TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

Department of Materials and Environmental Technology

PREPARATION OF SUSPENSIONS WITH POLY(IONIC LIQUID) FOR ELECTROSPINNING

POLÜMERISEERITUD IOONSE VEDELIKUGA SUSPENSIOONIDE VALMISTAMINE ELEKTROKETRUSEKS

MASTER THESIS

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Tallinn, 2018

AUTHOR'S DECLARATION

Hereby I declare, that I have written this thesis independently.
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Department of Materials and Environmental Technology

THESIS TASK

Student: Muhammad Nabeel Rahim

Study programme: Technology of Wood, Plastics and Textiles (KVEM)

main specialty: Plastic Technology

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Thesis topic:

PREPARATION OF SUSPENSIONS WITH POLY(IONIC LIQUID) FOR ELECTROSPINNING

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Thesis main objectives:

1. Develop conductive fibrous material using polymerized ionic liquid by using the technique of electrospinning.
2. Synthesis and polymerization of IL and preparation of suspensions with PIL for electrospinning
3. Electrospinning the suspensions and studying the morphology of the electrospun fibers

Thesis tasks and time schedule:

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CONTENTS

PREFACE

I am highly obliged to express the gratitude for the people who inspired and helped me in any way during my Master studies, especially my supervisor Dr. Illia Krasnou who has helped me to the greatest extent to achieve the desired results of my thesis, and without his help it wouldn't have been possible to have such accomplishments. I would also like to thank all the faculty members of the department for their help and support especially Vikotoria Gudkova, Dr. Natalja Savest, Prof. Andres Krumme and Dr. Elvira Tarasova for the guidelines provided for equipment and apparatus, calculations and motivation for research, the people who were in charge of the lab and my class fellows who always kept everything organized and inspired me to work hard.

I would like to give a huge thanks to my friends and family who supported me during the highs and the lows throughout my life, without them it wouldn't have been possible to achieve all the success I have in my life. In the end, my heartiest gratitude to Tallinn University of Technology which gave me a chance to study in Estonia and provided me with all the support required during my studies, all the Estonian people who welcomed me with open hearts and made my stay here wonderful.

During the thesis studies, an imidazole based poly (ionic liquid)(PIL) Poly(1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide was synthesized by the free radical polymerization (FRP) of the ionic liquid monomer which was obtained in the presence of AIBN as an initiator under the presence of UV light. The structure of the IL and PIL was confirmed using FTIR and NMR spectroscopy. Carbon particles and polyacrylonitrile (PAN) was used to make suspensions of different composition of PIL-PAN & IL-PAN which were then used for electrospinning after testing their rheology and the SEM images of the mats obtained showed uniform coating with fibers of the polymer (PAN/PIL) on the carbon particle.

Key words: Ionic liquid, Poly(ionic liquid), Polymerization, Synthesis, Electrospinning, FTIR, SEM, Fibers.

List of abbreviations and symbols

IL	Ionic liquid
ILs	Ionic liquids
PIL	Poly (ionic liquid)
RAFT	Reversible Addition-Fragmentation chain Transfer
FRP	Free radical polymerization
SEM	Scanning electron microscope
UV	Ultraviolet
FTIR	Fourier Transform Infrared spectroscopy
DMF	N, N- dimethylformamide
DMSO	Dimethyl sulfoxide
ATRP	Atomic radical polymerization
AC	Activated Carbon
BHT	Butylated hydroxy toluene
AIBN	Azobisisobutyronitrile
$[PF6]^-$	Hexafluorophosphate
Cl^-	Chloride ion
Br^-	Bromide ion
I^-	Iodide ion
BF_4^-	Tetra fluoroborate
T_m	Melting point
AA	Acrylic acid
Cu	Copper
Li	Lithium
EmimBr	1-Ethyl-3-methylimidazolium bromide
$EmimBF_4$	1-Ethyl-3-methylimidazolium tetrafluoroborate

INTRODUCTION

Ionic liquids have gained interest of researchers in the field of physics, chemistry and materials sciences because they have low melting temperature (below 100), high conductivity, thermal and chemical stability, and lower vapor pressure. Polymers which have Ionic liquid (IL) as repeating units, show great qualities as of ILs and can be used for different applications including reaction media, hybrid nanocomposites, dispersants membranes, etc. Recently, monomers with IL groups have been polymerized to synthesize a variety of PILS [1].

In the present development, PILs are being synthesized by two processes which are the polymerization of the IL monomer by the techniques of FRP, which is an uncontrolled process while atomic radical polymerization (ATRP) or reversible addition fragmentation chain transfer (RAFT) can be used for the controlled polymerization. Free radical polymerization (FRP) is the easiest to carry out because of the less specifics to control while ATRP can be used to synthesize well controlled PILS with limits in the section of disproportionation of the catalyst and halogen loss by hydrolysis [2].

PILs can be categorized as polyelectrolytes because they exhibit the electrochemical properties of the IL and the polymer nature of the polymer present in the backbone [3]. These properties have drawn a lot of interest in PILs in the electrospinning processes to produce nanofibers which can exhibit good conductive properties.

It is evident from the recent studies that due to the dual nature of PILs they can be used to synthesize fibers of smaller sizes than to conventional polymers [4]. However, there is a gap in the field of electrospinning of PILs which if filled can make us able to produce fibers with size ranges that can then be employed in various fields like biomedical sensors, conductive materials etc. [5], [6].

In this research, suspensions of PIL are made using various combinations of PIL and conventional polymer (Polyacrylonitrile) to prepare a suitable suspension for electrospinning for conductive fibers.

CHAPTER1. LITERATURE REVIEW

1. Ionic liquid

1.1 Introduction

Ionic liquid(IL) is a salt consisting of cation and/or anions - and have freezing point below 100 ˚C. ILs usually exhibit very good specific conductivity and it’s thermal stability is also very high. ILs are gaining a lot of interest of the researchers specifically because of their low vapor pressures which can be helpful in solving the problem by employing them in different applications instead of the conventional volatile organic liquids [7]. ILs are stable in air and water with a non-volatile and non-flammable nature. A specific type of ILs which is gaining a lot of attention in the present studies is room temperature ILs, which exists in the liquid form at room temperature [8]. Another type of IL on which a lot of research has been done in the recent past is PIL which is the polymerized ionic liquid.

1.1 Structure and properties

The classification of ILs is not usually done based on their chemical structure because sometimes it can be hard to classify them solely on their structure because they may present the structural properties of molten salts, molecular liquids, ionic crystals and surfactants. Due to this reason, an IL can be associated to more than one group at a time and the most appropriate way to classify ILs is on presence of the kind of cations and the functional group [9].

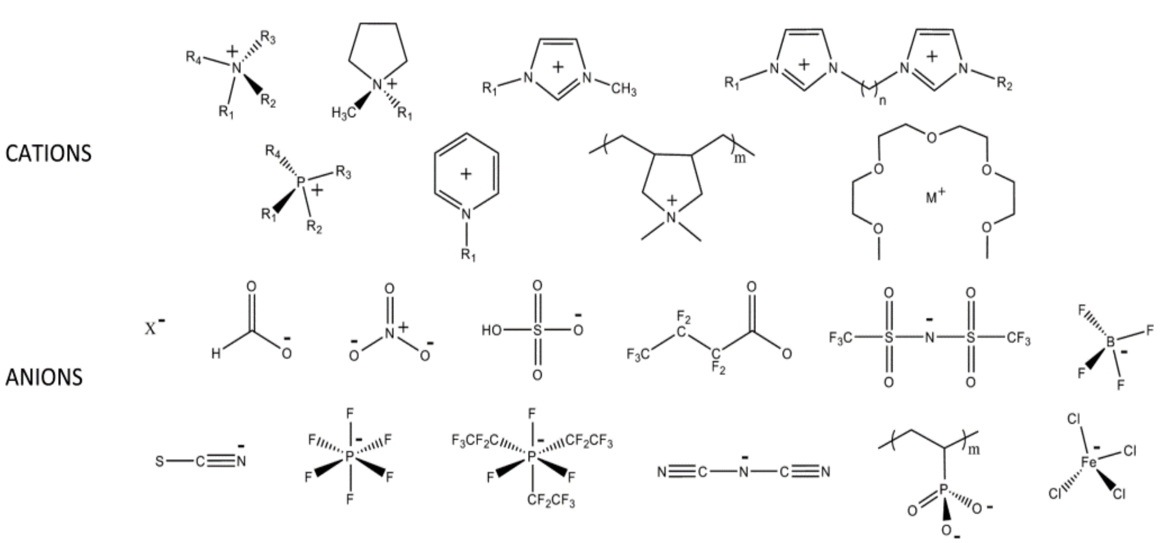


Figure 1. Chemical structures of cations and anions present in ILs

ILs consists of inorganic anions, e.g., Cl−, Br−, I−, BF4−, PF6− etc. and organic cations which can be imidazolium, pyrrolidinium or quaternary ammonium. Figure 1. Shows the classification of the ILs based on structure of the anions and cations present in them.

1.2.1 Melting point

The melting point of ILs depends on the structure of the ions present. Studies show that the melting point of ILs can increase or decrease depending on the symmetry of the ions because if the symmetry is increased then it can make the settlement of ions in the ILs structure to be more efficient which results in the increase of the IL melting point, similarly the melting point changes depending on the alkyl chain length [9]. Figure 2. Represents the melting point (T_m) of ILs as a function of the alkyl chain length

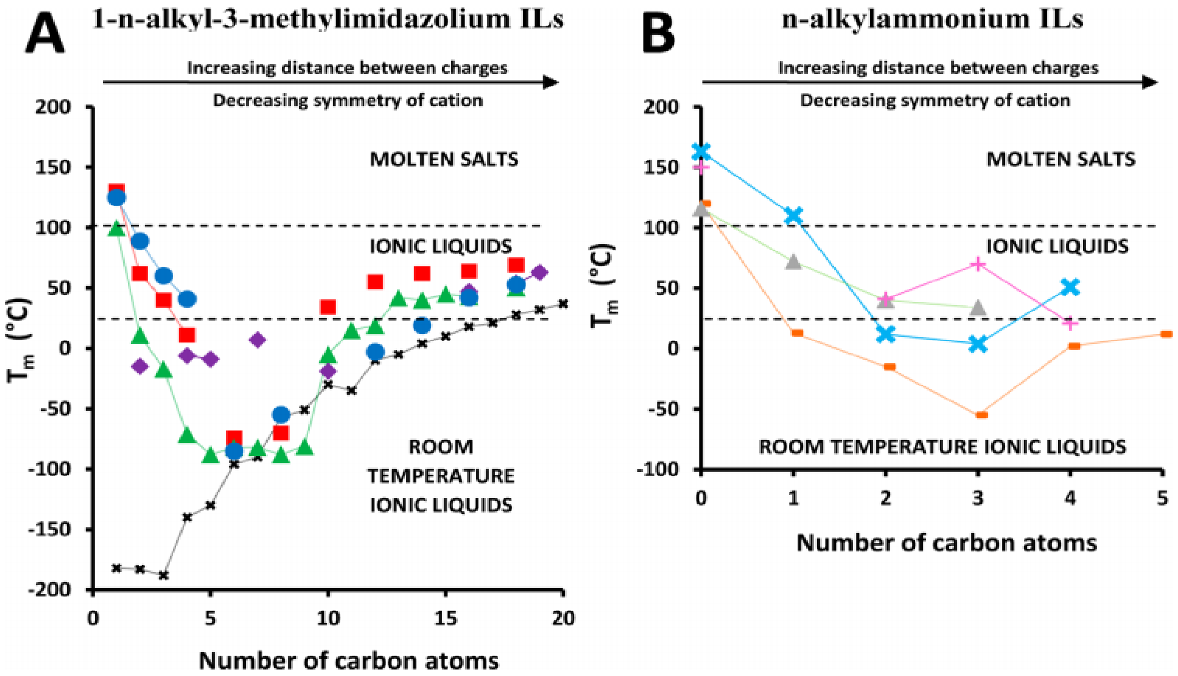


Figure 2. Melting point as a function of alkyl chain length

The representation is between the ILs based on imidazolium (A) and ammonium (B) ions and it can be seen that increasing the number of carbon atoms, which increases the alkyl chain, increases the melting point.

1.2.2 Conductivity

The conductivity of ILs depends on the presence of mobile ions. An IL is considered to be a good if it has more mobile ions which can only happen if the IL is liquid at room temperature. Generally, the pure ILs have low conductivity, the reason behind this is water or other solvent compatibility of ILs. A poor IL can be categorized as the ones which are solid at the room temperature. In this case, increasing the temperature of the IL can render it liquid and the conductivity increases, but this limits the application of such ILs in electrochemical applications [10]. The most typical range of IL conductivity is from 1.0 mS/cm - 10.0 mS/cm [11].

1.2.3 Thermal stability

Thermal stability of ILs can be represented as the function of type of anion present, studies show that the size of the anion can change the stability, the more the size of the anion, the more is the thermal stability. The presence of different cations have little to no effect on the stability, whereas the anion reported to have the highest grade of thermal stability is $[Tf_2N]^-$ [12]. ILs starts decomposing at high temperatures, which make them suitable for applications where high thermal stability is required. One of the most common techniques to measure the stability is by the thermogravimetric analysis [13].

1.2.4 Vapor pressure

One of the most focused properties of ILs is their low vapor pressure, e.g., $[C_4mim][PF_6]$ is one of the IL which even under very high vacuum cannot be evaporated. These properties of ILs are an area of interest especially to be used in the applications to replace organic solvents. The low vapor pressure of the ILs is attributed to their low triple points which are a result of their low melting point [14]. Vapor pressure of ILs is also considered to be important because it is the property which enables to measure the thermal stability of ILs [15]. A comparison of the changes in the vapor pressures of ILs and other solvents with the change in temperature can be seen in figure 3.

