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Synthesis and characterization of polymeric ionic liquid through free radical polymerization of acryloyl imidazolium-based ionic liquid monomer

Tesi di laurea sperimentale

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Abstract

This thesis investigates the synthesis of polymeric ionic liquid [(poly-acryloyloxy)$^6C_6C_1$im][NTf$_2$], by free radical polymerization of acryloyl imidazolium-base ionic liquid monomer [(acryloyloxy)$^6C_6C_1$im][NTf$_2$]. Moreover, the smartest synthetic route to obtain this monomer was investigated. Two different synthesis were compared. The first one started from the preparation of the monomer 6-chlorohexyl acrylate followed by substitution and metathesis to reach ionic liquid monomer. The second one started from synthesis of the ionic liquid [(HO)$^6C_6C_1$im]Cl followed by metathesis and esterification in order to get ionic liquid monomer [(acryloyloxy)$^6C_6C_1$im][NTf$_2$].

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Introduction

Combining the proprieties of two or more different materials always have been leading to extraordinary results. Such combination should be become a new way for improvement of properties of existing materials and development of new ones. Taking this into consideration, the combination of unique structural design and physical proprieties of room temperature ionic liquids (RTILs) or ionic liquid (ILs) (Fig. 1) with the performance of polymers can open a window of opportunity for the application of the produced novel material.

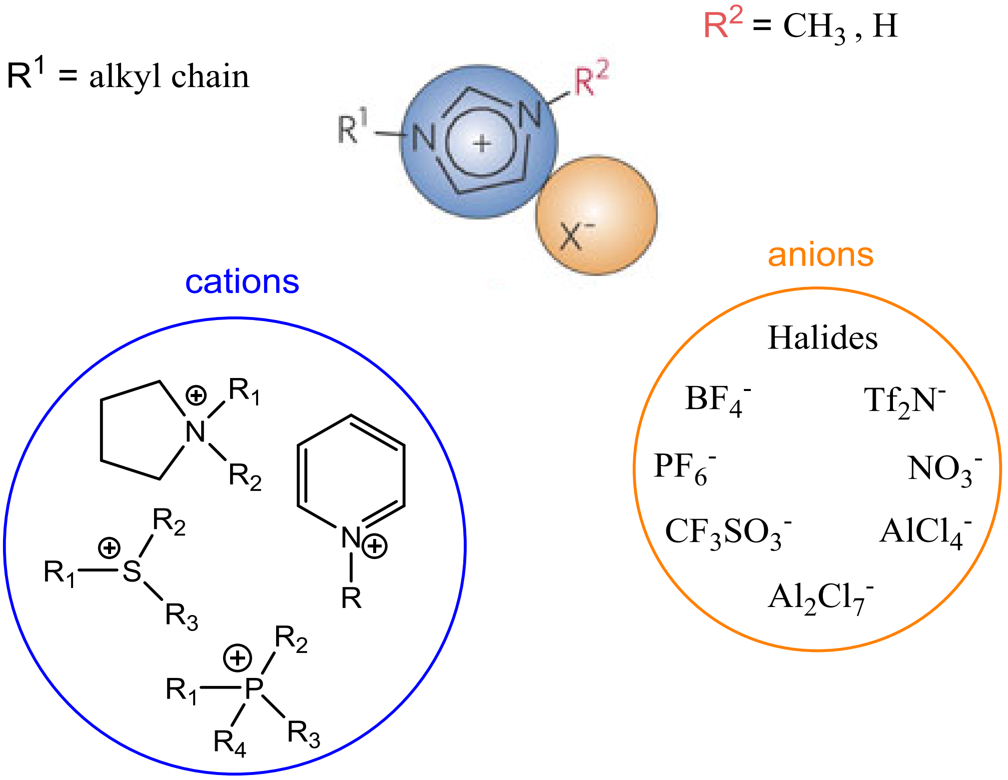


Fig. 1 Typical ionic liquids assembly[1].

The development of environmentally friendly catalysts and solvents for organic chemistry is an area of considerable importance. The use of ionic liquids as non-volatile solvents and non-metallic catalysts is very promising from both economic and environmental points of view[2]. Most of the research and industrial applications related to ionic liquids were associated to their applications in “green” chemistry as substitutes to volatile organic solvents. Thanks to their atypical proprieties, the field of application of ionic liquids has been extensively diversified during the past few years and they can be found in several technological fields such as catalysis[3], organic and polymer chemistry, electrochemistry[4], analytical chemistry[5], energy[6], nanotechnology[7] and biotechnology[8], among others. In the case of polymer science, ionic liquids are being investigated as "green" solvents in polymerization processes[9], promising solvents for cellulose[10], co-catalysts/initiators in polymerization reactions[11], specialty additives for polymers and in the development of functional polymers[12]. Interestingly, in the last years, the functionalization of polymers using some of ionic liquid has been carried on as a way of developing a new class of polyelectrolytes which here will be referred as polymeric/polymerized ionic liquids (PILs) also known in the scientific literature as poly(ionic liquid)s. The idea of creation of a new generation of polymers come from the particular properties of the functional groups associated to ionic liquids. One of their features is the chemical structure of polyelectrolytes with repeating monomer unit - cations and anions. PILs have inside of them a combination of the properties of IL (ionic conductivity, thermal stability, tuneable solution properties and chemical stability) and essential properties of polymer. This kind of polyelectrolyte differ from the classical polyelectrolyte by nature of counter-anion and counter-cations. The common polyelectrolytes have hydrophilic anions such as halides (Cl^-, Br^-, I^-) and the cations are typically metals (Li^+, Na^+ or K^+). The new polyelectrolyte ions could include presents hydrophobic anions ($[BF_4]^-$, $[PF_6]^-$, $[(CF_3SO_2)_2N]^-$ and $[CF_3SO_3]^-$) while the counter-cations are large organic ions (dialkyl imidazolium, alkylpyridinium, tetraalkylammonium and alkylpyrrolidonium). Thus, it can be concluded that PILs in general should be soluble in organic solvents but not in water contrary to classic polyelectrolytse, which are water soluble due to their hydrophilic character and high ion dissociation ability [13].

When consider PILs as polyelectrolytes they can be classified as polycations bearing a cations in the backbone's part of the monomer unit, polyanions with an anion or polyzwitterions having both anion and cations in their monomer units. The great variety of the potential combinations of the cations and anions allows a number of PILs to be synthesised by different routes resulting in different types of copolymers (either random, alternating or block copolymers) and macromolecular architectures (branched, dendritic or ramified) (Fig. 2).

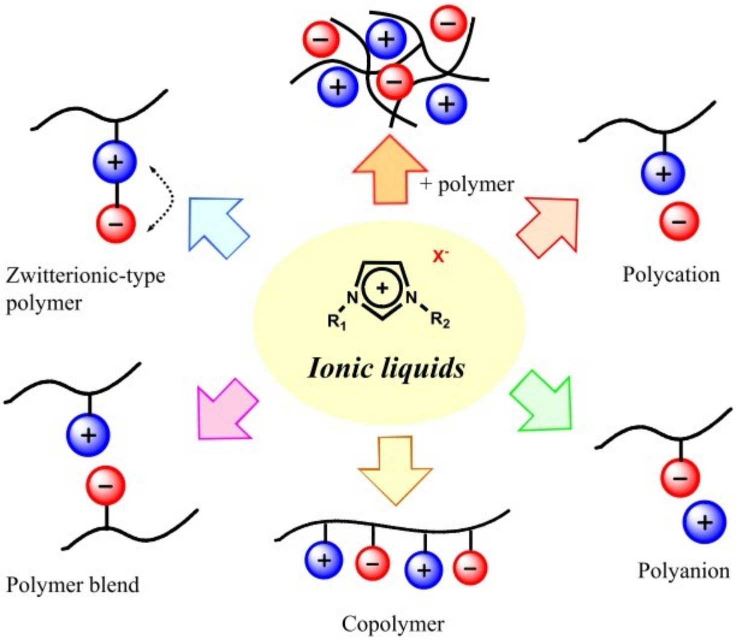


Fig. 2 The schematic illustration of a strategy to prepare PILs with different manners[14].

1 Ionic Liquids

The first mention of an ionic liquid was published about 100 years ago, in 1914 by Paul Walden, who observed the special physical properties of ethylammonium nitrate [15]. Then the field was dominated by a small number of narrow research, but today every chemist is likely to be well aware of the existence of ionic liquids and know that they are an useful addition to the existing range of solvents. In fact in the last 20 years there was an explosive increase in number of publications on ILs in every field of chemistry. Much of the interest in ionic liquids has been focused on their possible use as "green" alternative to volatile organic solvents[16]. The interest of replacing classical solvents comes from some simple physical properties of ILs[17]:

- They are good solvents for a large number of both organic and inorganic materials, with unusual combinations of reagents and can be brought into the same phase.
- They are often composed of poorly coordinating ions, so they have the possibility to be highly polar yet non-coordinating solvents.
- They are immiscible with a number of organic solvents and provide a non-aqueous, polar alternative for two-phase systems. Hydrophobic ionic liquids can also be used as immiscible polar phases with water.
- They are non-volatile due to their low vapour pressure, hence they may be used in high-vacuum systems and eliminate many contamination problems. This non-volatility also leads to most ionic liquids being non-flammable under ambient conditions[18].

Moreover, exposure risk to ionic liquids is much lower than it is for a volatile solvents, and they have no damaging atmospheric photochemistry[16].

1.1 Properties

One of the main application of ILs is in "green" chemistry because they are creating a cleaner and more sustainable chemistry and therefore receiving increasing interest as environmental friendly solvents for many synthetic and catalytic processes[16,18,19]. Another advantage is the possibility to perform a fine tuning of their physicochemical properties by suitable choice of cations and anions; therefore, ILs have been recognized as "designer-solvents"[20].

The mains physical and chemical properties of ILs are discussed below.

1.1.1 Handling

Two aspects need to be considered when operateing with any material:

- the possible hazard of the material to those expose to it

and

- what are the possible destructive effects of the material itself.

It is believed that there are no problems to keep and to work with ionic liquids in the air. Of course, the sensitivity of an ionic liquid to moisture and air, in particular to water and oxygen, is a chemical phenomenon and depends on the identity of the component ions of the ionic liquid[21]. Some ionic liquids, such as those containing the ions $[PF_6]^-$, $[SbF_6]^-$ and $[BF_4]^-$ undergo hydrolysis; in many cases the toxic and corrosive acid, HF, is formed[22]. Even when ionic liquid components are not hydrophilic, failure to protect the ionic liquids from atmospheric moisture may lead to considerable concentrations of water within it. The hydrophilicity of ionic liquid is largely determined by the nature of the anion[23] (Fig. 3). However, even ionic liquid with the least miscibility with water will contain considerable concentrations of bonded water molecules if not handled under the inert atmosphere, and this can lead to a dramatic changes in both physical and chemical proprieties[24].

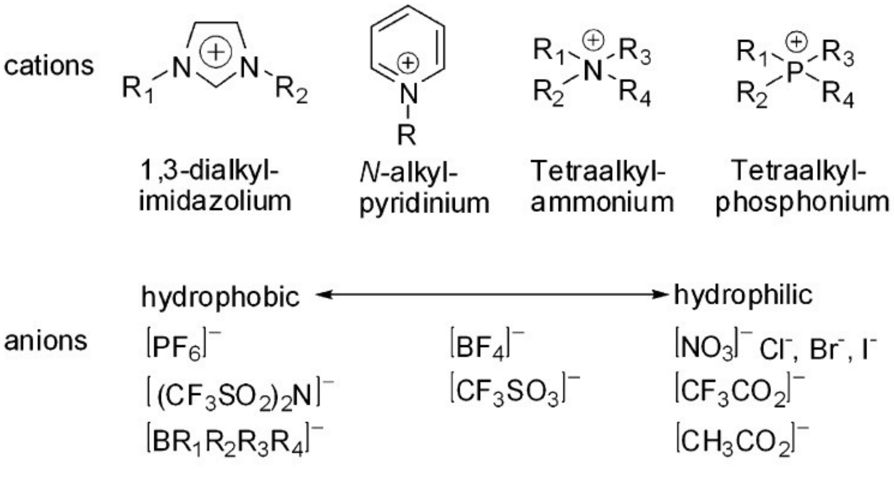


Fig. 3 Most commonly used cations and anions in the formation of ILs[25].

Oxygen-sensitivity has proven to be far less problematic. This because ionic liquids are rarely made using easily oxidised ions, the solubility of oxygen in most ionic liquids is relatively low[26], and it can be removed under vacuum.

The term “green” often used for ionic liquids essentially came from their low vapour pressure that makes them non-volatility solvents. But there was never a statement, that they are a safer replacement for the common solvents because ILs ions are non-toxic. No one IL has undergo a complete study to determine its hazards or non-toxicity. Despite several studies have shown the connection between the length of alkyl chains on the cations, or the change of the anion, and their toxicity, the negative effects were not meaningful enough to be sure of a structure-toxicity relationships[21]. Rather the determination of ILs as a “green” chemical was based on the fact that their insignificant vapour pressures means that accidental exposure to ionic liquids is far less likely than of volatile organic carbons.

1.1.2 Melting point

Melting point is a fundamental physical property of compounds, which has been found to have a wide use in chemical identification.

In ILs structure reduced Coulombic interactions between ions restrict the ion-pair formation required for volatilisation of salts. This is the reason for the low vapour pressure of ILs which allows ILs to have high upper temperature limits, determined by decomposition of IL rather than by vaporisation. The nature of the ionic liquids, containing organic cations, restricts upper stability temperatures, with pyrolysis generally occuring between 350 – 450 °C if no other lower temperature decomposition pathways are accessible[27].

The shapes and sizes of ions in ionic liquids are important in determining the melting points of the salts. Large difference in ions sizes results in decreased of melting points[28]. For example, an increase in anion size gives a rise to reductions in the melting points of salts through the reduction of the Coulombic attraction contributions and increasing covalency of the ions.

However attractive forces and ion sizes affect not only melting points of the components but also other properties of ILs such as their dissolution ability and solubility. If, for example, there is a requirement for an IL to have strong H-bond accepting character (of the anion), then it should be anticipated that this will also give rise to hydrogen-bonding interactions between ions, resulting in greater attractive forces and elevated melting points.

1.1.3 Viscosity

Viscosity is the physical property that characterize the flow resistance of simple fluids. Newton's viscosity law defines the relationship between the shear stress and shear rate of a fluid subjected to a mechanical stress. The ratio of shear stress to shear rate is a constant, at a given temperature and pressure, and is defined as the viscosity or coefficient of viscosity. Newtonian fluids have a constant viscosity regardless of the strain rate begin applide. Low-molecular-weight pure liquids are examples of Newtonian fluids. Non-Newtonian fluids do not have a constant viscosity and will either thicken or thin when strain is applied. Polymers, colloidal suspensions, and emulsions are examples of non-Newtonian fluids.

Compared to the conventional organic solvents, ILs are viscous liquids being 1–3 orders of magnitude more viscouse than common organic solvents[29]. This high viscosity may negatively affect the process. The viscosities of ILs are governed essentially by van der Waals interactions and hydrogen bonding. Alkyl chain length makes the salt more viscous, due to an increase in van der Waals interactions and additional hydrogen bonds. Alkyl chain ramification increases the viscosity due to reduced rotation freedom (and increased van der Waals). The Arrenihus equation (Eq. 1.1) is also applicable in ionic liquid systems to describe the temperature dependence of the dynamic viscosity for unbond liquid electrolytes[30]:

$$\eta = Ae^{\epsilon/RT}$$

Eq 1.1 Temperature dependence of the dynamic viscosity[30].

where η is the viscosity coefficient, $A = \eta_\infty$, ϵ is the activation energy for viscous flow, R is gas constant, and T is the temperature in K.

Temperature and the presence of additives are also important factors which affect the viscosity of ILs. The viscosity will obviously when the temperature is increased or an organic solvent is added to the ionic liquids[31].

