyl-1-vinylimidazolium trifluoromethylsulfonylimide)**

The polymer did not precipitate as the literature had suggested;<sup>40</sup> therefore a more extensive procedure was used.

As such, 10 mL (1.80 mmol) of the above solution was added to a centrifuge tube, to which a 30 mL solution of lithium trifluoromethanesulfonimide (LiTFSI, 1.70 g, 5.92 mmol) and mix vigorously. Transferred solution to 6-8,000 MWCO dialysis bag (swelled in distilled water and rinsed 3x in methanol) and dialyzed against methanol over night. LiTFSI (0.50 g, 1.74 mmol) was added to the dialysis bag and dialyzed against methanol for 48 hours. More LiTFSI (0.50 g, 1.74 mmol) was added to the dialysis bag and transferred bag to Soxhlet extractor to dialyze against methanol for 1 week. The dialysis bad was removed from the Soxhlet extractor and precipitated polymer solution in cyclohexane. A clear precipitate was seen attached to the sides and the solvent was decanted. Transferred precipitate to an inert glove box to dry. Dissolved precipitate in methanol (10 mL) and cast a film on a glass plate. Once the solvent has mostly evaporated, the plate placed on a hot plate at 100°C for 1 hour.

The film was collected for future testing. Yield = 0.17 g, 23.1%,  $T_g$  onset: heating = 84.16-90.81°C, cooling = 93.75-96.93°C

**Poly(3-ethyl-1-vinylimidazolium dicyanamide)**

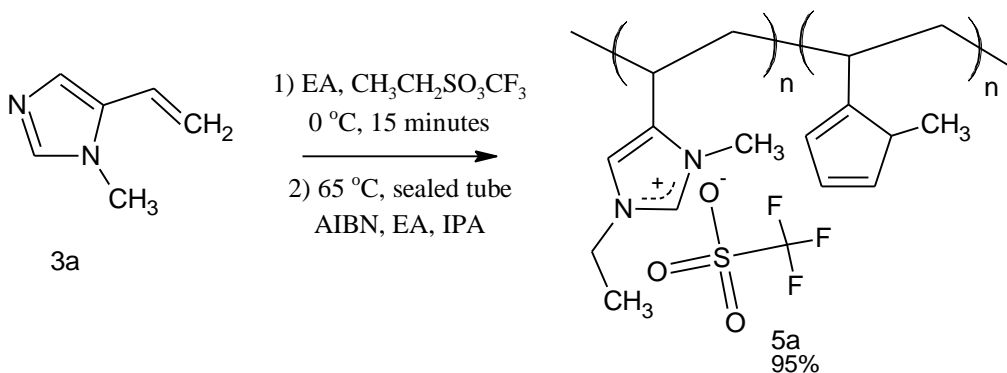
10 mL (1.89 mmol) of the above solution was added to a centrifuge tube, to which a 25 mL methanol solution containing sodium dicyanamide (0.85 g, 9.55 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.12 g, 32.5%,  $T_g$  onset: heating = 89.64°C, cooling = 119.77°C

**Poly(3-ethyl-1-vinylimidazolium dihydrogen phosphate)**

7 mL (1.32 mmol) of the above solution was added to a centrifuge tube, to which a 10 mL water solution containing ammonium dihydrogen phosphate (0.30 g, 2.61 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.55 g, 177.4%,  $T_g$  onset: no heat capacity changes were seen on the thermogram, for the heating or cooling cycle, in the temperature range of -50 – 220°C.

**Synthesis of poly(1-ethyl-3-methyl-4-vinylimidazolium trifluoromethane sulfonate-co-1-methyl-5-vinylimidazole)**

Freshly distilled 3a (1.09 g, 10.1 mmol) and ethyl acetate (30 mL, 305 mmol) were charged to a 250 mL three-neck round bottom flask, equipped with gas inlet valve, Teflon® adapter with thermometer, addition funnel, and magnetic stir bar. The solution was cooled to 0°C, by immersion into an ice-water bath, and stirred under an argon blanket. To the addition funnel, ethyl trifluoromethane sulfonate (1.79 g, 10.1 mmol, 1.0 eq) was added and dripped into the reaction vessel over a 30 minute period. The reaction vessel was kept at 0°C and allowed to stir for 15 minutes. After 15 minutes, a solution was made of AIBN (0.03 g, 0.183 mmol) by dissolution in ethyl acetate (10 mL). The AIBN solution (1 mL) and isopropanol (2 mL) were added to the reaction vessel, stirred for 2 minutes, and then was transferred to a polymerization tube. The solution was degassed by three freeze-thaw cycles by freezing the contents in liquid nitrogen (-192°C). The tube was then flame sealed and immersed in a water bath at 65°C for 20 hours. Yield = 2.70 g, 95%,  $M_n = 14,126$  g/mol,  $M_w = 15,962$  g/mol, PD = 1.13.



**Scheme 13. Synthesis of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate)-co-poly(1-methyl-5-vinylimidazole)**

**Anion exchange of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate-co-1-methyl-5-vinylimidazole)**

A solution with the concentration of 0.054 g/mL of 5a was used for the anion exchange.

**Poly(1-ethyl-3-methyl-4-vinylimidazolium tetrafluoroborate-co-1-methyl-5-vinylimidazole)**

10 mL (1.89 mmol) of the above solution was added to a centrifuge tube, to which 5 mL of 48% tetrafluoroboric acid (79.5 mmol) in water was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and rinsed several times with methanol to remove excess HBF<sub>4</sub>, in order to prevent the decomposition of the polymer; the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.35 g, 82.4%, T<sub>g</sub> onset: heating = 110.52-116.15°C, cooling = 124°C

**Poly(1-ethyl-3-methyl-4-vinylimidazolium hexafluorophosphate-co-1-methyl-5-vinylimidazole)**

10 mL (1.89 mmol) of the above solution was added to a centrifuge tube, to which a 25 mL methanol solution containing LiPF<sub>6</sub> (1.32 g, 8.68 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.42 g, 79.2%, T<sub>g</sub> onset: heating = 154.7-161.5°C, cooling = none observed

**Poly(1-ethyl-3-methyl-4-vinylimidazolium hexafluoroarsenate-co-1-methyl-5-vinylimidazole)**

5 mL (0.945 mmol) of the above solution was added to a centrifuge tube, to which a 5 mL methanol/water (50/50) solution containing KAsF<sub>6</sub> (0.43 g, 1.89 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.23 g 74.7%, T<sub>g</sub> onset: heating = 117.64-124.04°C, cooling = 116.92°C

**Poly(1-ethyl-3-methyl-4-vinylimidazolium trifluoromethylsulfonylimide-co-1-methyl-5-vinylimidazole)**

10 mL (1.89 mmol) of the above solution was added to a centrifuge tube, to which a 25 mL methanol solution containing LiTFSI (0.54 g, 1.89 mmol) was added. The solution was shaken vigorously and an oil separated out on the bottom. The top layer was removed and the tube was transferred to a glove box with inert atmosphere for further drying. The oil turned into a brittle film. Yield = 0.10 g, 12.7%, T<sub>g</sub> onset: heating = 57.95-63.17°C, cooling = 68.11-73.92°C

**Poly(1-ethyl-3-methyl-4-vinylimidazolium dicyanamide-co-1-methyl-5-vinylimidazole)**

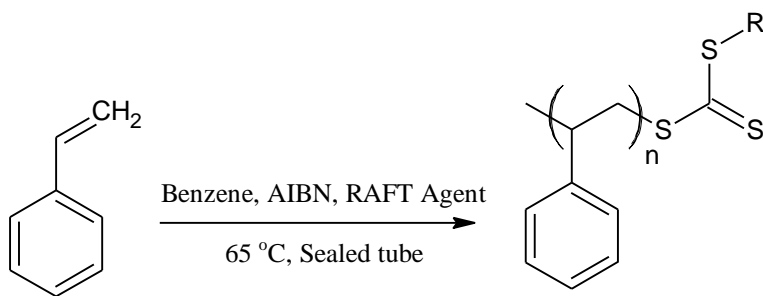
10 mL (1.89 mmol) of the above solution was added to a centrifuge tube, to which a 25 mL methanol solution containing sodium dicyanamide (0.85 g, 9.55 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.15 g, 39.1%, T<sub>g</sub> onset: heating = 109.77°C, cooling = 135.79°C

**Poly(1-ethyl-3-methyl-4-vinylimidazolium dihydrogen phosphate-co-1-methyl-5-vinylimidazole)**

7 mL (1.32 mmol) of the above solution was added to a centrifuge tube, to which a 10 mL water solution containing ammonium dihydrogen phosphate (0.40 g, 3.48 mmol) was added. The solution was shaken vigorously and a precipitate formed. The solution was centrifuged, decanted, and the tube was transferred to a glove box with inert atmosphere for further drying. Yield = 0.85 g, 274.2%,  $T_g$  onset: no heat capacity changes were seen on the thermogram, for the heating or cooling cycle, in the temperature range of -50 – 220°C.