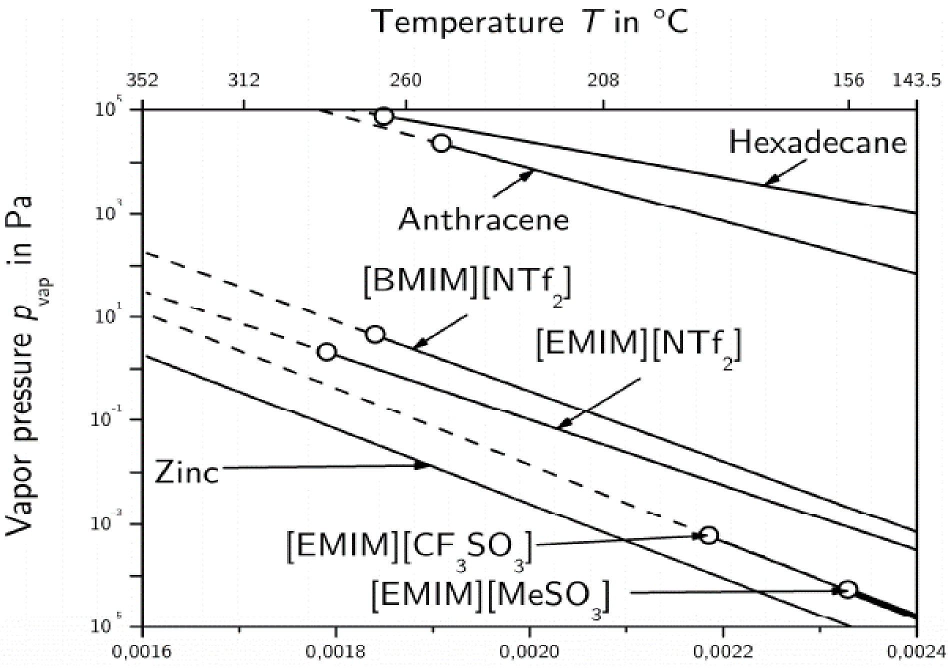


Figure 3. IL vapour pressure comparison

2. Poly(ionic liquid)s

2.1 Introduction

Poly(ionic liquid)s (PILs), are the polyelectrolytes which contain a combination of the properties of both the polymers and the ILs, which can be modified according to the application. PIL is a macromolecule which has repeating units of monomers of IL connected to the polymer backbone, an illustration can be seen in figure 4 where ILM is the IL monomer.

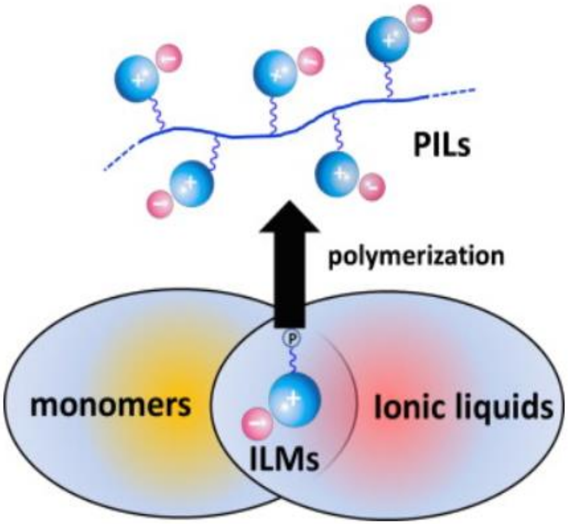


Figure 4. Representation of PILs

PILs can be used to make colloidal dispersions with great stabilities, this make them gain a great interest in various applications, e.g., gas separation, thermoresponsive materials, biomedical applications, as solid polymer electrolytes in fuel cells and batteries etc. and can obtain better stability, processability and increase the durability [16], [17].

2.2 Structure and properties

PILs can be divided into two categories, anionic and cationic PILs depending on the presence of type of ion on the polymer backbone [16], figure 5 illustrates some of the cationic and anionic PILs.

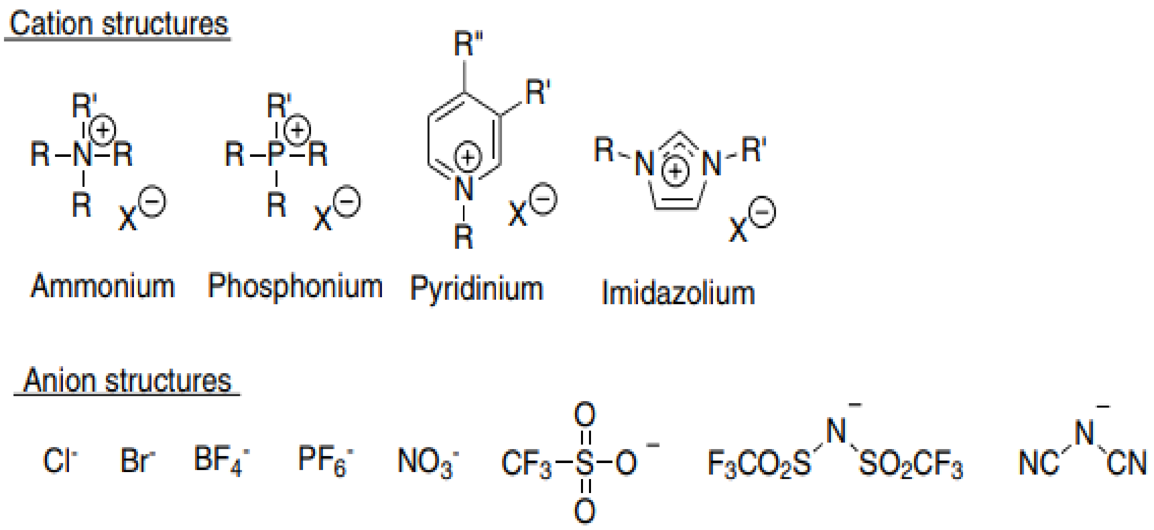


Figure 5. Anionic & cationic PILs

Polymerizable ILs are the ILM which can be synthesized by the radical polymerization of the ILs. Figure 6, shows examples of the polymerizable ILs which have polymerizable groups at anionic or the cationic site. In scheme (a), the anions are exchanged with the anion of the IL and cationic site at (b). Figure 7. represents the covalent attachments of the methacrylyol, vinyl and vinylbenzyl groups to the cationic sites.

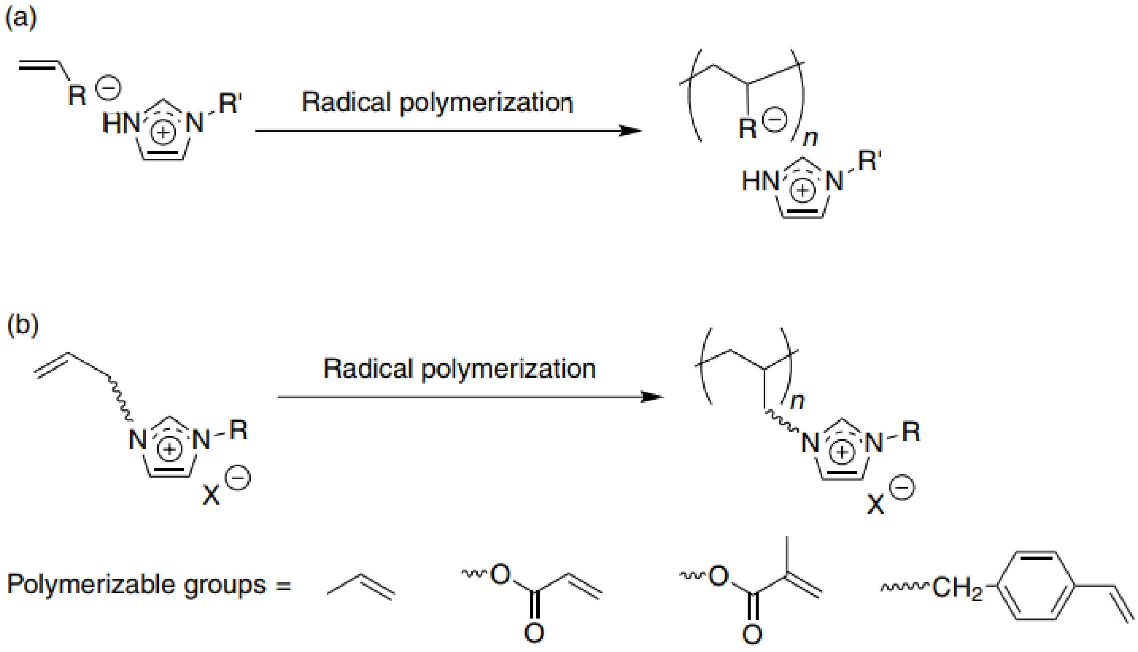


Figure 6. Polymerizable ILs at cationic & anionic sites

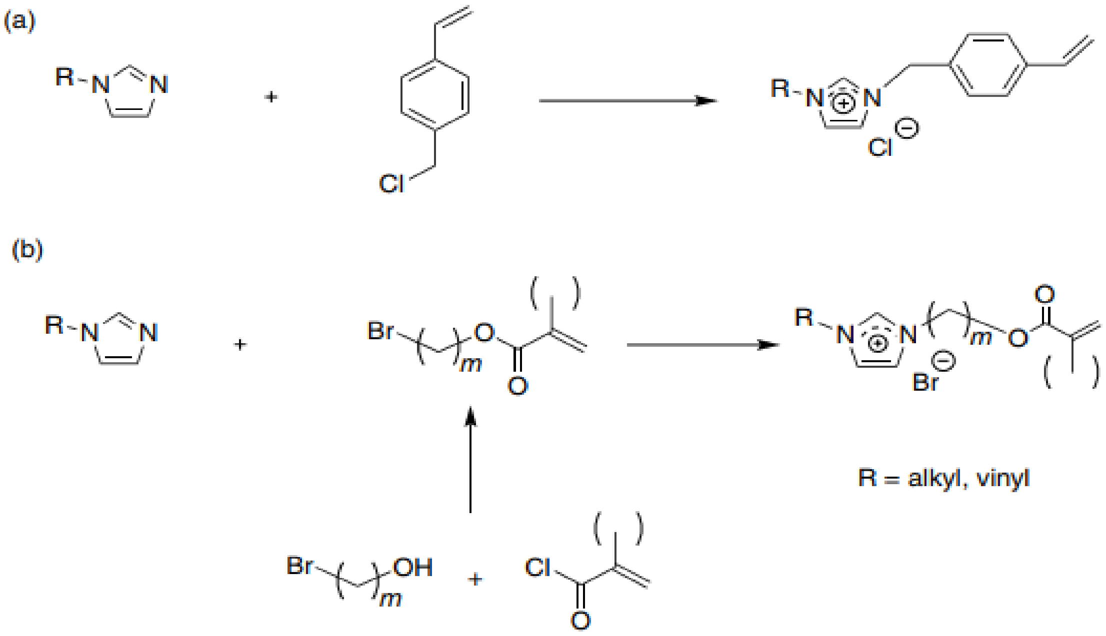


Figure 7. Synthesis of polymerizable ILs with group (a) vinylbenzyl (b) methacrylate

2.2.1 Conductivity

PILs usually are gel-like transparent materials, the properties from the polymer and inherit the conductive properties from the ILs. Due to these properties they can be used in electrochemical devices like capacitors, solar and fuel cells ad batteries. PIL monomers have a higher conductivity as compared to PILs as they go through polymerization because of the presence of polymer chain. Electrical conductivity of the PILs depends on the chemical nature and the structure of the polymer, molecular weight and the glass transition temperature T_g of the IL. Recent studies show that the decrease in the conductivity after polymerization can be addressed by either changing the structure of the material, to increase the mobility of ion, or by changing the concentration of the carrier ions. The conductivity dependence on the alkyl chain length can be seen in Figure 8 according to which, increasing the number of carbon atoms in the alkyl chain increases the conductivity of the PILs [19].

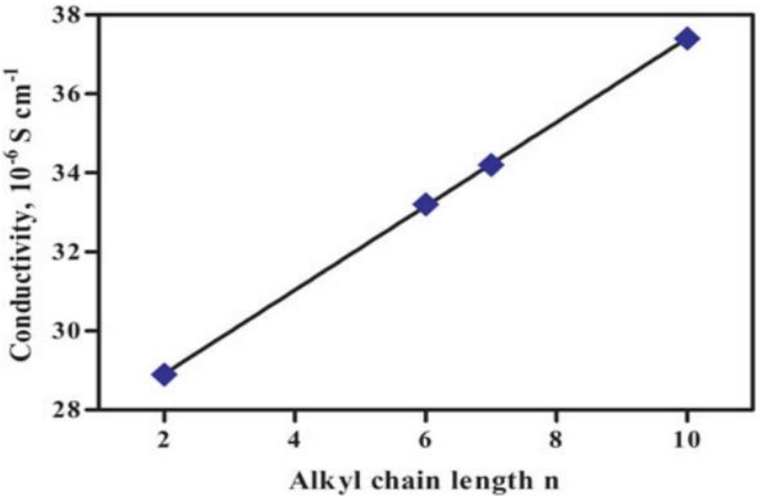


Figure 8. Conductivity as a function of alkyl chain length

2.2.2 Thermal stability

PILs inherit the properties of polymers and most of the high performance polymers are used at high temperatures, therefore, the thermal stability of PIL possesses great importance. The thermal decomposition of PILs is greatly dependent on the polycation backbone nature, e.g., the thermal stability decreases to a great extent if the double bonds in PILs are oxidized. Anion structures can also make the thermal stability to change, all the polyanions having SO_3^- ions exhibit similar thermal stability. Typical ranking of various anions in terms of stability in cationic PILS is $N(CN)^-_2$ < PF_6 < BF_4 <$CF_3SO_3^-$ < $(FSO_2)_2N$ < $(CF_3SO_2)_2N^-$. Thermal stability is similarly changed by the cations, increasing the substituent length of the cation increases the stability, whereas it changes proportionally if the alkyl spacer between the IL and the polymer chain increased or decreased [20].

2.2.3 Glass transition temperature

One of the most important properties of PILs for the employment on different applications is its glass transition temperature T_g, it is a polyelectrolyte which have an increase the ionic conductivity in the rubbery state than in the glassy state. T_g of PILS depends on the type and arrangement of the ions and the rigidity of the polymers and will range from -70 ˚C to less than 200 ˚C. The decrease in the anion size or the delocalization of the cation results in the decrease of the glass transition temperature. The resistant to heat is the lowest in anion like $(CF_3SO_2)_2N^-$, $(FSO_2)_2N$ and $N^-(CN)_2$ [20].