As for melting point, the variation in the structure of ionic liquid leads to changes in the viscosity of neat ionic liquids. The effect of cation is smaller when compared to the anion effect.

The viscosity of pure ionic liquids is affected by the addition of co-solvents; i.e., significant decrease in viscosity depends on the solvent added and the extent of resulting dissociation of ionic liquids into ions. The effect of several compatible co-solvents including water, benzene, dichloromethane, and acetonitrile on viscosity of ionic liquids has been already investigated[32–34]. This suggests that the organic co-solvents solvates the constituent ions of the molten salt, resulting in a decrease in aggregation of these ions.

1.1.4 Polarity

Ionic liquids are considered to be polar solvents, but can be non-coordinating (mainly depending on the ionic liquid's anion). Solvatochromatic studies indicate that ionic liquids have polarities similar to those of short-chain alcohols and other polar, aprotic solvents (DMSO, DMF, etc.)[30]. That is, the polarity of many ionic liquids is found between the of water and chlorinated organic solvents, and varies depending on the nature of the ionic liquid components. For example, the exchange the anion Cl^- to $[PF_6]^-$, causes the change of miscibility with water, from complete miscibility to total immiscibility respectively. Similarly, the lipophilicity of an ionic liquid is modified by the degree of its cation's alkyl chain substitution.

Hydrogen-bonding plays a fundamental role in the properties of ionic liquids, in this case the key factors are: donor ability of the cations toward the polar or dipolar solutes, hydrogen-bond accepting functionality of anions and π–π or (C–H)–π interactions. Ionic liquids tend to be immiscible with alkanes and other non-polar organic solvents and hence can be used in two-phase systems. Similarly, it is possible to design ILs that are hydrophobic and can be used in aqueous/IL biphasic systems[33].

The most common measure of polarity used by chemists is the dielectric constant (ε_r). It is a physical phenomenon that could be measured by different methods, for example by microwave dielectric spectroscopy[35] or by combining the cohesive energy densities (CEDs) and the heats of vaporization[36]. Usually molecular solvents with $\varepsilon_r < 9$ are considered to be nonpolar, those with $9 < \varepsilon_r < 15$ are moderately polar, and values in the range $15 < \varepsilon_r < 30$ characterize the solvent as polar, but not exceptionally so. Liquids with ε_r in excess of 50 are considered to be highly polar. The dielectric constant of the ionic liquids appears to be related to the ability of the ionic liquids to enter into hydrogen bond networks. Hence, for anions the dielectric constant varies such that $[HCO_2]^-$ > $[C_2OSO_4]^-$ ≈ $[NO_3]^-$ >> $[OTf]^-$ > $[BF_4]^-$ > $[NTf_2]^-$ ≈ $[PF_6]^-$, which is the order of the decreasing basicity of the ions, and for cations the order is $[(HO)^2C_2NH_3]^+$ > $[C_2NH_3]^+$ > $[C_nC_mim]^+$. The dielectric constant has also been found to decrease as the length of the alkyl chain on the cations increased. These effects are similar to the behaviours seen for molecular solvents[21].

1.1.5 Electrochemical properties

The early history of ionic liquid research was dominated by their application as electrochemical solvents. They often have wide electrochemical potential windows, they have reasonably good electrical conductivity and solvent transport properties, they have wide liquid ranges, and they are able to solvate a wide variety of inorganic, organic, and organometallic species[33].

A key criterion for selection of a solvent for electrochemical studies is the electrochemical stability of the solvent[37]. An electrochemical solvent is a media for a reaction and it should not react with either analyte of a product and also should not be involved in electrochemical reactions over a wide potential range. The range of voltages, the potential “window”, in which a solvent is electrochemically inert depends on the oxidative and reductive stability of the solvent. In the case of ionic liquids, the potential window depends primarily on the resistance of the cation to reduction and the resistance of the anion to oxidation[33]. In addition, the presence of impurities can play an important role in limiting the potential windows of ionic liquids.

Cyclic voltammetry is the most common and simple method to determine the potential window of an ionic liquid. The measurement is performed with the application of a voltage to the electrode and monitoring of the corresponding current flow[38]. The potentials where the maximum and minimum background currents are obtained due to oxidation and reduction processed represent the potential window of the ILs. Normally the range of this electrochemical potential window is ± (3.0-5.0) V[33].

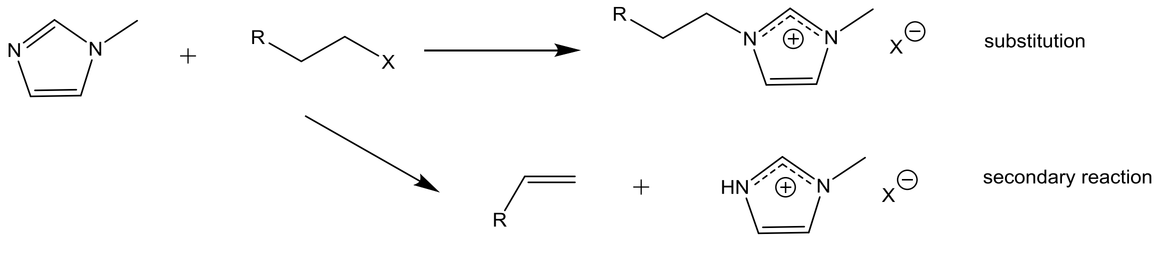
The impurities brought with the starting materials or formed during the synthesis can have a huge impact on the potential limits. For example the presence of moisture can affect both limits as water can be reduced and oxidized within the potential window of many ionic liquids, and contamination with significant concentrations of halide ions bring to observe a appreciably reduction of anodic potential [32,39].

1.2 Synthesis

As already mentioned, in the last 20 years has been an increase in the number of ionic liquids publications and group researching them. The most common method of ionic liquids synthesis is based on alkylation of amines/phosphine/sulphide (a smaller number for the last two) to produce an intermediate salt, which then is followed by anion exchange to produce the ionic liquid. In common organic reactions impurities that can be formed are removed via distillation, but for most ionic liquids this technique cannot be applied because of their high boiling temperature. Hence, the possibility to obtain high purity ionic liquids is a key factor when synthetic protocols are selected[19].

The impurities presented in ionic liquid can come from different sources. Generally, starting materials usually contain contaminations, ergo, it is important to perform a purification step, typically distillation of a starting materials from a suitable drying agent (under an inert atmosphere), prior to their use.

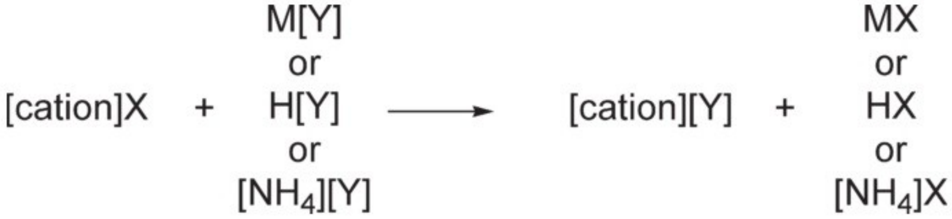
Once reactants are purified, the alkylation step can be performed. During this step it is important to work under inert atmosphere avoiding the presence of moisture and air. This nucleophilic substitution is highly exothermic[21]. Overheating of the reaction mixture leads to the formation of secondary products from the competing reaction (Scheme 1). Hence, the reaction is usually performed in the presence of an appropriate solvent (for example, ethyl acetate), the reactants are added slowly drop-wise to prevent "hot-spot", and the reaction mixture is cooled with ice, which extends the time of reaction but reduces the temperature and prevents the formation of the elimination products.



Scheme 1 Substitution and secondary reaction[21].

Most of the halide salts of cations used in ionic liquids are solid at room temperature, allowing purification of the intermediate salts by re-crystallisation, most often from acetonitrile; ethyl acetate can be added to increase the rate of precipitation of the salt and removal of unreacted starting materials. Finally, the ionic liquid salt is dried in vacuum, and sometimes, at elevated temperatures.

Generally, halide IL are used as intermediate for metathesis reaction with a metal, ammonium, or conjugate acid of the required anion (Scheme 2) to obtain desired ionic liquid. For hydrophobic IL, this step can be done in aqueous solution[40] with the product separating during the reaction. The aqueous solution is washed a few times with dichloromethane to separate the newly formed IL from the aqueous solution, which is subsequently isolated from dichloromethane solution by means of vacuum distillation. The ionic liquid is not completely dry at this stage, and any remaining water is removed under vacuum. This is usually conduced at elevated temperatures, but care is required because overheating can lead to decomposition of the ionic liquid[18]. For hydrophilic IL, the metathesis is usually performed in a water-immiscible organic solvent[23]. The new produced hydrophilic IL is recovered by an appropriate separation method and then it is purified by using small volumes of water to remove any residual halide salt. The greater the miscibility of the produced ionic liquid with water, the less effective this process is, leading to either low yields or halide contamination of the ionic liquid[41].



Scheme 2 Metathesis[21].

At this stage ionic liquids are often coloured or contain other impurities, such as unreacted starting materials or by-products that come from secondary reactions. These are typically removed by the use of sorbents such as activated charcoal, alumina, or silica[42]. However, these methods of purification could reduce the yields of the synthesis and further filtration is needed to remove any remaining particles of the sorbent material from ionic liquid[43].

The general preparation of ionic liquid as described above forms the vast majority of the syntheses described in the literature, nevertheless the details of the synthesis vary between each ionic liquid.

2 Polymeric Ionic Liquids

Despite that ILs have been known for more than a century and have been intensively studied during last two decades the idea to polymerise ionic liquid monomers is relatively new. The interest in polymeric ionic liquids (PILs) comes from the possibility of a combination of the unique properties of ILs with the polymeric macromolecular architecture, which results in a creation of materials with new functions and properties. The major advantages of using a PIL instead of an ionic liquid are the enhanced mechanical stability, improved processability, durability and spatial controllability over the IL species[25].

Furthermore, rapid advances in the chemistry and physics of PILs have developed novel and versatile polyelectrolytes that have expanded the traditional design of solid polyelectrolytes into more complex and versatile directions with pronounced strength in energy, environment, and catalysis applications[44].

They are commonly reported to have rather broad glass transition temperature (T_g) ranges, despite their high charge density. There are many reports describing unconventionally low T_g of PILs, even as low as −60°C[45].

The chemical nature of PILs determines their solubility in many types of organic solvents, from polar to non polar. The nature of the anion plays a key role in defining the solubility of PILs. This is why PILs with the same cationic backbone structure but different anions can be soluble in different solvents[44].

The concept of PILs is based on the traditional route of their synthesis - polymerization of particular ionic liquid monomers (Fig. 4).

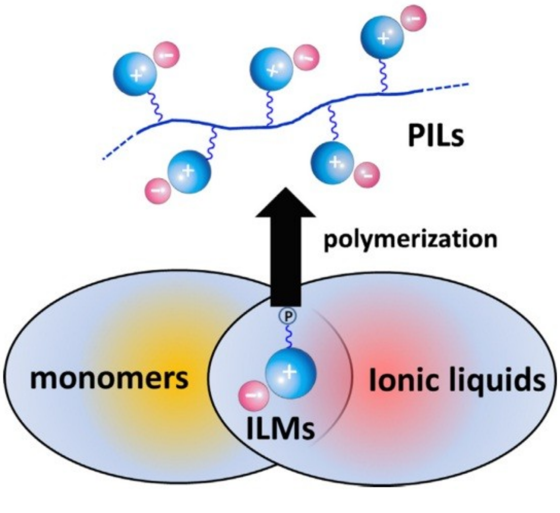


Fig. 4 Illustration of the relationship between ILs and PILs[44].

Therefore, PILs, similar to common polymers, are derived from corresponding monomers. The physical properties of PILs and ILs are sometimes closely but not necessarily related to each other.

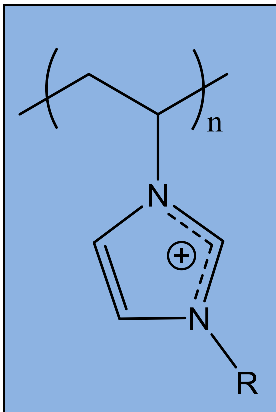
2.1 Properties

In analogy to the case of ILs, PILs are finding applications in many different technological fields. The interest in polymeric ionic liquids comes from the possibility to extend the properties and classical applications of polyelectrolytes. This is giving a rise to a new family of functional polymers with particular properties and new applications. Some of this properties are described below.

2.1.1 Solubility

A strong influence of the nature of the counter-anion on PILs solubility behaviour has been found. This behaviour is seen, for example, in poly(1-vinyl-3-ethylimidazolium) X^- where the halide anion (Cl^-, Br^- and I^-) is soluble in water but when the anion is substituted by $[BF_4]^-$, $[PF_6]^-$, $[CF_3SO_3]^-$ or $[(CF_3SO_2)_2N]^-$ the polymer is not soluble in water anymore but becomes soluble in some organic solvents [13] (Table 1).

Table 1 Solubility of poly(1-vinyl-3-ethylimidazolium) X^- in different solvents[13].

	X^-	H_2O	MeOH	Acetone	THF
	Br^-	+	+	−	−
	$[BF_4]^-$	−	±	+	−
	$[PF_6]^-$	−	−	+	−
	$[CF_3SO_3]^-$	−	+	+	−
	$[(CF_3SO_2)_2N]^-$	−	−	+	+

(+ = Soluble , − = Insoluble, ± = Partly soluble, R = Et)

A similar behaviour has been shown independent of the type of PILs having imidazolium, alkylammonium or pyridinium cationic backbones[46].

The behaviour of PILs in solution is expected to have similarities to those one of polyelectrolytes. Conventional polyelectrolytes in aqueous solution show repulsive electrostatic interactions among ionic groups, which leads to a viscoelastic behaviour. Polyelectrolytes in solution show rheological properties extremely different from neutral solutions of polymers. Normally the chains of polyelectrolytes are set far apart from each other due to repulsive interactions. The polymer coil expands as the polymer concentration decreases. In the presence of added salts, the polyelectrolytes behave like non-ionic polymers and chain expansion is not observed. This is known as the "polyelectrolyte effect". For PILs it is still unknown whether they show a similar solution behaviour in organic solvents than polyelectrolytes in water or if they behave as neutral polymers[13].

2.1.2 Thermal stability and glass transition temperature (T_g)

PILs are often considered to be highly thermo-stable polymers. However, in direct comparison to the corresponding IL species, their thermal stability is limited by the chemical structure of the polymer backbone. PILs will undergo depolymerization, scission, or thermal degradation at some temperatures that the ionic liquids can survive. To be able to overcome this limitation, the basis of the main chain needs to be carefully designed bearing in minds its thermostability [44].

On the other hand thermal stability of PILs is also defined by the counter-anion. The influence of the counter-anion is observed for example when studying the thermal stability of the solid polymers. Figure 5 shows the thermo gravimetric analysis (TGA) of poly(1-vinyl-3-ethylimidazolium) X^-[13]. It is clearly seen that anion structure influences the thermal stability in the order $[CF_3SO_3]^- > [(CF_3SO_2)_2N]^- > [C_{12}H_{25}C_6H_4SO_3]^- > [PF_6]^- > [Br]^- > [C_{16}H_{34}PO_4]^-$.

