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Synthesis and Characterization of Ionic Liquid Monomers and Polymers Derived from 2-substituted-1,3-dialkyl-4(5)-vinylimidazolium salts

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August 2012

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

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Abstract

In the present research, 1-butyl-2,3-dimethyl-4-vinylimidazolium trifluoromethane sulfonate (triflate) was synthesized and polymerized. This is the first report of the synthesis and polymerization of this ionic liquid monomer. The resulting polymer was characterized by NMR, GPC and thermal analysis (DSC and TGA). The number average molecular weight of the polymer was ~39,600 g/mol (PD = 1.75). The polymer was ion-exchanged to create the trifluoromethyl sulfonylimide (TSFI) and hexafluorophosphate (PF_6^-) polymer derivatives. Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) and poly(1-butyl-2,3-dimethyl-4-vinylimidazolium TFSI) were characterized by TGA and all the three polymers were characterized by DSC. The TGA showed that poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) and poly(1-butyl-2,3-dimethyl -4-vinylimidazolium TFSI) had the same decomposition temperature profiles, with mass loss beginning at 400^{o} C and ending at 510^{o} C. Glass transition characteristics were evaluated by DSC. Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium hexafluorophosphate) exhibited the lowest onset glass transition temperature, 78 ^{o}C, as compared to 94 ^{o}C for poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) and 96 ^{o}C for poly(1-butyl-2,3-dimethyl-4-vinylimidazolium TFSI).

Table of Contents

List of Figures

List of Schemes

Background

Room temperature ionic liquids (RTILs) are ionic salts that melt near and below room temperature. Their low melting points are achieved by incorporating a bulky asymmetric cation and a large, charge-delocalized anion into the structure, which stops the ions from packing uniformly. Ionic liquids are typically comprised quaternary sulfonium, phosphonium, or ammonium cations paired with anions of low Lewis basicity (BF_4^-,PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, etc.). Ionic liquids have attracted considerable attention in recent years due to their interesting and potentially useful physicochemical properties, including high ion conductivity, chemical stability, non-flammability, and near absence of vapor pressure.[1,2]

The discovery, in the early 1990's, of hydrolytically stable liquid, 1,3-dialkylimidazolium tetrafluoroborate and hexafluorophosphate salts[3], led to an explosive growth in the number of publications relating to the synthesis, properties and applications of this unique class of materials that came to be known as room temperature ionic liquids (RTILs). Activity initially centered on the use of ionic liquids as battery electrolytes and the proposition that ionic liquids are "green" solvents and candidates to replace volatile organic compounds. Ionic liquids can be used in place of traditional solvent-based electrolytes which tend to promote corrosion, are prone to leak, are volatile, and are flammable. Ionic liquids have no volatile organic components and no significant vapor. Ionic liquids can act as solvents in which reactions can be performed; and, because the liquid is a molten ionic salt, such reactions often give distinct selectivity and reactivity when compared with reactions in more conventional organic solvents.

Today the focus has shifted to "task specific ionic liquids" [4,5] and studies of the utility of ionic liquids in advanced electrochemical devices[6] ranging from lithium ion batteries[7], to fuel cells[8], capacitors[9], solar cells[10] and actuators[11]. Recently there has been growing interest in the polymeric forms of ionic liquids. Solid-state polymer electrolytes are believed to offer a means by which to eliminate the potential disadvantages of liquid electrolytes including leakage, flammability, toxicity, and instability. Because of the mobility of the anionic and cationic components of ionic liquids, the function of some devices would be improved if conventional ionic liquids could be replaced by film-forming ionic liquid/polymer gel electrolytes or ionic liquid polymers in which the mobility of the ions is constrained. [12] There are, effectively, two options for the realization of ionic liquid-based polymer electrolytes:

1.) plasticization of a pre-formed non-ionic polymer with an ionic liquid[13], or polymerization of a nonionic monomer in an ionic liquid to form "ion-gels," [14,15] and;
2.) synthesis of ionic liquid polyelectrolytes by quaternization of an ammonium polymer or synthesis and subsequent polymerization of an ionic liquid monomer[16], which is being pursued in the present research.

When polymer ionic liquids (ILs) are used as electrolyte materials, they have a significant deficiency in regards to their conductivity. Small molecular ionic liquids exhibit very high ionic conductivity. Ionic conductivity in poly(ionic liquids) is typically dramatically reduced. For example, the ionic conductivity of 1-ethyl-3-vinylimidazolium TFSI salt is around 10^{-2} S cm^{-1} at room temperature, it drops to about 10^{-6} S cm^{-1} after polymerization [29]. This conductivity drop can be understood in terms of the decrease in mobility of ions in polymerized systems. Binding of ions in covalent bonds (polymerization) reduces the mobility of the tethered ionic unit and the mobility of the counter ion is limited by the glass transition temperature (T_g) of the polymer. Crosslinking also lowers ion conductivity. [17]

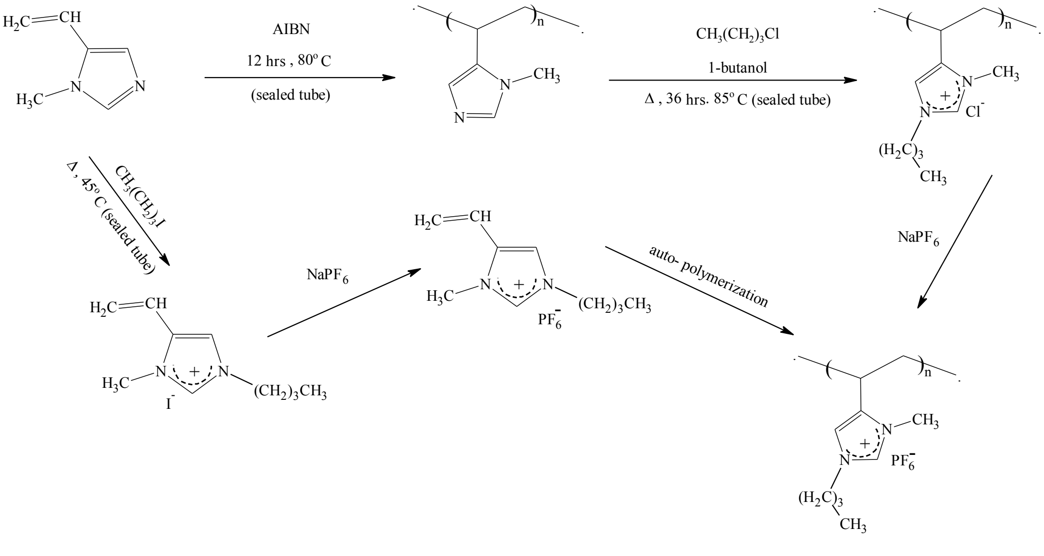
In the 1970's, the synthesis and polymerization of a series of 3-alkyl-1-vinylimidazolium salts, was reported by Salamone and his coworkers. [18,19] In that same time period, Salamone et al., published a series of papers on the synthesis and spontaneous polymerization of 4-vinylpyridinium salts.[20,21] In the early 1990's, Fife and coworkers reported the synthesis,[22] polymerization[23] and thermal properties[24] of a series of isolable, storage stable, 4-vinyl-N-alkylpyridinium salts. Thus, N-methyl-, ethyl-, butyl- hexyl- and dodecyl-4-vinylpyridinium triflates were synthesized by alkylation of 4-vinylpyridine with appropriate triflate esters. The N-methyl- and N-dodecyl- salts melted at 119°C and 62°C, respectively. The N-ethyl-, butyl-, and hexyl-4-vinylpyridinium triflates were viscous liquids at room temperature. All of these salts were readily polymerized free-radically, thermally, and anionically - with weakly basic nucleophiles. The most active current research group in the study of ionic liquid polymers is that of Hiroyuki Ohno at the Tokyo University of Agriculture and Technology. Ohno et al., have published on the preparation and polymerization of N-vinylimidazolium tetrafluoroborate,[25] zwitterionic N-vinylimidazolium sulfonates[26] and sulfonamides, ionic liquid monomer couples generated by neutralization of 1-vinylimidazole with vinylsulfonic acid or 3-sulfopropyl acrylate,[27] 1-ethyl-3-vinylimidazolium trifluoromethyl-sulfonylimide, 1-acryloyloxyalkyl-3-alkyl-imidazolium salts, [28,29,30,31] ion-gels comprised of copolymers of 1-acryloyloxy-3-ethylimidazolium salts with difunctional ionic liquid monomers in conventional ethylmethylimidazolium ionic liquids[32] and hydroboration polymerization of 1,3-diallyimidazolium bromide with subsequent ion exchange with lithium bis(trifluoromethylsulfonyl)-imide.[33] The objectives of Ohno's work in ionic liquid polymers have been to maintain levels of ionic conductivity similar to that in the monomeric ionic liquids by synthesizing ionic liquid polymers having flexible spacer segments between the imidazolium cation and the vinyl group[43] and to create compositions in which only the target ions (Li^+, H^+, I^-, etc.) can migrate[6].