2.2.4 Solubility

The solubility of PILs depends on the polymer chain, size and the structure of the anion, e.g., the same PILs which show good solubility in alcohol and water with halogen anion becomes hydrophilic by the inclusion of bis(trifluoromethanesulfonyl)imide, whereas the spacer and cation play no role in solubility. A delocalization in the anion can make the PIL lose its solubility in DMSO and some alcohols while the solubility in acetonitrile can be increased if the PIL backbone contains aliphatic than aromatic groups. Similarly, PILs with acrylate groups show more solubility in alcohols as compared to methacrylate groups. All these properties show that the solubility of the PILs can be controlled by controlling the type of ions and the reactive groups [20].

2.2.5 Applications

Electrochemical devices

When compared to non-ionic polymers, polymer electrolytes made from PILs have high conductivities and thermal stabilities with greater extents of compatibilities and non-flammability. Therefore, the use of PILs in electrochemical devices in increased in the past decade.

1. Fuel cells

A rather cleaner form of energy is considered to be produced by fuel cells because of little to no polluting emission are caused during the process of energy conversion. A common electrolyte used for such fuel cells is Nafion, but due to its low thermal stability, it can’t be used at temperature above 80 ˚C. In this case, the use of a protic ILs can make the fuel cells to work at much higher temperatures because of the proton carriers which are non-aqueous and extremely low values of volatility. PILs can be used as redox couples and serve as charge transfer materials and can offer better photovoltaic performances as compared to conventional electrolytes.

2. Batteries

PILs present in the gel form have immobilized polymer electrolytes, due to this property they have gained interest in the application in Lithium ion batteries. An example of Lithium ion battery made for PIL is the one made from a dicationic PIL and LiTFSI electrolyte. This kind of PIL can be used in metal batteries and works at room temperature, it is also considered to be one of the safest electrolytes for Li based batteries.

3. Supercapacitors

One of the important property that is required to be present in a supercapacitor is its light weight. Previously, liquid and quasi-solid electrolytes were used, which can add to the weight of supercapacitors. To address this problem, solid PILs can be used to produce light weight supercapacitors with greater extent of stability, but one problem with it is the fall in the stability as the capacitor ages. One of the most commonly studies PIL which can provide stability with good ranges of conductivity is the one based on pyrrolidinium [21].

Smart materials

PILs can be used in smart materials which are responsive to physical, chemical, bio-chemical stimuli. Such PILs have gained attention in smart application and studied on the basis of their responsiveness to redox reactions, light, pH and temperature.

1. pH actuators

Imidazolium based PILs combined with poly(acrylic acid) results in a highly charged and nanopourous polyelectrolyte which is then suitable for the use in sensing application like pH triggered actuators. One such example of the membrane produced using imidazolium based PIL is shown in figure 9., which shows the reaction scheme of the polymerization of an imidazolium based ILM with acrylonitrile and acrylic acid(AA).

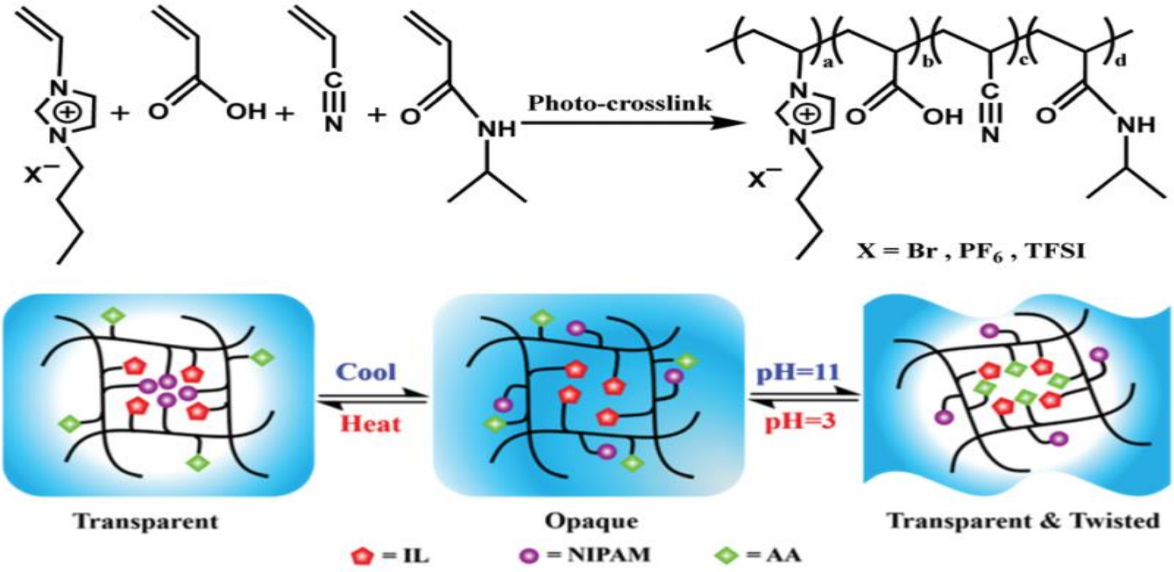


Figure 9. Cross-linking of imidazolium based PIL membranes for sensing applications

2. Solvent responsive materials

PIL gels have anions that can form complexes which can convert the gel to shape memory gel. Such gels can absorb certain types of solvents, like water, and swell quickly to show a fast reaction. This allows them to be used as actuators because they can offer fast and easy to detect actuation with great responsiveness. Actuators made from shape memory PIL gels are can also be used to detect vapours in wet and dry conditions.

3. CO_2 triggered actuators

CO_2 is present in all the biological matter which renders it to have good biocompatibility. There are numerous reactions which require the removal of CO_2. Imidazolium based PIL gels are not only good actuators, they can also be used for the removal of CO_2 from such reactions. The most interesting thing about this king of PIL gels is that, on reaction with CO_2, they are a changed to a transparent gel, absorbing the CO_2 and return to the original form when N_2 is passed through. These properties make such gels to be cost effective in CO_2 removal in appropriate reactions [21].

3. Synthesis of Poly(ionic liquid)s

There are three ways developed to date to synthesize PILs which are post-modification of polymer chain with ILM, step growth polymerization and direct chain growth polymerization. These types of polymerizations can be done using free radical polymerization which is an uncontrolled process or by ATRP/RAFT techniques to undergo controlled reactions [21].

3.1 Free radical polymerization (FRP)

FRP is one of the most common and widely used technique to synthesize PILs. This particular method is widely accepted because it can work at higher concentrations and works well even if there are impurities, other functional groups or moisture present in the starting materials [21], [23]. It is difficult to obtain high conversion rates and high molecular masses using FRP because of the presence of high electrostatic repulsion in ions. Moreover, the rate or polymerization is decreased as the charge density decreases [20]. FRP is driven by the solvents used in ILs, initiators, structure of the IL, polarity and viscosity [22]. Figure 10 shows a three step reaction used to synthesize Methacryloyl based IL using FRP. First step includes the formation of an ester by treating methacrylyol chloride with hydroxy haloalkane followed by the reaction with N-alkyl imidazole to make methacrylyol polymerizable IL and which in the presence of an initiator is polymerized in the third and the final step. Whereas, a one-step polymerization process for vinylimidazolium based IL is shown in figure 11, where the IL is quaternized with a haloalkane in the presence of a thermal initiator AIBN [23].

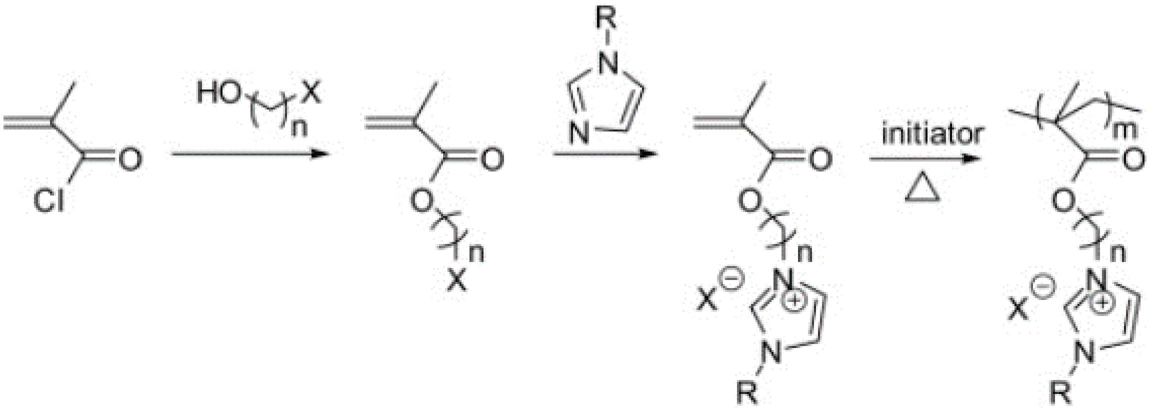


Figure 10. Three step polymerization of methacrylyol based IL

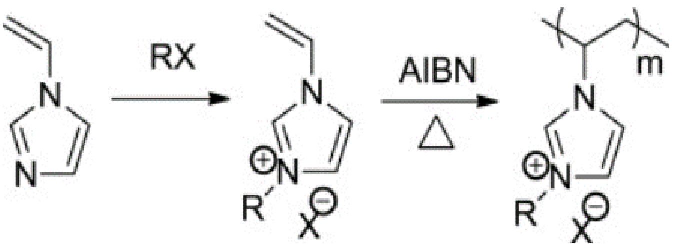


Figure 11. One step polymerization of vinylimidazolium based IL

Synthesis scheme of a PIL homopolymer, which has an IL group at each repeating unit, is shown in figure 12. N-vinyl-2-pyrrolidone is copolymerized in the presence of methanol and AIBN with 1-vinyl-butylimidaolium [23].

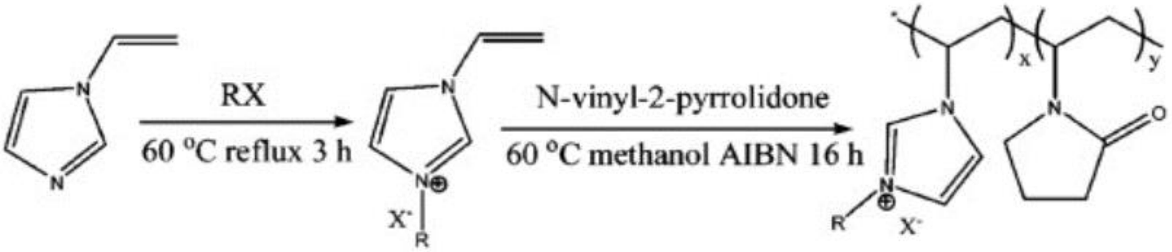


Figure 12. PIL copolymerization process

3.2 Living/controlled polymerization

Recent developments in controlled polymerization have made the researchers to synthesize polymeric materials with much more precise properties for various applications. PILs can be synthesized using controlled polymerization to achieve better and improved macromolecular structure, molecular weight and viscosity. The most typical processes for controlled polymerization are ATRP and RAFT [23].

3.2.1 Atom transfer radical polymerization (ATRP)

ATRP is a type of living polymerization which can be used to predict polydispersity, molecular weight and structure of PILs. The downside of using this process is that it can be affected by the presence of impurities, ionic species and can result in lower conversion rates [24], [25]. In this type of polymerization process, conversion directly affects the molecular weight of PIL produced. Concentration of the IL monomer is another important feature to be managed because low concentrations of ILM can lead to incomplete polymerization. Catalyst that are found to have a controlled reaction and proper conversion rate for the control of molecular weight are Cu(I)Br/2,2′-

bipyridine and Cu(I)Br/1,1,4,7,10,10-hexamethyltriethylenetetramine. Figure 13 represents the conversion of a styrene based IL to PIL using ATRP [23].

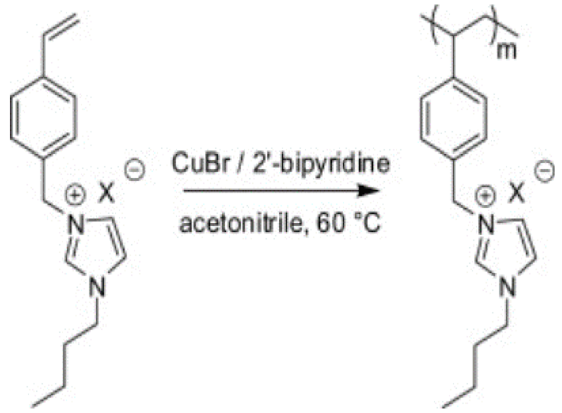


Figure 13. ATRP of 1-butyl-3-vinylimidazolium tetrafluoroborate using copper based catalyst

3.2.2 Reversible addition fragmentation chain transfer (RAFT)

During ATRP a complex mixture is formed which contain the PIL and the copper ions from the catalyst. This problem can be solved using RAFT polymerization as it contains no metal source and is known to be an effective technique to be used for the synthesis of block copolymers. Figure 14. Shows the reaction scheme of a double block copolymer using RAFT where a metharcyloyl based IL is polymerized in methanol solution to give a water-soluble copolymer [23].

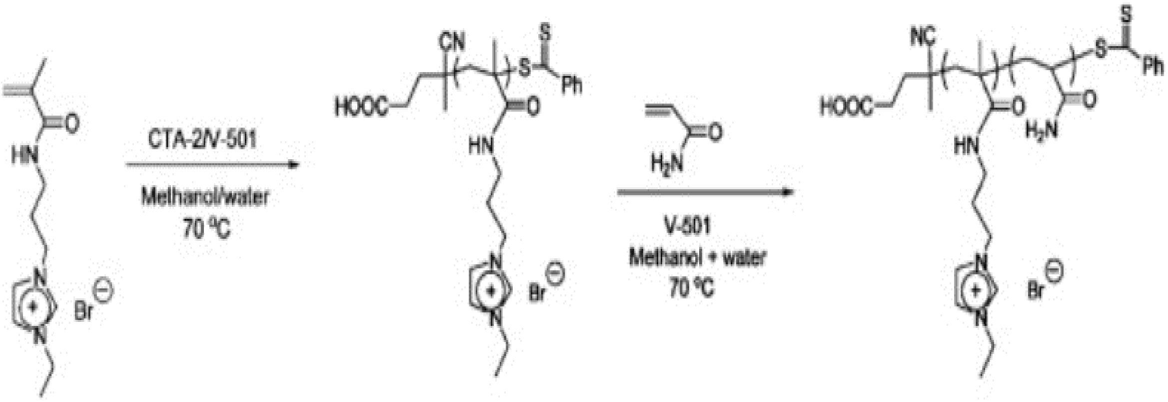


Figure 14. RAFT polymerization of metharcyloyl based IL

3.3 Chemical modification

PILs can be synthesized by doing some chemical modifications in the already existing polymers. In this way the modified polymers posse's similar properties and structures as of PILs. PILs formed this way possess naturally adopted monomer, structure and degree of polymerization. Using this technique enables to obtain the PILs, which are impossible to synthesize using the typical polymerization techniques, by modifying a precursor polymer with defined properties. Imidazolium based PIL can be prepared using this method which is a two-step procedure, it includes the grafting of N- alkyl imidazole on the halo alkyl in repeating units throughout the polymer and to react the imidazole containing polymer with haloalkane.