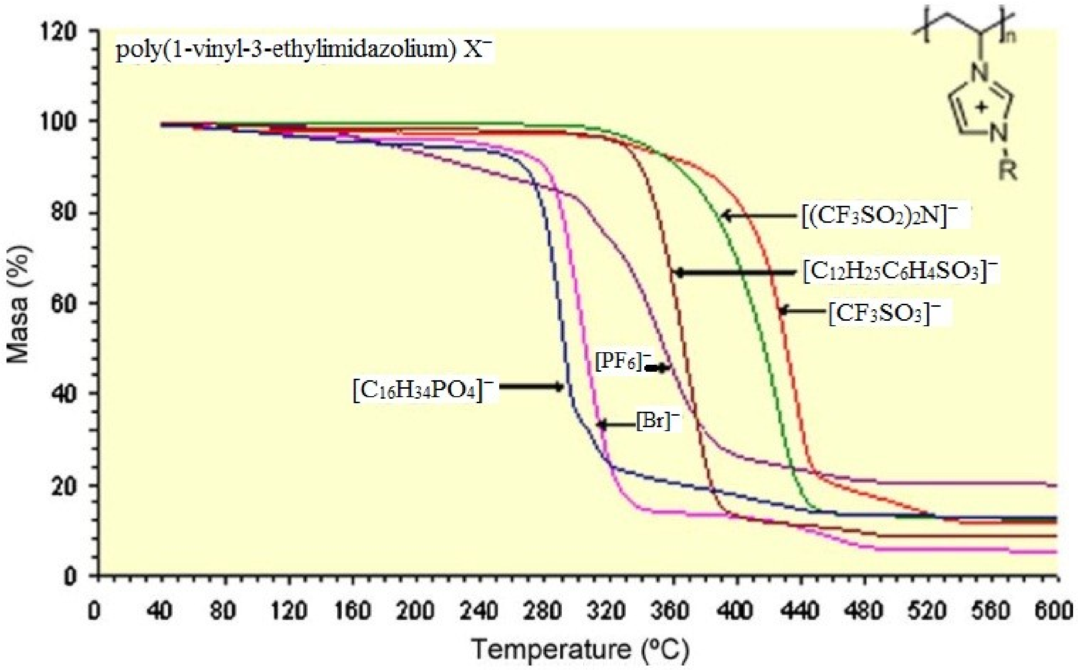


Fig. 5 TGA of poly(1-vinyl-3-ethylimidazolium) X^- at a heating rate of 10°C/min under nitrogen atmosphere[13].

The glass transition temperature (T_g), similarly to T_m, of PILs depends on the chemical composition of the polymer backbone together with the type of counter-anion. In literature are found different example that describe this behaviour, for example the glass transition temperature of poly(1-vinyl-3-ethylimidazolium) X^- is 19°C when the X^- counter anion was $[(CN)_2N]^-$, 60°C for $[(CF_3SO_2)_2N]^-$, 173°C for $[CF_3SO_3]^-$ and 235°C for Br^- [47].

In general, the temperature affects the ion mobility and there is a dependence of the polymer electrolytes conductivity with the rise of the temperature. An increase in the temperature creates a fast movement of the ions and consequently an increase in the ion conductivity. On the other hand, since polymeric materials are malleable with the increase in pressure the general free volume for the ion mobility will be reduced and consequently the same for the PIL's conductivity.

2.1.3 Conductivity

Ion conductivity is a fundamental and the most interesting to explore physical property of PILs. They may avoid some of the disadvantages of liquid electrolytes, such as leakage and flammability, in the application areas of batteries and fuel cells. Moreover, the nature of PIL allows the production of ion-conductive materials with defined size, shape and geometry, such as thin films, fibers, coatings and even complete circuits[44].

The polymerization of IL monomers in general results in lower ionic conductivity compared to the corresponding IL monomers. This is because of both the considerable increase in glass transition temperature and covalent bonding of the polymerizable ions which reduces the number of mobile ions [46]. Types of IL monomers, cations, anions, the space between the polymerizable group and the cation (for methacryloyl-based IL monomers), the alkyl chain on the imidazolium ring (for N-vinylimidazolium-based IL monomers), the presence of networks, the moisture, etc. all affect the structural parameters of PILs that influence their ion conductivity.

2.1.4 Processability and water sensibility

Taking advantage of their polymer nature, PILs can be easily manufactured via some classical polymer processing methods, such as extrusion, spin coating and electrospinning.

Also the water sensitivity is a common characteristic of ILs and PILs. Absorbed water is not always beneficial for processing and practical applications. Obviously, the conductivity is affected by the presence of water. To remove moisture from ILs high temperatures and vacuum conditions should be applied due to affinity of some ILs towards water molecules. However various established purification techniques for polymers can be used for PILs and simplify this process. For example, the freeze-drying or precipitation of PILs from their solution into a water miscible organic solvent can largely remove the water trapped in the PILs[44]. If necessary this procedure can be repeated a few times to remove residual moisture or a foamy precipitate can be dried at high temperatures and under vacuum conditions.

2.2 Synthesis

PILs can be synthesized using two approaches:

1) direct polymerization of ionic liquid monomers (ILMs),

2) incorporation of the IL in the existing polymers.

In each approach the use of common polymerization techniques, such free radical polymerization[25,49], atom transfer polymerization (ATRP)[50], ring opening metathesis polymerization (ROMP), etc. is necessary.

In the case of unsaturated acrylate, acrylamide or vinyl type ionic liquids monomers the polymerization can be performed in bulk[45,51], in solution[52] and in emulsion[53]. Many types of strategies are possible for the polymerization techniques and so offer distinct advantages as well as limitations with respect to molecular features of PILs.

The highly sensitive to impurities IL monomers can be used in a polymerization technique, in which the obtained species are tolerant to impurities and moisture, that is the free radical polymerization technique[33].

2.2.1 Free radical polymerisation

Free radical polymerisation is one of the most popular approaches used in the polymer industry to produce a wide range of polymers. The interest for this technique is linked to the easy chemistry and because it is tolerant to many functional groups and impurities.

The polymerization is defined as radical polymerisation when the kinetic chain carriers are free radicals. A free radical is a molecular fragment obtained from homolytic dissociation of a covalent bond, in which the resulting unpaired electron is not involved in any bond. This unpaired electron makes the free radical highly reactive species. They can add to molecule containing multiple bonds like ethylene, styrene, vinyl chloride, butadiene, etc.[54].

Free radical polymerization is a chain reaction consisting of a sequence of three steps: *initiation*, *propagation* and *termination*.

- *Initiation* step involves two reactions. First the production of primary radical (R*) and second the addition of this formed radical to the monomer (M) molecule to produce the chain-initiating radical (P_1^*) (Scheme 3). The primary radical was obtained by the homolytic dissociation of an initiator species I by thermal, photochemical, or redox methods.

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^*$$

$$\mathrm{R}^* + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1^*$$

Scheme 3 Initiation.

where k_d and k_i are the rate constants for the dissociation and initiation step, respectively.

- *Propagation* consists of the growth of P_1* by the successive additions of large numbers (hundreds and perhaps thousands) of monomers (M). Each addition creates a new radical that has the same identity as the previous one, except that it is larger by one monomeric unit (Scheme 4).

$$\mathrm{P}_n^* + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{(n+1)}^*$$

Scheme 4 Propagation.

where k_p is the rate constant for propagation.

Propagation with growth of the chain to high polymer proportions takes place very rapidly. The value of k_p for most monomers is in the range 10^2–10^4 L mol^{-1} s^{-1}.

- *Termination* is the annihilation of the radical centers which occurs by bimolecular reaction between radicals. Two radicals react with each other by combination (coupling) (Schema 5a) or, more rarely, by disproportionation (Schema 5b). Termination can also occur by a combination of coupling and disproportionation.

a. $$\mathrm{P}_n^* + \mathrm{P}_m^* \xrightarrow{k_{tc}} \mathrm{P}_{(n+m)}$$

b. $$\mathrm{P}_n^* + \mathrm{P}_m^* \xrightarrow{k_{td}} \mathrm{P}_n + \mathrm{P}_m$$

Scheme 5 **a**)Coupling and **b**)disproportionation.

where k_{tc} and k_{td} are the rate constants for termination by coupling and disproportionation, respectively. The termination step can be also expressed by Scheme 5c

$$P_n^* + P_m^* \xrightarrow{k_t} \textit{ending polymer}$$

Scheme 5c Termination.

where k_t is rate constant for the termination step, and is described in Eq. 2.1

$$k_t = ak_{tc} + (1 - a)k_{td}$$

Eq 2.1 Rate constant of the termination step[55].

where a and $(1-a)$ are the fractions of termination by coupling and disproportionation, respectively. The term *ending polymer* means the cessation of growth for the propagating radical.

Typical termination rate constants are in the range of 10^6–10^8 L mol^{-1} s^{-1} or orders of magnitude greater than the propagation rate constants. The much greater value of k_t (whether k_{tc} or k_{td}) compared to k_p does not prevent propagation because the radical species are present in very low concentrations and because the polymerization rate is dependent on the one-half power of k_t only.

In a polymerizations reaction the kinetic rate is a fundamental guideline to determine the yields of polymer. Furthermore, it allows to an understanding of the relation of conversion-time and the tendency of molecular weight distribution.

2.2.2 Preparation of ionic liquid monomers

An ILM is an ionic liquid that contains in its chemical structure one or more polymerizable units. It is possible to describe five basic forms of ILMs (Fig. 7). The polymerizable unit can be located either on the cation (Fig. 7A) or anion (Fig. 7B). ILMs with two polymerizable units separated on the cation and anion (Fig. 7C), or located on the cations (Fig. 7D and E) already built into a PIL networks.

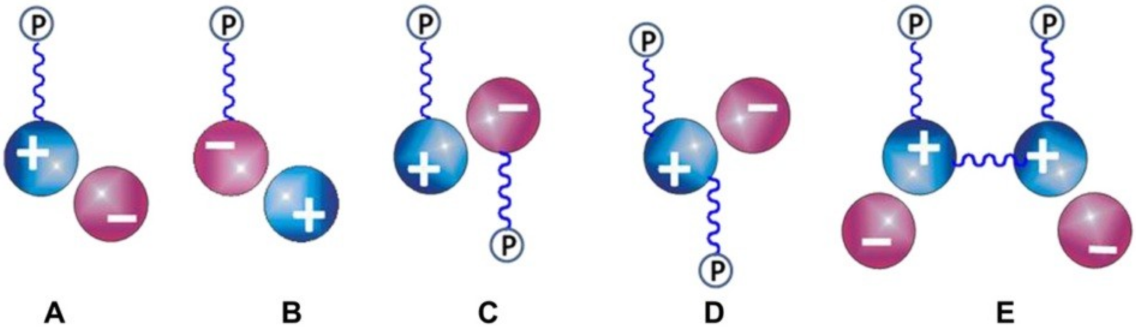
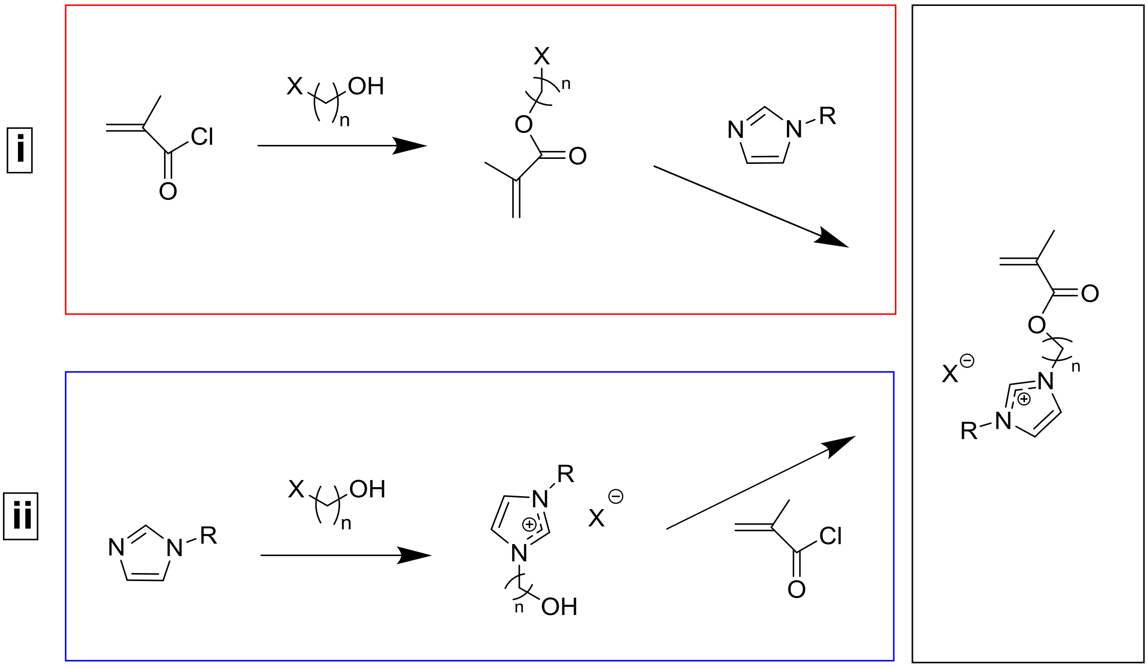


Fig. 7 Basic stuctures of ILMs. “P” represents a polymerizing unit in an ILM [25].

The IL monomer with a polymerizable unit on the cation (Fig. 7A) is the dominant and the most studied precursor of PILs. In free radical polymerizations the cation unit of ILMs can have one of three standard forms: acrylate/methacrylate, acrylamide or vinyl group based. The synthesis of acryloyl/(meth)acryloyl functionalized ILMs is accomplished through two different synthetic routes, as illustrated in Scheme 6.



Scheme 6 Synthetic routes for acryloyl/(meth)acryloyl functionalized ILMs [25,56].

i. In the first synthetic method – firstly, the (meth)acryloyl group is introduced by esterification of a hydroxyl-containing haloalkane with (meth)acryloyl chloride. In the second step, the ester reacts with N-alkyl imidazole molecule by nucleophilic substitution and the product is on IL monomers with a dialkylimidazolium cation covalently connected to the (meth)acrylate part.

ii. In the second synthetic method, the ionic liquid is produced by simple nucleophilic substitution between N-alkyl imidazole molecule with hydroxyl-containing haloalkane. Following the (meth)acryloyl group addition by esterification of (meth)acryloyl chloride with ionic liquid.

The last step for the routes i and ii is the polymerization similar to other common (meth)acrylates in the presence of initiators, such as 2,2'-azobis(2-methylpropionitrile) (AIBN).

In literature, wide attention has been paid to these kind of IL monomers[4,45]. Hence, each review treat acrylate/methacrylate with different variables which allow the chemical and physical proprieties of IL monomers to be modulated [2,4,44,45,57]:

1) the spacer between the (meth)acryloyl and imidazolium groups,

2) the alkyl chain on the imidazolium ring, and

3) the anion.

3 Aim of this study

The main goal of this study is the polymerization of the ionic liquid monomer, [(acryloyloxy)$^6C_6C_1$im][NTf_2] (Fig.8).

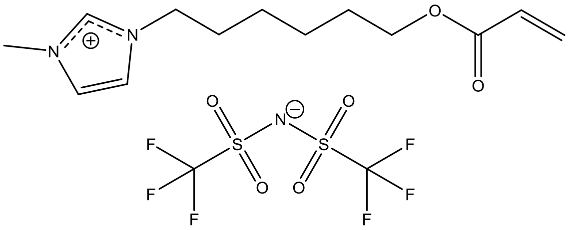
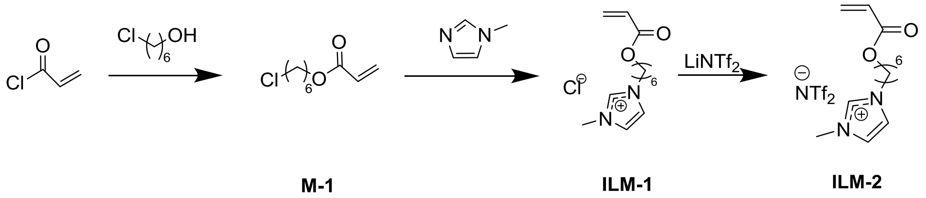


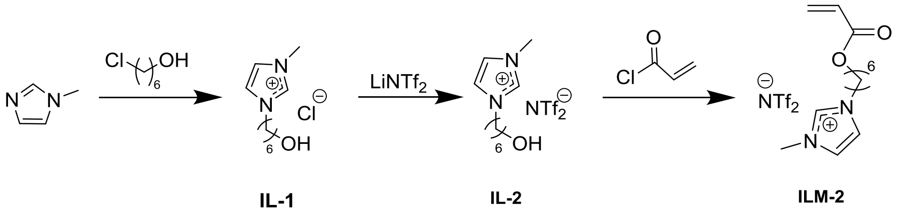
Fig. 8 [(acryloyloxy)$^6C_6C_1$im][NTf_2].