There are other groups that have been active in synthesizing and characterizing ionic liquid polymers. The group of Marcilla and Mecerreyes from the Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastian and their coworkers synthesized and polymerized N-vinyl-3-alkylimidazolium halide monomers, ion exchanged the resultant polymers, and evaluated the solubility characteristics of the polymer families having Cl^-, Br^-, BF_4^-, $PF_6^{-,}$ $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(CF_3CF_2SO_2)_2N^-$ and ClO_4^- anions. [34] Youquing Shen's group at the University of Wyoming[35,36] has synthesized poly(ionic liquids) containing ammonium and imidazolium moieties and demonstrated that these polymers were capable of selectively absorbing and sequestering CO_2. Shen's group also worked on living (RAFT) polymerizations of ionic liquid vinylbenzyl monomers.[37,38]

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 homopolymers and copolymers 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_4^-, 373° C versus 322° C, respectively. Elabd 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.

In 2007, Vygodskii, *et al*, [39] synthesized a series of poly(3-ethyl-1-vinylimidazolium salts), which varied among Br-, $(CF_3SO_2)_2N^-$, $(CN)_2N^-$, and $CF_3SO_3^-$. 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 derivatives with differing anions, by ion exchange with various silver and lithium salts. The monomers were 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 most stable anion in Vygodskii's set was the trifluoromethylsulfonylimide, which degraded over a temperature span of 325℃ to 485℃. Vygodskii, *et al*, also, for the first time, reported glass transition temperatures for these poly(ionic liquids) using the technique of thermomechanical analysis. The glass transition temperatures were found to range from 19° C for the dicyanamide polymer salt to 235° C for the bromide polymer salt.

In exploratory research at RIT, Jun Wang[40] and Darren Smith[41] focused on 4- and 5-vinylimidazolium salts and their corresponding polymers. Since the imidazolium moiety in these polymers is not covalently connected to the polymer backbone at one of the nitrogen atoms on the imidazole ring, the 1-methyl-3-alkylimidazolium group has more conformational degrees of freedom than does the imidazolium moiety in 1-vinyl-3-alkylimidazolium polymers. Jun Wang synthesized poly(1-methyl-3-butyl-5-vinylimidazolium salts) by quaternization of poly(1-methyl -5-vinylimidazole), a polymer analogous reaction, and by polymerization of ionic liquid 1-methyl-3-butyl-5-vinylimidazolium salts. The polymer obtained in the polymer analogous reaction was not fully quaternized. Direct alkylation of 1-methyl-5-vinylimidazole with n-butyl iodide produced a quantitative yield of 1-butyl-3-methyl-4-vinylimidazolium iodide. However, quaternization with n-butylchloride yields a quaternary monomer that polymerizes spontaneously. Since polymerization of the iodide salt does not yield high molecular weight polymer, Wang performed an ion exchange of the iodide salt with lithium hexafluorophosphate. This yielded 1-butyl-3-methyl-4- vinylimidazolium



Scheme1. Synthetic route of poly(1-methyl-3-butyl-5-vinylimidazolium salts)

hexafluorophosphate, which was not able to be crystallized and had a monomeric T_g of -12° 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, i.e., the monomer spontaneously polymerizes during a subsequent to the ion exchange.

Darren Smith built on the work of Wang to synthesize 1-alkyl-3-methyl-4- vinylimidazolium salts that can be polymerized in a controlled fashion. Smith synthesized 1-ethyl-3-methyl -4-vinylimidazolium triflate and polymerized it free-radically to yield poly(1-ethyl -3-methyl-4-vinylimidazolium triflate), which had a M_n = 13,088g/mol (PD = 1.11, in DMF), an onset decomposition temperature of 467^oC and an onset glass transition temperature of 115^oC. For comparison, Smith also synthesized poly(3-ethyl-1-vinylimidazolium triflate) which has a glass transition temperature of 127°C (higher than poly(1-ethyl-3-methyl-4-vinylimidazolium triflate)). It was found that the 4-vinyl imidazolium polymer also has greater thermal stability than the 1-vinylimidazolium polymer. After the ion exchange of the polymers to dicyanamide, trifluoromethylsulfonylimide (TFSI), tetrafluoroborate, hexafluorophosphate, and hexafluoroarsenate, the resulting lowest glass transition temperatures are obtained with imidazolium trifluoromethylsulfonyl imide (TFSI) salt.

The work of Darren Smith has provided an attractive option for poly(ionic liquid) membranes that can be used in lithium ion batteries and super capacitors, etc. However, the acidity of the proton at the 2-position of the imidazole ring is particularly problematic in that it can be the source of chemical and electrochemical instability. 2-methylimidazolium monomers mitigate this problem. The present research is particularly concerned with the synthesis, polymerization, and thermal characteristics of 1,3-dialkyl-2-methyl-4-vinylimidazolium salts and the polymers derived therefrom, as shown in Figure 1.

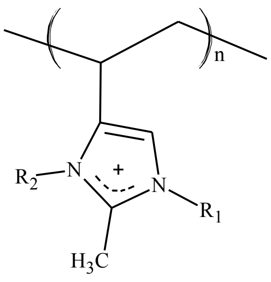


Figure 1. **Structure of poly(2-methyl-1,3-dialkyl-4-vinylimidazolium salt), where R_1 varies from methyl, ethyl and butyl and R2 varies from methyl and butyl.**

Experimental

Materials

4-imidazoleacrylic acid (99%), butyllithium (1.6M solution in hexane), sec-butyllithium (1.4M solution in cyclohexane), 1,1,1,3,3,3-hexamethyl disilazane (99.9%), ethyl vinyl ether(⩾98.0%), *N,N'*-Dimethylformamide(anhydrous, 99.8%), benzene (anhydrous, 99.8%), 1-Bromobutane (99%), methyl trifluoromethansulfonate (⩾98%)， Bis(trifluoromethane)-sulfonimide lithium salt, Methyl sulfoxide (99.6+%), ammonium hexafluorophosphate (99.99%), were obtained from Sigma-Aldrich and used as received.

4-*tert*-butylcatechol (99%), Potassium tert-butoxide (pure, 1M solution in THF, AcroSeal), triphenylmethyl chloride (98%), iodomethane (stabilized, 99%), methyl alcohol (reagent ACS, 99.8%), tetrahydrofuran (stabilized, 99+%), ethanol (pure, denat, 95%, with 5% wood spirit), potassium carbonate (reagent ACS, anhydrous), ammonium sulfate (reagent ACS), sodium bicarbonate (p.a.), were obtained from ACROS Organics and used as received.

Ethyl acetate (AR ACS, 99.5%), hydrochloric acid (AR ACS), chloroform (AR ACS),

dichloromethane (AR ACS), were obtained from Mallinckrodt Chemicals and used as received.

Diethyl ether (anhydrous) and acetone (certified ACS), were obtained from Fisher Scientific and used as received.

Magnesium sulfate (Anhydrous Powder) and acetic acid (glacial) were obtained from J.T.Baker and used as received.

Triethylamine (99%) was obtained from Lancaster Synthesis and used as received.

Acetonitrile (GR ACS) was obtained from EMD Chemicals and used as received.

2,2’-azobisisobutyronitrile (AIBN, 98%, recrystallized from methanol).

1-silyl-4-vinylimidazole was prepared by Darren Smith using a procedure analogous to that reported by Kawakami, et al. [42]

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)，methanol-d4(Aldrich, 99.96 atom % D) and (methyl-sulfoxide)-d6 (ACROS Organics, 99.9 atom % D).

Thermal gravimetric analysis was carried out under nitrogen atmosphere with a TA Instruments TGA 2050. The temperature was increased from 25-600^oC at 20^oC/min under a nitrogen atmosphere, and then held at 600^oC for 10 minutes under an air atmosphere.

Glass transition data was gathered using a TA Instruments DSC 2010 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^oC for 15 minutes on a hot plate to remove moisture, then capped and sealed. Samples were ramped to 150^oC then cooled to -50^oC at a rate of 20^oC/min. After that, the samples were ramped to 200^oC then cooled to -50^oC at a rate of 20^oC/min. The temperature was held for 1 minute at the end of each heating and cooling cycle. Tg values are reported as Tg onset, Tg peak and Tg mid temperatures. An example of the 15-step analysis process is described below.

Step 1 – Heat from 22^oC to 150^oC at 20^oC/min

Step 2 – Hold 1 minute

Step 3 – Cool from 150°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

Step 8 – Hold 1 minute

Step 9 – Heat from -50°C to 200°C at 20°C/min

Step 10 – Hold 1 minute

Step 11 – Cool from 200°C to -50°C at 20°C/min

Step 12 – Hold 1 minute

Step 13 – Heat from -50°C to 200°C at 40°C/min

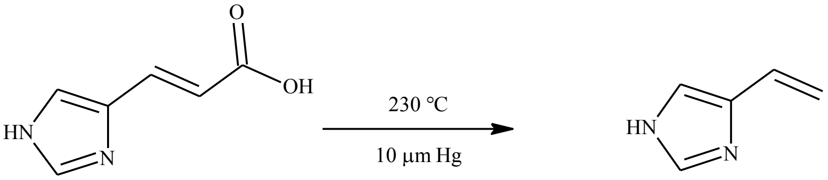
Step 14 – Hold 1 minute

Step 15 – Cool from 200°C to -50°C at 5°C/min

Molecular weight and polydispersity were determined using an Agilent 1100 series gel permeation chromatograph with two Agilent Zorbax PSM 60-S columns (in series). The sample was eluted at 35°C, using *N,N'*-dimethylformamide as the solvent.