One such example is given in figure 15 where poly(p-chloromethylstyrene) (PCMS) was used as a precursor polymer after synthesis using RAFT polymerization. Poly (1-butyl-3-vinylbenzylimidazolium chloride) was synthesized by treating PCMS with 1-butylimidazole, which quaternized the chloromethyl units and resulted in a PIL with similar properties as of PCMS [23].

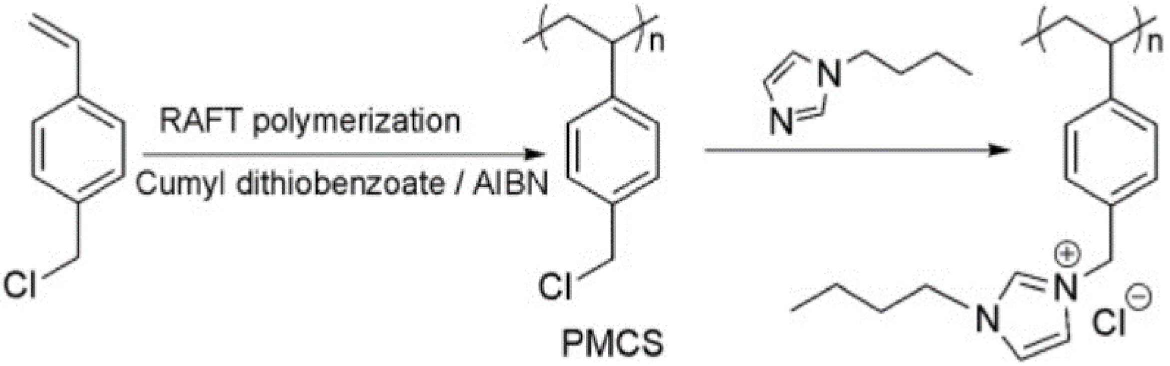


Figure 15. Chemical modification of PCMS to synthesize poly(1-butyl-3-vinylbenzylimidazolium chloride)

4. Electrospinning

4.1 Introduction

Electrospinning is a technique used to produce fibers from natural and synthetic polymer solutions/suspensions using electrostatic forces. Fibers made by this method could have a diameter range of 2nm to several micrometres [26]. The process of electrospinning can be employed to produce fibers with controlled pore structure and in a consistent micron range. In the process of electrospinning, the axial directed flow of the polymer in an electric field is responsible for polymer fibers. Typically, a polymer solution is used to make a jet, which is then electrically charged using high voltages to make highly charged fibers. These fibers are then collected on an oppositely charged collector, which can be a round rotating drum or a flat surface and the collection of the fibers depend on surface shapes, rheology of the solution and the applied electrical charge while the fiber size and its length can be increased or decrease by changing the voltage [26], [27], [28], [29], [30].

A typical setup of electrospinning apparatus is shown in figure 16, consisting four main components. First component is the needle through which the polymer solution (second component) flows when an electric field is applied using a power supply (third component). The fibers then sprayed are collected at a charged metal collector [33].

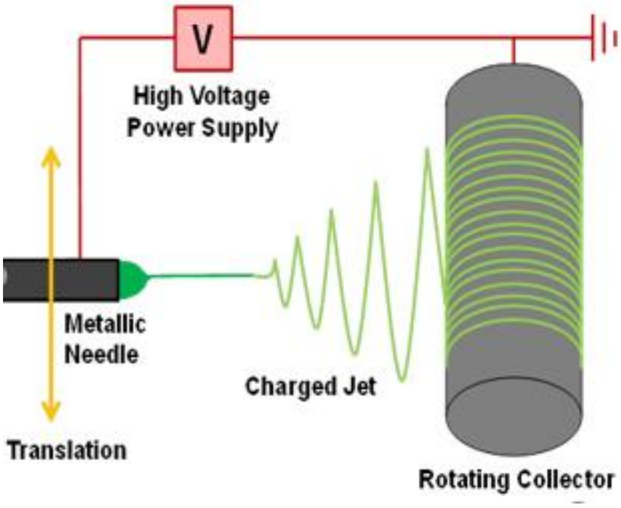


Figure 16. Electrospinning apparatus scheme

4.2 Electrospinning parameters

The fiber morphology in the electrospinning process is driven by process, solution and ambient parameters. Controlling these parameters help to create fibers with desired diameters and morphology [26].

4.2.1 Solution Parameters

4.2.1.1 Concentration

A minimum concentration of the polymer solution is required for the electrospinning process to work properly. If the concentration of the solution is low then due to low viscosity, the jet formed presents a lot of beads on fibers, which on increasing the concentration will change its shape from spherical, spindle and uniform fibers are obtained finally as the viscosity of the polymer solution is increased. Optimum concentration of the solution can be defined as the concentration at which the solution can maintain a continuous flow to form continuous fibers, as at low concentration and viscosity, beads are formed and at high concentration and viscosity, solution can’t flow properly. Polymer solution concentration has a direct relation with the diameter fiber as increasing or decreasing the concentration affect the diameter accordingly [26].

4.2.1.2 Molecular weight

Another important parameter to control the morphology of the electrospun fibers is molecular weight as it can affect the electrical and rheological properties like surface tension, conductivity, viscosity etc. A polymer solution with lower molecular weight results in lower viscosities even at higher concentrations, which is not suitable for electrospinning, as such solution will have a high chance of bead formation. High molecular weight solutions are found to be more appropriate for this process because of the larger average diameters of the formed fibers. A solution having high molecular weight will have comparatively more chain entanglements, therefore even at lower concentrations, such solution can maintain an appropriate and suitable amount of viscosity for electrospinning. Also, if high intermolecular forces are present in the solution the high molecular weight is not always required [26].

4.2.1.3 Viscosity

Viscosity is one of the most important parameters in electrospinning and it controls the morphology and size of the electrospun fiber. Optimal viscosity is required for electrospinning as low viscosity will form beads or no formation of fibers and high viscosity can make the spinneret to block. The maximum viscosity of the solution for spinning ranges from 1 to 215 poise. As discussed above, molecular weight, concentration and polymer viscosity are interrelated. A longer stress relaxation time is shown at high viscosity which breaks the continuous flow of the polymer melt. If the viscosity of the polymer solution is known, one can also determine the concentration ranges at which uniform and continuous fiber formation can be done using electrospinning [26].

4.2.1.4 Surface tension

Surface tension is a function of solvent composition and reduced values of surface tension can help obtain the fibers with less amounts of beads formed during the process. High surface tension results in a non-uniform spray and formation of beads. Upper and lower boundaries of the electrospinning process for a specific solution can be measured by surface tension in the case when other variables are kept constant [26].

4.2.1.5 Conductivity

The charged ions present in the polymer solution are responsible for the formation of jet formation. The conductivity of a solution can be determined by the types of solvent used and the presence of ions and their structure. Increasing the conductivity of the polymer solution decreases the fiber diameter and increasing the conductivity too much will result in bead formation and longer jet formation. Highly conductive polymer solutions are also not suitable for electrospinning as they tend to form jets which are prone to bending and producing non-uniform diameter due to their highly unstable nature [26].

4.2.2 Processing parameters

4.2.2.1 Voltage

For the formation of fibers, a specific amount of voltage has to be applied. This optimal voltage allows the solution to be induced with required charges. The value of the voltage applied to start the process depends on the shape of the drop of polymer solution on the spinneret. Fibers with larger diameters can be formed by increasing the voltage as it increases the polymer ejection. If the voltage is increased above the upper limit, it results in the stretching of polymer solution which causes the electrospun fibers to have narrower diameters [26].

4.2.2.2 Flow rate

The jet velocity and the transfer rate of the fibers from the spinneret to the collector is determined by the polymer solution flow rate. If the flow rate is too high, it results in an increase in the fiber and pores diameters and cause bead formation because of the less drying time given to the fiber before it is collected. Decreasing the flow rate can solve this problem as it can allow more time to the solvent to evaporate [26].

4.2.2.3 Collector

Collector is a charged conductive space used to collect the electrospun fibers. Most commonly used type of collector is aluminum foil, other materials can also be used to collect fibers like wire mesh, conductive paper, conductive cloth etc.

Fiber morphology also depends on the distance between the collector and the tip. Optimal distance is the one that allows the formation of uniform fibers, If the tip is too close to the collector, flat fibers are formed and increasing the distance results in rounder fibers [26].

Rotation speed is another important variable which enables to determine alignment of the fibers. The crystal orientation of the fibers is improved if the alignment is in fiber axis direction [31]. The rate of evaporation of the solvent from the polymer solution can be increased by creating a ventilation effect using a rotational high-speed collector [32].

4.2.3 Ambient parameters

Ambient parameters like temperature and humidity can affect the electrospinning process, e.g., if a polymer solution is electrospun at a higher temperature then its viscosity is decreased and as a result the fiber diameters are decreased. Similarly, an increase in the humidity can cause the fibers to have circular pores. Low humidity can allow the solvents to dry faster as compared to high viscosity [26].

Aim and objectives

The main aim of the study is to develop conductive fibrous material using polymerized ionic liquid by using the technique of electrospinning.

Objectives

- Synthesis of ionic liquid and the polymerizable ionic liquid (Ionic liquid monomer)
- Polymerization of the ILM using free radical photo-initiated polymerization
- Preparation of suspensions with PIL for electrospinning
- Studying the morphology of the electrospun fibers

CHAPTER2. EXPERIMENTAL WORK

1. Synthesis of PILs

In this work, to study the properties of PILs, we have gone through three major processes. The first step includes the synthesis of an IL followed by its treatment to create an ILM, and finally the polymerization step. A methacrylate imidazolium based PIL, 1-[(6-methacryloyloxy)hexyl]-3-methylimidazolium bromide, was synthesized in this research by following the process reported by Põhako-Esko et al.[34] which is shown in figure 17.

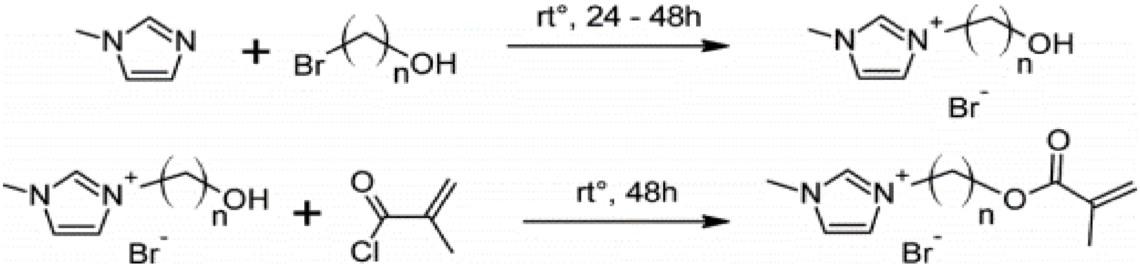


Figure 17. Synthesis of methacrylate imidazolium based ILM

1.1 Materials

The materials used for the synthesis of 1-[(6-methacryloyloxy)hexyl]-3-methylimidazolium bromide were; 1-methylimidazole (Sigma-Aldrich), 6-bromo-1-hexanol (Aldrich), Methacrylyol chloride (Aldrich), 2,6-di-tert-butyl4-methylphenol (BHT; Fluka), Acetonitrile (ACN; Aldrich) used as received.

1.2 Synthesis of IL 1-(6-hydroxyhexyl)-3-methylimidazolium bromide

First step in the synthesis of PILs is the preparation of Ionic Liquid monomer. In this step a reaction is made between 1-methylimidazole and 6-bromo-1-hexanol. Both substances are reacted in a round bottom flask in a molar ration of 1:1. The reaction takes 48 hours to complete in inert atmosphere of Nitrogen. After the reaction is completed, the mixture kept under vacuum at 1.1 mbar for 12 hours to remove the traces of 6-bromo-1-hexanol, followed by washing the product 3 times with toluene to remove unreacted 1-methylimidazole and again put under vacuum for another 12 hours. The reaction between 1-methylimidazole and 6-bromo-1-hexanol is shown in figure 1 which yielded a viscous transparent liquid.

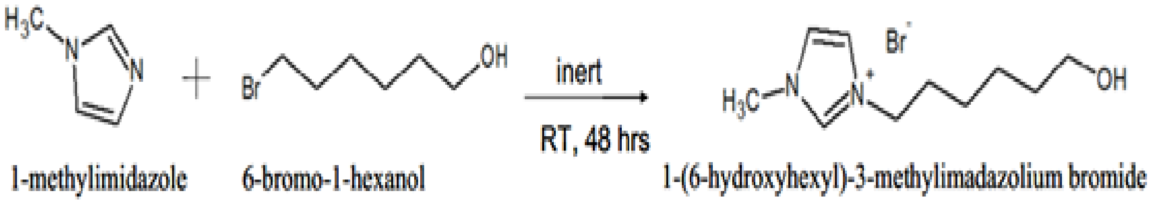


Figure 18. Synthesis of transparent and viscous alkylated ionic liquid

1.3 Synthesis of ILM 1-[(6-methacryloyloxy)hexyl]-3-methylimidazolium bromide

The ionic liquid obtained from the previous step has to be reacted with methacrylyol chloride in acetonitrile media which works as a stabilizer and BHT (Butylated hydroxyl Toluene) to prevent localized oxidation. The reaction between methacrylyol chloride and 1-(6-hydroxyhexyl)-3-methylimadazoium bromide is shown in Figure 2.