In order to obtain [(poly-acryloyloxy)$^6C_6C_1$im][NTf_2] it is needed to synthesise the corresponding ILM. For this reason I focused my attention on the study of the optimal route to synthesise polymerisable [(acryloyloxy)$^6C_6C_1$im][NTf_2].
Two different synthetic methods were investigated. The first one started with the synthesis of 6-chlorohexyl-acrylate (M-1) and consequent reaction of M-1 with methylimidazole producing ILM-1, which finely undergo anion substitution which resulted in synthesis of desired ILM-2 (Scheme 7).



Scheme 7 First synthetic route[2,58].

On the other hand, the second route started with synthesis of the corresponding amide ionic liquid which the was esterificated in order to produced ionic liquid monomer (ILM-2) (Scheme 8).



Scheme 8 Second synthetic route[56].

This study also considered the formation of product and by-products for each route in order to apply all available data to determine the optimal/smartest synthetic route for the desired cationic PIL.

4 Experimental

In this chapter, two different synthetic routes which were applied to produce ILMs followed by polymerization are described. All products that were obtained are synthesised following established protocoles[2,56–58].

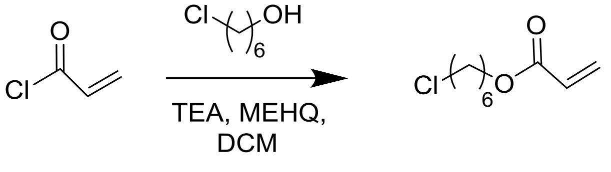
4.1 Materials and methods

1-Methylimidazole (≥ 99%, Fluka) was dried in vacuum distillation over KOH (85-100.5%, Aldrich). Acryloyl chloride (≥ 97%, Aldrich), 6-bromo-1-hexanol (≥ 97%, Aldrich), 6-chloro-hexanol (96%, Aldrich) were used without further purification. Reagent-grade chloroform (≥ 99.0-99.4%, Aldrich), dichloromethane (≥ 99%, Aldrich), diethyl ether (≥ 99.5%, Aldrich), acetonitrile (99.8%, Aldrich), methanol (99,8%; Aldrich) and ethyl acetate (99,8%; Aldrich) were used without further purification; while 1,4-dioxane (99,8%; Aldrich) and tetrahydrofuran (≥ 99%, Aldrich) were distilled under an inert atmosphere over potassium (99.15%, Aldrich) and benzophenone (≥ 99%, Aldrich). 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich), triethylamine (99%, Aldrich), hydrochloric acid (min. 37%, Aldrich), sodium sulphate anhydrous (Aldrich), lithium bis(trifluoromethylsulfonyl)amide (≥ 99%, Aldrich), 4-methoxyphenol (MEHQ, 99%, Aldrich), silver nitrate (99%, Aldrich) and sodium chloride were used without further purification.

^{1}H and ^{13}C NMR spectra were obtained on a Oxford AS400 and a Varian Gemini 400 spectrometers operating at 400MHz. All NMR data were processed using ACDLABS 12.0 software. All chemical shift are reported in ppm (δ) relative to deuterated dimethyl sulfoxide (DMSO-d_6), referenceto the chemical shift. The following abbreviation were used for NMR peak multiplicities: s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet.
Mass spectrometry was carried out using a Waters MicroMassZQ 4000.

4.2 First synthetic route

4.2.1 6-Chlorohexyl-acrylate, (**M-1**).



M-1

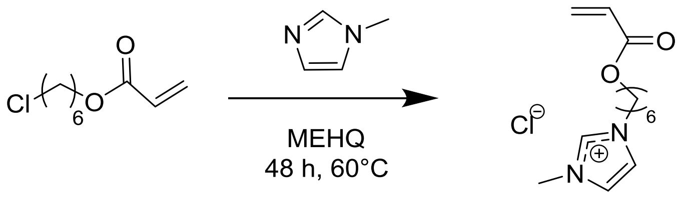
Schema 9 Esterification of acryloyl chloride[58].

A solution of 6-chloro-hexanol (6.83 g, 50 mmol), triethylamine (15 mL, 108 mmol) and a small amount of 4-methoxyphenol (MEHQ) in dichloromethane (25 mL) were cooled down to 0°C. Then diluted in dichloromethane (25 mL) acryloyl chloride (6.68 g, 50 mmol) was added to the solution dropwise while vigorously stirring and maintaining the temperature close to 0°C. The system was maintained under a nitrogen flow. After 30 min the resulting orange-coloured mixture was filtered, washed successively with 2x12.5 mL of 1 M hydrochloric acid and 2x25 mL of distilled water. For each washing 1mL of brine (saturated aqueous solution of sodium chloride) was added. Then the organic layer was dried with sodium sulphate and the solvent was evaporated under vacuum to obtain an orange liquid which claimed to be 6-chlorohexyl-acrylate.
Yield: 8.91 g, 93%.

^{1}H NMR (400 MHz; DMSO-d_6), δH: 6.33 (dd, 1H, ***H***−CH=CH−), 6.17 (dd, 1H, CH_2=C***H***−), 5.93 (dd, 1H, H−C***H***=CH−), 4.10 (t, 2H, CO_2−C***H***$_2$−), 3.62 (t, 2H, −C***H***$_2$−Cl), 1.72 (m, 2H, −C***H***$_2$−), 1.62 (m, 2H, −C***H***$_2$−), 1.46-1.30 (m, 4H, −C***H***$_2$−).

^{13}C NMR (400 MHz; DMSO-d_6), δC: 165.7 (***C***=O), 131.4 (***C***H_2=CH−), 128.3 (CH_2=***C***H−), 64.3 (CO_2−***C***H_2−), 45.2 (−***C***H_2−Cl), 29.3 (−***C***H_2−), 30.8 (−***C***H_2−), 26.5 (−***C***H_2−), 24.9 (−***C***H_2−).

4.2.2 3-(6-(Aryloyloxy)hexyl)-1-methyl-1*H*-imidazol-3-ium chloride, [(acryloyloxy)^{6}C$_6$C$_1$im]Cl (**ILM-1**).



M-1 **ILM-1**

Scheme 10 Nucleophilic substitution[2].

To M-1 (4.94 g, 26 mmol), at room temperature, a small amount of MEHQ was added and the 1-methylimidazole (1.77 g, 21 mmol) was added dropwise under a flow of nitrogen. The reaction was heated at 60°C for 48 h. The obtained viscous crude material was dissolved in a smaller volume of chloroform, filtered and precipitated a minimum of two times in diethyl ether. Finally, the solvent was evaporated and the orange viscous oil was dried under vacuum.

Yield: > 1%.

^{1}H NMR (400 MHz; DMSO-d$_6$), δH: 9.19 (s, 1H, N−C***H***−N), 7.79 (t, 1H, N−C***H***=CH), 7.72 (t, 1H, CH=C***H***−N), 6.32 (dd, 1H, ***H***−CH=CH−), 6.16 (dd, 1H, CH$_2$=C***H***−), 5.94 (dd, 1H, H−C***H***=CH−), 4.16 (t, 2H, CO$_2$-C***H***$_2$−), 4.10 (t, 2H, −C***H***$_2$−N), 3.85 (s, 3H, N−C***H***$_3$), 1.79 (m, 2H, −C***H***$_2$−), 1.61 (m, 2H, −C***H***$_2$−), 1.41-1.21 (m, 4H, −C***H***$_2$−).

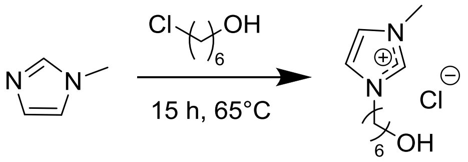
^{13}C NMR (400 MHz; DMSO-d$_6$), δC: 165.5 (***C***=O), 136.6 (N−***C***H−N), 131.4 (***C***H$_2$=CH−), 128.4 (CH$_2$=***C***H−), 123.5 (N−***C***H=CH), 122,3 (CH=***C***H−N), 63.9 (CO$_2$-***C***H$_2$−), 48.6 (−***C***H$_2$−N), 35.7 (N−***C***H$_3$), 29.2 (−***C***H$_2$−), 27.8 (−***C***H$_2$−), 25.1 (−***C***H$_2$−), 24.7 (−***C***H$_2$−).

m/z: (ESI$^+$) 237 ([(acryloyloxy)^{6}C$_6$C$_1$im]$^+$, 100%).

(ESI$^-$) 35 (Cl$^-$, 100%).

4.3 Second synthetic route

4.3.1 3-(6-Hydroxyhexyl)-1-methyl-1H-imidazol-3-ium chloride, $[(HO)^6C_6C_1im]Cl$ (**IL-1**).



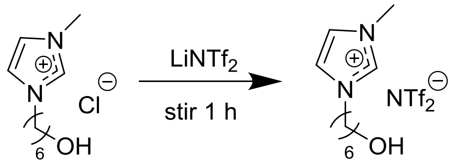
IL-1

Scheme 11 Nucleophilic substitution[56].

6-Chloro-hexanol (4.00 g, 29 mmol) was added dropwise under a flow of nitrogen to 1-methylimidazole (2.21 g, 27 mmol) at room temperature. The temperature was then increased to 65°C and the solution left to stir for 15 h. After cooling to room temperature the obtained crude material was washed with 11x10 mL of diethyl ether. The produced IL was dried at 65°C in high vacuum overnight to obtain a transparent oil.
Yield: 3.60 g, 61%.

^{1}H NMR (400 MHz; DMSO-d_6), δH: 9.30 (s, 1H, N−C***H***−N), 7.82 (t, 1H, N−C***H***=CH), 7.75 (t, 1H, CH=C***H***−N), 4.45 (bs, 1H, −O***H***), 4.17(t, 2H, $-CH_2-OH$), 3.87 (s, 3H, $N-CH_3$), 3.38 (t, 2H, $-CH_2-N$), 1.78 (m, 2H, $-CH_2-$), 1.46-1.18 (m, 6H, $-CH_2-$).

4.3.2 3-(6-Hydroxyhexyl)-1-methyl-1*H*-imidazol-3-ium bis((trifluoromethyl)sulfonyl)amide, $[(HO)^6C_6C_1im][NTf_2]$ (**IL-2**).



IL-1 **IL-2**

Scheme 12 Metathesis of IL-1[56].

A solution of lithium bis(trifluoromethylsulfonyl)amide (3.45 g, 12 mmol) in 10 mL of distilled water was added to a solution of IL-1 (2.21 g, 10 mmol) in 15 mL of distilled water. After stirring for 2 h at room temperature the aqueous layer was separated with 4x10 mL of dichloromethane. The organic layer was dried over anhydrous sodium sulphate anhydrous. The absence LiCl in the product was confirmed by the silver nitrate test to aqueous layer. Finally, the solvent was evaporated using a rotary evaporator and the transparent product was dried in high vacuum at 65°C overnight.
Yield: 4.36 g, 94%.

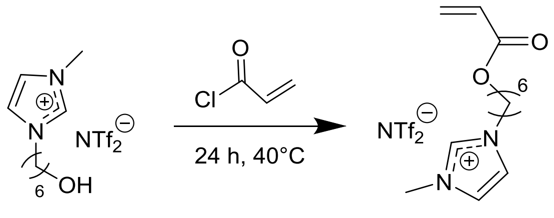
^{1}H NMR (400 MHz; DMSO-d_6), δH: 9.10 (s, 1H, N−C***H***−N), 7.76 (t, 1H, N−C***H***=CH), 7.69 (t, 1H, CH=C***H***−N), 4.35 (bs, 1H, −O***H***), 4.15 (t, 2H, −C$\boldsymbol{H}_2$−OH), 3.85 (s, 3H, N−C$\boldsymbol{H}_3$), 3.38 (t, 2H, −C$\boldsymbol{H}_2$−N), 1.78 (m, 2H, −C$\boldsymbol{H}_2$−), 1.48-1.18 (m, 6H, −C$\boldsymbol{H}_2$−).

^{13}C NMR (400 MHz; DMSO-d_6), δC: 136.5 (N−***C***H−N), 123.6 (N−***C***H=CH), 122,2 (CH=***C***H−N), 119.5(q, −***C***F$_3$, J^{C-F} = 321.4 Hz), 60.5 (HO-***C***H$_2$−), 48.7 (−***C***H$_2$−N), 35.7 (N−***C***H$_3$), 32.2 (−***C***H$_2$−), 29.4 (−***C***H$_2$−), 25.4 (−***C***H$_2$−), 24.8 (−***C***H$_2$−).

^{19}F NMR (400 MHz; DMSO-d_6), δF: −78.8 (s, −C$\boldsymbol{F}_3$).

m/z: (ESI$^+$) 183 ($[(HO)^6C_6C_1im]^+$, 100%),
(ESI$^-$) 280 ($[NTf_2]^-$, 100%).

4.3.3 3-(6-(Acryloyloxy)hexyl)-1-methyl-1*H*-imidazol-3-ium bis((trifluoromethyl)-sulfonyl)amide, [(acryloyloxy)^{6}C$_{6}$C$_{1}$im][NTf$_{2}$] (**ILM-2**).



IL-2 **ILM-2**

Scheme 13 Esterification of IL-2[56].

IL-2 (3.69 g, 7.96 mmol) was slowly added dropwise at 0°C to the acryloyl chloride (0.81 g, 8.25mmol). The stirring was continued at 0°C for 1 h, then the temperature was increased to 40°C and the solution left stirring for 24 h. The obtained oil was thoroughly washed with 6x15 mL of diethyl ether. After evaporation of all the ether the obtained pail yellow oil was dissolved in 20 mL of distilled water and stirred for 1 h a solution of lithium bis(trifluoromethylsulfonyl)amide (1.50 g, 12 mmol) in 10 mL of distilled water. Then a bi-phase solution was obtained by addition of 4x20 mL of dichloromethane. The organic layer was dried over sodium sulphate anhydrous. The silver nitrate test was performed to confirm the absence of LiCl in the obtained ILM. At last the solvent was evaporated on a rotary evaporator and the obtained pale yellow oil was dried in high vacuum at 65°C overnight.

Yield:1.65 g, 40%.

^{1}H NMR (400 MHz; DMSO-d$_{6}$), δH: 9.07 (s, 1H, N−C***H***−N), 7.74 (t, 1H, N−C***H***=CH), 7.68 (t, 1H, CH=C***H***−N), 6.32 (dd, 1H, ***H***−CH=CH−), 6.16 (dd, 1H, CH$_{2}$=C***H***−), 5.94 (dd, 1H, H−C***H***=CH−), 4.13 (t, 2H, CO$_{2}$−C***H***$_{2}$−), 4.08 (t, 2H, −C***H***$_{2}$−N), 3.82 (s, 3H, N−C***H***$_{3}$), 1.78 (m, 2H, −C***H***$_{2}$−), 1.60 (m, 2H, −C***H***$_{2}$−), 1.40-1.21 (m, 4H, −C***H***$_{2}$−).

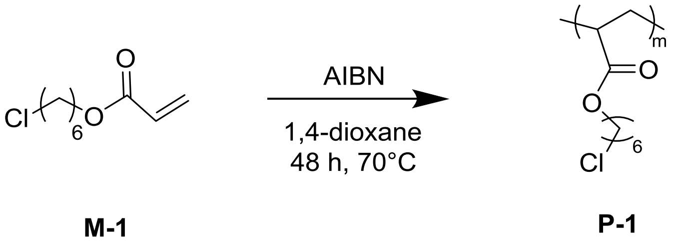
^{13}C NMR (400 MHz; DMSO-d$_{6}$), δC: 165.9 (***C***=O), 136.9 (N−***C***H−N), 131.7 (***C***H$_{2}$=CH−), 128.8 (CH$_{2}$=***C***H−), 124.0 (N−***C***H=CH), 122,7 (CH=***C***H−N), 119.92 (q, −***C***F$_{3}$, $J^{C\text{-}F}$ = 322.1 Hz), 63.5 (CO$_{2}$−***C***H$_{2}$−), 49.1 (−***C***H$_{2}$−N), 36.1 (N−***C***H$_{3}$), 29.6 (−***C***H$_{2}$−), 28.2 (−***C***H$_{2}$−), 25.5 (−***C***H$_{2}$−), 25.1 (−***C***H$_{2}$−).