### **RAFT polymerization of Styrene**

In a glove box, styrene (5.75 g, 55 mmol, 97.0 eq, purified as above) and 2,2'-[carbonothioylbis(thio)]bis[2-methyl-propanoic acid] (0.16 g, 0.567 mmol, 1.0 eq), benzene (30 mL, 0.337 mol, distilled over Calcium hydride) were charged to a polymerization tube. The polymerization tube was removed from the glove box and stirred/heated until the RAFT agent dissolved. To the solution, AIBN (0.01 g, 0.0609 mmol, purified as above) was added and the solution was degassed by three freeze-thaw cycles. The polymerization tube was flame sealed and placed in an oil bath heated at 90°C for 20 hrs. The tube was removed from the oil bath and precipitated in hexanes. The first precipitation was dissolved in benzene and freeze dried to yield 0.27 g of yellow polymer. The hexanes solution was rotatory evaporated until a yellow oil was formed and yielded 1.06 g. The molecular weights were tested on the gel-permeation chromatograph and the first precipitation had a  $M_n = 4,025$  g/mol and  $M_w = 4,318$  g/mol with a poly-dispersity of 1.07, while the second precipitation had a  $M_n = 3,602$  g/mol and  $M_w = 3,856$  g/mol with a poly-dispersity of 1.07.



**Scheme 14. RAFT polymerization of styrene**

### **Attempted addition of 1-methyl-5-vinylimidazole block**

To a polymerization tube, poly(styrene) macromolecule (0.83 g, 0.231 mmol, 3600 g/mol), benzene (11 mL, 123.4 mmol), 3a (0.41 g, 3.80 mmol), and AIBN (0.04 g, 0.244 mmol) were charged. Three freeze-evacuate-thaw cycles were run on the solution and the tube was flame sealed and transferred to an oil bath at 110°C and left overnight to polymerize. Some of the solution was added to an excess of hexanes and a precipitate formed. The precipitate was dissolved in analytical grade DMF and tested on the GPC. The results from the GPC showed two peaks, one with a molecular weight of 3600 g/mol and the other with a molecular weight of 1200 g/mol. The data from the GPC showed that the monomer, 3a, homopolymerized faster than being blocked to the poly(styrene) macromolecule, thus the formation of a block copolymer using the RAFT agent 2,2'-[carbonothioylbis(thio)]bis[2-methyl-propanoic acid], was unsuccessful.



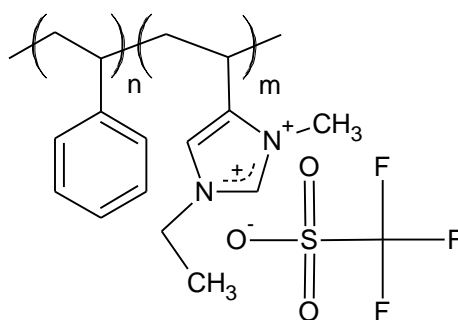
## Results and Discussion

Room temperature ionic liquids (RTILs) are salts with melting points that are often below room temperature and are comprised of quaternary sulfonium, phosphonium, or ammonium (imidazolium, pyridinium, pyrrolidinium) cations in combination with anions that have low Lewis basicity, such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ , etc. The use of these RTILs in advanced electrochemical devices, such as lithium ion batteries,<sup>1</sup> fuel cells,<sup>2</sup> capacitors,<sup>3</sup> solar cells,<sup>4</sup> and actuators,<sup>5</sup> are being explored. The function of such devices might be improved if the small molecular ionic liquids were replaced by film-forming ionic liquid polymers.<sup>6</sup> The current issue is that reducing the mobility of the cationic or anionic components of the ionic liquid causes the ion conductivity to be significantly diminished. It has been proposed that diminished ion conductivity can potentially be mediated by reducing the dimensionality of ion diffusion in nanostructured, precision block copolymers or polymer blends.<sup>6</sup>

Given the mobility of the anionic and cationic components of ionic liquids, the function of these batteries, fuel cells and capacitive devices, could possibly be improved if the conventional ionic liquids were replaced by film-forming ionic liquid/polymer gel electrolytes or poly(ionic liquids) where the mobility of the ions will be restricted.<sup>14</sup> Film-forming ionic liquid/polymer gel electrolytes have been formed by plasticization of a polymer with an ionic liquid,<sup>15</sup> or the formation of an ion gel by polymerization of nonionic monomer in an ionic liquid.<sup>16, 17</sup> Poly(ionic liquids) have been synthesized by quaternization to yield sulfonium, phosphonium, or ammonium polymers and the polymerization of ionic liquid monomers.<sup>18</sup> The strategy of plasticization has been explored in transducers,<sup>19</sup> sensors,<sup>20</sup> secondary lithium batteries, fuel cells, and other electrochemical devices.<sup>21, 22</sup>

The focus of most research groups dealing with vinylimidazoles, are 3-alkyl-1-vinylimidazolium salts. Wang and Smith speculated that tethering the imidazolium ring to the polymer backbone at the 4- or 5- position of the imidazole ring, there would increase the conformational degree of freedom over that of when the imidazole ring is tethered at the 1- position. It was speculated that this increase in degrees of freedom would result in a lower the  $T_g$  and increased the ion mobility.<sup>43</sup>

The objectives of the present research were to synthesize the monomer, 1-ethyl-3-methyl-4-vinylimidazolium triflate, polymerize, ion exchange the polymer to develop a family of poly(1-ethyl-3-methyl-4-vinylimidazolium salts), and characterization of the thermal properties of the polymer by TGA and DSC. The thermal properties of polymers would then be compared to the analogous poly(3-ethyl-1-vinylimidazolium salts). Reduced dimensionality was envisioned by formation of a block copolymer by anionic or RAFT copolymerization of the  $\alpha,\beta$ -unsaturated 4(5)-vinylimidazolium monomer. A styrene block copolymer is depicted in Figure 5.



**Figure 5.** Precision block co-polymer, Styrene-b-3-ethyl-1-methyl-5-vinylimidazolium triflate.

### *Monomer Synthesis and Polymerization*

Several approaches were considered as potential synthetic routes for the quaternization of 1-methyl-5-vinylimidazole. The first approach was to continue the exploratory research of

Wang and Smith,<sup>43</sup> where 1-methyl-5-vinylimidazole was directly quaternized with 1-iodobutane. The synthesis of 1-butyl-3-methyl-4-vinylimidazolium iodide is quantitative. The iodide monomer is storage stable at 0°C; however, the monomer is difficult to polymerize because the iodide anion, which acts as a free-radical scavenger. The iodide salt of the 1-vinylimidazolium monomer was polymerized to low conversion, by Salamone, *et al.*<sup>26</sup> An effort was made to ion exchange 1-butyl-3-methyl-4-vinylimidazolium iodide with lithium hexafluorophosphate. Thus, the iodide monomer was readily dissolved in cold water and a water solution of excess lithium hexafluorophosphate was added. The anion exchange occurred quickly and the imidazolium hexafluorophosphate monomer oiled out and floated to the top of the solution. Even though the water was cold, the wet hexafluorophosphate monomer polymerized almost immediately (perhaps an anionic polymerization initiated by water). However, because of the fact that 1-ethyl-3-methyl-4-vinylimidazolium triflate was later found to polymerize thermally at ambient temperature, thermal polymerization of the 1-butyl-3-methyl-4-vinylimidazolium hexafluorophosphate cannot be ruled out. To avoid polymerization, Wang anion exchanged 1-butyl-3-methyl-4-vinylimidazolium iodide at -78°C and was able to isolate sufficient quantities of hexafluorophosphate monomer for characterization (<sup>1</sup>H-NMR and T<sub>g</sub> by DSC). In the present research an attempt was made to suppress polymerization during ion-exchange by dilution of the salt with a water immiscible organic solvent as it oiled out. This however, also did not work, as the monomer still polymerized. This route was, accordingly, abandoned as a route to the synthesis of 1-alkyl-3-methyl-4-vinylimidazolium salts and their controlled polymerization to form poly(1-alkyl-3-methyl-4-vinylimidazolium) salts.

The next approach was the direct alkylation of the 1-methyl-5-vinylimidazole monomer with *N*-ethyl bis((perfluoroalkyl)sulfonyl)imide, which was analogous to the work done on *N*-

alkyl imidazole by DesMarteau, *et al.*<sup>46</sup> The DesMarteau direct alkylation path was rejected, after several attempts to obtain a pure alkylating agent failed. Careful examination of the work of DesMarteau revealed that the formation of the ionic liquid was accomplished at elevated temperatures (70°C). Since an elevated temperature would lead to thermal polymerization upon alkylation, the idea of using an alkylation process analogous to that developed by DesMarteau was abandoned.