Synthesis of 4(5)-vinylimidazole

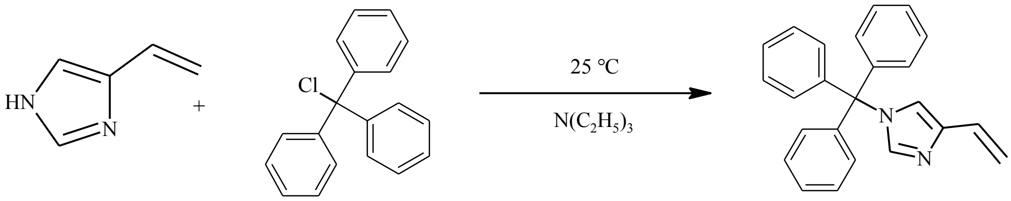
4(5)-vinylimidazole was synthesized by decarboxylation of urocanic acid. The procedure employed was analogous to that of Overberger, et al[43]. Thus, urocanic acid (3.70 g, 26.8mmol) was charged to a 50 mL single-neck round bottom flask. The flask was then connected to an elbow and a 50ml three-neck round bottom flask was connected to the other side of the elbow. The three-neck round bottom flask was immersed in a ice water bath during the reaction and also connected to a 50ml two-neck round bottom flask , which was placed in a liquid-nitrogen bath. The system was connected to the vacuum line through the two-neck round bottom flask. The single-neck flask was first heated in an oil bath at 120°C under vacuum (10μmHg) for 30 minutes and cooled to room temperature. Then it was heated again in the oil bath at 230°C under vacuum (10μmHg) for 2 hours until the residue in the flask all turned dark black. The yellow oil collected in the three-neck round bottom flask was crude 4(5)-vinylimidazole. The reaction vessel was allowed to cool down to room temperature and removed from the vacuum. The 4(5)-vinylimidazole was then cooled in refrigerator (5 °C) overnight to obtain a yellow crystalline material. Yield=1.46g, 58%.



Scheme 2. Synthesis of 4(5)-vinylimidazole

1-trityl-4-vinylimidazole

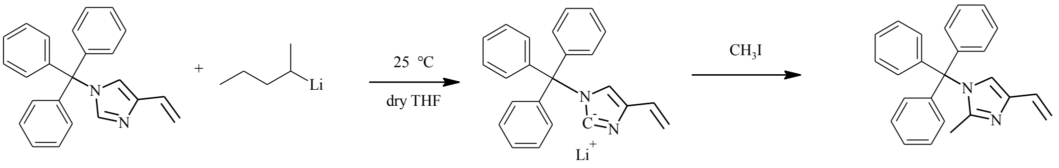
1-trityl-4-vinylimidazole was synthesized by a procedure analogous to that of Schiavone, et al. [44] Thus, crude 4(5)-vinylimidazole (10g, 106.4mmol) and anhydrous *N,N'*-Dimethylformamide (200ml) were charged to a 500ml single neck round bottom flask. The flask was placed in ice water bath and triphenylmethyl chloride (32.6g, 117.0mmol) was added portionwise over a 15 minute period. Then triethylamine (25.8g, 255.3mmol) was charged to the solution. The flask was equipped with a reflux condenser and the reaction mixture was stirred under room temperature for 20 hours. The suspension was then poured into a 500ml solution of hydrochloric acid (12ml of 37%) and water and stirred vigorously for 10 minutes. The white precipitate was isolated by vacuum filtration, washed with water and air dried overnight, resulting in a white, dry solid of 1-trityl-4-vinylimidazole. Yield=36g, 100%.



Scheme 3. Synthesis of 1-trityl-4-vinylimidazole

1-trityl-2-methyl-4-vinylimidazole

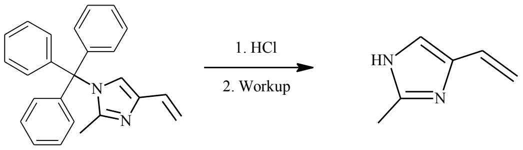
The synthesis of 1-trityl-2-methyl-4-vinylimidazole was carried out by a procedure analogous to that reported by Schiavone et al.[43] Thus, 1-trityl-4-vinylimidazole (12g, 35.7mmol) and dry tetrahydrofuran (600ml, dried from sodium and benzophenone) were charged to 1L three-neck round bottom flask. The flask was equipped with ground glass stopper, rubber serum cap, reflux condenser with gas inlet valve and magnetic stir bar. The flask was then placed in ice water bath and stirred under argon. *Sec*-butyl lithium (25.5ml, 36mmol, 1.4M solution in cyclohexane) was injected dropwise from a 50ml syringe, through the rubber serum cap and into the flask. The reaction mixture, which turned deep red upon addition of *sec*-butyl lithium, was stirred in an ice water bath for 15 minutes and for 2 hours at room temperature. Iodomethane (3ml, 46.4mmol) was then injected from a 5ml syringe through the rubber serum cap and into the flask by. The solution turned yellow and was stirred at room temperature for 30 minutes. Distilled water (100ml) was added to stop the reaction. THF was removed by rotary evaporation and the residue was partitioned between chloroform and water. The chloroform solution was dried over magnesium sulfate. The solution was then filtered and the solvent was removed under reduced pressure, leaving a yellow solid of 1-trityl-2-methyl-4-vinylimidazole. Crude yield=9.3g, 74.4%.



Scheme 4. Synthesis of 1-trityl-2-methyl-4-vinylimidazole

2-methyl-4-vinylimidazole

The synthesis of 2-methyl-4-vinylimidazole was carried out by deprotection of 1-trityl-2-methyl-4-vinylimidazole. In a typical procedure, 1-trityl-2-methyl-4-vinylimidazole (5.7g, 16.4mmol) was charged to a 500ml single neck round bottom flask equipped with a reflux condenser. 200ml of a 5% acetic acid-methanol solution was then added to the flask. The reaction mixture was placed in a 75 °C oil bath and refluxed for 40 minutes. The solvent was removed by rotary evaporation and 50ml of distilled water was added. A white precipitate formed immediately. The precipitate was centrifuged down and the water layer was decanted to another 200ml single neck round bottom flask. The water was ultimately removed *in vacuo*, yielding 2-methyl-4-vinylimidazole as a clear yellow oily residue. Yield = 0.45g, 25%.



Scheme 5. Synthesis of 2-methyl-4-vinylimidazole

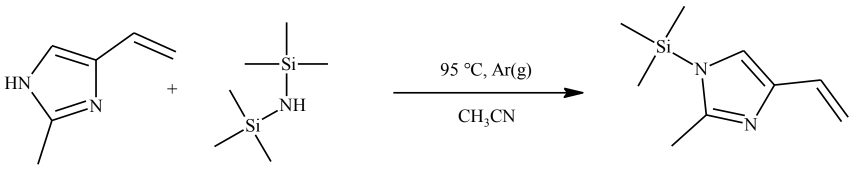
The reaction was then increased in scale to prepare 25.5g of crude1-trityl-2-methyl-4-vinylimidazole.

Recrystallization of 2-methyl-4-vinylimidazole

10.5g of crude 2-methyl-4-vinylimidazole was charged to a 250 ml Erlenmeyer flask and was dissolved in a minimum amount of ethyl acetate. The solution was cooled under room temperature for 1 hour and then stored in a refrigerator over weekend. Needle-like white crystals were formed in the solution and were collected by vacuum filtration. Yield=8.65g, 82.4%.

1-trimethylsilyl-2-methyl-4-vinylimidazole

The synthesis of 1-trimethylsilyl-2-methyl-4-vinylimidazole was carried out in a procedure analogous to that used by Kawakami and Overberger[42] to prepare 1-trimethylsilyl-4-vinylimidazole. Thus, 2-methyl-4-vinylimidazole. (1.0g, 6.0 mmol), 1,1,1,3,3,3-hexamethyldisilazane (1.1g, 6.0 mmol), acetonitrile (50 mL), ammonium sulfate (catalytic amount), and 4-*tert*-butyl catechol (catalytic amount) were charged to a 100 mL single neck round bottom flask. The flask was equipped with a reflux condenser, 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 resulting clear yellow oil was 1-trimethylsilyl-2-methyl-4-vinylimidazole. Yield=0.75g, 70%.



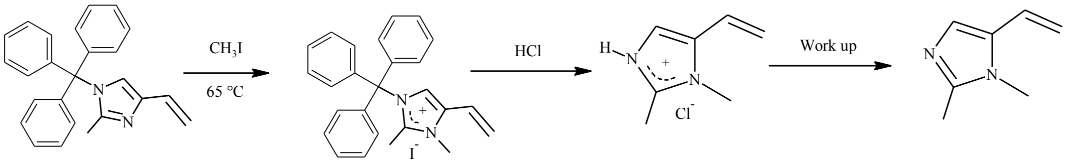
Scheme 6. Synthesis of 1-trimethylsilyl-2-methyl-4-vinylimidazole

1,2-dimethyl-5-vinylimidazole

The synthesis of 1,2-dimethyl-5-vinylimidazole was carried out, in low yield - as described below, by methylation and hydrolysis of 1-trityl-2-methyl-4-vinylimidazole. 1,2-dimethyl-5-vinylimidazole was also obtained by methylation and hydrolysis of 1-trimethylsilyl-2-methyl-4-vinylimidazole.