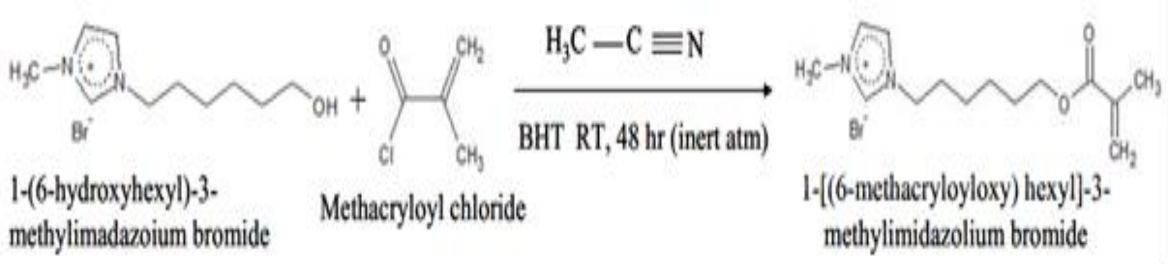


Figure 19. Synthesis of ILM

After the completion of the reaction in 48 h, the ILM was vacuumed and treated with diethyl ether three times followed by vacuumation for 12 h.

1.4 Polymerization of ILM 1-[(6-methacryloyloxy)hexyl]-3-methylimidazolium bromide (PIL2)

The ILM was processed further to create imidazolium based PIL using the technique of free radical polymerization. The monomer was mixed with methanol as a solvent due to its low boiling point and a mixture was formed. AIBN was added to the mixture as an Initiator and purged with nitrogen for 30 minutes to prevent any side reactions, following a 24 hr. reaction at a temperature of 70 °C. In order to check if the mixture has reached the extent to desired polymerization, a small amount of the mixture was added to a cold mixture of acetone. The reaction was carried out in normal light and the reaction mixture did not precipitate in acetone which showed that polymerization was not achieved. In order to achieve polymerization of the ILM, it was then put under ultraviolet light for another 24 h. in a petri dish. A viscous film of polymer was formed, which was then dissolved in methanol to put in the conical flask. The mixture was then added to acetone to precipitate for 12 h and after that some amount of the polymer was precipitated while leaving the other dissolved in acetone which indicated polymerization was carried out

1.5 Synthesis of 1-Ethyl-3-methylimidazolium bromide (EmimBr)

1-Ethyl-3-methylimidazolium bromide [EmimBr] was prepared by reacting 82g of methylimidazolium with 163g of bromoethane in a ratio of 1:2 respectively. The reaction is carried out for 24 hours at a temperature of 37 ˚C in the presence of N_2. A solid salt was obtained which was then liquefied by keeping in the oven at a temperature of 80 ˚C. Removing the unreacted starting materials involves, washing with Ethyl Acetate for two times and washing one time with a mixture of Methanol and Acetone (1:10) and dried in vacuum for 12 hour.

1.5.1 Ion exchange from Br to BF_4

ILs having BF_4 cation as it is reported to show the best stability and conductivity [35], to test this the Br ion of EmimBr was exchanged with BF_4. Equimolar quantities of EmimBr and $NaBF_4$ were dissolved in 40ml of acetonitrile in a flask and allowed to react for 48 hours at room temperature. NaBr was filtered from the reaction solution and the resulting EmimBF4 was washed with 30ml of dichloromethane for 20 minutes. White particles precipitated at the bottom were again filtered and the ionic liquid was kept in vacuum to dry. Solubility tests done on the ILs are discussed in chapter 3 section 3.3.

1.6 Electrospinning

A syringe pump was used for pumping the carbon suspensions and the fibers were collected at a rotating drum collector using aluminum foil. The parameters of the process were adjusted during the process because each solution had its own working parameters to obtain continuous fibers. Feed rate for all the suspensions was set at 1ml per hour while the distance between the tip of the needle and voltage were variable for different suspensions. The applied voltage ranged from 10 kV to 20 kV, while the distance range was 12-15 cm. Electrospinning process for all the suspensions was done at ambient conditions.

1.7 Testing methods

1.7.1 Fourier transform infrared (FTIR) spectroscopic analysis

FTIR is an analytical tool which make use of infrared light to cause absorption in the molecular bonds and results in vibrational movements to estimate the chemical composition and the structure of the substance being analyzed [37], [38]. Radiations are absorbed by the chemical bonds because of the vibrations in middle infrared region ranging from 400 to 4000 cm^{-1} with each functional group having a unique absorption frequency and the unknown samples can then be recognized [39].

1.7.2 Rheology Test

The stability of the suspensions was studied using Anton Paar PhysicaMCR501 rheometer, Germany, with cone-plate (25mm in diameter) measuring geometry. These test shows the stability of the solid carbon particles suspended in the liquid solvent and the polymer used in our research.

1.7.3 Nuclear magnetic resonance (NMR) spectroscopic analysis

The magnetic properties of every chemical substance are unique, and NMR is based on this concept [41]. Substances with different chemical structures have electrons in their nuclei using which the can bond with other substances and each of those substances have specific electrons shells. There is a magnetic field associated to these electrons and every substance resonates at a specific frequency depending on the number of electrons. Once the frequency date is obtained, Fourier transform is used to determine the corresponding chemical structures and the compounds.

In our experiments, Hydrogen NMR (HNMR) was used to determine the chemical structures. An example of HNMR of ethanol is given in figure 20., where ethanol is subjected to HNMR and the three hydrogen groups present in ethanol are detected at different frequencies, the peak obtained are directly proportional to the number of hydrogen atoms [40].

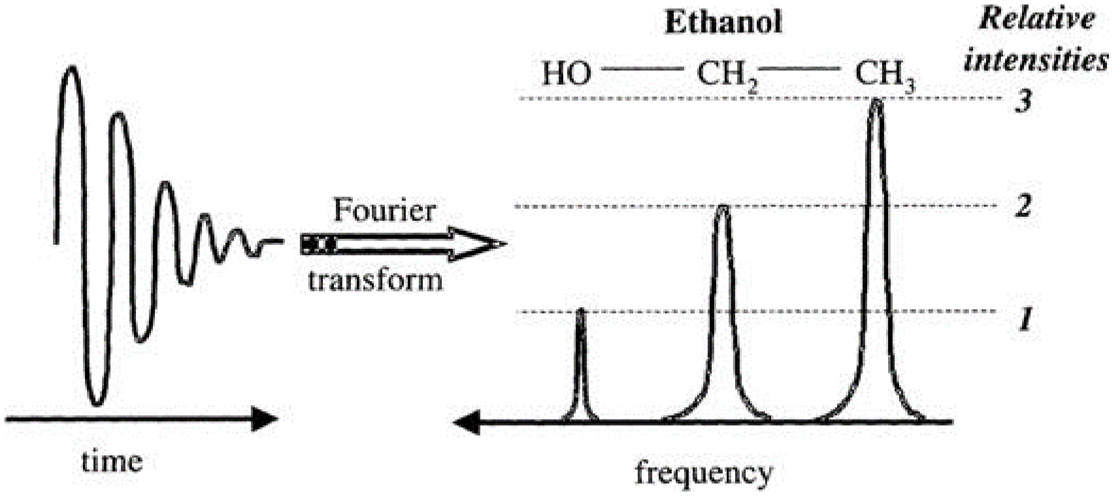


Figure 20. HNMR of Ethanol

1.7.4 Conductivity

The conductivity of the mats made by electrospinning using the PIL and polymer suspensions was measured using the High Resistance Meter HR2 from AlphaLab. The readings were taken after the drying of the mats to eliminate any effects of the solvents on the conductivity of the mats.

1.7.5 Scanning electron microscopic (SEM) analysis

In scanning electron microscope a sample is subjected to a beam of electrons which are created using a filament, most common filament being tungsten wire. These electrons have high acceleration energies ranging from 2 to 1000KeV and they passes unabsorbed through a thin sample and absorbs in thicker specimen giving the information about the specimen in both cases using the information from the particles (electrons, photons, x-rays) emitted from the surface of the sample. Information about electrical behavior of the specimen, chemical composition, topography and crystalline structure can be obtained using SEM [42]. In our research, a Tabletop scanning electron microscope TM-1000 Hitachi was used to study the morphology of the electrospun suspensions.

CHAPTER3. RESULTS AND DISCUSSION

1.1 FTIR ANALYSIS

FTIR analysis of the synthesized IL monomers, PIL liquids and other solutions made during the research was done to confirm the chemical structures. Figure 21 shows a comparison between the IR spectra of IL monomer (1-[(6-methacryloyloxy)hexyl]-3-methylimidazolium bromide)(red) and polymer (PIL2)(blue). The presence of carbon-carbon bond in monomer is shown by red line, which is at 1710 cm^{-1}. The overlapping of C-O and C-N bond appears at 1162 cm^{-1}. The peak at 2938 cm^{-1} shows the -C-H- stretching of alkyl groups. N-H and O-H bonds can be given to the peak at 3405 cm^{-1}. The transformation of IL monomer to PIL (scheme 1) is accompanied by the conversion of α β ester unsaturated ester to ester which is evident by the peak at 1668 cm^{-1} in PIL FTIR curve.

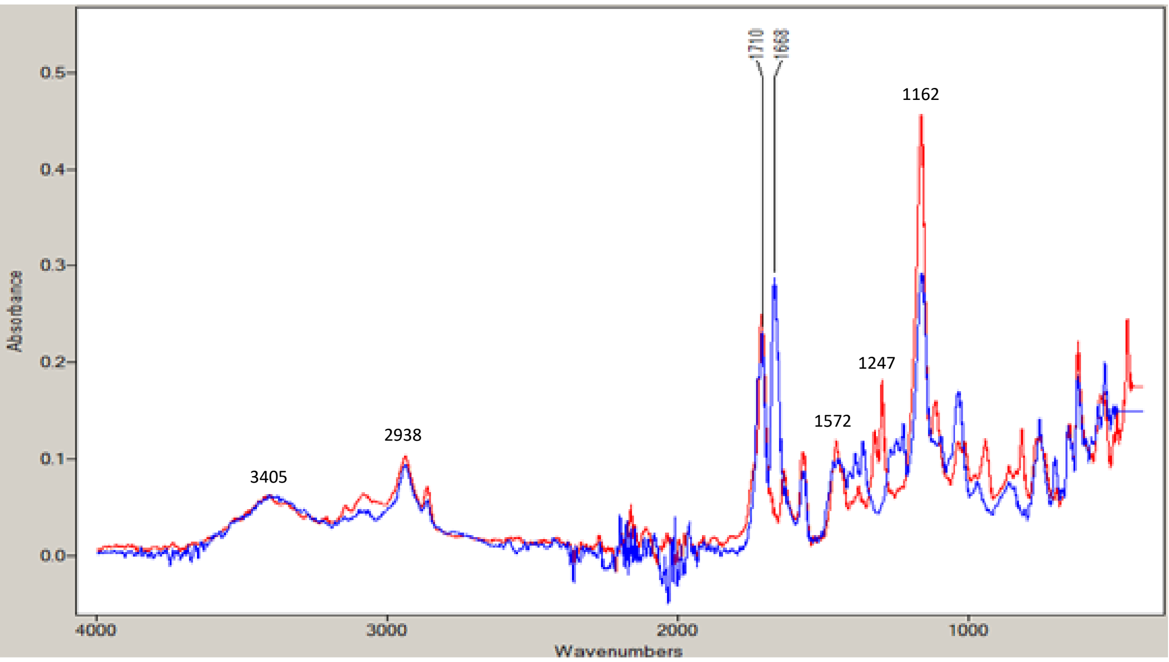
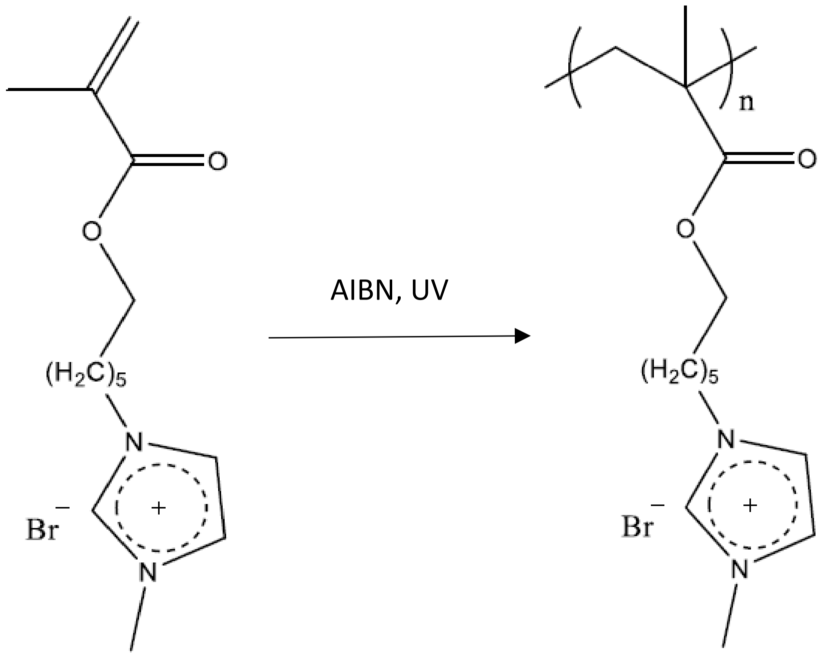


Figure 21. IR spectra of IL monomer (1-[(6-methacryloyloxy)hexyl]-3-methylimidazolium bromide) (red) and PIL (blue)



Scheme 1: ILM polymerization to PIL

EmimBr was prepared specifically to study the effects of ion exchange and solvent solubility (discussed in chapter 3.2). Figure 22 shows the FTIR results for EmimBr (BLUE) compared with EmimBF$_4$ (RED) which was the ILM obtained after the ion exchange. The peak at 3415 shows the presence of moisture in EmimBr which is then removed after ion exchange. The peaks at 1570, 1458 represent the stretching of C-C, C-N stretching in the imidazole ring with C-O and C-N overlapping around 1167 and C-H bending out-of-plane around 754 and 701. The peaks at 3139 and 2938 can be given to C-H stretching of the alkyl groups. The peak at 3070 can be attributed to =C–H stretching.

