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Novel organic and inorganic ionogels:
preparation and characterization



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LIST OF ORIGINAL PUBLICATIONS

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- II. **Põhako-Esko, K.**; Timusk, M.; Saal, K.; Lõhmus, R.; Kink, I.; Mäeorg, U. Increased conductivity of polymerized ionic liquids by an non-polymerizable ionic liquid additive. *J. Mater. Res. (submitted)*.
- III. **Põhako, K.**; Saal, K.; Kink, I.; Bredihhin, A.; Mäeorg, U. Synthesis of allyl hydrazine: a comparative study of different methods. *Arkivoc* **2008**, IX, 116–125.
- IV. **Põhako, K.**; Saal, K.; Bredihhin, A.; Kink, I.; Mäeorg, U. New method for synthesis of 3-hydrazinopropyl trimethoxysilane. *Proceedings of the Estonian Academy of Sciences.* **2011**, 60, 1, 64–68.

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- I. Synthesis and characterization of ionic liquids. Responsible for preparation of the manuscript.
- II. Synthesis and characterization of ionic liquids. Responsible for preparation of the manuscript.
- III. Synthesis and characterization of all investigated compounds. Responsible for preparation of the manuscript.
- IV. Preparation of experimental work. Responsible for preparation of the manuscript.

ABBREVIATIONS AND SYMBOLS

ACN	acetonitrile
AIBN	azobisisobutyronitrile
APTES	(3-aminopropyl)trimethoxysilane
BF_4^-	tetrafluoroborate
BHT	2,6-di- <i>tert</i> -butyl-4-methylphenol
BMIM	1-butyl-3-methylimidazolium
Boc	<i>tert</i> -butoxycarbonyl
CNT	carbon nanotube
DMF	dimethylformamide
DMSO	dimethylsulphoxide
EMIM	1-ethyl-3-methylimidazolium
Et	ethyl
EtOH	ethanol
FT-IR	Fourier transformation infrared spectroscopy
HPMS	(3-hydrazinopropyl)trimethoxysilane
IL	ionic liquid
MS	mass spectroscopy
NMR	nuclear magnetic resonance spectroscopy
ORMOSIL	organically modified silica
PEO	poly(ethylene oxide)
PF_6^-	hexafluorophosphate
PIL	polymerized ionic liquid
R	alkyl group
SILC	supported ionic liquid catalyst
SILP	supported ionic liquid phase
T_d	decomposition temperature
TEA	triethylamine
Tf^-	trifluoromethane sulphonate
TFSI ⁻	(trifluoromethanesulphonyl)imide
T_g	glass transition state temperature

For ionic liquids following notation was used: [cation][anion].

INTRODUCTION

Ionic liquids are salts that are liquid at ambient temperature. These unique compounds have extraordinary physico-chemical properties like extended liquidus range, negligible vapour pressure, good chemical and thermal stability and high ionic conductivity. The feature that makes ionic liquids so special and holds the greatest potential is the tuneability of their properties. The characteristics of ionic liquids can be influenced by choice of suitable cations and anions.

Ionic liquids have been in the focus of intense research for more than 20 years. The broad liquidus range and non-volatility made ionic liquids attractive first as an environmental friendly replacement for conventional organic solvents. However, the utilization of ionic liquids as unique materials rather than just the alternative reaction media has opened up new frontiers in material science. Ionic liquids can be used in different fields: as electrolytes in electrochemical devices, like batteries and fuel cells, in separation sciences, analytical chemistry, tribology, bioengineering if just to mention a few.

Regardless of the unique properties, the exploitation of ionic liquids can be complicated in certain applications because of the problems related to the liquid state, for example possible leakage or difficulties in obtaining or maintaining a predefined physical shape. So there is a challenging need to immobilize ionic liquids into solid state in order to retain their properties. Hybridization of ionic liquids with other organic and inorganic materials results in different type of ionogels. Ionogels are hybrid materials in which ionic liquid is physically or covalently bound to an organic or inorganic matrix. Ionogels supply solutions for ionic liquids fluidity problems although from development of these materials, several new unique properties have also emerged that open up further horizons in the field of ionic liquids.

In the present thesis a literature overview about ionogels is given. Preparation, properties and possible practical applications of various types of ionogels are covered. Experimental work carried out in frame of the thesis was focused on the preparation of two new hybrid materials, which can be classified as an organic and an inorganic chemical ionogel. The novel organic ionogel was developed with the aim to prepare a transparent and flexible material with tuneable ionic conductivity and mechanical properties. The research on the inorganic ionogels was concentrated on development of the synthesis method for hydrazinosilanes, which analogous to aminosilanes can be used for preparing ionic liquid like structures on various surfaces.