^{19}F NMR (400 MHz; DMSO-d$_{6}$), δF: −78.4 (s, −C***F***$_{3}$).

m/z: (ESI^{+}) 237 [(acryloyloxy)^{6}C$_{6}$C$_{1}$im]$^{+}$, 100%),
(ESI^{-}) 280 ([NTf$_{2}$]$^{-}$, 100%).

4.4 Polymerization

4.4.1 Poly-6-chlorohexyl acrylate, (**P-1**).

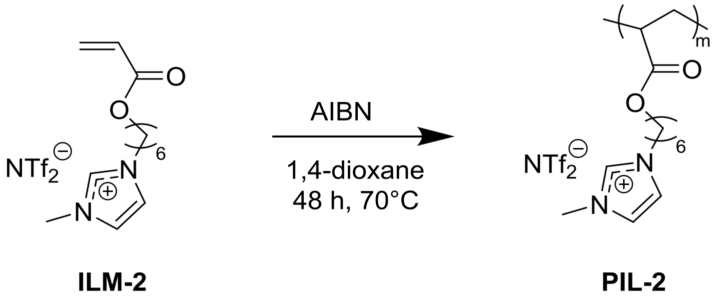


Scheme 14 Polymerization of M-1[58].

In a glass vial M-1 (1.17 g, 6.142 mmol) was dissolved in 6 mL of 1,4-dioxane in the presence of AIBN (0.020 g, 0.1228 mmol). After triple freeze-thaw-pump cycles the vial was sealed under vacuum and heated for 48 h at 70°C. The obtained viscous crude material was dissolved in a small volume of THF and precipitated two times into an excess of methanol. The obtained orange product was dried under high vacuum.

^{1}H NMR (400 MHz; DMSO-d_6), δH: 3.98 (bs, 2H, $CO_2{-}C\boldsymbol{H}_2{-}$), 3.61 (bs, 2H, $-C\boldsymbol{H}_2{-}Cl$), 2.17 (bs, 1H, $-C\boldsymbol{H}$), 1.72 (bs, 2H, $-C\boldsymbol{H}_2{-}$), 1.56 (bs, 2H, $-C\boldsymbol{H}_2{-}$), 1.70-1.20 (bs, 6H, $-C\boldsymbol{H}_2{-}$).

4.4.2 Poly-3-(6-(acryloyloxy)hexyl)-1-methyl-1*H*-imidazol-3-ium bis((trifluoromethyl)sulfonyl)amide, [(poly-acryloyloxy)$^{6}C_6C_1$im][NTf$_2$] (**PIL-2**).



Scheme 15 Polymerization of ILM-2[56,57].

In a glass vial ILM-2 (0.77 g, 1.488 mmol) was dissolved in 2 mL of 1,4-dioxane in the presence of AIBN (0.0048 g, 0.02976 mmol). After triple freeze-thaw-pump cycles the vial was sealed under vacuum and heated for 48 h at 70°C. The obtained viscous crude material was dissolved in a small amount of acetonitrile and precipitated two times into an excess of ethyl acetate. The obtained pale yellow product was dried under high vacuum.

Yield: 0.34 g, 44 %.

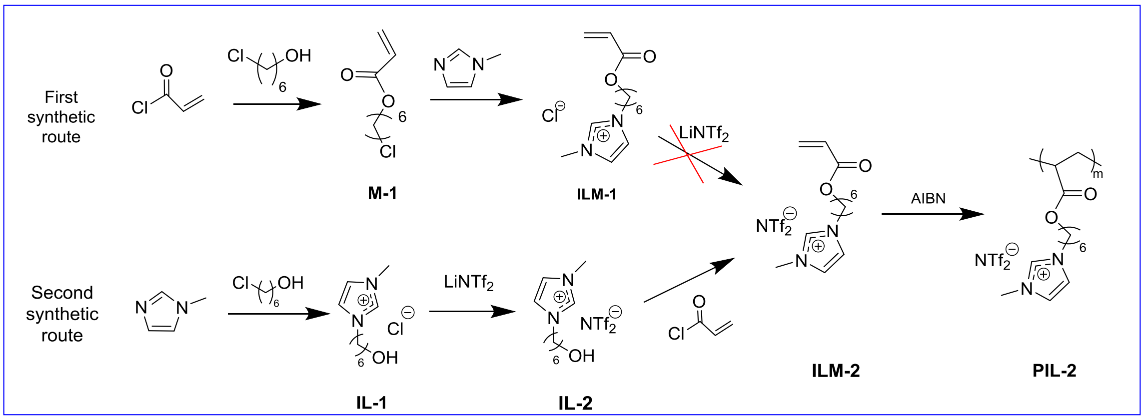
^{1}H NMR (400 MHz; DMSO-d$_6$), δH: 9.04 (bs, 1H, N−C***H***−N), 7.66 (bs, 2H, N−C***H***=C***H***−N), 4.10 (bs, 2H, CO_2-C***H***$_2$−), 3.88 (bs, 2H, −C***H***$_2$−N), 3.83 (bs, 3H, N−C***H***$_3$), 2.13 (bs, 1H, −C***H***) 1.75 (bs, 2H, −C***H***$_2$−), 1.50 (bs, 2H, −C***H***$_2$−), 1.20-1.70 (bs, 6H, −C***H***$_2$−).

^{19}F NMR (400 MHz; DMSO-d$_6$), δF: −78.8 (s, −C***F***$_3$).

5 Results and Discussion

5.1 Synthesis of ionic liquid monomers

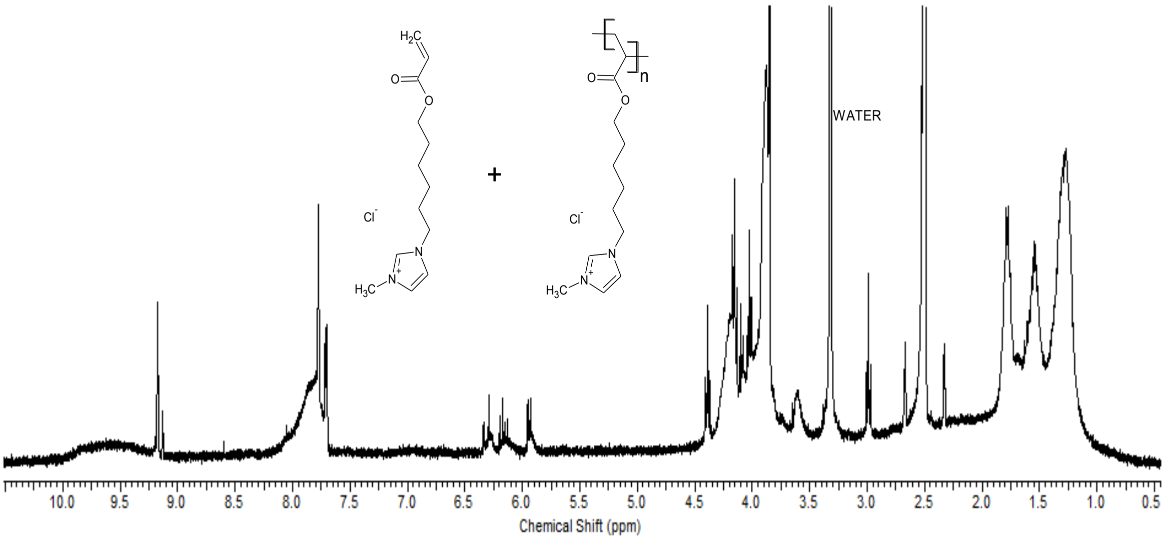
Ionic liquid monomer [(acryloyloxy)^{6}C$_6$C$_1$im][NTf$_2$] (ILM-2) was synthesised via two different routes (Scheme 18). However, the routes did not lead to the same results, due to different issues during the synthesis.



Scheme 18 Synthetic routes for ILM-2[2,56–58].

In fact, in the first synthetic path the metathesis reaction of ILM-1 cannot proceed. This because the resulting ILM-1 influenced the next step. Therefore, I synthesised two ionic liquid monomers which differ by the type of counter-anion: the Cl$^-$ for the first one (ILM-1) and [(CF$_3$SO$_2$)$_2$N]$^-$ for the second one (ILM-2). The counter-anion [(CF$_3$SO$_2$)$_2$N]$^-$ is water-immiscible and affords the utilisation of organic solvent.

In the first synthetic route the monomer, 6-chlorohexyl acrylate (M-1), reacted with an N-alkyl imidazole molecule at 60°C for 48 h. During the synthesis it was possible to see that the orange crude product became more viscous. It is possible to identify the structure of ILM-1 from ^{1}H-NMR spectrum (Spectrum 1) by the very narrow peaks combined with broader signals from other by-products.

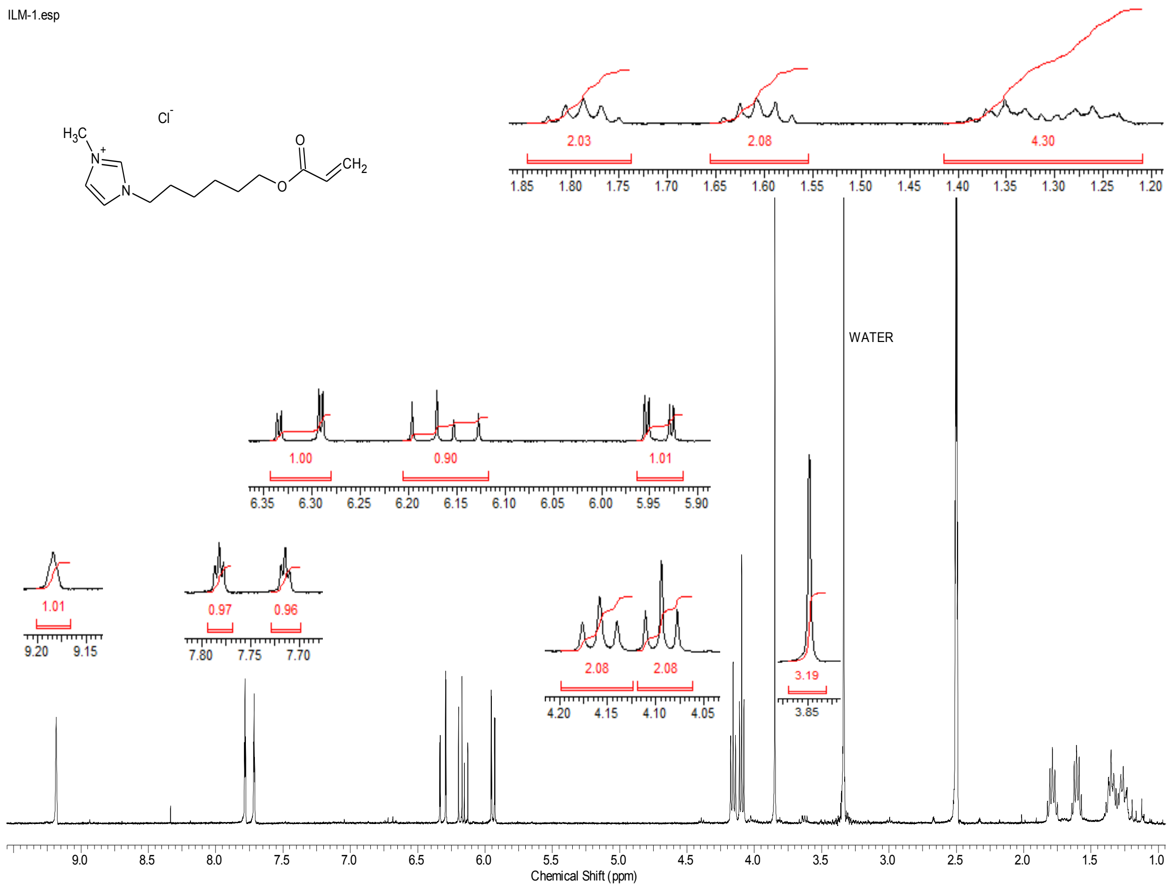


Spectrum 1 ^{1}H-NMR of crude reaction of ILM-1.

This broad signals are in the aliphatic region 1.00 – 2.10 ppm, in the range 3.60 − 4.50 ppm and in the aromatic region, 7.55 – 10.10 ppm. These are a typical polymer signals shape. It is hypothesised that there is a mixture of small amount of ILM-1 and more of polymerised ILM-1. The features of these by-product came from the imidazole broad signals at 7.55 – 10.10 ppm, the signal of methylene bonding with heteroatoms, 3.60 − 4.50 ppm, and the four methylenes of lateral chain, 1.00 – 2.10 ppm. The characteristic weak narrow signals of ILM-1 are the vinyl group in the range of 5.75 – 6.45 ppm while the other are partly covered from the broad signals of polymer.

The explanation of the presence of these broad peaks can be attributed to the operative conditions. Due to the elevated temperature and prolonged reaction time, a homolytic dissociation of the double bond occurred, hence the polymerization of ILM-1 started.

This route clearly results in a low product of the yield (> 1%) (Spectrum 2). The low yield is due to the necessary continuous purification to remove the product from the polymer.

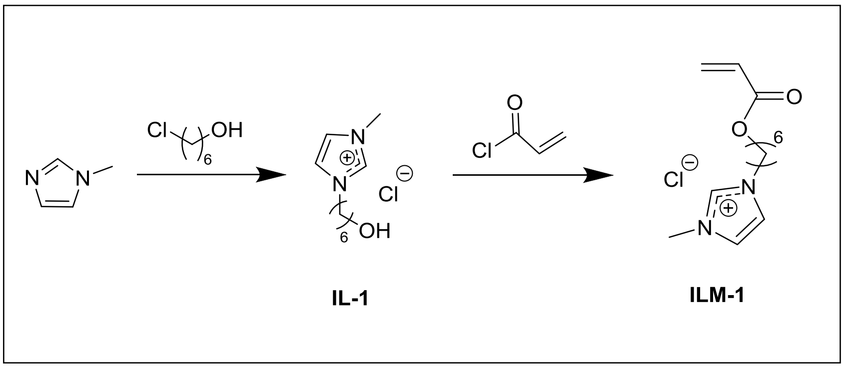


Spectrum 2 ^{1}H-NMR of ILM-1.