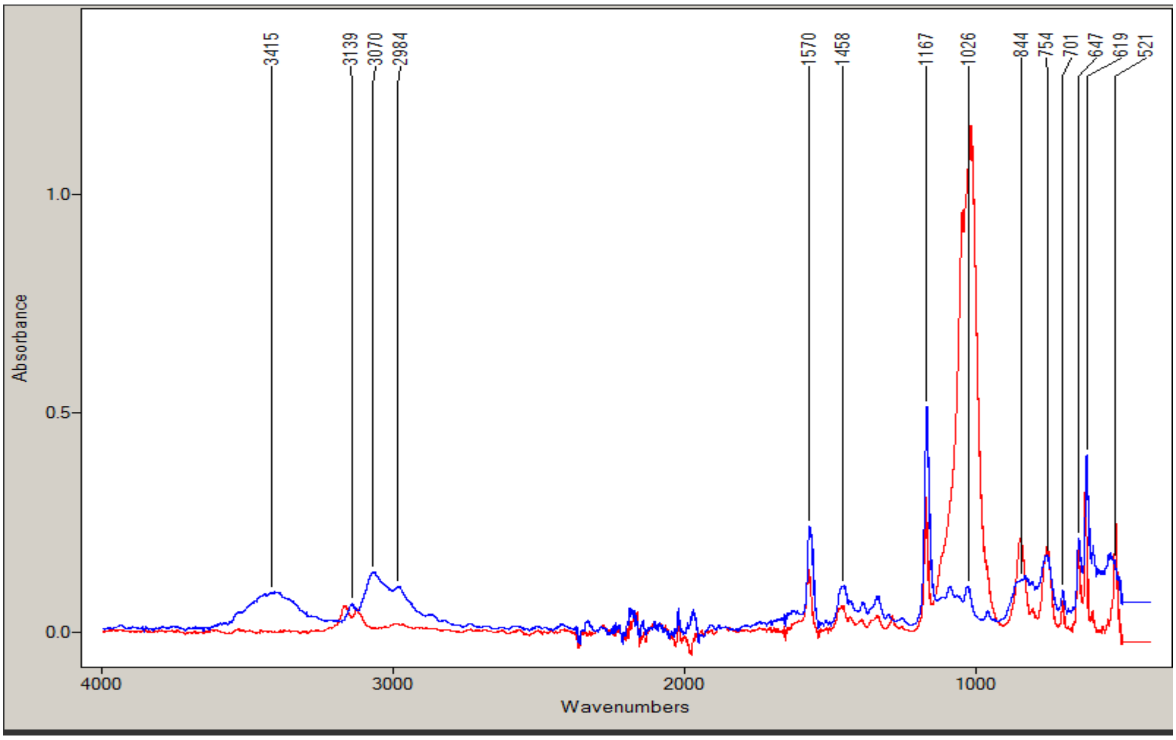


Figure 22. Comparison between EmimBF4 (red) & EmimBr (blue)

Similarly, 1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide was subjected to polymerization and ion exchange in two different ways. It was polymerized before and after the ion exchange (Br to BF_4) and the resulting PILs were studied using FTIR analysis.

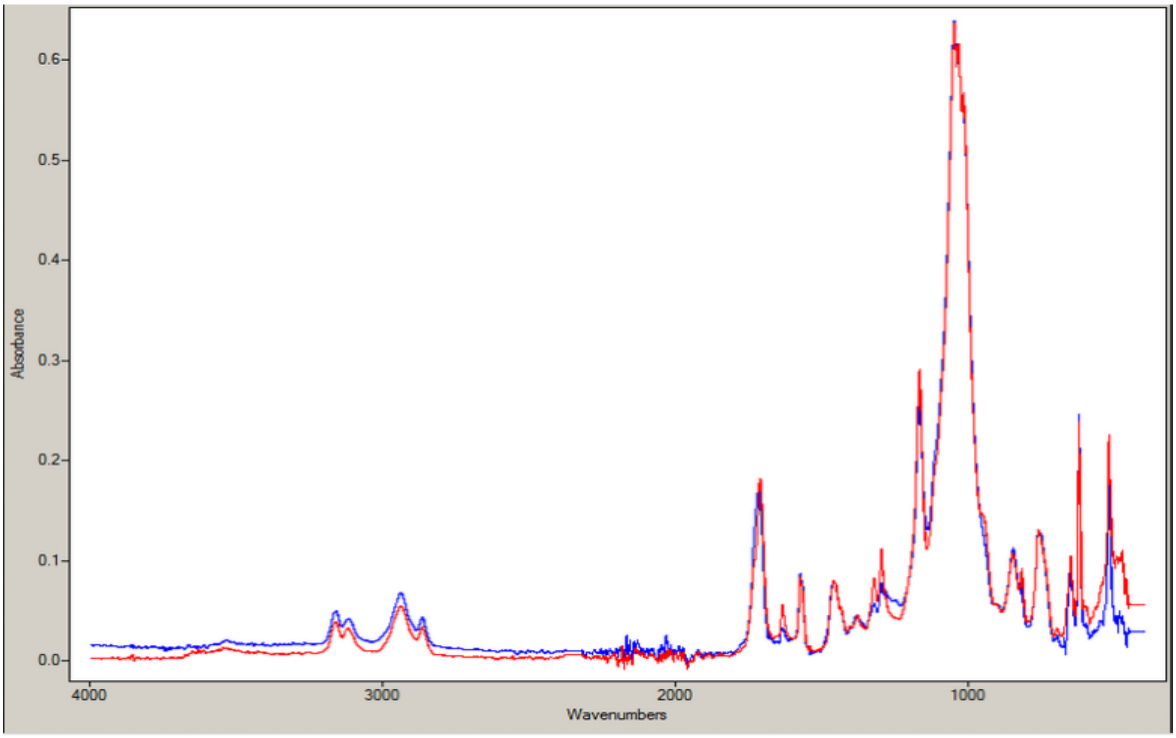


Figure 23. PIL2 polymerization before (blue) vs after (red) ion exchange

The results obtained from the FTIR spectrum for PIL2 polymerization before (blue) and after (red) the ion exchange can be seen in figure 23. Wavenumbers between 3500 to 4000 cm^{-1} represents the presence of moisture in the compound, according to this data obtained PIL 2 which was polymerized after ion exchange shows better properties when taking moisture into account. However, apart from water, both the samples showed identical chemical structure.

The result from FTIR analysis of ion exchanged PIL 2 is also compared with PIL 2 without any ion exchange, which can be seen in figure 24. The peak at 3043 cm^{-1} in PIL 2 shows the presence of hydrogen bonding which suggests presence of water in our sample. It makes obvious that ion exchange process removes moisture from our sample and better results are obtained. Whereas, the peak at 1049 cm^{-1} represents the shift of ion from Br to BF_4 ion.

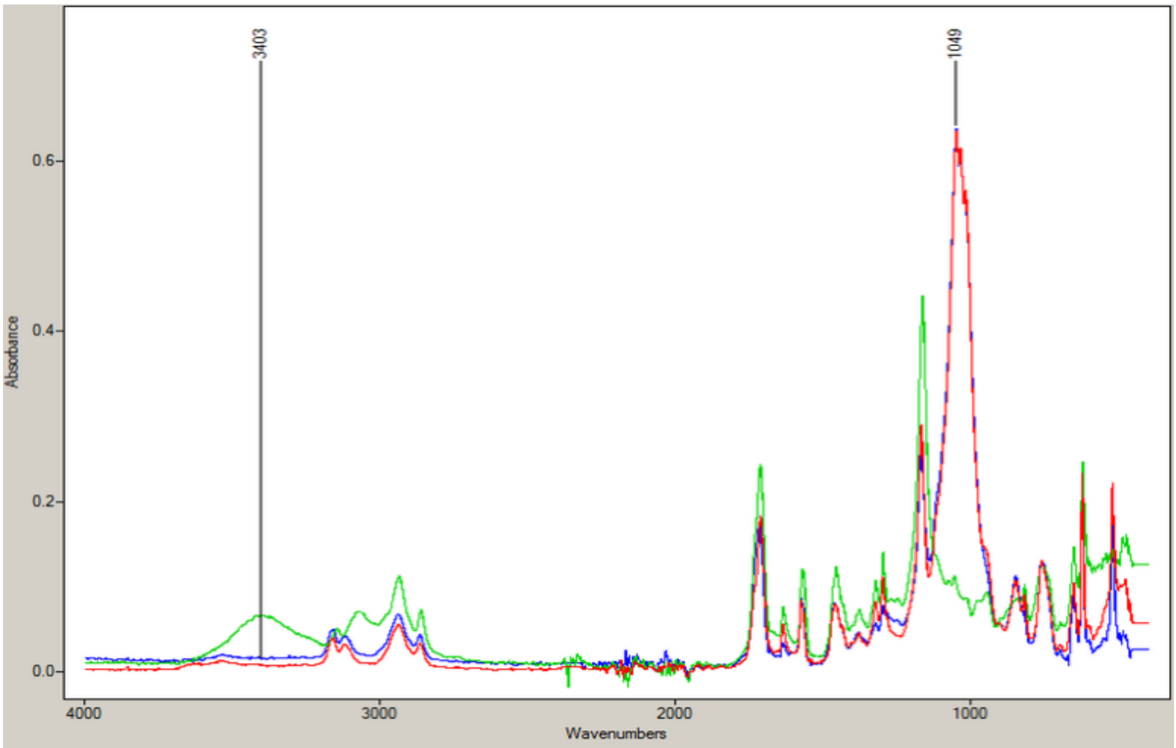


Figure 23. PIL2 polymerization before (blue) vs after (red) ion exchange vs PIL 2 (green)

1.2 NMR ANALYSIS

NMR analysis of poly(1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide) was done. In the Figure 24 the HNMR spectra obtained from the PIL and the monomer is illustrated. The monomer structure is identified by the protons of -N-CH-N and -N-CH=CH- are corresponded by the chemical shift peaks 9.29 (s, 1H) and 7.77 (s, 1H) respectively. -CH_2-CH_2-N-, CH_2-CH_2-O- were identified by the protons of the 6C chains with the chemical shift values of 1.82 (q, 2H), 1.64 (q, 2H) and, 1.34 (m, 4H). CH_2=C bonds are absent from the spectra of the PIL which proves that the polymerization was successful.

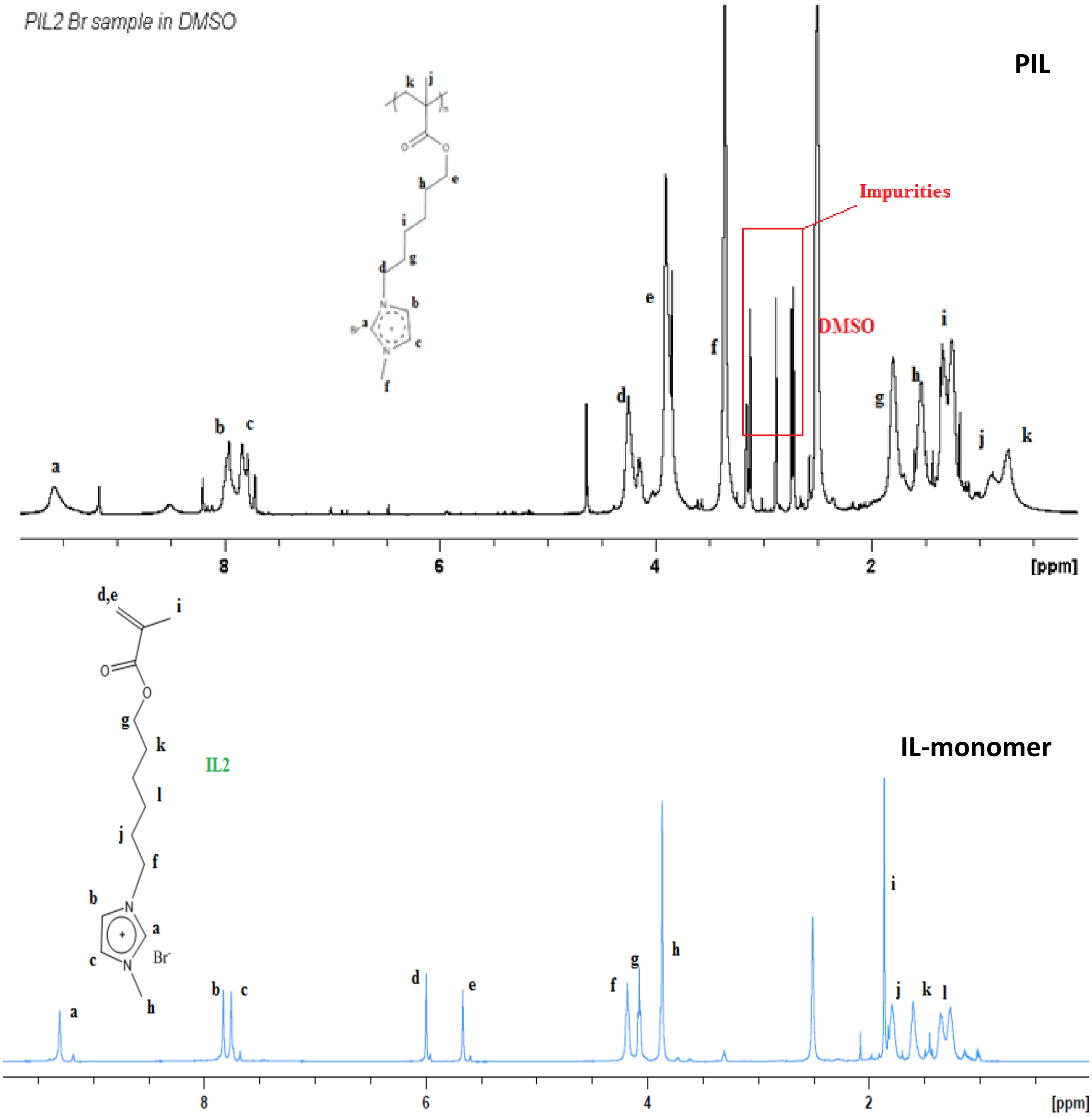


Figure 24. HNMR spectra of PIL and the monomer

1.3 Solubility tests

A comparison between the solubility of EmimBr and $EmimBF_4$ is shown in table 1. It can be seen that the anion exchange from Br to BF_4 have little to no impact on the solubility of EmimBr, it only became insoluble in Dicholoromethane and Chloroform and still soluble in water, which our main focus is.