I. LITERATURE OVERVIEW

I.1. Ionic liquids

I.1.1. Definition and history

Ionic liquids are a diverse group of salts which are liquid at ambient temperature [1]. An earlier definition restricts that ionic liquids should have melting point below 100°C but this temperature limit was chosen quite arbitrary.

The history of ionic liquids may be viewed from two perspectives: the first one being a relatively recent discovery of new materials – the so-called ionic liquids, and the second one a renaissance of the chemistry of molten salts dating back to the 19th century. In progress of the field of ionic liquids three milestones can be pointed out. As the first synthesized ionic liquid ethyl-ammonium nitrate $[\text{EtNH}_3][\text{NO}_3]$ reported by Paul Walden in 1914 is generally acknowledged [2]. Next step towards modern ionic liquids were studies in pyridinium and imidazolium based chloroaluminates to find replacement for LiCl/KCl molten salt electrolytes used in thermal batteries [2]. Although research on these compounds dates back to 1940s, the real breakthrough came in 1992 when Wilkes and Zaworotko reported air- and water-stable ionic liquids [3].

According to the definition, ionic liquids consist entirely from ions. There are many cations and anions that can be combined to form ionic liquids. The number of combinations is almost unlimited and according to speculations could provide up to 10^{18} different structures [4]. Cations are usually, but not limited to, bulky asymmetric organic molecules. The cationic centre often involves a positively charged nitrogen or phosphorus. General requirement for an anion is low coordinating power. Anions are usually weakly basic inorganic or organic compounds that have a diffuse or protected negative charge [1].

Based on the cation ionic liquids can be divided into three groups (Figure 1): (1) five- and six-membered aromatic heterocyclic and benzo-fused heterocyclic cations, (2) ammonium, phosphonium and sulphonium based cations, (3) saturated heterocyclic cations.

The anions can be divided into following groups (Figure 2): (1) anions formed from Lewis' acids like AlCl_4^- , (2) halides: F^- , Cl^- , Br^- , I^- , (3) PF_6^- , BF_4^- , (4) amide and imide anions like TFSI^- , (5) alkylsulphates RSO_4^- , alkylsulphonates RSO_3^- , (6) alkylphosphates R_2PO_4^- , alkylphosphinates R_2PO_2^- and alkylphosphonates R_2PO_3^- , (7) alkylcarboxylates like acetate CH_3CO_2^- .

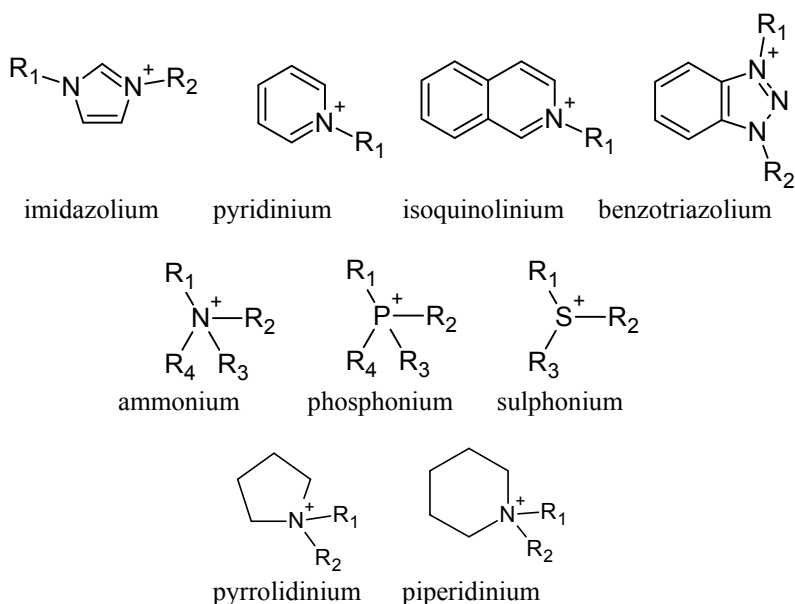


Figure 1. Cations used for formation of ionic liquids.

Special group of ionic liquids are functionalized ionic liquids, also named „task specific ionic liquids“ [5]. These are defined as ionic liquids in which a functional group is covalently tethered to the cation, anion or zwitterionic form of the salt. The functional group provides additional properties, like chemical, optical, magnetic, physical or biological, which can then be employed to perform a specific task.