The final option was to alkylate by a process analogous to that of Fife, *et al.*,<sup>30</sup> in which, 4-vinylpyridine was directly quaternized with various alkyltriflate esters. Through this route, while using ethyl triflate to directly quaternize 1-methyl-5-vinylimidazole and 1-vinylimidazole, we were able to isolate 1-ethyl-3-methyl-4-vinylimidazolium triflate and 3-ethyl-1-vinylimidazolium triflate, respectively, both monomers were obtained as white crystalline solids at subzero temperatures. The <sup>1</sup>H NMR of 1-ethyl-3-methyl-4-vinylimidazolium triflate is seen in Figure 6.

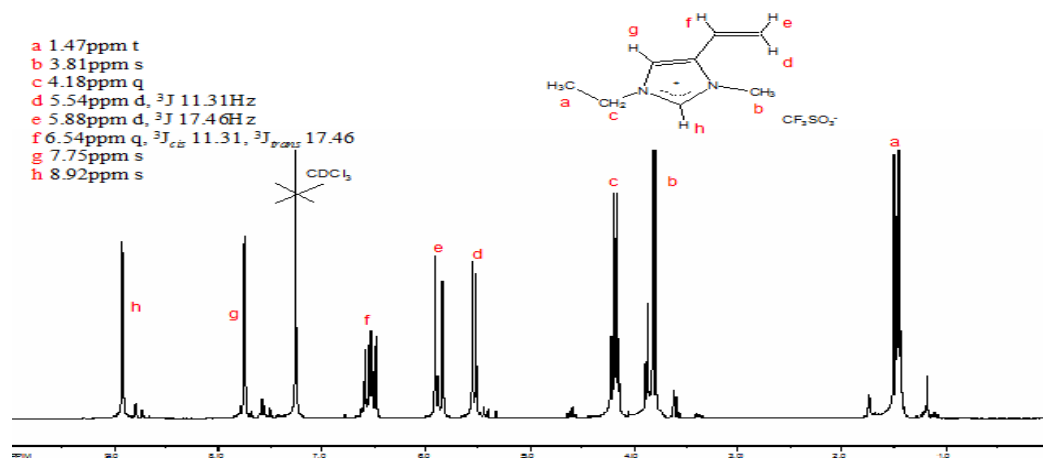


Figure 6. <sup>1</sup>H NMR of 1-ethyl-3-methyl-4-vinylimidazolium triflate

Both triflate monomers were polymerized free-radically using AIBN by dissolution in ethyl acetate; 1-ethyl-3-methyl-4-vinylimidazolium triflate required the addition of isopropanol as a co-solvent. The respective monomer solutions were polymerized in classic sealed Carius tubes, which had been degassed in three freeze-thaw cycles prior to being flame sealed and heated at 65°C for 16 hours to yield polymer which precipitated from the ethyl acetate solution and was isolated as a white powder. The  $^1\text{H}$  NMR of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) can be seen in Figure 7.

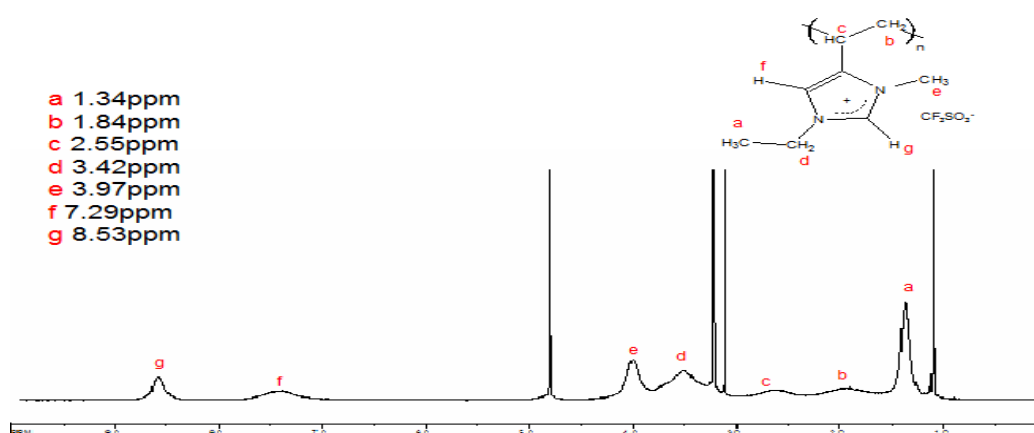
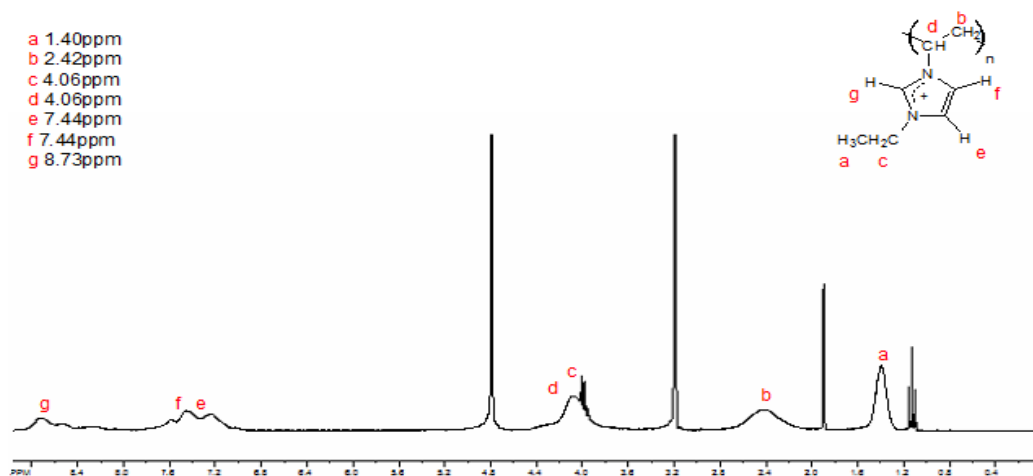


Figure 7.  $^1\text{H}$  NMR of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate)

In the  $^1\text{H}$  NMR of the monomer and polymer of 1-ethyl-3-methyl-4-vinylimidazolium triflate, significant shifts in the assignments can be seen between the two spectra. The relative chemical shifts of the methyl and methylene hydrogen atoms bonded to the nitrogen atoms in the imidazolium ring are different in the monomer and polymer. It appears that in the monomer, the methyl group is shielded by the cone of electron density around the vinyl group; in the polymer, there is no shielding and the chemical shift of the peak of the methyl group moves to 3.97  $\delta$ . The ionic liquid monomer of 3-ethyl-1-vinylimidazolium triflate was synthesized and polymerized

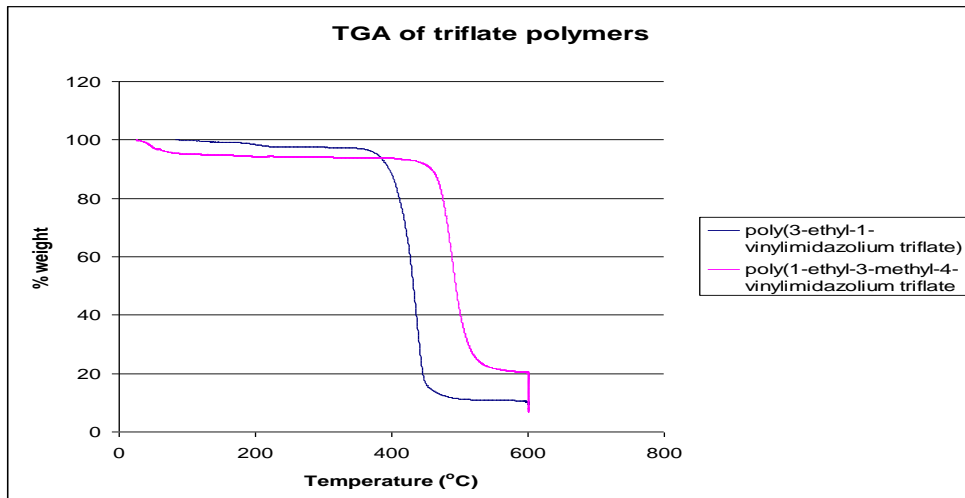
under similar conditions to that of the 1-ethyl-3-methyl-4-vinylimidazolium triflate. An  $^1\text{H}$  NMR of poly(3-ethyl-1-vinylimidazolium triflate) can be seen in Figure 8.