Table 1. Solubility of EmimBF4 and EmimBr

Soluble in	$EmimBF_4$	EmimBr
Water	Yes	Yes
THF	Yes	Partly soluble
Ethanol	Yes	Yes
DMF	Yes	Yes
Dichloromethane	No	Yes
DMSO	Yes	---
Acetonitrile	Yes	Yes
Ethyl Acetate	No	No
Methanol	Yes	Yes
Formic Acid	Yes	Yes
Chloroform	No	Yes
Ethyl Ether	No	No

1.4 Stability Tests

1.4.1 Suspension preparation

Rheology tests were done on the initial suspensions/solutions preparation for electrospinning.

The following samples were prepared during this process.

1. PAN solutions with different concentrations were made, DMSO was used as a solvent because PAN shows good solubility in it as compared to other solvents. 3,5 and 9% of PAN solution in 5ml of DMSO were made using magnetic stirring.
2. Activated carbon (Kuraray) suspensions were made in Hexane. 1,3,5 and 7% of kuraray suspension weres made in 5ml of hexane, sonicated for 1 hour under the thin ultrasonication tip at 50% power using Bandelin Sonopuls sonification device. The sonication was done in

three intervals of 20 minutes each because of the extremely volatile nature of hexane. After each interval, the amount of evaporated hexane was measure and pure hexane was added to fill the gap.

3. 7% of PAN solution in DMSO and 7% of kuraray suspension in hexane were mixed in a ratio of 1:1 and a 5ml suspension was made under ultrasonification at 50% power for 1 hour and tested for stability and the results were compared to pure DMSO and the solution of 9% PAN in DMSO [36]. A suspension of polymer and activated carbon was obtained.

1.4.2 Rheology results

Rheology tests were done on PAN solution in DMSO and the suspension of PAN+DMSO & KURARAY+HEXANE. It can be seen in figure 25 that the viscosity of the different concentrations of PAN solutions has a linear relation to angular frequency from $10^0 – 10^{1.5}$ and then increase until reaching a common point at $10^{2.5}$. Figure 26 shows the viscosity curves obtained on the emulsion of PAN and kuraray, it can be seen that the stability of Emulsion at day 1 is almost identical to the tests made on day 2. Here one problem is that if the emulsion is not kept in air tight conditions there is a possibility that hexane evaporates, and it affects the stability of our emulsion, and this issue can be solved if the solution prepared is electrospun immediately.

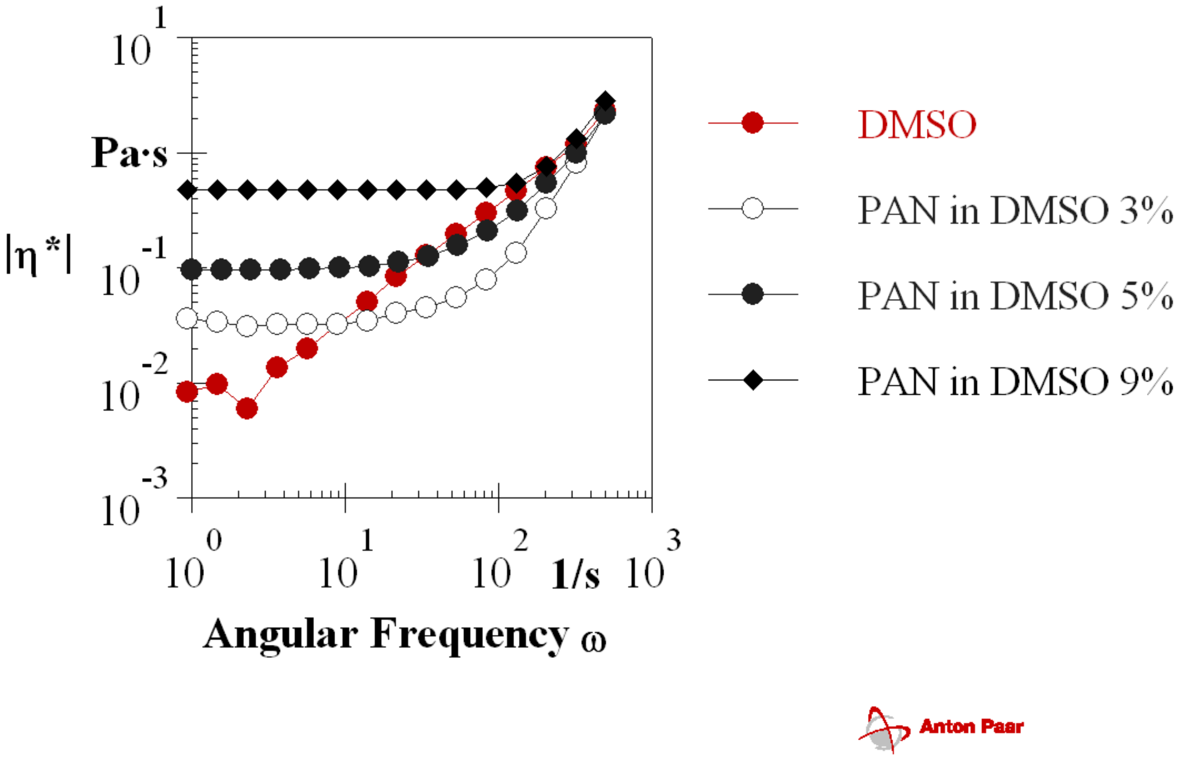


Figure 25. Comparison of pure DMSO to PAN solutions

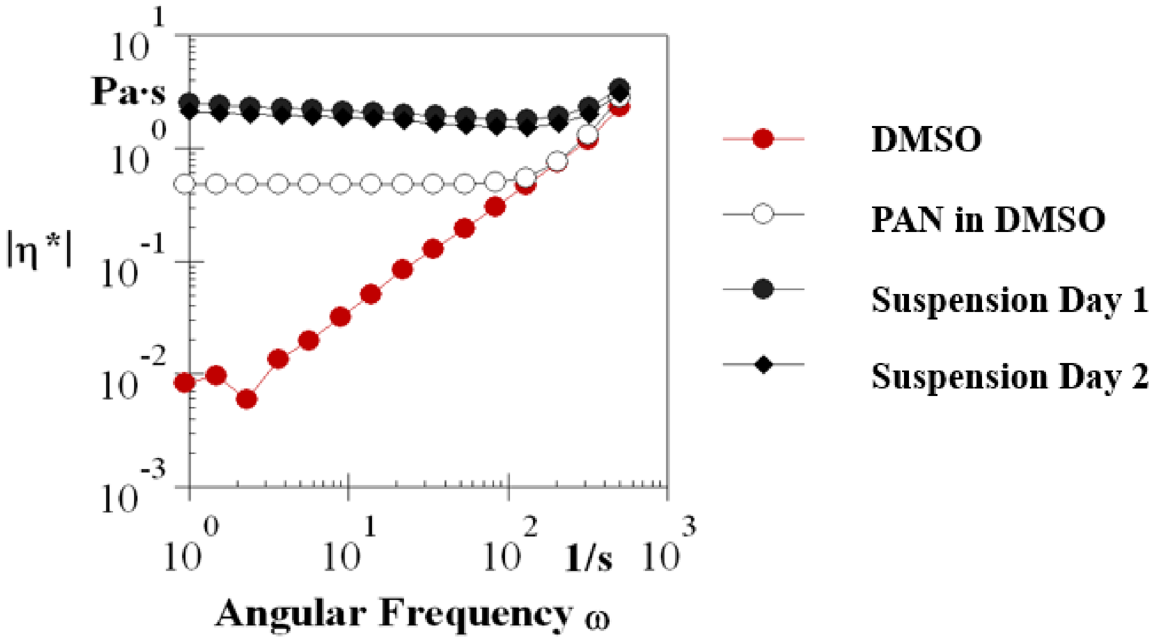


Figure 26. Stability of Emulsion (PAN + KURARAY)

1.4.3 Microscopy of suspensions

Stability of the kuraray suspensions in hexane was tested used microscopy. The smallest patches can be seen in figure 27, which represents 1% kuraray solution. All the concentration showed bigger agglomerates comparatively.

Figure 28 shows the microscopic image of the suspension of PAN and Kuraray suspension, prepared for electrospinning, and its visual assessment shows that the emulsion reached a good level of homogeneity. Black spots seen here are the kuraray particles and white substance is PAN covering most of the space. The stability and the homogeneity this emulsion showed, made it suitable for electrospinning.

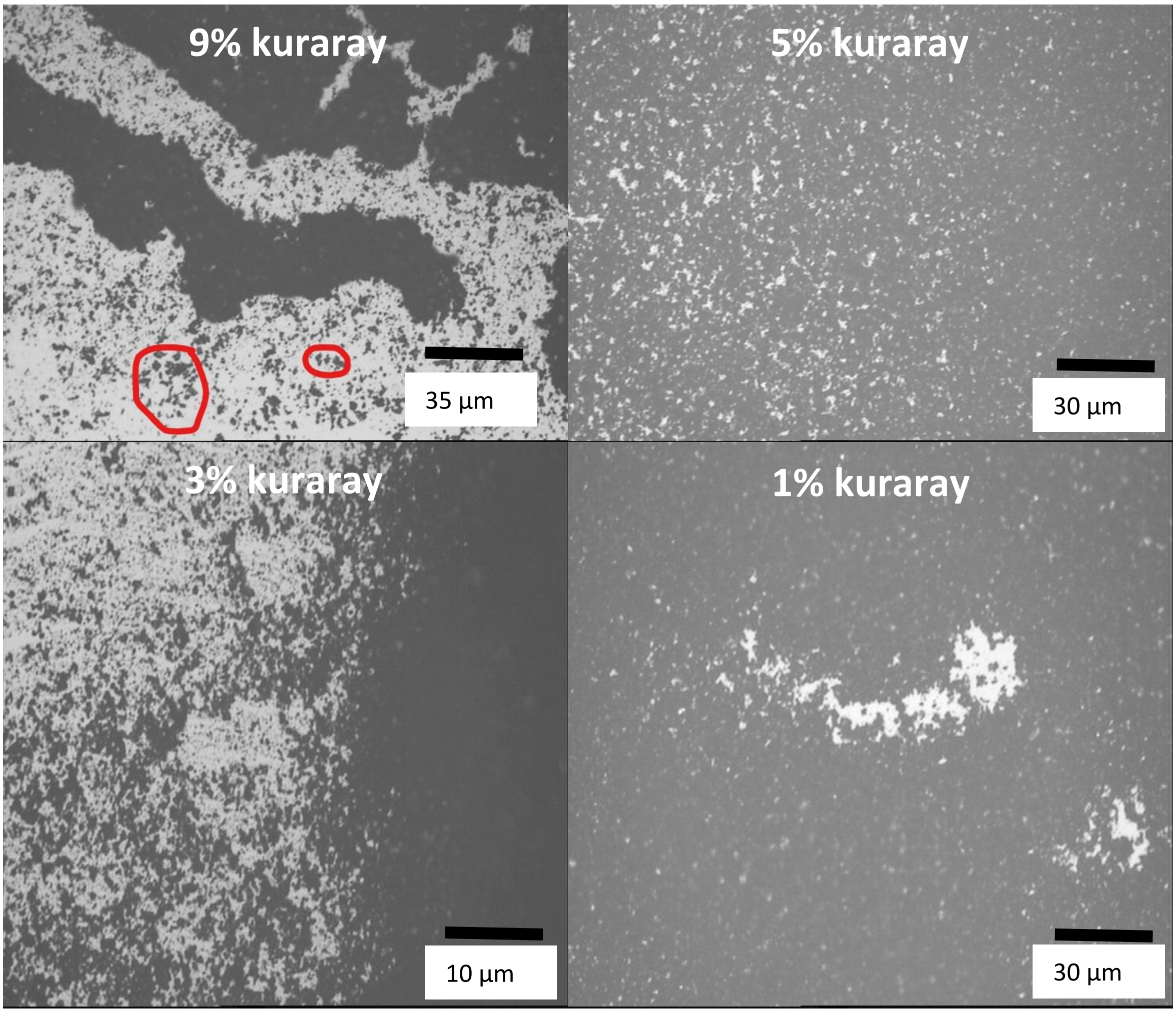


Figure 27. Microscopy of kuraray suspensions

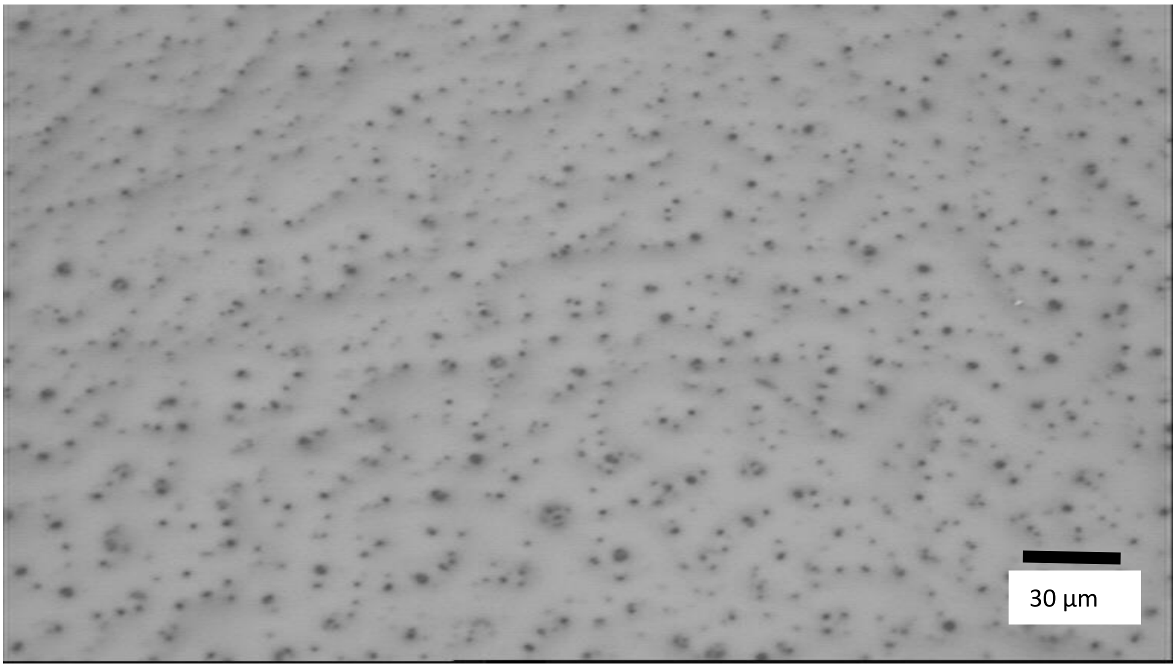


Figure 28. Microscopic image of suspension (9% Kuraray in Hexane + 9% PAN in DMSO)

1.5 Electrospinning of suspensions

1.5.1 Suspension preparation

IL/PIL/PAN suspensions were made mixing with a suspension of kuraray in hexane using the process explained below.