Methylation and hydrolysis of 1-trityl-2-methyl-4-vinylimidazole

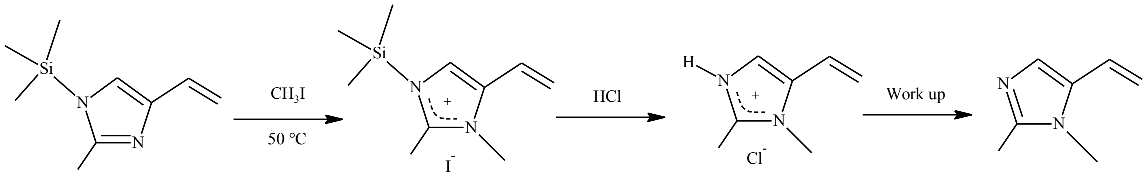
In a typical procedure, 1-trityl-2-methyl-4-vinylimidazole (2g, 5.7mmol), nitromethane (25ml) and iodomethane (0.45ml, 6.3mmol) were charged to a glass pressure vessel. The vessel was capped with a crown cap, placed in a 65 °C water bath and heated overnight. The solution turned brown. The supernant solvent was removed and the dark brown residue was dissolved in 100ml of dichloromethane. 100ml of a 5% acid-water solution was added and the mixture was stirred vigorously for 2 hours. Sodium carbonate was added to neutralize the excess acid and the aqueous solution was extracted exhaustively with three 100ml aliquots of dichloromethane. The dichloromethane was dried over magnesium sulfate and filtered. The solvent was then removed by rotary evaporation, yielding a yellow oily residue of 1,2-dimethyl-5-vinylimidazole. Yield=0.26g, 37.4%.



Scheme 7. Synthesis of 1,2-dimethyl-5-vinylimidazole(1)

Methylation and hydrolysis of 1-trimethylsilyl-2-methyl-4-vinylimidazole

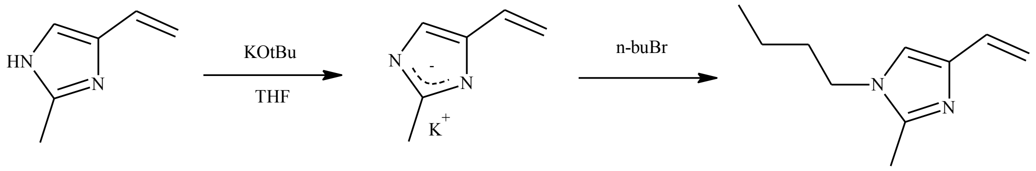
1-trimethylsilyl-2-methyl-4-vinylimidazole (0.36g, 2mmol), acetonitrile (30ml) and iodomethane (0.125ml, 2mmol) were charged to 100ml single neck round bottom flask equipped with magnetic stir bar and reflux condenser. The solution was stirred in a 50° C oil bath for 20 hours. In order to hydrolyze the trimethylsilyl group, 25ml of a 5% acid-water solution was poured into the reaction mixture and stirred vigorously for 1 hour. The reaction mixture was neutralized by sodium bicarbonate. After acetonitrile was substantially removed *in vacuo* , the aqueous layer was extracted with 3 aliquots of diethyl ether and the ether layer was dried over magnesium sulfate. The solution was then filtered and the solvent removed by rotary evaporation, resulting in a yellow oily residue of 1,2-dimethyl-5-vinylimidazole. Yield=0.244g, 53.3%.



Scheme 8. Synthesis of 1,2-dimethyl-5-vinylimidazole(2)

1-butyl-2-methyl-4-vinylimidazole

Crystalline 2-methyl-4-vinylimidazole (2.15g, 19.7mmol) and 20ml of tetrahydrofuran were charged to a 150ml round bottom flask, equipped with Y-tube, rubber stopper, reflux condenser with gas inlet, and magnetic stir bar. Under an argon blanket, the suspension was allowed to stir and the vessel was immersed in ice bath. Then potassium *tert*-butoxide (39.5ml, 39.5mmol) was injected into the flask through rubber stopper on one neck of the Y-tube by syringe. The reaction mixture, which turned milky white, was allowed to stir for 15 minutes. The vessel was cooled in a cold water bath while n-butyl bromide (2.55ml, 23.7mmol) was added drop-wise. The mixture was stirred under Ar at room temperature overnight. Then the solvent was evaporated under reduced pressure and the yellow oily residue was dissolved in 50 ml of diethyl ether. The solution was added to 100mL of dilute hydrochloric acid (5%) and stirred vigorously. The mixture was then transferred to a 500mL separatory funnel and shaken vigorously. After the separation, potassium carbonate was added to the aqueous layer until the pH value of the solution increased to 11. The aqueous layer was then extracted three times with 100 mL aliquots of diethyl ether 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 light yellow oil, yield = 0.8 g, 25%.

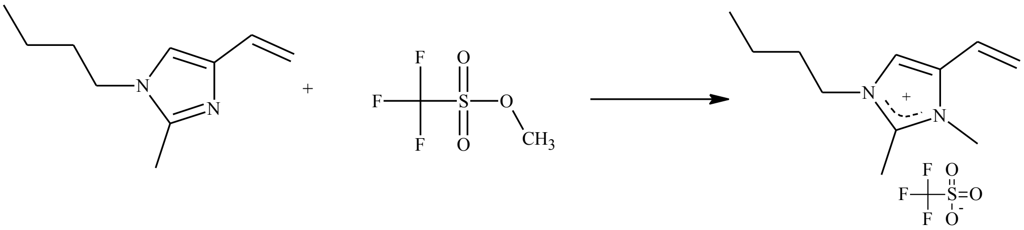


Scheme 9. Synthesis of 1-butyl-2-methyl-5-vinylimidazole

Crude 1-butyl-2-methyl-4-vinylimidazole (1.50 g, 9.15mmol) was charged to a 10mL single-neck round bottom flask, equipped with a short path distillation apparatus. The vacuum was pulled down to 50 µmHg. The flask was immersed in an ice bath and the cow-type receiver was immersed in liquid nitrogen. The clear colorless product was stored at 0 °C. Yield=0.84g, 56.0%.

1-butyl-2,3-dimethyl-4-vinylimidazole

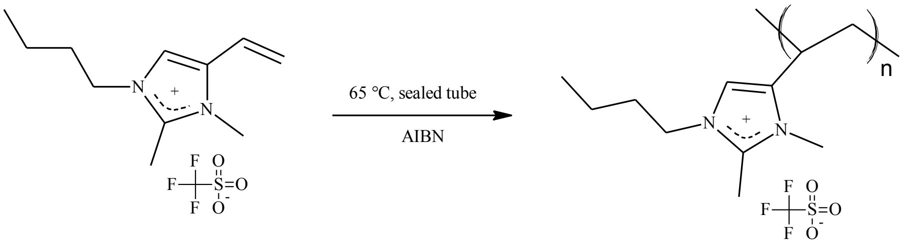
Freshly distilled 1-butyl-2-methyl-4-vinylimidazole (0.84g, 5.12mmol) and 8ml dichloromethane was charged to a 50ml single neck round bottom flask, equipped with Y-tube, rubber stopper, reflux condenser with gas inlet, and magnetic stir bar. The vessel was immersed in ice bath. Under an argon blanket, methyl trifluoromethansulfonate (0.69ml, 6.14mmol), which was dissolved in 10ml of dichloromethane, was added drop-wise by 20mL syringe. The reaction mixture was stirred at 0°C for 2 hours. Then the Y-tube and reflux condenser were removed while the distillation apparatus was set up. The reaction vessel was still immersed in the ice bath and the receiver was immersed in liquid nitrogen. The vacuum was pulled down to remove dichloromethane and unreacted methyl trifluoromethane sulfonate, resulting in a white crystalline solid of product. Yield=1.68g, 100%. MP=45 °C, 760mmHg.



Scheme 10. Synthesis of 1-butyl-2,3-dimethyl-5-vinylimidazolium triflate

Polymerization of 1-butyl-2,3-dimethyl-4-vinylimidazolium trifluoromethane sulfonate

1-butyl-2,3-dimethyl-4-vinylimidazolium trifluoromethane sulfonate (1.68g, 5.80mmol) was dissolved in ethyl acetate (8mL) and ethanol (2mL) and transferred to a polymerization tube at 0°C. A solution was made of AIBN (0.02 g, 0.122 mmol) by dissolution in ethyl acetate (10mL). The AIBN solution (1mL) 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. The tube was then flame sealed and immersed in a water bath at 65°C for 20 hours. A viscous polymer solution formed as a result of the polymerization process. The resulting polymer solution was uncapped and transferred to a 500ml Erlenmeyer flask and 300ml of diethyl ether was added. The solution was shaken vigorously and a white polymer precipitate formed. The suspension was centrifuged, decanted, and combined, resulting in a white fluffy polymer. The polymer turned hard plastic-like after further drying in the glove box with inert atmosphere. Yield=1.68g, 100%. M_n = 39,637 g/mol and M_w = 69,371 g/mol with a poly-dispersity of 1.75.



Scheme 11. Polymerization of 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate

<u>**Anion exchange of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium trifluoromethane sulfonate)**</u>

A “stock solution” with a concentration of 0.02 g/mL of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium trifluoromethane sulfonate) in methanol was used for the anion exchange.

Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium trifluoromethylsulfonylimide)

10 mL (0.69mmol) of the above <u>stock solution</u> was added to a centrifuge tube, to which 10 mL of lithium trifluoromethylsulfonylimide (0.87mmol) in methanol was added. The solution was shaken vigorously and a precipitate formed. The suspension was centrifuged, decanted, and rinsed twice with methanol to remove excess LiTFSI. In order to prevent hydration of the polymer, the tube was transferred to a glove box with inert atmosphere for further drying.

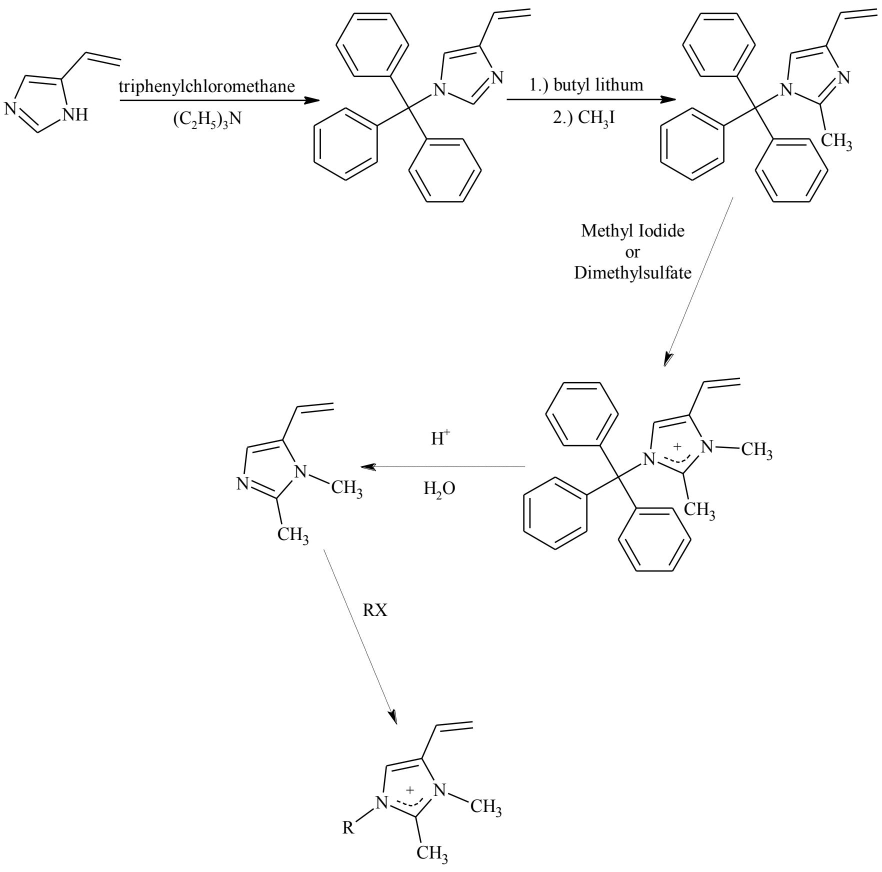
Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium hexafluorophosphate)

10 mL (0.69mmol) of the stock solution was added to a centrifuge tube, to which 10 mL of ammonium hexafluorophosphate (0.92mmol) in methanol was added. The solution was shaken vigorously and a precipitate formed. The suspension was centrifuged, decanted, and rinsed twice with methanol to remove excess NH_4PF_6. In order to prevent hydration of the polymer, the tube was transferred to a glove box with inert atmosphere for further drying.

Results and Discussion

The objectives of the present research were to synthesize monomeric 1,3-dialkyl-2-methyl -4-vinylimidazolium salts (the alkyl group could be methyl, ethyl or butyl), the corresponding polymers and copolymers and to ion exchange these polymers to yield derivatives with different anions. The characterization of the thermal and electrical properties of these polymers was a primary objective. Several approaches were considered as potential routes to synthesize the target monomers.

The first approach starts with crude 4(5)-vinylimidazole, and is outlined in Scheme 12.

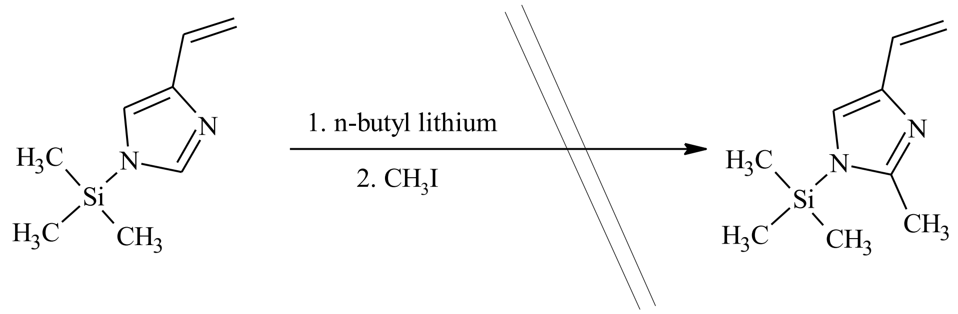


Scheme 12. Option 1 – Quaternization of 1-trityl-2-methyl-4-vinylimidazole

The 1-position of 4(5)-vinylimidazole is first blocked by the trityl group. Then the 1-trityl-4-vinylimidazole is treated with n-butyllithium and iodomethane to methylate the

2-position.These two steps are analogous to those in the procedure that published by Schiavone, et al. [43] for methylation of 4(5)-vinylimidazole at the 2 position. The quaternization of this molecule can be achieved by adding another equivalent of iodomethane to alkylate the 3-position. After that, the trityl group will be removed in an acidic condition so that the 1-position can be alkylated by another alkylation reagent (ethyl triflate or butyl iodide). This route has been put into practice and the yield was quantitative in the first two steps. When n-butyl lithium was added in the second step, a scarlet color was observed in the reaction mixture, indicating that the 2-lithio imidazole anion was formed. The color of the reaction mixture turned into pale yellow as soon as iodomethane was injected. Thus, 1-trityl-2-methyl-4-vinylimidazole was successfully made. The quaternization and deprotection processes were carried out sequentially without isolation of the quaternary dimethyltritylimidazolium iodide. However, the ^{1}H NMR spectra did not show a positive result for the anticipated 1,2-dimethyl-5-vinylimidazole. According to the NMR spectra and TLC results, there were at least two kinds of imidazole compounds in the product, which indicated that some unknown unexpected reactions were happening during the quaternization. These products could not be separated by column chromatography. The speculation is that the iodide removed some of the trityl groups before hydrolysis and quaternized product was formed during work up. Thus, an alternative non-nucleophilic alkylation reagent--dimethyl sulfate was used to do the quaternization. The product, however, was not improved. Therefore, the synthetic direction has been switched to the second route.

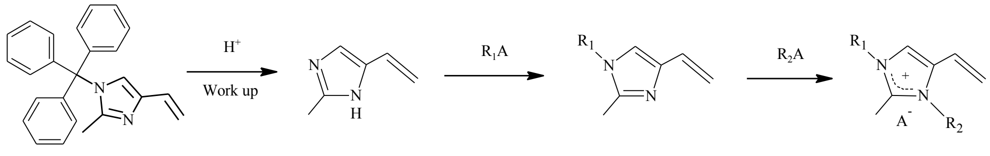
Another option which was attempted was to methylate 1-trimethylsilyl-4-vinylimidazole at the 2-position. As compared to the trityl group, the trimethylsilyl group is easier to remove and separate from the imidazole product. The resulting 2-methyl-4-vinylimidazole would subsequently be alkylated and quaternized to yield the desired molecule.



Scheme 13. Option 2 - Attempted lithiation and alkylation of 1-trimethylsilyl-4-vinylimidazole

An effort was made to methylate 1-trimethylsilyl-4-vinylimidazole; however, when treated with n-butyllithium 1-trimethylsilyl-2-lithio-4-vinylimidazole was not formed. The failure of the reaction was evidenced by the absence of the characteristic scarlet color for the 2-imidazole anion.

A third option was to remove the trityl group in 1-trityl-2-methyl-4-vinylimidazole prior to alkylation. The resultant 2-methyl-4(5)-vinylimidazole could then be alkylated in either one step to give the symmetrical 1,3-disubstituted-2-methyl-5-vinylimidazolium salt or in two steps, using two different alkylating agents, to yield asymmetric structured monomers, as shown in Scheme 14.



Scheme 14. Option 3 - Alkylation of 2-methyl-4(5)-vinylimidazole

In the present research, pure crystalline 2-methy-4-vinylimidazole was prepared by a procedure analogous to that of Schiavone. Instead of using hydrochloric acid water solution to cleave the trityl group, the 2-methyl-1-trityl-4-vinylimidazole was directly dissolved in 5% acetic acid methanol solution and refluxed. Methanol, being more volatile than waster, was easily removed *in vacuo*. The crude product was obtained as a yellow oily liquid at ambient temperature. The ^{1}H NMR of 2-methyl-4-vinylimidazole is shown in Figure 2.