**Figure 8.**  $^1\text{H}$  NMR of poly(3-ethyl-1-vinylimidazolium triflate)

#### *Thermal gravimetric analysis of imidazolium polymers*

Thermal gravimetric analysis of the triflate polymers showed that the 4-vinylimidazolium polymer has greater thermal stability than the 1-vinylimidazolium polymer. The TGA results for the 1-vinylimidazolium triflate matched that published by Marcilla *et al.*<sup>42</sup> Under nitrogen, poly(3-ethyl-1-vinylimidazolium triflate) suffered extensive mass loss from 400°C to 448°C, while poly(1-ethyl-3-methyl-4-vinylimidazolium triflate), lost significant mass in the range of 467°C to 527°C. The increased thermal stability is thought to be due to the difference in the tethering point of the imidazolium ring to the polymer back-bone. Although the length of the carbon-carbon bond is longer than that of the carbon-nitrogen bond, the energy required to break the carbon-carbon bond is still greater by 40kJ/mol.<sup>47</sup>



**Figure 9. TGA of poly(3-ethyl-1-vinylimidazolium triflate) and poly(1-ethyl-3-methyl-4-vinylimidazolium triflate)**

#### *Controlling factors in the glass transition of ionic polymers*

In studies of ionene and polyphosphate polymers, Tsutsui and Tanaka,<sup>48</sup> found that the glass transition temperatures of ionic polymers could be correlated to cohesive energy densities.

$$CED_{ionic} = N_A e^2 \left( \frac{\rho}{M} \frac{q_c}{a} \right) \quad (1)$$

Equation (1) is that of the cohesive energy density found for ionic polymers, where  $N_A$  is Avogadro's number,  $e$  is the electronic charge,  $\rho$  is the polymer density,  $M$  is the molecular weight per skeletal ion, and  $a$  is the equilibrium distance between the center of the anion and the cation.

$$T_g = K_1 \left( N_A e^2 \left( \frac{\rho}{M} \frac{q_c}{a} \right) \right)^n \quad (2)$$

Equation (2) shows that the glass transition temperature is approximately equal to the cohesive energy density multiplied by a coefficient,  $K_1$ . The coefficient varies from polymer to

polymer; however, the glass transition temperature is inversely proportional to the distance between the anion and the cation.

In 1980, Pfeiffer<sup>49</sup> found that the glass transition of ionic polymers is based on the molar ionic cohesive energy, universal gas constant, and factor (n). The factor (n), in equation 2, is related to the intramolecular interactions. Pfeiffer tested several ionic polymers and found that approximately  $2/3 \Delta C_p$  is attributed to intersegmental interactions and  $1/3$  of  $\Delta C_p$  related to intramolecular interactions. A similar relationship was found between the specific heat and the degrees of freedom.

In the present research, the anions that were employed differ in geometry and polarizability. The triflate salt is a classic semi-spherical “hard anion” in which the electrons surrounding the sulfonate group are not highly polarizable. Trifluoromethylsulfonimide is a bent, tetrahedral, plasticizing anion in which the anionic charge on the nitrogen atom is soft and polarizable. Dicyanamide is a less solvating, bent, tetrahedral, anion in which the anionic charge is soft polarizable and delocalized over an ambident anion. Tetrafluoroborate, hexafluorophosphate and hexafluoroarsenate are a family non-nucleophilic complex anions derived from Lewis acids in which the volume of the anion increases from 0.073 to 0.109 to 0.121 nm<sup>3</sup>, respectively.<sup>50</sup>

#### *Anion Exchange and glass transition of poly(3-ethyl-1-vinylimidazolium) salts*

Poly(3-ethyl-1-vinylimidazolium triflate) was ion exchanged with  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{N}(\text{CN})_2^-$  and  $\text{H}_2\text{PO}_4^-$ . This family was created by dissolving poly(3-ethyl-1-vinylimidazolium triflate) in methanol and mixing with solutions consisting of excess amounts of salts, with the desired anions, in methanol or methanol/water. The anion exchanged



polymer would precipitate as the solubility characteristic changed, to where the new polymer was not soluble in methanol. The polymers were rinsed thoroughly with methanol and allowed to dry in an inert atmosphere prior to being tested on the DSC.

The samples were dried in an argon atmosphere by heating in an open DSC pan at 100°C for 15 minutes. The DSC pans were then sealed and the glass transition characteristics of the family of 1-vinyl polymers were evaluated by DSC. DSC scans were repeated until essential reproducibility in the glass transition was observed. The onset glass transition temperatures of the 1-vinylimidazolium polymer salts and the zwitterionic propane sulfonate polymer are shown in Table 2.

**Table 2: Heating cycle scan, onset Glass Transition temperatures (°C) for poly(3-ethyl-1-vinylimidazolium salts) (NVIm)**

Anion Name	NVIm	
	Heating Cycle T <sub>g</sub> , Scan #1	Heating cycle T <sub>g</sub> , Scan #2
Propansulfonate Zwitter	137	164
Triflate	128	129
Dicyanamide	89	90
TFSI	91	84
Tetrafluoroborate	97	98
Hexafluorophosphate	173	163
Hexafluoroarsenate	119	123

The triflate polymer exhibited a glass transition temperature at ~128°C. The transition was well defined on the heating cycle and was also reflected in the cooling cycle.

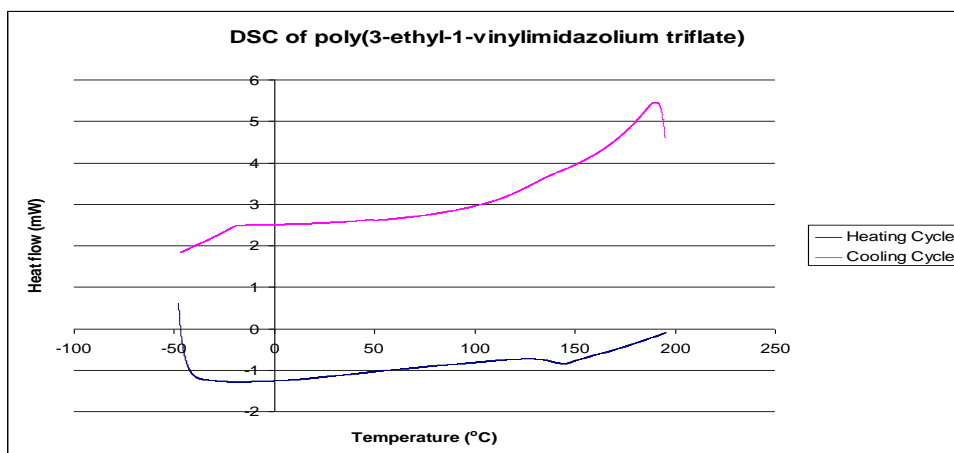


Figure 10. DSC scan of poly(3-ethyl-1-vinylimidazolium triflate) from -50°C to 200°C

The glass transition of the zwitterionic propanesulfonate, was more difficult to define. The transitions in this polymer were broadened and much less distinct than the transitions of the triflate. As such, the glass transitions measured in separate heating cycles ranged from 137°C to 164°C. A corresponding broad glass transition was also observed in the cooling cycle.

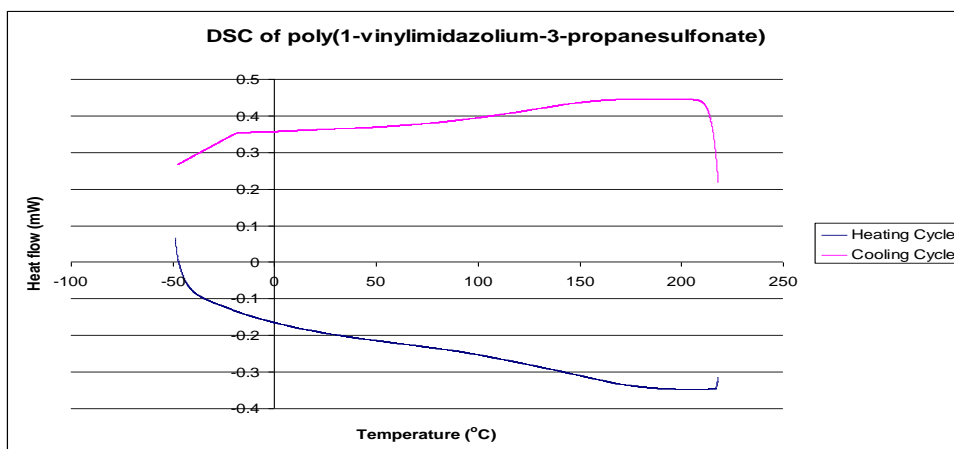


Figure 11. DSC scan of poly(1-vinylimidazolium-3-propanesulfonate) from -50°C to 220°C

The lowest glass transition temperatures were seen with the poly(3-ethyl-1-vinylimidazolium salts) of the soft, polarizable anions. The amide group, trifluoromethylsulfonylimide (TFSI) and dicyanamide salts exhibited heating cycle glass transitions around 90°C. A significant difference in  $T_g$  was however observed in the cooling cycle where the cooling cycle onset for the TFSI salt was 95°C and that for the dicyanamide salt was 120°C. The thermograms for the TFSI and dicyanamide polymer salts are displayed in Figures 12 and 13, respectively.