1. 10ml solution of 7% PAN in DMSO

2. IL/PIL is added to the above solution in 7% by weight to the amount of PAN.

3. The above solution is mechanically stirred at room temperature for 24hr.

4. 5ml kuraray solution is prepared in Hexane using thin tip ultrasonic finger.

5. The solution is ultrasonicated for 1 hr in 3 intervals of 20 minutes at a power of 50% and 9 % cycles. Complete process was done at room temperature while the heat produced during the sonication process was aided using cool water.

6. Hexane is volatile and after 20 minutes the weight of the system is measured as evaporated hexane is added.

7. Finally, 5ml suspensions of PAN(in DMSO) with activated carbon(in hexane) in a ratio of 1:1 & 2:3, PAN+PIL(in DMSO) with activated carbon (in hexane) in a ratio of 2:3 are made using same ultrasonification process as above.

1.5.2 Electrospinning parameters

Electrospinning of the above solutions was done using a conventional electrospinning setup in ambient conditions. The voltage applied for the above solution was 15kV for the PAN suspensions and by the addition of PIL the voltage had to be increased to 18kV for the process to run. A drum collector with aluminium foil was used at a distance of 15cm from the syringe.

1.5.3 Scanning electron microscopy of electrospun mats

SEM is a type of electron microscope which uses a focused beam of electrons on the surface of the material to produces the images. Suspensions were electrospunned and SEM images of the mats were taken to study the morphology.

Figure 29. the left image shows the SEM results of an electrospun mat using a suspension of PAN and kuraray in a ratio of 2:3, respectively. Kuraray is uniformly coated by PAN and from the porous structure of PAN fiber obtained may be due to the porous nature of PAN or due to the evaporation of hexane in the suspension during the drying of the mat. Whereas, on the right image the SEM image of the same suspension in a ratio of 1:1 is shown, PAN fibers completely cover kuraray which can reduce the conductivity, therefore, the best working suspension is in a ratio of 2:3 of PAN & kuraray respectively. Figure 30 shows the SEM images of PAN+IL(left)/PIL(right) in Kuraray, while these images cannot be used to define the structure, but it can be still seen that the structure is uniform, and the presence of fibers can also be seen.

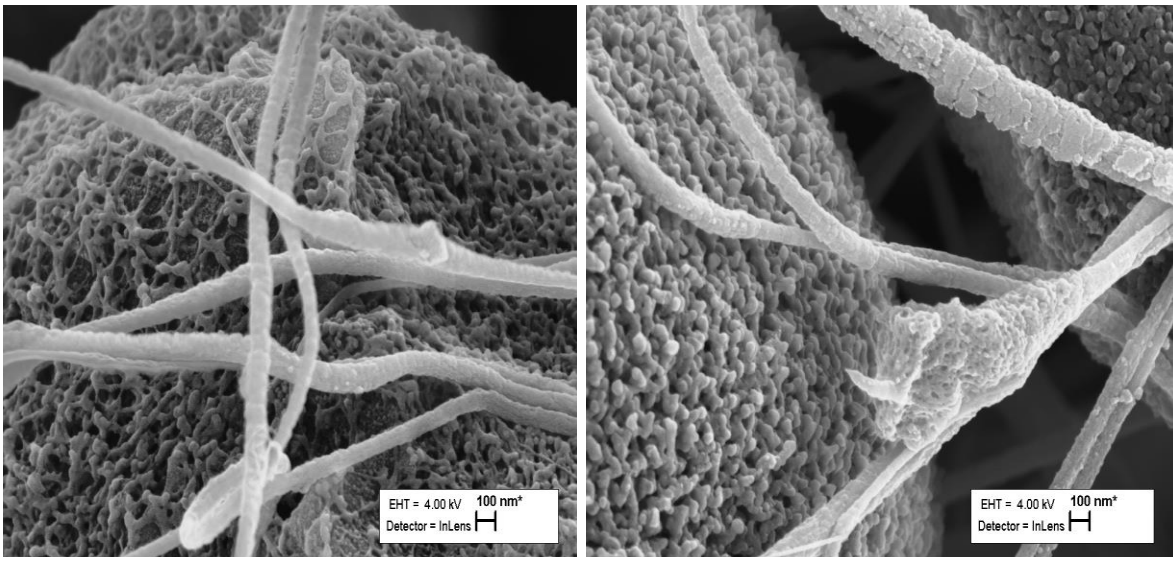


Figure 29. SEM image of PAN/KURARAY mat in a ratio of 2:3 (left) & 1:1 (right)

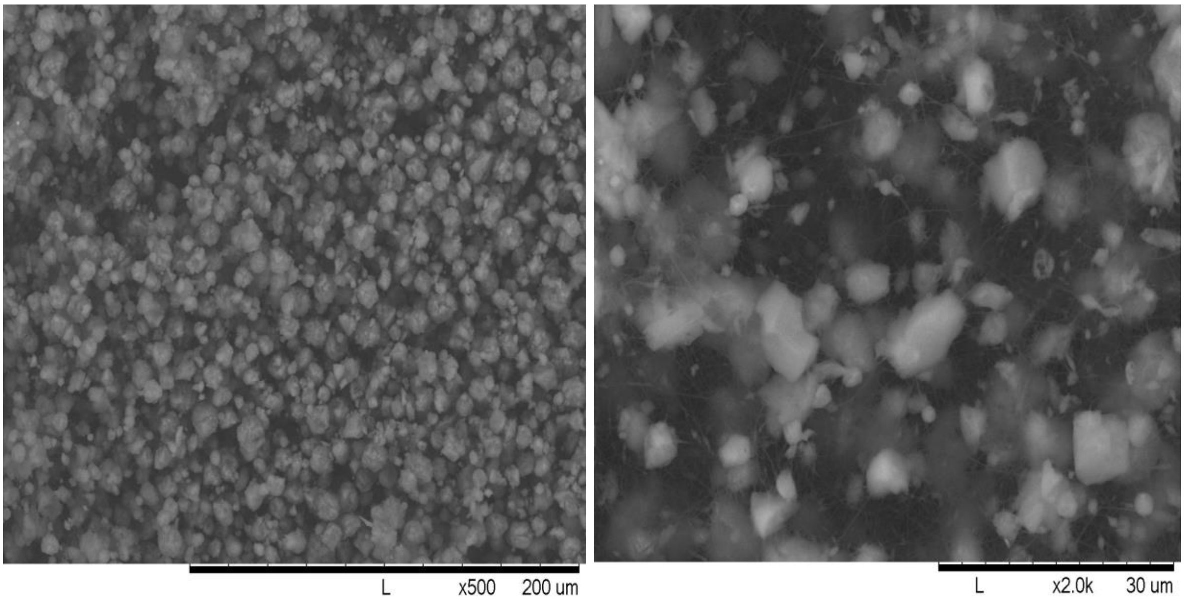
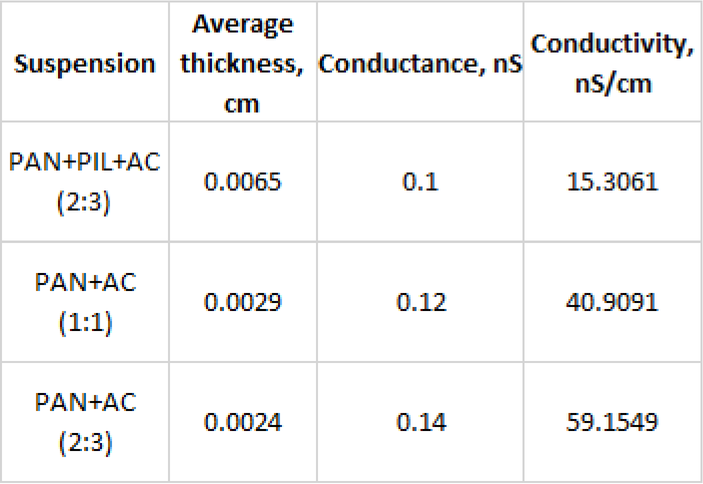


Figure 30. SEM image of PAN+IL/KURARAY mat in a ratio of 2:3 (left) & PAN+PIL/KURARAY 2:3 (right)

1.6 Conductivity

The conductance of the electrospun mats was measured using 2-point high resistance meter and the conductivity was calculated and the date is shown in table 1. The conductivity results of the mats made from the suspension of AC in PAN shows that the conductivity increases by increasing the amount of activated carbon as it is a conductive material and the most important in providing the conductivity to the mats. The conductivity for the AC in PAN (1:1) is 40.90 nS/cm and it increase to 59.15 nS/cm by increasing the amount of AC in PAN 3:2. Whereas, adding PIL to the same suspension decrease the conductivity of the resulting mat to 15.30 nS/cm. This may happen due the fact that PIL has low conductivity and as a result it makes the conductivity of the overall mat to be low. Another factor that can have an effect on the conductivity is the quality and the uniformity of the mat.

Table 1: Conductivity of electrospun mats



Suspension	Average thickness, cm	Conductance, nS	Conductivity, nS/cm
PAN+PIL+AC (2:3)	0.0065	0.1	15.3061
PAN+AC (1:1)	0.0029	0.12	40.9091
PAN+AC (2:3)	0.0024	0.14	59.1549

Conclusions

During this study, an ionic liquid monomer, 1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide, was successfully synthesized and its polymerization was done using AIBN initiator for free radical photo-initiated polymerization technique.

FTIR and NMR analysis was done to confirm the structure of the synthesized IL & PIL. Ion exchange was done on the IL and solubility tests were performed, which showed no change in the solubility of the IL. PIL suspensions were successfully made using ultrasonification technology and their flow stability was tested by performing rheology tests. These stable suspensions were used for conventional electrospinning to produce conductive fibers. The mats obtained from the process were used to study the morphology of the fibers.

Conductivity of the electrospun mats made from PIL suspensions was calculated. It was seen that increasing the amount of AC to PAN suspension from 1:1 to 3:2 increased the conductivity of the mat from 40.9 nS/cm to 59.15 nS/cm. It was noticed that the addition of PIL to the suspension of AC in PAN (3:2) decreased the conductivity of the mat to 15.30 nS/cm. The morphology tests on the AC in PAN mats showed the formation of fibers around 100 nm while the mats made from PIL suspensions made more of a coating with some fibers. Morphology of the fibers of PIL suspensions still remain under question as the conductivity and the SEM results of the mats were not conclusive. However, the studies show that PIL can be used to make suspensions for electrospinning for producing conductive coating, and more studies must be done to improve the production of conductive fibers.

SUMMARY

In this study, an imidazole based ionic liquid monomer, 1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide, was synthesized by a two-step process. Quaternization of 1-methylimidazole with 6-bromohexanol was done followed by the acylation of the resulting IL with methacryloyl chloride to form the ionic liquid monomer. The resulting ionic liquid monomer was polymerized using the photo-initiated free radical polymerization in the presence of AIBN as an initiator. Poly(1-[(6-methacryloyloxy) hexyl]-3-methylimidazolium bromide) (PIL) was obtained after 48 hr process and the structure of the ILM and PIL was confirmed using NMR & FTIR analysis techniques. PIL was used to make suspensions to be used for electrospinning process. Suspension of different concentrations were made using polyacrylonitrile as the main electrospinning polymer, activated carbon as a filler and DMSO and hexane as solvents. Fibrous mats were made using these suspensions from electrospinning followed by the conductivity and morphology tests. It was seen that the mats made from PIL showed a coating feature with fibers and a low conductivity as compared to PAN and activated carbon mats. Moreover, the morphology results obtained were not conclusive and left a question to be studied in continuation of these studies.

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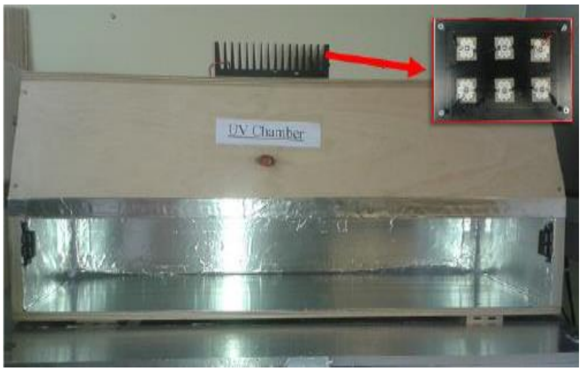
Appendix

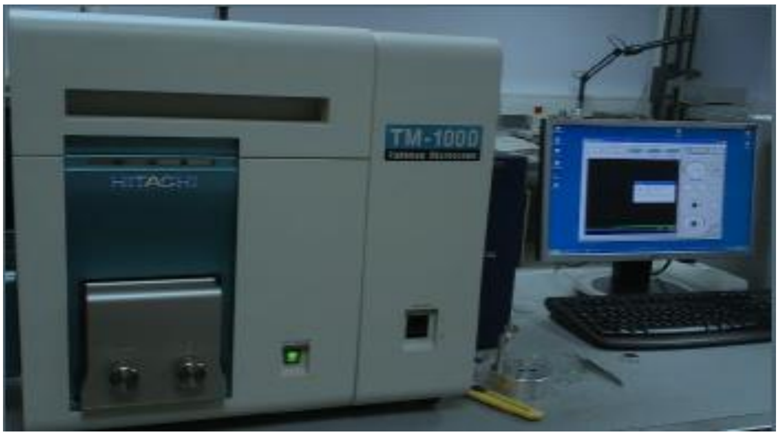
Electrospinning setup

FTIR spectrometer, INTERSPEC 200-X



UV chamber

Optical microscope, Zeiss



SEM microscope, TM1000, HITACHI

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