From Spectrum 2 we can see:

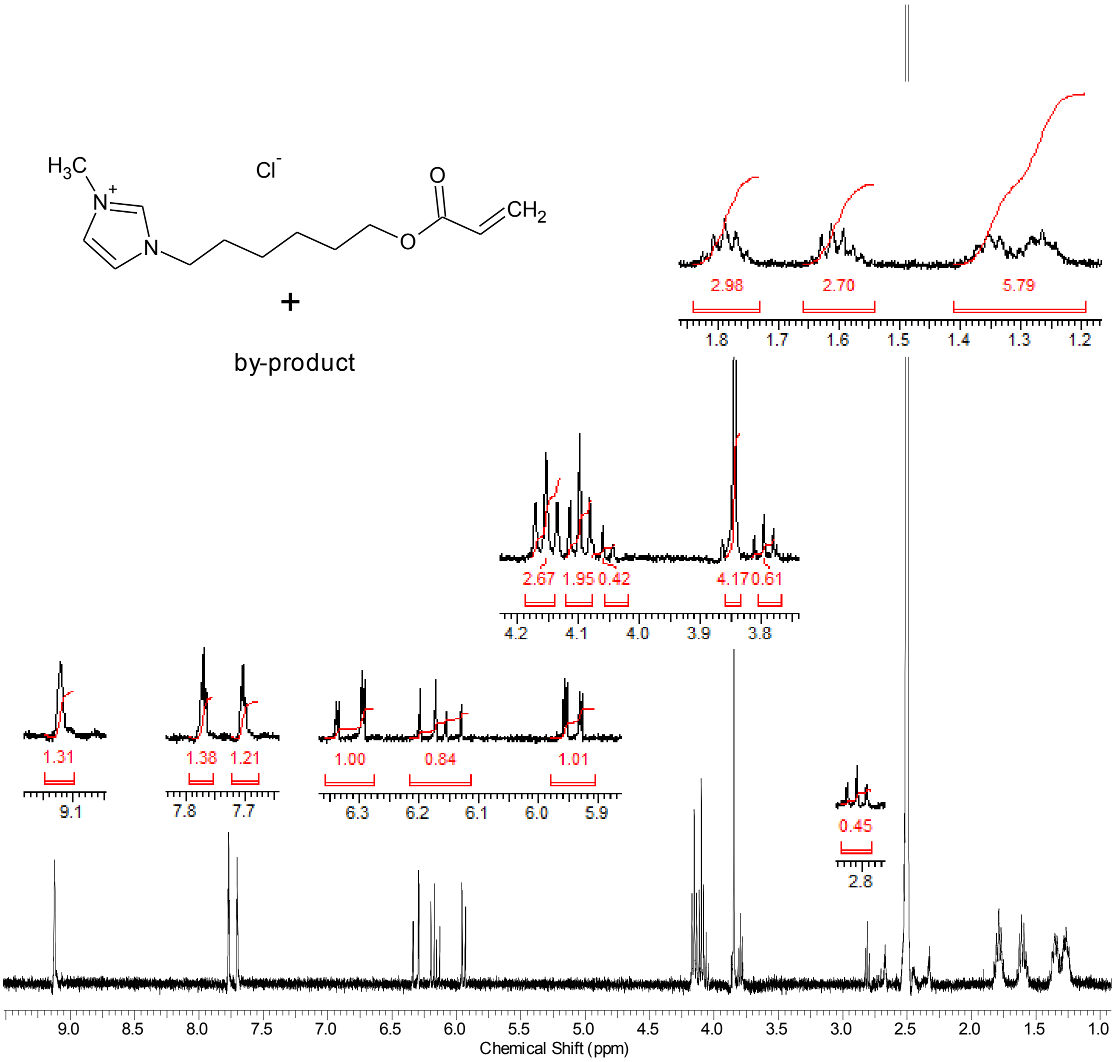
- 7.70 – 9.20 ppm signals of imidazole ring
- 5.90 – 6.35 ppm signals of vinyl group
- 4.05 – 4.20 ppm signals of methylene bonding with heteroatoms
- 3.85 ppm signal of methyl on the imidazole ring
- 1.20 – 1.65 ppm signals of methylene aliphatic chain

In order to solve the problem of purification the same ionic liquid monomer was prepared by applying another synthetic route. The synthesis of ILM-1 was carried out in bulk with the same amount of IL-1 ($[(HO)^6C_6C_1im]Cl$) and acryloyl chloride (Scheme 19). In this route the MEHQ inhibitor was not used.



Scheme 19 Alternative synthetic route for ILM-1.

The results of this synthetic route reinforce the idea about the role of acryloyl chloride and at which synthetic step it should be added. The resulting product was characterised by ^{1}H NMR analysis (Spectrum 3).



Spectrum 3 ^{1}H NMR of ILM-1 by alternative route.

From Spectrum 2 we can see:

- 7.70 – 9.20 ppm signals of imidazole ring
- 5.90 – 6.35 ppm signals of vinyl group.
- 4.05 – 4.20 ppm signals of methylene bonding with heteroatoms and by-product
- 3.85 ppm signal of methyl on the imidazole ring
- 3.75 ppm signal of by-product
- 2.75 ppm signal of by-product
- 1.20 – 1.65 ppm signals of methylene aliphatic chain.

Figure 9 presents ^{1}H NMR analysis of the two ILM-1 obtained by the first (red) and alternative (black) route.

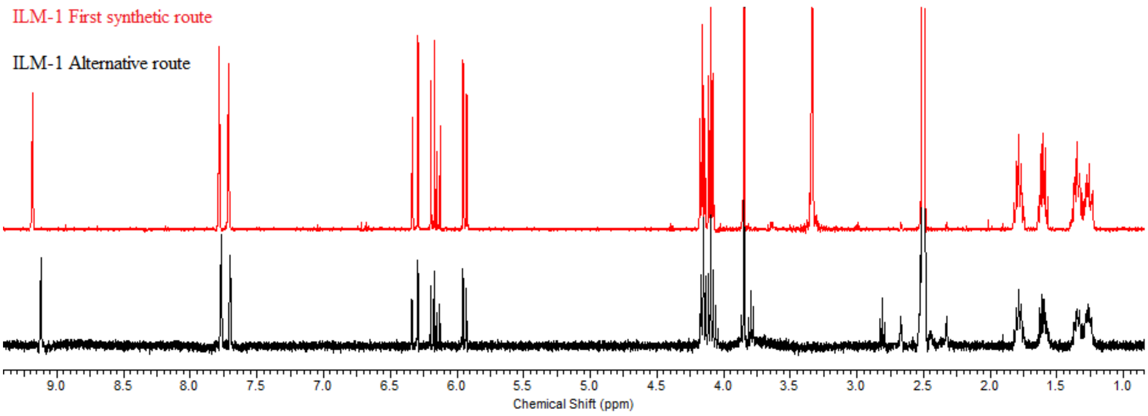


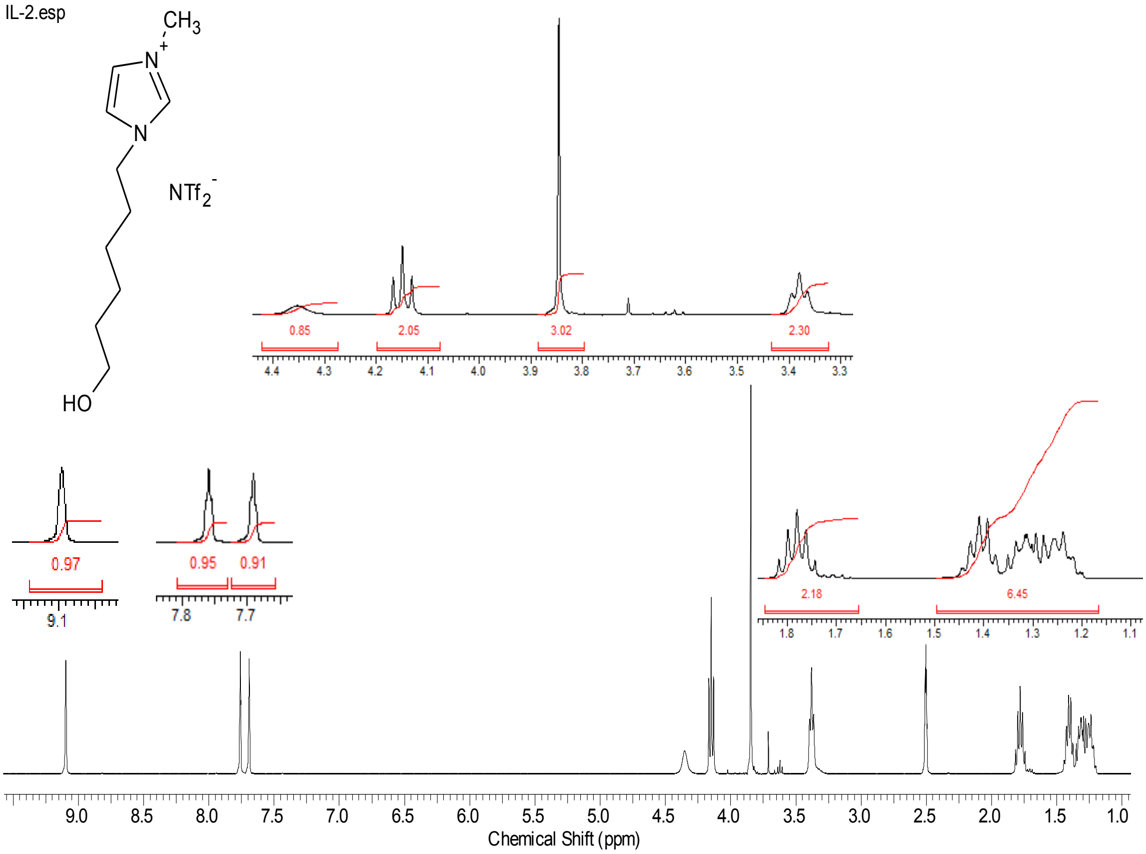
Fig. 9 Comparison ^{1}H NMR analysis of ILM-1(first synthetic route) and ILM-1(alternative route).

The advantage of this alternative route was the amount and the appearance of crude ionic liquid monomer (ILM-1). The amount of product obtained by this alternative route is substantially greater than by the first one. It is a transparent ionic liquid monomer and it's less viscous than the orange product obtain via Scheme 1. However, from ^{1}H-NMR spectra is possible to see two triplets at 2.79 ppm and 3.78 ppm. This signals are related to the presence of by-products which will be explained in the esterification using the second synthetic route (see below).

As it was mentioned above, the addition of acryloyl chloride is a main step where undesirable by-products could be generated. In the second synthetic route the starting material (acryloyl chloride), prone to esterification, was added at the last step after synthesis of ionic liquid (Scheme 13).

At the beginning we synthesised the water-soluble ionic liquid (IL-1) and by metathesis reaction ionic liquid (IL-2) was obtain with the counter anion $[NTf_2]^-$. The metathesis reaction is the most common approach in preparation of water immiscible ionic liquid[33]. The resulting IL-2 was extracted from aqueous solution into dichloromethane (DCM). The presence of chloride ions in the washing solutions can be detected by testing with $AgNO_3$. Although the chloride ion by-product has limited solubility in DCM, it is much more soluble in the ionic liquid/DCM mixture. Thus, when this method was employed, it was important that the DCM extracts were washed with small amounts of water to minimize the chloride ion content in the final product. Generally, anion affects solubility more than cation and $[NTf_2]^-$ anion is hydrophobic (see above).

Both ionic liquids (IL-1 and IL-2) were dried in high vacuum at 65°C overnight to remove traces of moisture. Spectrum 4 reports the water-immiscible ionic liquid after purification. It is possible to confirm that obtained IL was dry by the absence of the water signal (3.33 ppm) .



Spectrum 4 ^{1}H-NMR of IL-2.

From Spectrum 4 we can see:

- 7.65 – 9.15 ppm signals of imidazole ring
- 4.35 ppm signal of hydroxyl
- 4.15 ppm signals of methylene bonding with hydroxyl
- 3.35 ppm signal of methylene bonding with imidazole ring
- 3.85 ppm signal of methyl on the imidazole ring
- 1.20 – 1.85 ppm signals of methylene aliphatic chain

But the most important results came from ^{19}F-NMR, ^{13}C-NMR and ESI^{-} which confirm the substitution of counter anion (Fig. 10) being the mass 280 m/z of $[NTf_2]^-$ from ESI^{-}. Additional information could be obtained by ^{13}C-NMR spectra. In fact, the signals in range (114 – 125) ppm have quartet multiplicity ($J^{C\text{-}F}$ = 321.40 Hz) provides that the central carbon is coupled to the three vicinal fluoride. From ^{19}F-NMR the singlet signal is the features of the interaction between the three fluoride bonding with carbon.

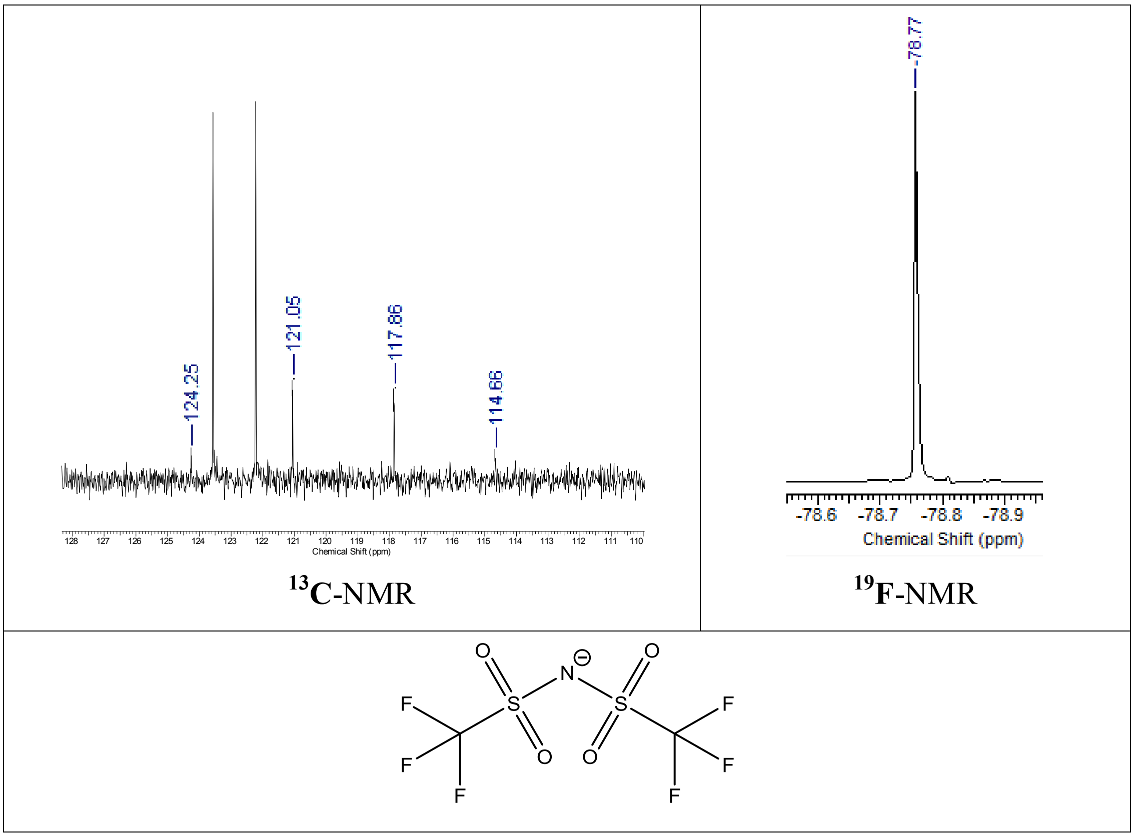
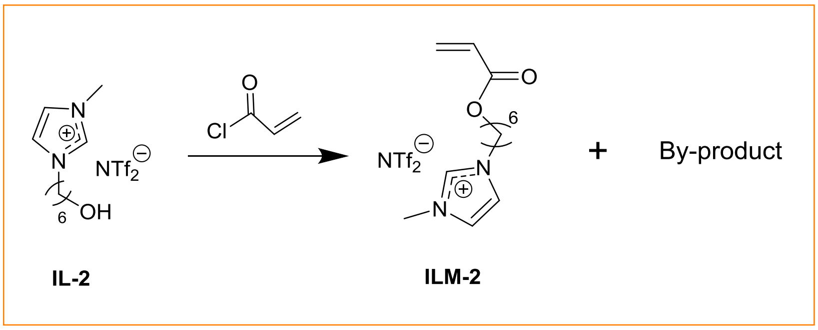


Fig.10 NMR analysis.