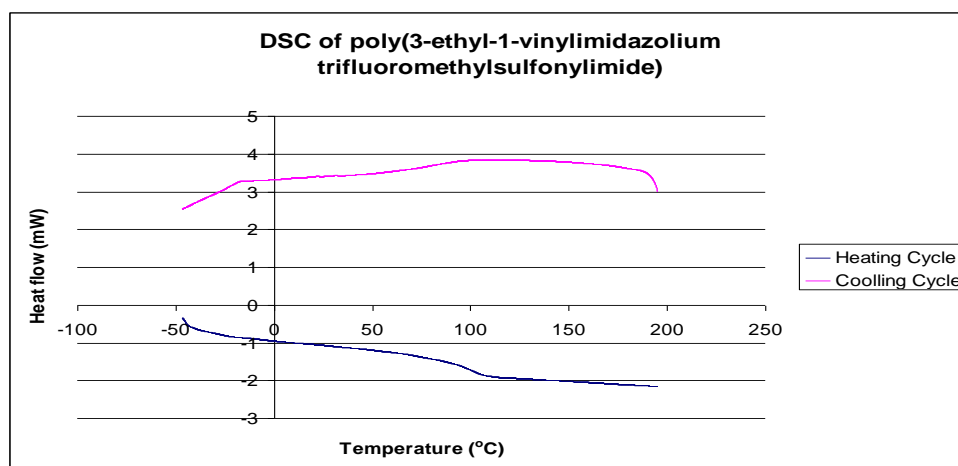


Figure 12. DSC scan of poly(3-ethyl-1-vinylimidazolium TFSI) from -50°C to 200°C

The TFSI salt had the lowest of the glass transitions (84°C - 90°C). The transitions of the TFSI were broad but well defined. The dicyanamide, less solvating and smaller than the TFSI, exhibited more defined transitions in both the heating and cooling cycles. The dicyanamide also had the second lowest glass transition of the anions tested (89°C - 90°C).

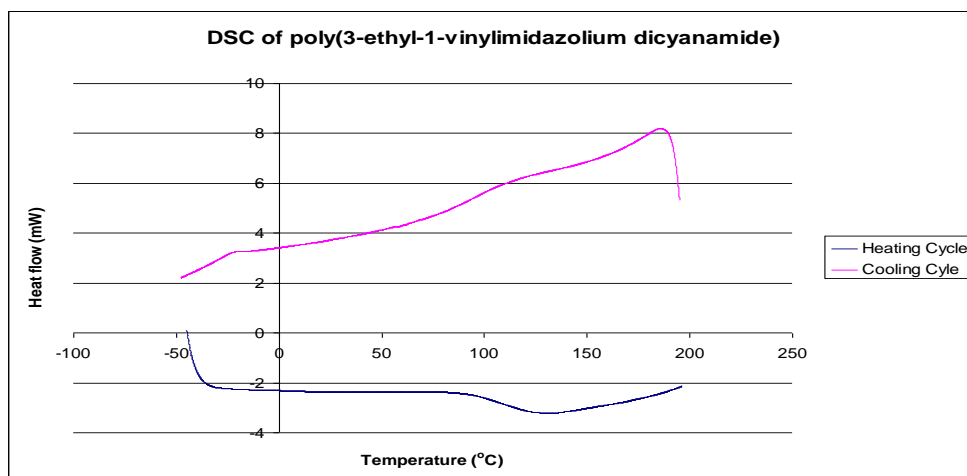


Figure 13. DSC scan of poly(3-ethyl-1-vinylimidazolium dicyanamide) from -50°C to 200°C

With the complex fluorinated anions,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{AsF}_6^-$  there was no apparent trend with size. The smallest of these anions, tetrafluoroborate had the lowest glass transition temperature ( $\sim 98^\circ \text{C}$ ). The transitions were well defined, had definitive starting and ending points on the heating cycle, and corresponding transitions were reflected in the cooling cycle. The lower glass transition of the tetrafluoroborate salt is possibly due to its smaller size and the tetrahedral geometry of the anion.

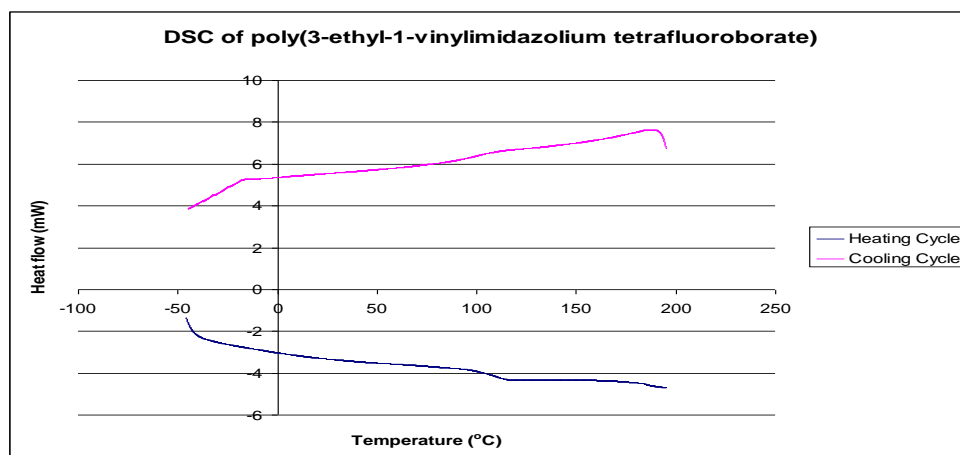
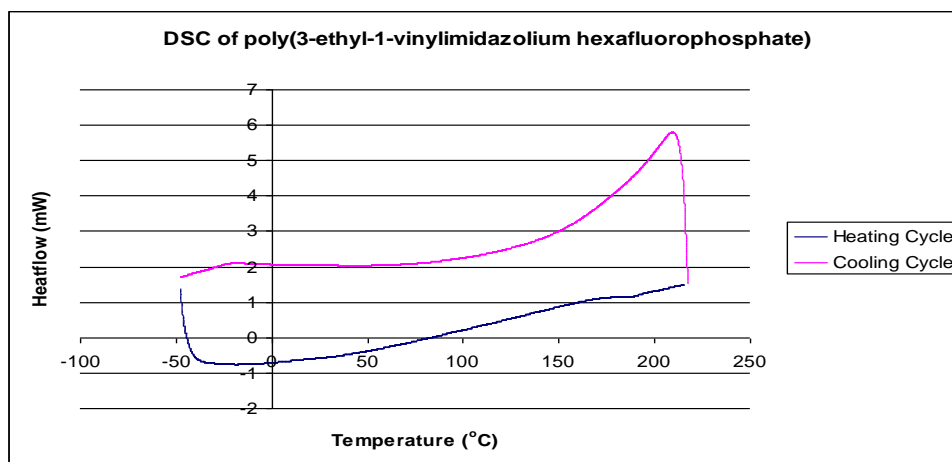


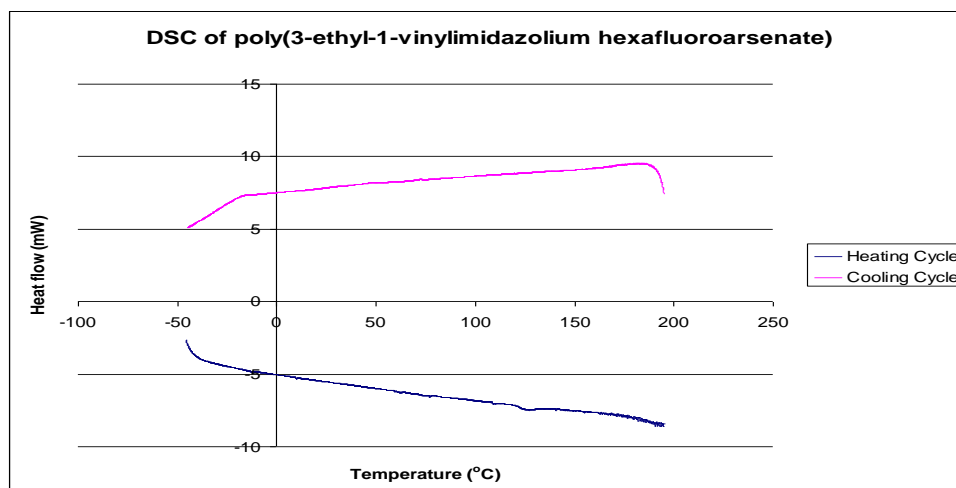
Figure 14. DSC scan of poly(3-ethyl-1-vinylimidazolium tetrafluoroborate) from -50°C to 200°C

The geometry of the hexafluorophosphate and hexafluoroarsenate anions is octahedral with  $\text{PF}_6^-$  being smaller than  $\text{AsF}_6^-$ . In separate scans, the glass transition of the imidazolium hexafluorophosphate polymer ranged from 163 to 173°C and. The thermogram exhibited a short and defined glass transition on the heating cycle; however, no transition was observed on the cooling cycle



**Figure 15.** DSC scan of poly(3-ethyl-1-vinylimidazolium hexafluorophosphate) from -50°C to 220°C

The glass transition of the imidazolium hexafluoroarsenate polymer was difficult to observe, as there happened to be a lot of noise in the baseline of the sample. A definitive glass transition was however seen on the heating cycle and repeated at 119°C and 123°C. No change in heat capacity consistent with a glass transition was discerned in the cooling cycle of the imidazolium hexafluoroarsenate polymer.