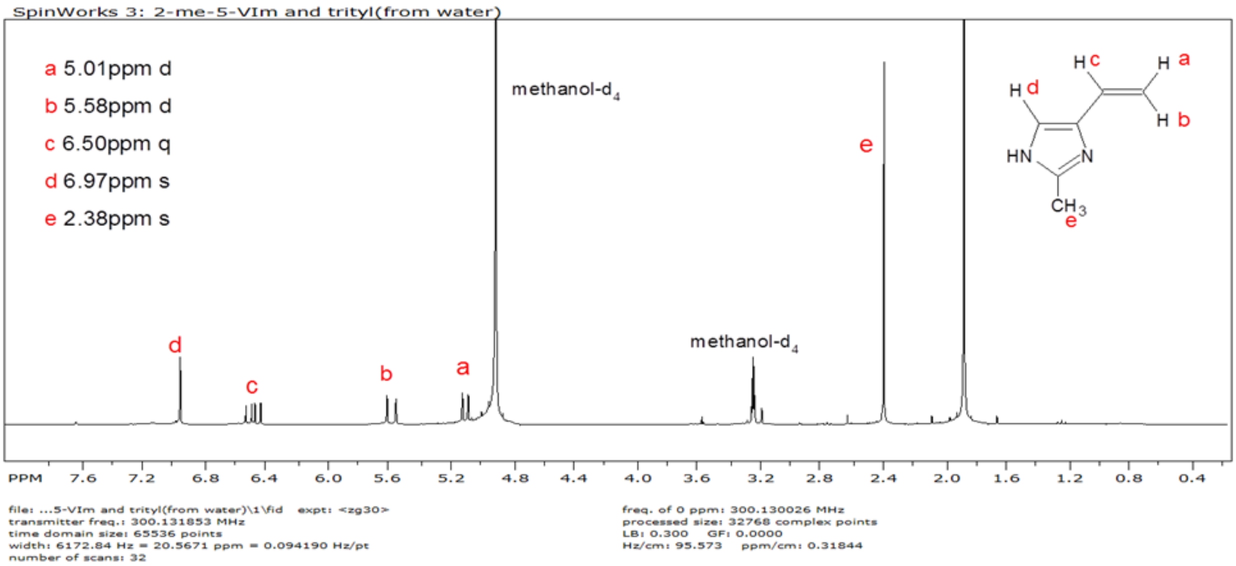


Figure 2. ^{1}H NMR of 2-methyl-4-vinylimidazole

Ha and Hb are in different chemical environments and they are coupled with each other and with Hc to yield split doublets. Hc is also a pair of split doublets, a result of coupling to both Ha and Hb. Hd on the imidazole ring shows a singlet at 6.97ppm and the methyl hydrogens at the 2-position exhibit a chemical shift of 2.38ppm. The sharp singlet at around 1.9ppm may come from residual cyclohexane, which was the solvent of n-butyl lithium.

The alkylation of 2-methyl-4-vinylimidazole was carried out under strongly basic conditions in tetrahydrofuran. The alkylation agent, n-butyl bromide was added to the potassium salt of 2-methy-4(5)-vinylimidazole, formed by reacting 2-methyl-4(5)-vinylimidazole with potassium *tert*-butoxide; and the mixture was stirred at room temperature for 12 hours. After removal of THF *in* *vacuo*, the product was dissolved in ether, extracted into 5% aqueous HCl, neutralized with potassium carbonate, extracted into diethyl ether which was dried over anhydrous $MgSO_4$. Removal of the ether yielded a light yellow oil. The ^1H NMR of 1-butyl-2-methyl-4-vinylimidazole is shown in Figure 3.

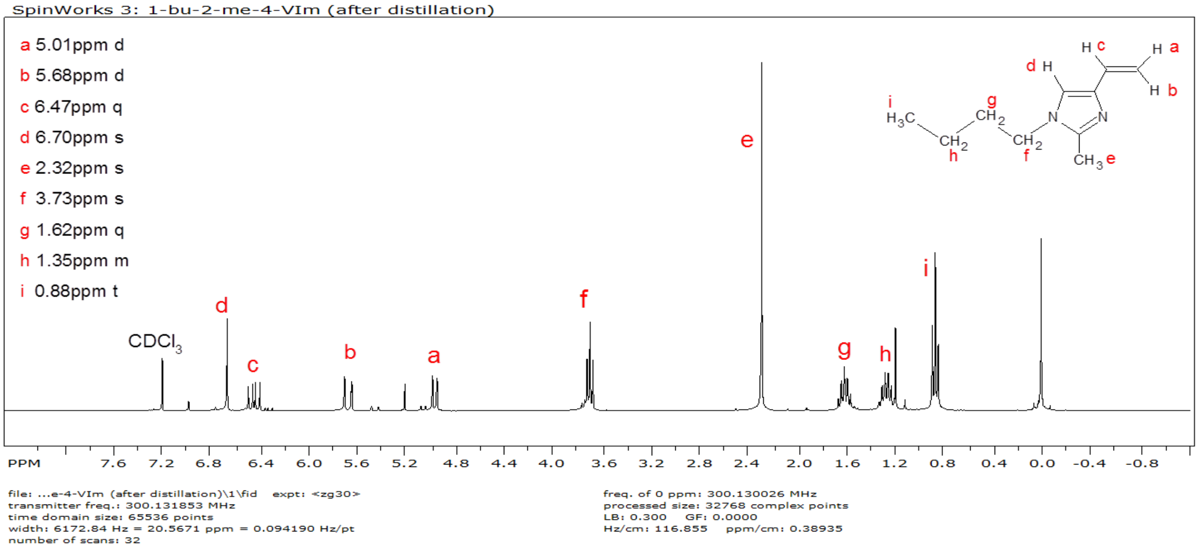
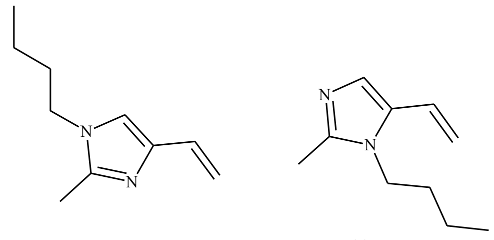


Figure 3. ^1H NMR of 1-butyl-2-methyl-4-vinylimidazole

The two possible products in this reaction are shown in Figure 4.



(1)

(2)

Figure 4. Structures of the two possible products

Compound (1) was expected to be the major product due to the steric hindrance to alkylation between the 2-methyl group and the vinyl group. The NMR spectrum verifies the formation of compounds (1) and (2). However, the fraction of compound (2) in the product mixture is very small. Given this outcome, the quaternization reaction was carried out on the mixed product.

The vacuum-distilled monomer mixture described above was quaternized by reaction with methyl trifluoromethansulfonate in dichloromethane. After addition of a trace amount of 4-tert-butyl catechol and removal of the solvent and unreacted materials *in vacuo at* 0°C, a white crystalline solid was obtained. To avoid polymerization, the monomer was stored at 0°C. The ^{1}H NMR of 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate is shown in Figure 5. The 3-position methyl hydrogen has a chemical shift of 3.73ppm. Hf is more up field than Hg because hydrogens on the methyl group are shielded by the cone of the pi-cloud of the vinyl group.

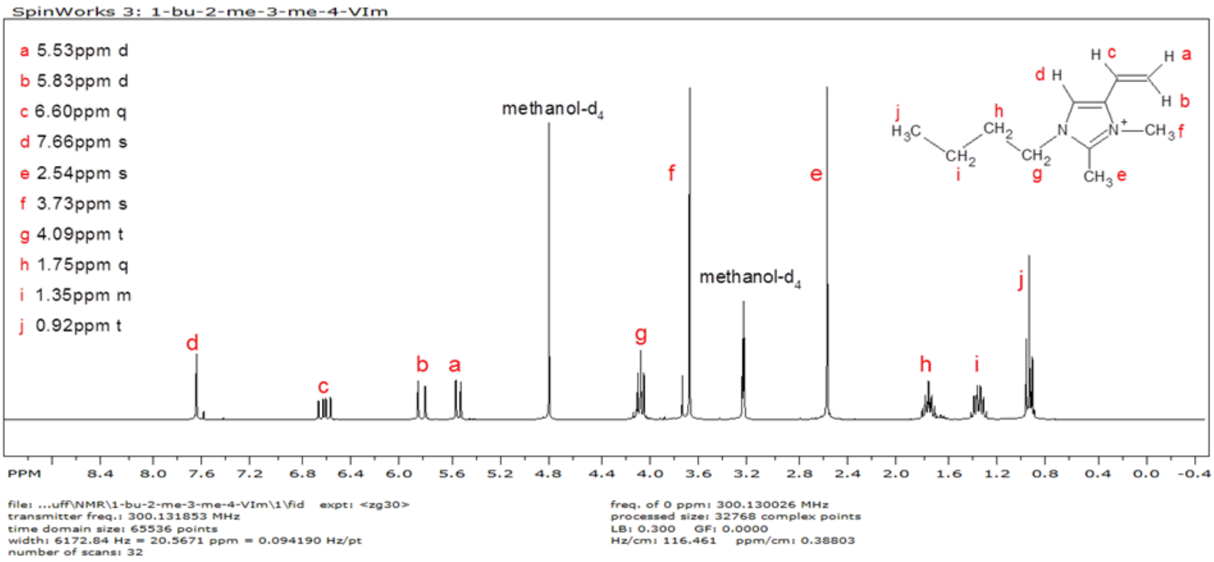


Figure 5. ^{1}H NMR of 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate

The triflate monomer was dissolved in ethyl acetate with ethanol as a co-solvent and polymerized free-radically using AIBN 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 20 hours to yield polymer which was precipitated from diethyl ether and was isolated and dried to give a white hard plastic. The ^{1}H NMR of poly(1-ethyl-3-methyl-4-vinylimidazolium triflate) can be seen in Figure 6. It is significant to note that, as compared to the ^{1}H-NMR spectrum of the monomer, the chemical shift of the methyl hydrogens, H_e, in the polymer now appear down field from the methylene hydrogens, Hf, attached at the 1-position of the imidazole ring. This is a result of the fact that, in the polymer, there is no shielding cone from a vinyl group.