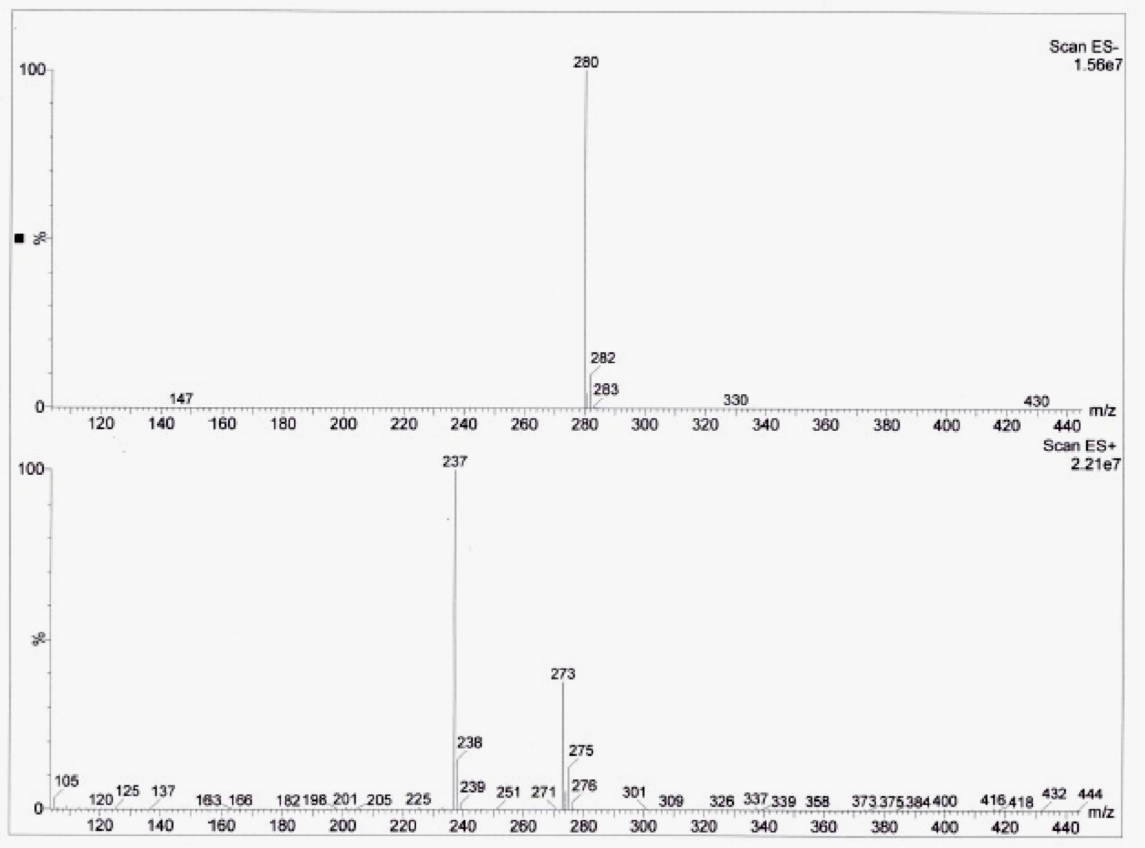
In the last step of the second synthetic route the esterification between IL-2 and acryloyl chloride occurred (Scheme 20). Usually in an esterification reaction, like in the synthesis of 6-chlorohexyl acrylate, triethylamine (TEA) is used to neutralise the forming hydrochloric acid. The neutralization causes a precipitate of the ammonium salt that is filtered and separated from the product. However, in our synthesis we did not used TEA avoiding the precipitation of the salt which would be very hard to remove from the crude product.



Scheme 20 Last step of second synthetic route.

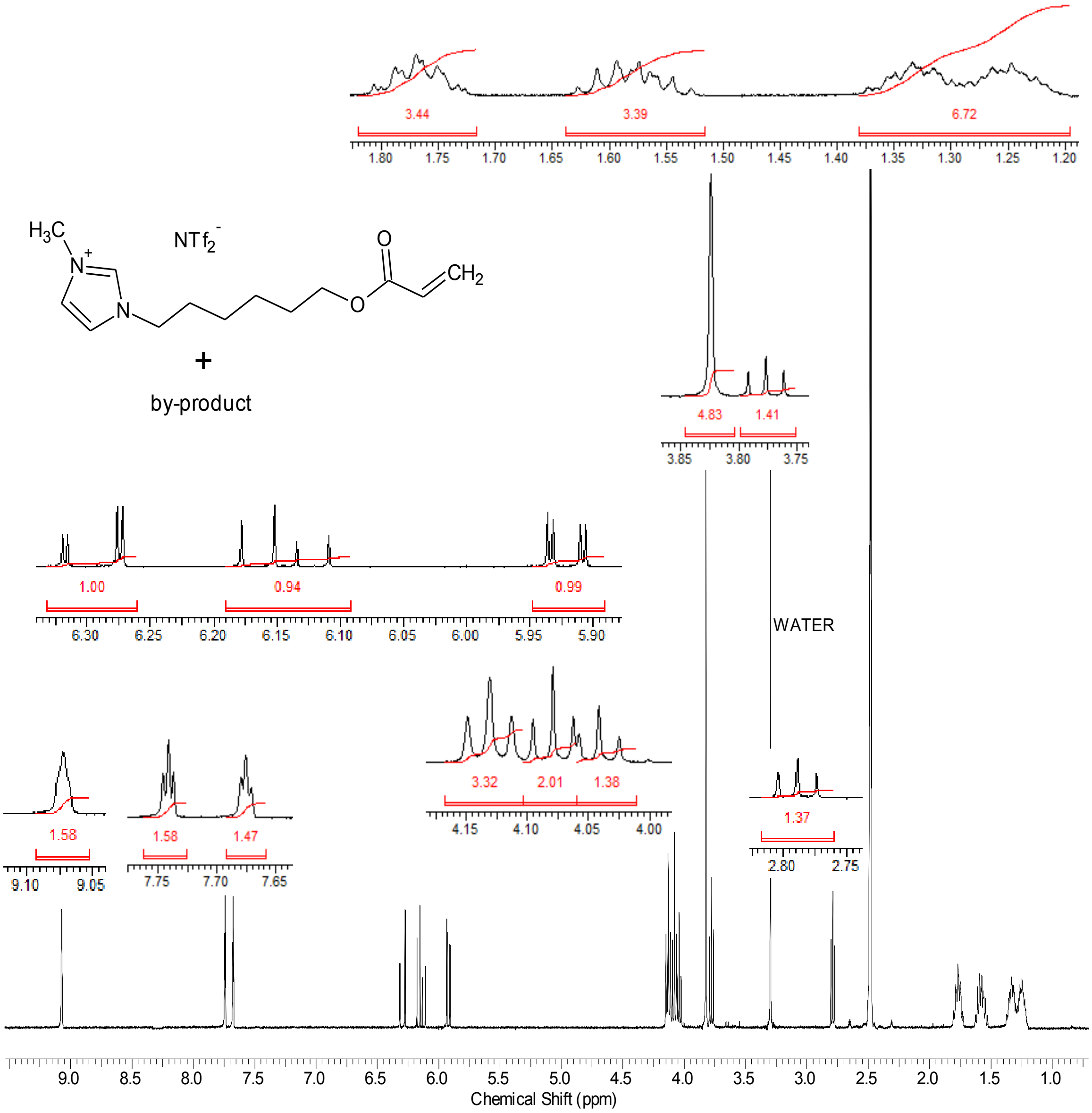
In the crude product of the reaction it is possible to find the desired monomer (ILM-2) with the presence of a by-product. In order to identify this by-product ^{1}H-NMR and mass analysis was performed.

From mass spectrometry (Spectrum 5) it is possible to see the signals of the counter anion $[NTf_2]^-$ (280 m/z) and counter cation $[(acryloyloxy)^6C_6C_1im]^+$ (237 m/z). Furthermore, in the ESI+ spectra the fragment at 273 m/z was found, it can be related to ILM-2 combined with one chloride ion.



Spectrum 5 Mass Spectrometry of ILM-2 and impurities.

In the ^{1}H-NMR analysis (Spectrum 6) the signals of vinyl group range 5.90 − 6.35 ppm were integrated to 1. It is possible to find the presence of by-product by the increase of the other ILM-2s' integrals. From the ^{1}H-NMR spectra the amount ILM-2 is roughly estimated as 60%, while the other 40% are attributed to the by-product.



Spectrum 6 ^{1}H-NMR of ILM-2.

At 2.78 ppm and 3.78 ppm there are two triplet with the same J coupling ($J^{H\text{-}H}$ = 6.25 Hz). It is possible to hypothesise that these two are bonded to heteroatoms, that in our system can be only a chloride (+273 m/z). Bearing in mind this, we could hypothesised that there is a by-product formed from the addition of the hydrochloric acid to the vinyl group leading to a β-connection with the carbonyl. The resulting by-product is 1-(6-((3-chloropropanonoyl)oxy)hexyl)-3-methyl-1H-imidazol-3-ium bis((trifluoromethyl)sulfonyl)amide, which will be referred to as IL-3 (Fig.11).

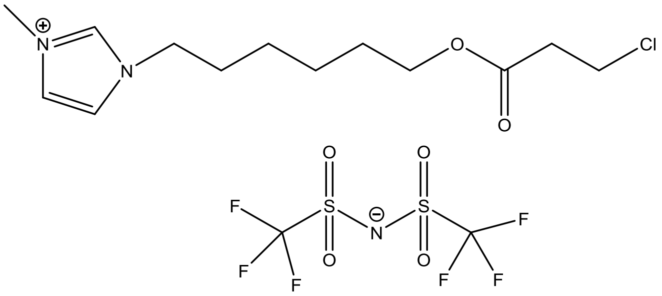
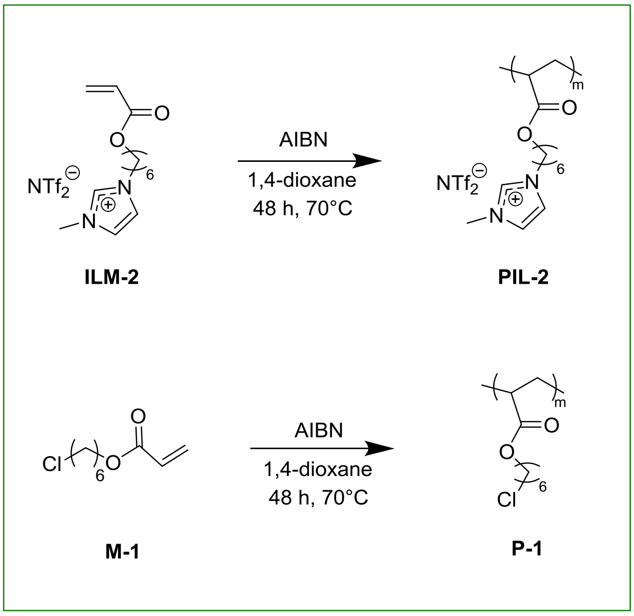


Fig.11 IL-3.

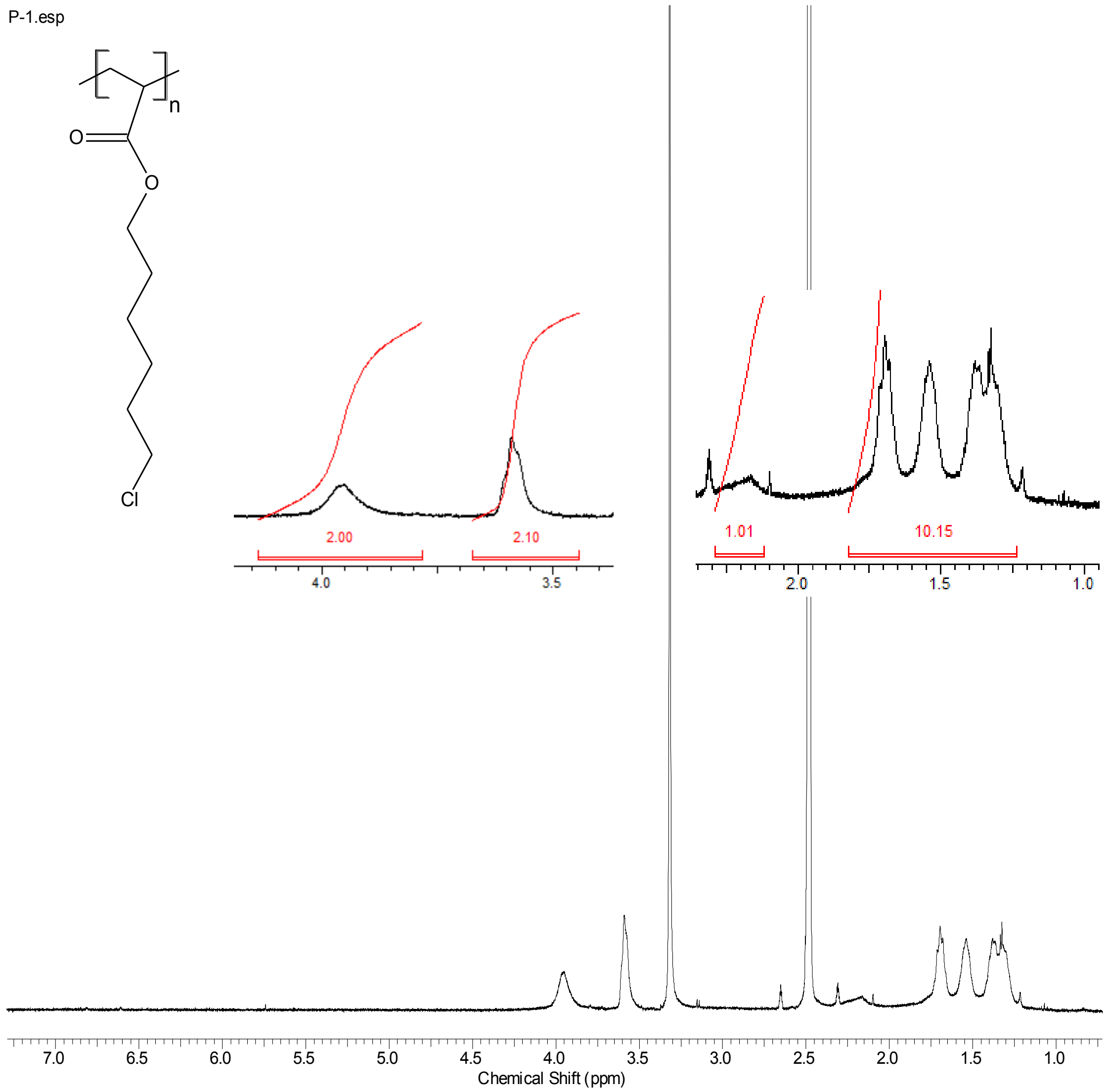
5.2 Polymerization

The polymerization of ILM-2 and M-1 was performed in the same operative conditions (Scheme 21). This choice arose from the necessity to confirm that the polymerization took placed and the possibility to compare the two polymers. Furthermore, polymerised ILM-2 precipitated in ethyl acetate while by-product ionic liquid IL-3 remained in solution.



Scheme 21 Polymerization of ILM-2 and M-1.