**Figure 16. DSC scan of poly(3-ethyl-1-vinylimidazolium hexafluoroarsenate) from -50°C to 200°C**

As proposed by Tsutsui and Tanaka,<sup>48</sup> it is tempting to think of correlating the difference in  $T_g$  of the  $\text{PF}_6^-$  and  $\text{AsF}_6^-$  polymers with cohesive energy density and the increased distance between the center of the anion and the cationic imidazolium group tethered to the polymer backbone. Unfortunately, sufficient data on a family of salts where size of the anion is the predominant variable is not in hand. It is clear from the DSC data of the poly(3-ethyl-1-vinylimidazolium salt) series, that the lowest glass transitions were realized with the soft polarizable amide anions.

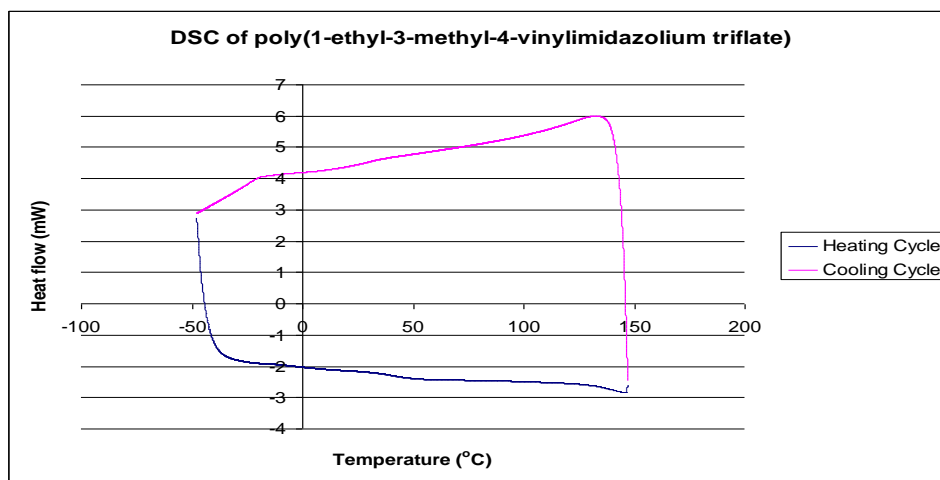
*Glass transition of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) and zwitterionic poly(1-methyl-5-vinyl-3-propane sulfonate)*

Poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) was synthesized and its glass transition was evaluated by DSC.

**Table 3. Onset Glass Transitions (°C) for heating cycle thermograms of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate and zwitterionic poly(1-methyl-5-vinyl-3-propane sulfonate)**

Anion	4-VIm	
	T <sub>g</sub> - Scan #1, °C	T <sub>g</sub> - Scan #2, °C
Zwitter	136	139
Triflate	115	115

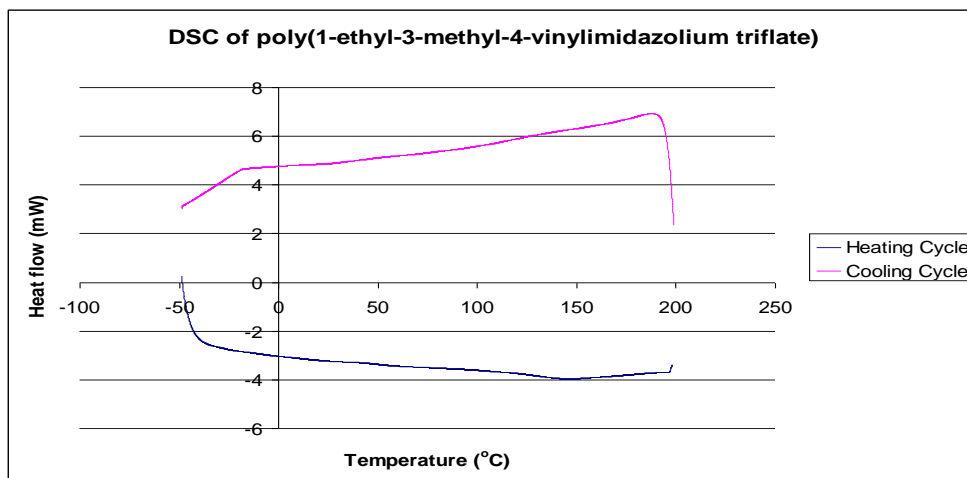
The initial scans showed a heat capacity change consistent with a second-order transition at around 40°C, thought to be the glass transition. This heat capacity change was observed on both the heating and cooling cycles. As compared to the 128°C T<sub>g</sub> of poly(1-ethyl-3-vinylimidazolium triflate), this apparent T<sub>g</sub> was almost 90°C lower. At first, this seemed to be a breakthrough supporting the hypothesis that changing the connection point of the imidazole ring to the polymer would have a dramatic effect on T<sub>g</sub>.



**Figure 17. DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) from -50°C to 150°C**

Repeated scans cycling to 200°C, showed the transition at 40°C along with a new heat capacity change at ~115°C. The heat capacity change at ~115°C was ultimately assigned as the glass transition. The 13°C difference between the T<sub>g</sub> of the 4-vinyl- and 1-vinyl triflate polymers

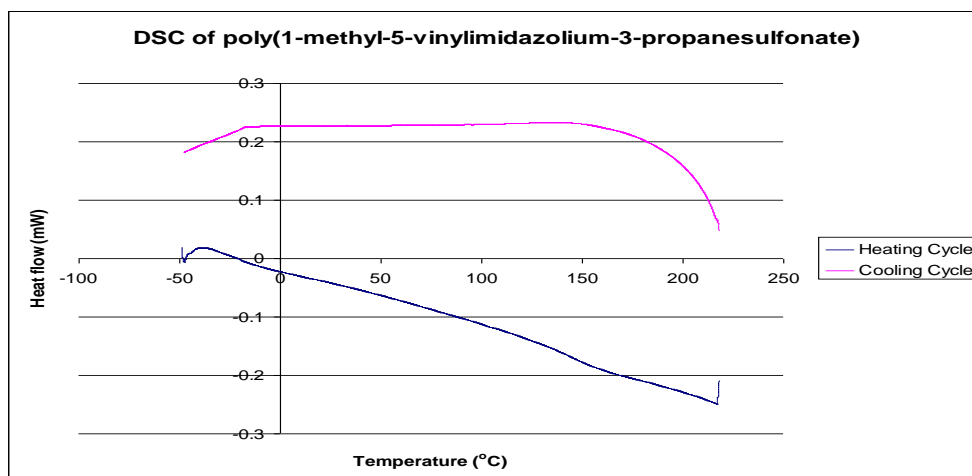
is closer to the anticipated result one might reasonably expect from attachment of the imidazole ring to the polymer backbone at the 4(5)-position.



**Figure 18. DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) from -50°C to 200°C**

The zwitterionic propanesulfonate of the 1-methyl-5-vinylimidazole was also synthesized and its  $T_g$  was measured by DSC. Compared to the 1-vinylimidazolium analogue, the heating cycle glass transition was more distinct (not as broad), appearing at  $\sim 137^\circ\text{C}$  for poly(1-ethyl-4-vinylimidazolium-3-propane sulfonate) *versus*  $137\text{-}164^\circ\text{C}$  for poly(1-vinylimidazolium-3-propane sulfonate).