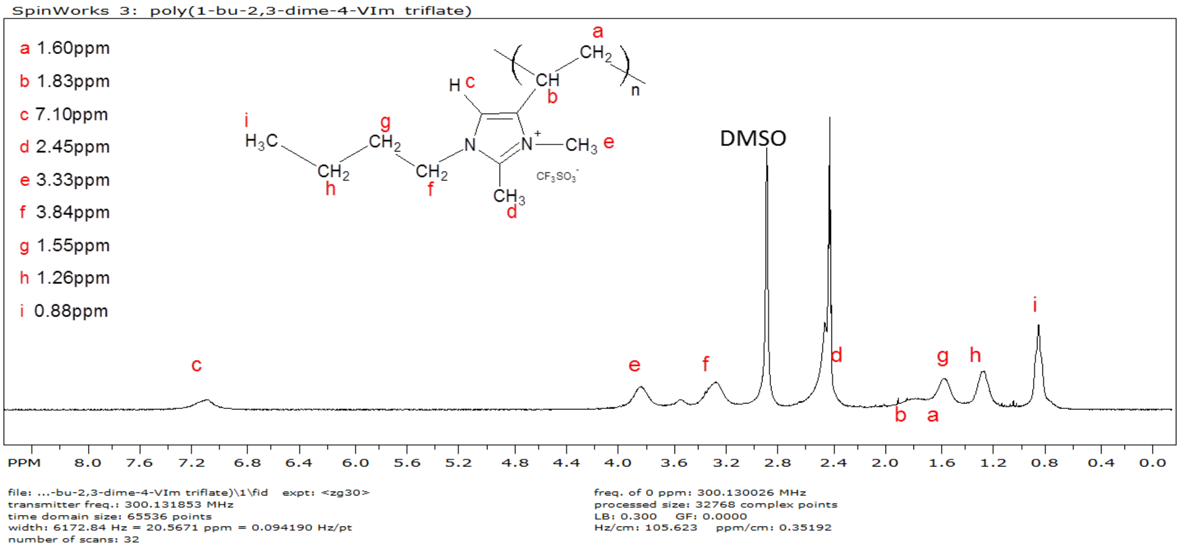


Figure 6. ^{1}H NMR of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate)

Anion Exchange of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium) salts

Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) was ion-exchanged with $(CF_3SO_2)_2N^-$ and PF_6^-. Separate solutions of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate), lithium TFSI, lithium PF_6^- in methanol were prepared. A stoichiometric excess of the respective salt solutions was mixed with the triflate polymer solution, resulting in the formation of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium TFSI$^-$) and poly(1-butyl-2,3-dimethyl-4-vinylimidazolium PF_6^-) which precipitate from the mixed methanol solutions. The precipitated polymers were washed with methanol and dried in the vacuum anti-chamber of a glove box.

Thermal gravimetric analysis of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium) salts

Thermal gravimetric analysis of the poly(1-butyl-2,3-dimethyl-4-vinylimidazolium salts) showed that the triflate polymer and the TFSI polymer have nearly identical thermal stability behavior. Under nitrogen, they both suffered extensive mass loss from 440°C to 500°C.

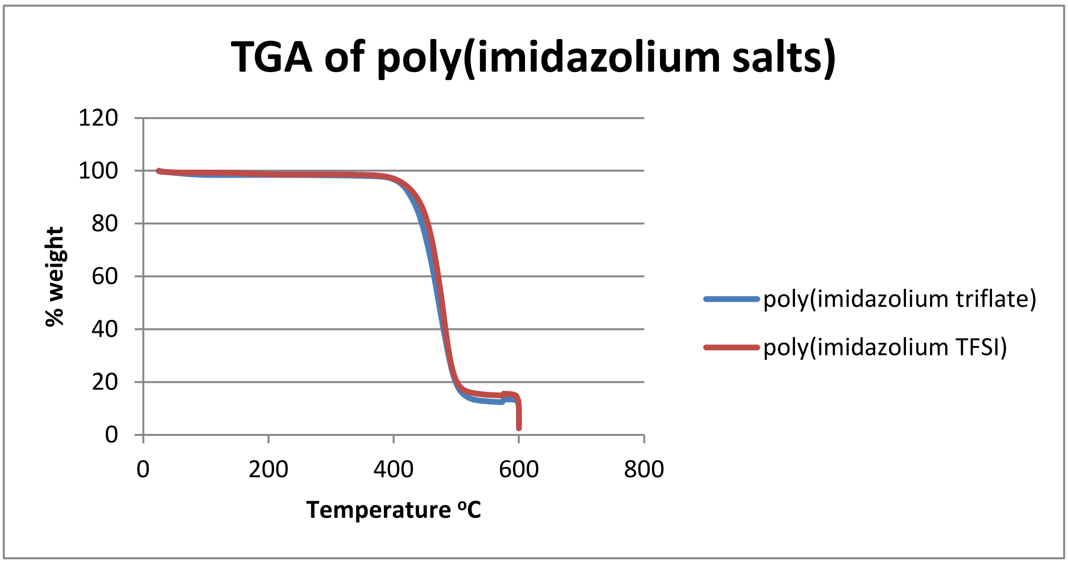


Figure 7. TGA of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) and poly(1-butyl-2,3-dimethyl-4-vinylimidazolium TFSI)

Glass transition of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium) salts

The DSC thermogram for poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) is shown in Figure 8.

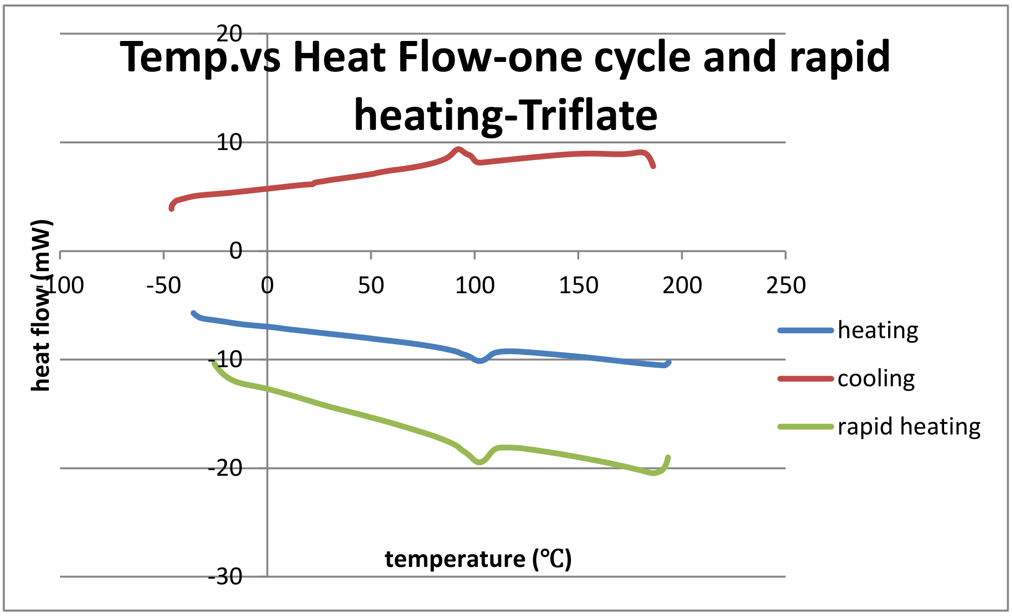


Figure 8. **DSC scan of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) from -50°C to 200°C**

A typical DSC thermogram of a glassy polymer exhibits a step change in heat capacity of the heating or cooling cycle, like that shown in Figure 9.

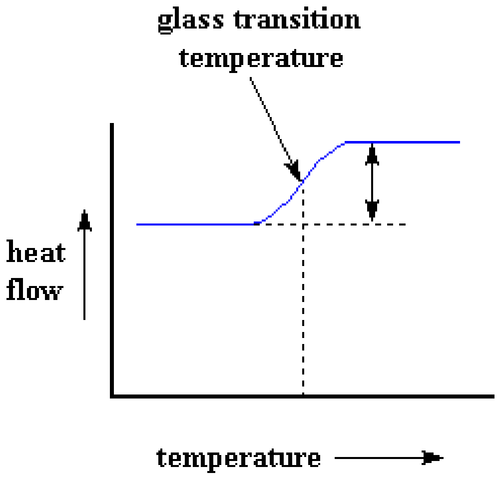


Figure 9. Typical DSC thermogram of a glassy polymer (heating cycle)

However, the heat capacity change around glass transition temperature for poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate) and the other two salts in this group of 2-substituted imidazolium polymers exhibits an unexpected peaked shape normally seen in aged polymer glasses. This excess enthalpy peak is a result of densification of the aged glass. The extremely rapid aging of the 2-substituted imidazolium polymers is unprecedented and one might speculate that it is related to the ionic liquid character of these polymers. In the heating cycle, the onset, mid and peak glass transition temperatures (Tg) are 94℃, 98℃ and 102℃. The peak and min Tg of triflate polymer measured in cooling cycle are 91℃ and 83℃, respectively. The thermograms for the TFSI and hexafluorophosphate polymer salts are displayed in Figure 10 and 11, respectively.