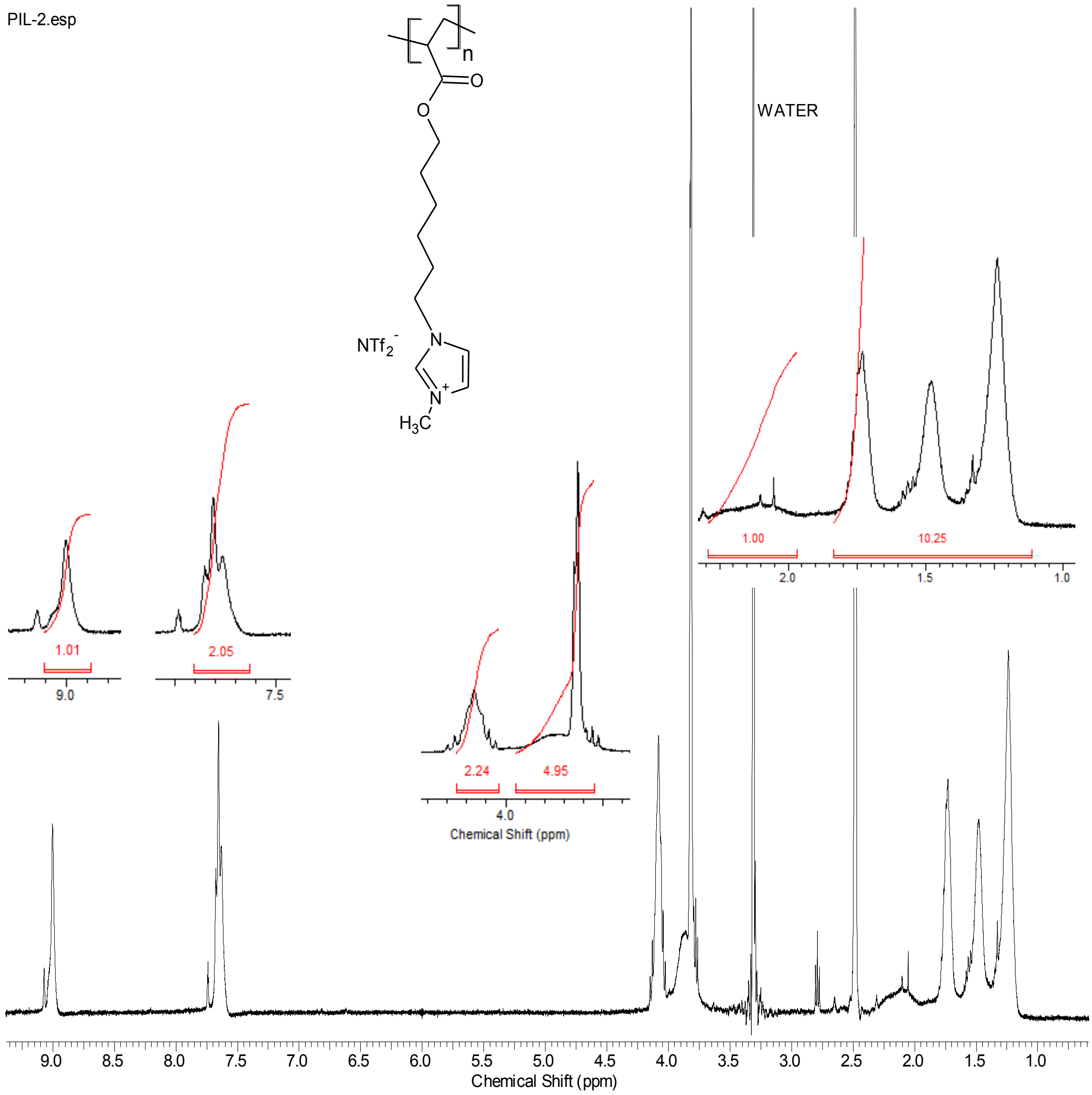
The orange crude P-1 was precipitated in methanol and analysed with ^{1}H-NMR (Spectrum 7).



Spectrum 7 ^{1}H-NMR of P-1.

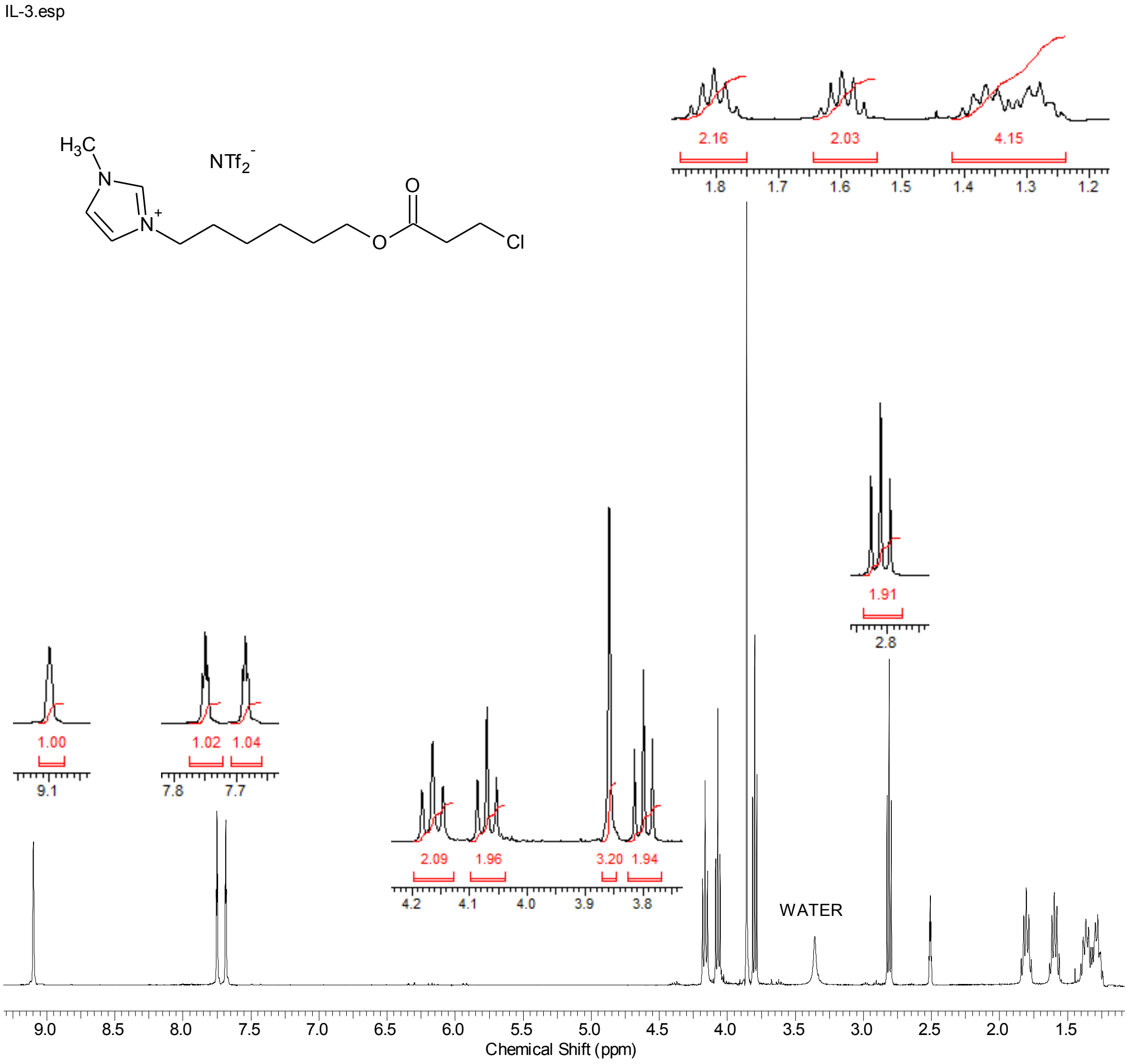
The broad signals are characteristic of polymers, and the lack of vinyl signal at 5.75 – 6.55 ppm confirms the complete polymerization of the monomer (M-1). The broad signal at 3.98 ppm and 3.61 ppm are the two protons bonding to ester group and chloride respectively. At 2.17 ppm is the signal of the proton linked to the carbons of the polymer chain. The residual signals at 1.00 – 1.75 ppm are eight protons of the aliphatic side-chain and two of the methilenic polymeric backbone.

The crude polymer (PIL-2) was precipitated in ethyl acetate as a pale yellow viscous oil. ^{1}H-NMR analysis showed the broad signals similar to P-1 in the aliphatic zone together with the broader signal of imidazolium protons (Spectrum 8).



Spectrum 8 ^{1}H-NMR of PIL-2.

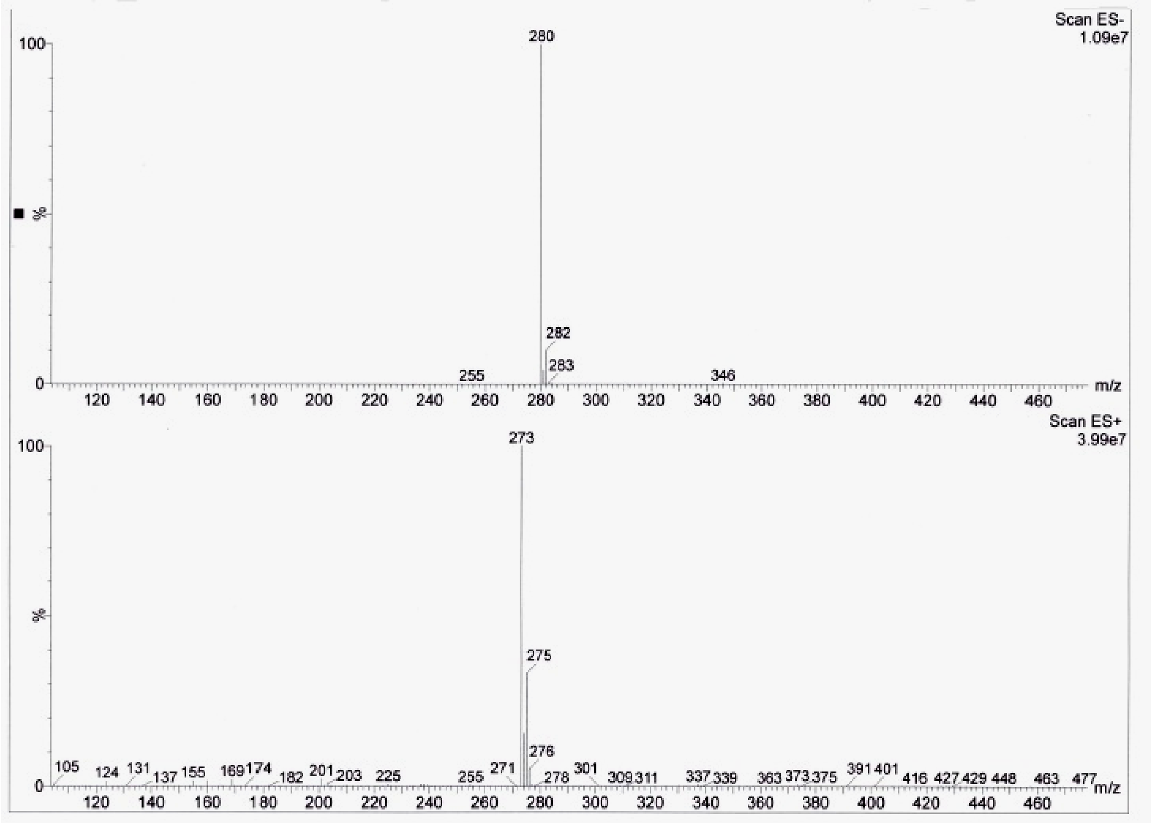
A small amount of ionic liquid (IL-3) can be still be found in the product, probably because it has strong interactions with the polymer in polymer tangle. However, IL-3 did not precipitated in the solution of ethyl acetate and after the evaporation of the solvent it was recovered as yellow oil. From its ^{1}H-NMR analysis (Spectrum 9) and mass spectroscopy (Spectrum 10) it is possible to see only the characteristic peaks of IL-3.



Spectrum 10 ^{1}H-NMR of IL-3.

From Spectrum 10 we can see:

- 7.65 – 9.10 ppm signals of imidazole ring
- 4.16 ppm signal of methylene bonding with ester group
- 4.08 ppm signal of methylene bonding with imidazole ring
- 3.85 ppm signal of methyl on the imidazole ring
- 3.80 ppm signal of methylene bonding with chloride
- 2.80 ppm signal of methylene bonding with carbonyl group
- 1.25 – 1.85 ppm signals of methylene in the aliphatic chain



Spectrum 10 Mass spectra of IL-3.

If ^{1}H-NMR spectra of ILM-2 (Spectrum 6) and IL-3 (Spectrum 9) were compared it is possible to see the absence of peaks related to protons of vinyl group in spectra of IL-3 (Fig. 12). The two triplets at 2.78 ppm and 3.78 ppm attributed to the methylenic groups previously discussed are also present in the spectrum of ILM-2 with impurities.

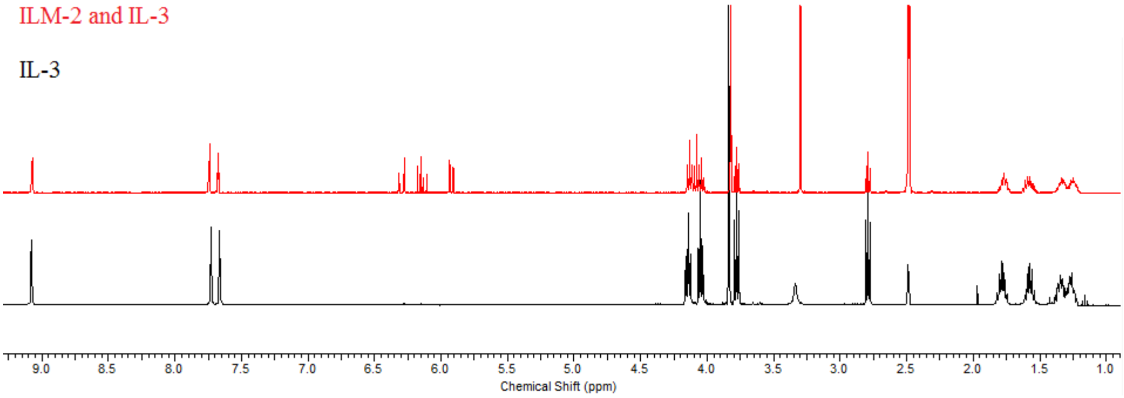
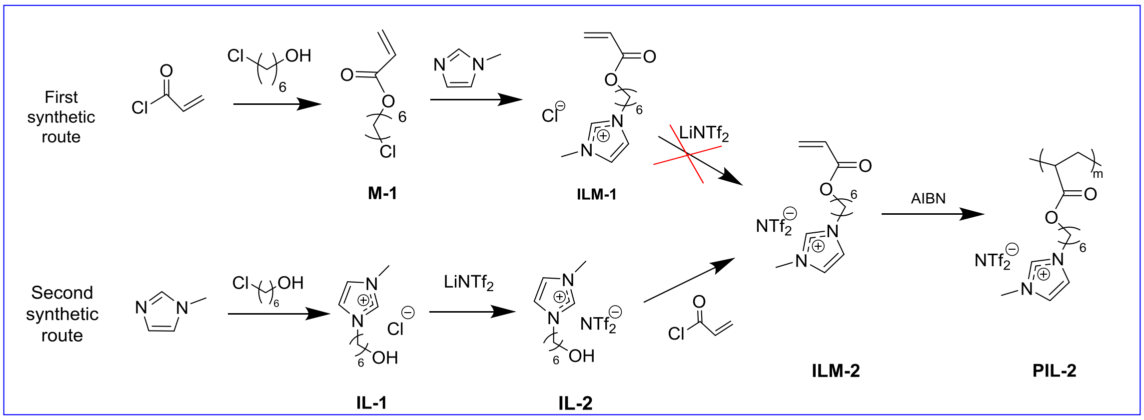


Fig. 12 Comparison ^{1}H NMR analysis of ILM-2 and IL-3.

Despite that it is assumed that IL-3 was the only possible impurity, the ionic liquid monomer (ILM-2) is not inhibited in the polymerization. So we did not afford other study of this by-product as it is beyond the scope of this thesis, due to the interest in just comparing of different routes of synthesis polymerizable ILMs with the aim to produce [(poly-acryloyloxy)$^6C_6C_1$im][NTf$_2$].

6 Conclusion

The aim of this work was to research the smartest route for the synthesise of $[(\text{acryloyloxy})^6C_6C_1\text{im}][\text{NTf}_2]$ (ILM-2), which was then polymerised to produce PIL-2 (Scheme 18).



Scheme 18 Synthetic routes for ILM-2[2,56–58].

The investigations confirms that the second route has some advantages over the first:

- In the first route, there is a competition between the principal reaction and undesired polymerization of ILM-1.
- In the first route, the metathesis reaction did not proceed due to the prolonged purification of ILM-1 and consequently reduced the amount of monomer available for the metathesis.
- The ILs used in the second route (IL-2) can be dried under vacuum and at elevated temperatures, and therefore a higher yield of its esterification can be reached in the absence of moisture.

The composition of the polymer PIL-2 has been confirm by ^{1}H-NMR spectroscopy. However, the thermal and morphological analysis were not performed due to the presence of small amount of impurities which are difficult to remove will disturb the results.

In the future studies these impurities should be investigated in order to improve the yield and quality of the obtained PIL.

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