**Figure 19. DSC scan of poly(1-methyl-5-vinylimidazolium-3-propanesulfonate) from -50°C to 220°C**

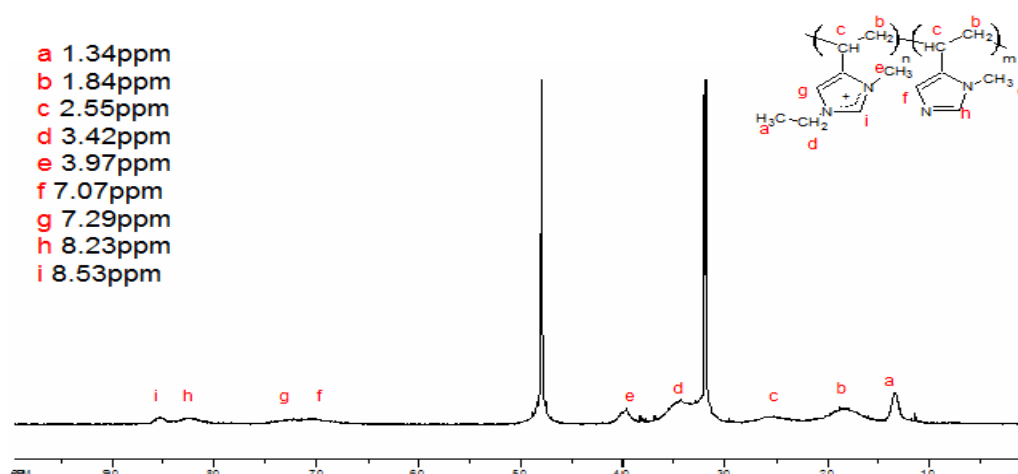
*Poly(1-ethyl-3-methyl-4-vinylimidazolium triflate-co-1-methyl-5-vinylimidazole)*

With only a small batch of triflate polymer initially synthesized, more had to be created and ion-exchanged to develop the family of anions, as was done with the 3-ethyl-1-vinylimidazolium polymer. A second batch of *1-ethyl-3-methyl-4-vinylimidazolium triflate* was synthesized, this time in ethyl acetate. Under the assumption that the alkylation with ethyl triflate was extremely rapid, the alkylation was carried out for only 15 minutes, not the 2 hour period previously employed. After polymerization, the polymer was dissolved in methanol and ion-exchanged, following the same procedures generally used with the 3-ethyl-1-vinylimidazolium triflate. (See the experimental section for specific details of the ion exchange of the copolymer) The trend in the glass transitions of the “new” 4-vinylimidazolium polymers was similar to that observed with the homopolymers of 3-ethyl-1-vinylimidazolium salts. However, there was a significant difference between the glass transition temperature of the initially synthesized 4-vinylimidazolium triflate polymer and the “new” triflate polymer subsequently synthesized in ethyl acetate.

**Table 4. Onset temperatures (°C) for the heating cycles of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) (4VIm)**

Anion Name	4VIm	4VIm
Triflate - Original	115	115
Triflate – “New”	146	149

Since the polymers from the two batches did not have the same glass transition temperature, there had to be a reason as to why they were not acting as predicted. A  $^1\text{H}$  NMR was taken of the “new” 4-vinyl triflate polymer and the spectrum was compared to that of the original polymer. Using the farthest down field peaks, which are unique to the imidazole ring, it was seen that there were four peaks above 7.00 ppm, instead of only two.



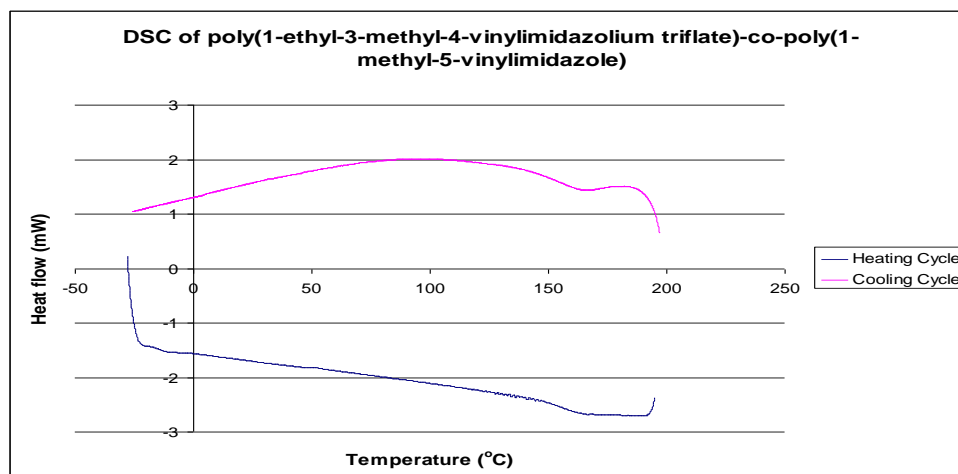
**Figure 20.  $^1\text{H}$  NMR of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate)-co-poly(1-methyl-5-vinylimidazole)**

The additional peaks mean that the polymer did not fully quaternize and that a random co-polymer of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) and poly(1-methyl-5-vinylimidazole) was synthesized in a ratio approximately 1:1.6. The spectrum can be seen in Figure 20. In this spectrum there are two peaks at 8.53 and 8.23 ppm and two peaks at 7.29 and 7.07 ppm. The spectrum of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate), Figure 7, shows

only peaks at 8.53 and 7.29 ppm, which shows that this latest batch is a copolymer. Due to the broadness of the peaks, there is an adherent error in the possible integrations; therefore the amount of the quaternized imidazole in the polymer is estimated to be between 30-50%. This was caused by a stoichiometric amount of ethyl triflate and 1-methyl-5-vinylimidazole being used, along with the change in solvent and the lower reaction time. The reaction mixture was not isolated prior to polymerization, as the solvent was ethyl acetate, which is a good polymerization solvent. The non-chlorinated solvent might have required additional time to mix, or at least the same two hours; however, since a kinetic study was not completed, no real conclusion can be made along those lines. The one conclusion that can be drawn from the  $^1\text{H}$  NMR is that the family of anions created from the second batch of triflate polymer was synthesized using a copolymer, which changes the glass transitions.

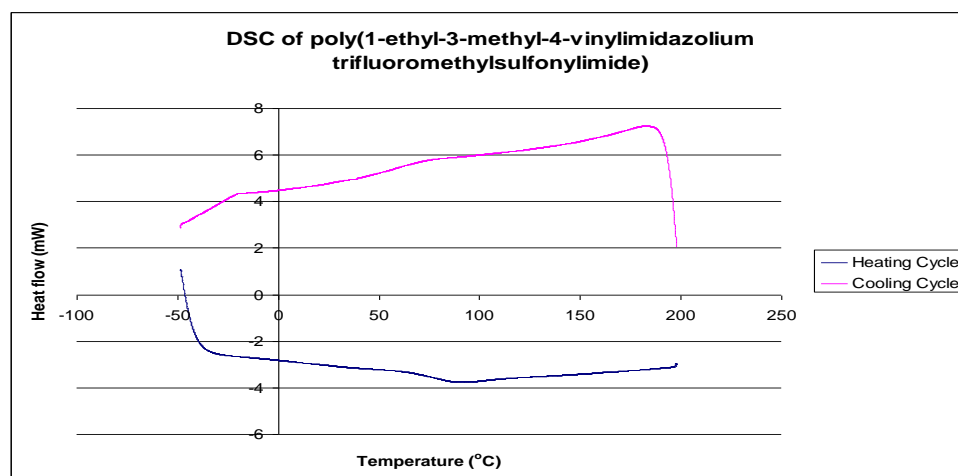
**Table 5. Onset Glass Transition temperatures ( $^{\circ}\text{C}$ ) for the heating cycles of copoly(1-ethyl-3-methyl-4-vinylimidazolium-co-1-methyl-5-vinylimidazole) (Copoly-4VIm)**

Anion Name	Copoly-4VIm	
	Heating Scan #1	Heating Scan #2
Triflate	146	149
Dicyanamide	111	108
TFSI	63	58
Tetrafluoroborate	116	110
Hexafluorophosphate	155	161
Hexafluoroarsenate	124	118



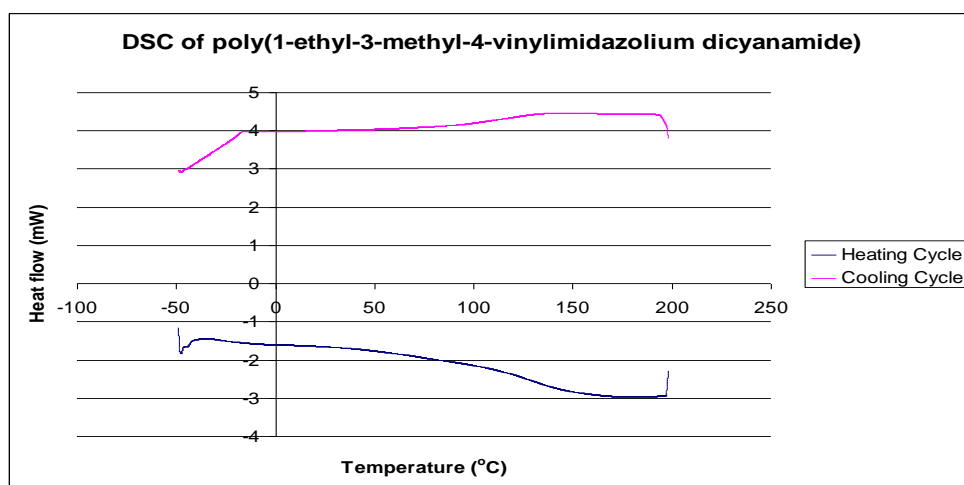
**Figure 21. DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate-co-1-methyl-5-vinylimidazole) from -50°C to 200°C**

In the figure above, an onset glass transition temperature can be seen on the heating cycle at ~150°C and ~173°C on the cooling cycle. The thermogram is not typical as the cooling cycle differs from what you would normally see, as there was no true flat baseline; instead a maximum is seen around 100°C with a steady decline following.