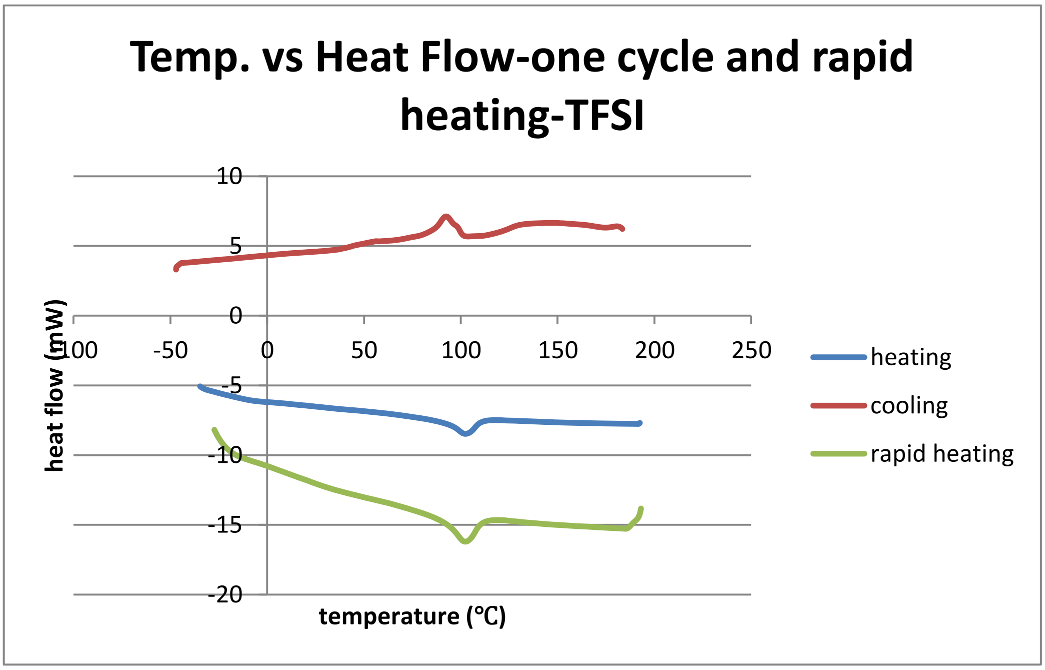


Figure 10. **DSC scan of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium TFSI) from -50°C to 200°C**

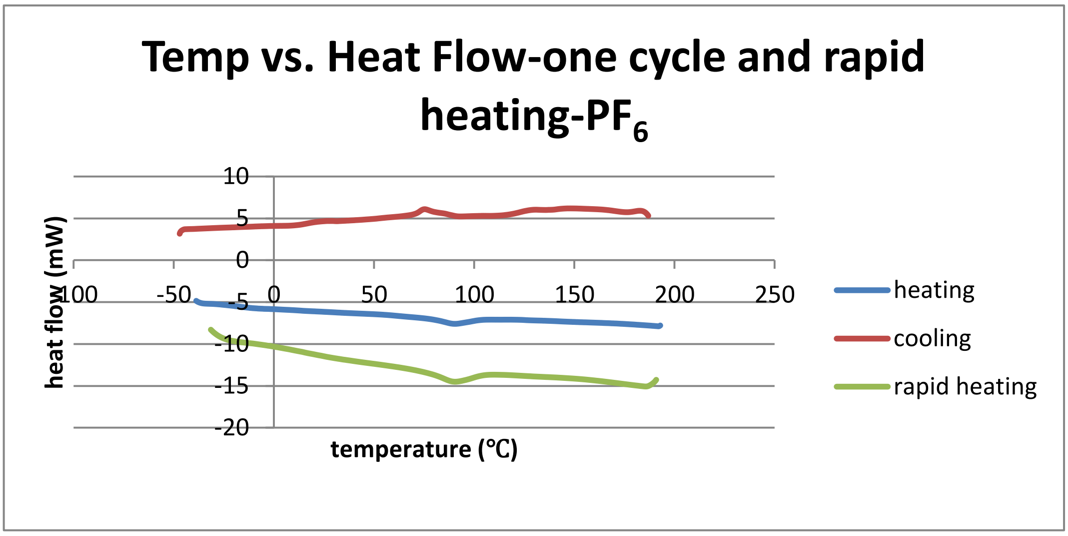


Figure 11. DSC scan of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium hexafluorophosphate) from -50°C to 200°C

They also showed the peak behavior at glass transition temperatures. The baseline in the heating cycles is relatively flat. The baseline in the cooling cycles, however, is anomalous exhibiting numerous fluctuations in heat capacity of unknown origin.

The TFSI salt exhibited a Tg of 96°C-102°C in the heating cycle and 92 °C-84 °C in the cooling cycle. The hexafluorophosphate anion is less solvating and smaller than TFSI-, yet it exhibits a somewhat lower Tg than that of the TFSI- salt. The glass transition characteristics of the three polymer salts are summarized in Table 1

Table1: Heating and cooling cycle scan, glass transition temperatures for poly(1-butyl-2,3-dimethyl-4-vinylimidazolium salts)

Salt	triflate	TFSI	PF_6
heating onset	94℃	96℃	78℃
heating mid	98℃	99℃	84℃
heating peak	102℃	102℃	90℃
cooling min	83℃	84℃	70℃
cooling peak	91℃	91℃	75℃

The surprising feature of the data in the above table is the lack of any significant or systematic variation of the glass transition with change of anion in and poly(1-butyl-2,3-dimethyl-4-vinyl -imidazolium salts).

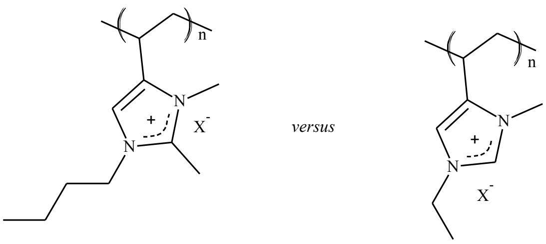
In Table 2, the glass transition temperatures of the triflate, TFSI and PF_6^- salts of the 1-ethyl-3-methyl-4-vinylimidazolium polymer and the 1-butyl-2,3-dimethyl-4-vinylimidazolium polymer are compared.

Table2. Comparison Glass Transition temperatures* of P23DM4VIm$^+$ polymers and P4VIm$^+$ polymers

Polymer composition	**Triflate**		**TFSI**		**PF_6^-**	
	P23DM4VIm$^+$	**P4VIm$^+$**	**P23DM4VIm$^+$**	**P4VIm$^+$**	**P23DM4VIm$^+$**	**P4VIm$^+$**
Heating cycle onset Tg	**94℃**	**145℃**	**96℃**	**72℃**	**78℃**	**187℃**
Heating cycle mid-point Tg	**98℃**	**153℃**	**99℃**	**88℃**	**84℃**	**200℃**

**Heating cycle, glass transition temperatures*

The glass transition temperatures of P4VIm$^+$ polymers drops significantly as the size of the counter anion is increased. P23DM4VIm$^+$ polymers did not follow this pattern. The triflate, TFSI and PF_6^- salts of P23DM4VIm$^+$ had very similar glass transition temperatures. It is speculated that since the cation of P23DM4VIm$^+$ is bulkier, with the 2-position substituted, the motion of the cation tethered to the polymethylene chain and the motion of the anion are largely decoupled. Thus, their Tg did not vary significantly with change in the size of the anions. The structures of the P23DM4VIm$^+$ and P4VIm$^+$ polymers are shown in Figure 13.



(X^-=triflate, TFSI and PF_6^-)

Figure 12. Structure of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium salts) and poly(1-ethyl-3-methyl-4-vinylimidazolium salts)

Conclusions

In this thesis work, three possible route for synthesis of 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate were explored and the target monomer was successfully synthesized by the third route. The quaternized monomer, 1-butyl-2,3-dimethyl-4-vinylimidazolium triflate was free-radically polymerized to yield poly(1-butyl-2,3-dimethyl-4-vinylimidazolium triflate), which had a M_n = 39,637g/mol (PD = 1.75, in DMF) and an onset decomposition temperature of 440^{o}C.

The polymer was ion-exchanged with TFSI and PF_6^- and the glass transition temperatures of the three polymers were measured by differential scanning calorimetry. Poly(1-butyl-2,3-dimethyl-4-vinylimidazolium hexafluorophosphate) exhibited the lowest onset glass transition temperature of 78 ^{o}C (heating cycle). As compared to 1-ethyl-3-methyl-4-vinylimidazolium polymer salts, the glass transition temperature of poly(1-butyl-2,3-dimethyl-4-vinylimidazolium salts) did not vary significantly when ion-exchanged with anions of differing size.

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