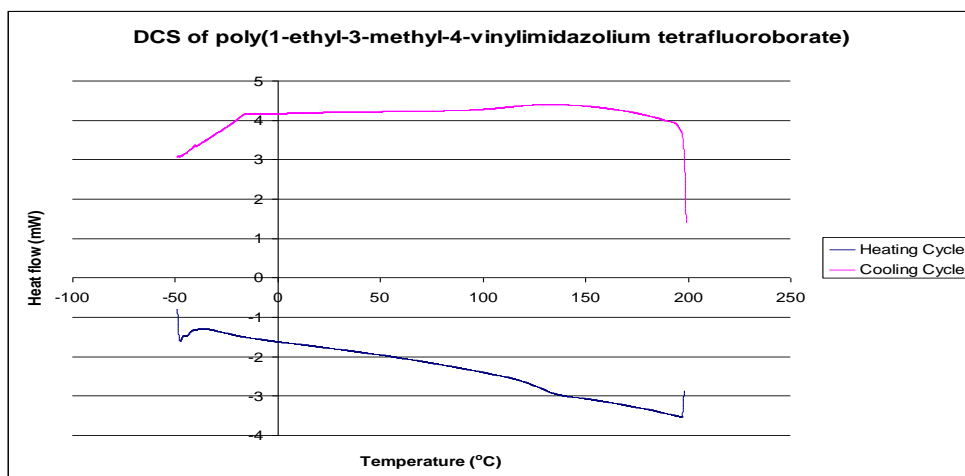
**Figure 22. DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium TFSI-co-1-methyl-5-vinylimidazole)**

Poly(1-ethyl-3-methyl-4-vinylimidazolium TFSI-co-1-methyl-5-vinylimidazole) exhibits a broad transition with an onset  $T_g$  at 58°C. The cooling cycle for this polymer has a more defined onset  $T_g$ , although the transition is still broad, at 68°C. The amides, TFSI in particular, were shown to have the lowest glass transition temperature of all the anions tested in both the 4-vinyl (co-polymer) and 1-vinyl polymers. The 4-vinyl co-polymer exhibited an onset glass transition that somewhat broad and not well defined. The cooling cycle  $T_g$  was not quite as broad as that in the heating cycle and the onset was slightly more defined. The onset of the glass transition on the heating cycle was ~110°C, while that on the cooling cycle was ~124°C.



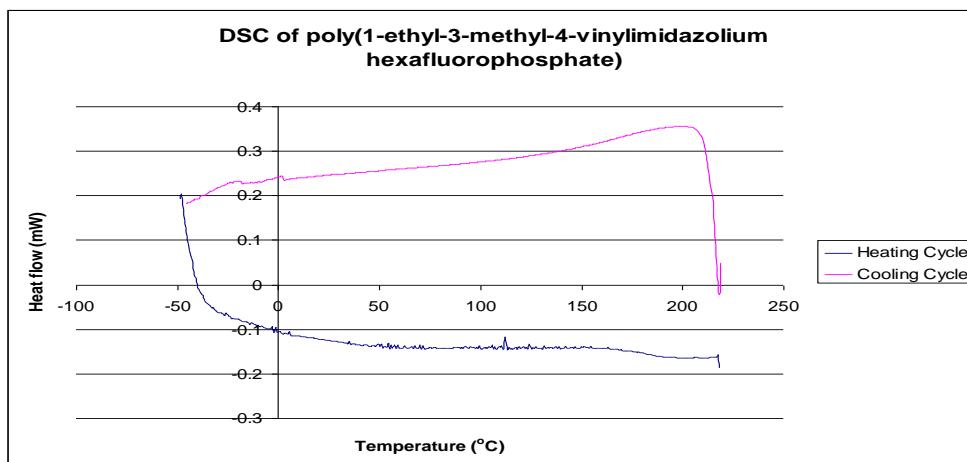
**Figure 23. DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium dicyanamide -co-1-methyl-5-vinylimidazole) from -50°C to 200°C**

Of the fluorinated 4-vinyl co-polymer samples, the tetrafluoroborate salt had the lowest glass transition (110-116°C on the heating cycle and ~124°C on the cooling cycle). The glass transitions were sharp and well defined.



**Figure 24. DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium tetrafluoroborate-co-1-methyl-5-vinylimiazole) from -50°C to -200°C**

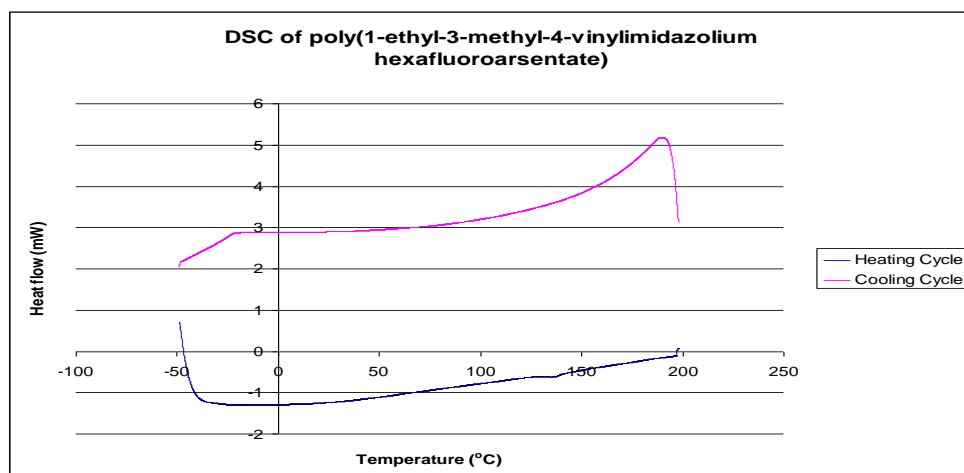
Although there was some noise on the heating cycle of the hexafluorophosphate; a well defined, shallow, glass transition could be seen at ~154°C. A corresponding the glass transition was observed in the cooling cycle.



**Figure 25. DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium hexafluorophosphate -co-1-methyl-5-vinylimidazole) from -50°C to 220°C**

A glass transition at 117-124°C was observed in 4-vinylimidazolium hexafluoroarsenate.

The glass transition was not discerned on the cooling cycle.



**Figure 26.** DSC scan of poly(1-ethyl-3-methyl-4-vinylimidazolium hexafluoroarsenate-co-1-methyl-5-vinylimiazole) from -50°C to 200°C

## Conclusions and Future Directions

In this thesis work, a robust synthetic route for the direct quaternization of 1-methyl-5-vinylimidazole, using ethyl triflate was developed using procedures analogous to those used by Fife, *et al.*<sup>30</sup> to synthesize 1-ethyl-4-vinylpyridinium triflate. The quaternized monomer, 1-ethyl-3-methyl-4-vinylimidazolium triflate was free-radically polymerized to yield poly(1-ethyl-3-methyl-4-vinylimidazolium triflate), which had a  $M_n = 13,088\text{g/mol}$  (PD = 1.11, in DMF), an onset decomposition temperature of 467°C and an onset glass transition temperature of 115°C (heating cycle).

Differential scanning calorimetry was used to measure glass transition temperatures in polymers derived from ionic liquid vinylimidazolium monomers. Poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) exhibits a glass transition temperature (~115°C) that is about 15 degrees lower than that for poly(3-ethyl-1-vinylimidazolium triflate) (~127°C). The 4-vinylimidazolium polymer also has greater thermal stability than the 1-vinylimidazolium polymer. The lowest glass transition temperatures are obtained with imidazolium trifluoromethylsulfonyl imide (TFSI) salts.

Zwitter-ionic monomers and polymers, poly(1-methyl-5-vinylimidazolium-3-propanesulfonate) and poly(1-vinylimidazolium-3-propanesulfonate) were also synthesized. The first priority for future work is the synthesis of the family of poly(1-ethyl-3-methyl-4-vinylimidazolium salts) based on true homopolymer. Other priorities include the synthesis and polymerization of 1-ethyl-2-alkyl-3-methyl-4-vinylimidazolium salts and device studies and evaluation of ion conductivity of all the polymers. Finally, in order to create self-assembling one and two dimensional nanostructured materials, the synthesis of block-co-polymers containing poly(ionic liquid) segments should be pursued.



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