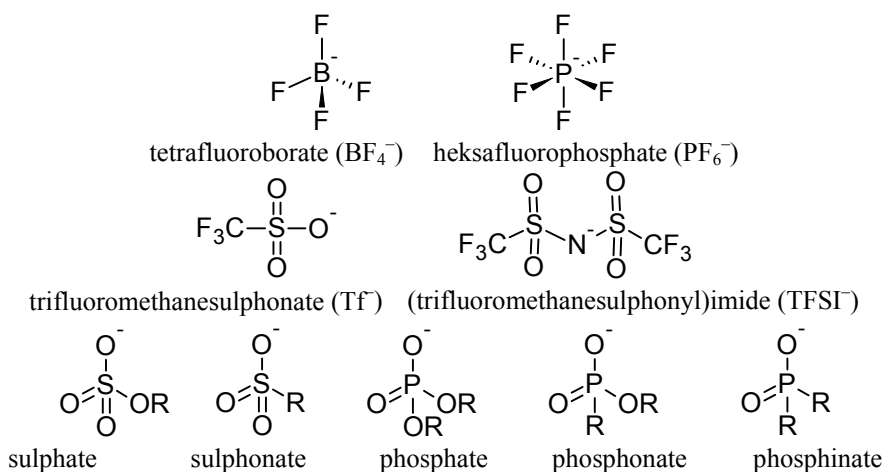


Figure 2. Anions used for formation of ionic liquids.

1.1.2. Physical properties

While early works in the field tended to presume that ionic liquids had uniform properties as a class, it is now widely recognized that they cover a very wide spectrum of properties. It is often declared that the characteristics of ionic liquids are tuneable and new ionic liquids with a unique set of properties can be prepared simply by changing the ions or their substitution patterns. The vast number of possible ionic liquids structures made clear, that it is impossible to individually study the characteristics of every single salt. Instead, it is necessary to determine how the properties of ionic liquids change as a function of anion/cation/substitution patterns and to identify relationships, which enable to predict the properties.

In the following sections some physical properties of ionic liquids are discussed in detail. This is accompanied with a list of factors that can influence these parameters and a brief description of underlying mechanisms.

1.1.2.1. Liquidus range and its limits

Wide liquidus range is the most unique characteristic of ionic liquids. Liquidus range of ionic liquids is much wider than for molecular compounds in general because it is defined by melting point or glass transition state temperature (T_g) and thermal decomposition rather than by vaporization as for common solvents. For example, water has the liquidus range of 100°C (0 to 100°C), but 1-alkyl-3-methylimidazolium salts typically have T_g in the range -90 to -70°C and thermal decomposition temperatures between 250–450°C [6]. The resulting liquidus range is therefore over 300°C.

Factors that determine the melting points of ionic liquids are electrostatic interactions and van der Waal forces. Electrostatic interactions between ions are influenced by size, charge and charge distribution. Larger anions with delocalized charge have weaker Coulombic interactions with cations and it leads to lower melting point of the salts. Same relationship stands true for cations as there is a significant difference between cyclic and aliphatic cations. Another influential characteristic is symmetry of the cation. Asymmetry of the cation causes a distortion from the ideal close-packing of ionic charges in the solid state lattice, a reduction in the lattice energy and hence depression of the melting point. Other parameters that affect melting point are chain length and branching of substituents and ability to form hydrogen bond [7].

Ionic liquids are known for very low vapour pressure. In early days of the field it was presumed that they even do not have a vapour pressure, but in 2006 it was demonstrated by Earle and co-workers that ionic liquids can be distilled [8]. Low vapour pressure is caused by the structural peculiarities of ionic liquids.

As ionic liquids are almost non-volatile the upper limit of liquidus range is determined by the decomposition due to pyrolysis at temperatures between

350–450°C [7]. For example, the decomposition of the imidazolium salts proceeds through E2 elimination on the N-substituent, which is the reversible reaction of $\text{S}_{\text{N}}2$ substitution carried out for preparation of imidazolium cations (section 1.1.3.1) [7]. Comparison of the decomposition temperatures for ionic liquids with different anions reveals that ionic liquids containing weakly coordinating charge-diffuse anions are more stable towards high temperature (stability order for anions: $\text{halides}^- < \text{PF}_6^- < \text{BF}_4^- < \text{TFSI}^-$) [9].

1.1.2.2. Electrochemical properties

Ionic liquids have good ionic conductivity and wide electrochemical window. Conductivities of ionic liquids at room temperature are in range of $0.1\text{--}18\text{ mS cm}^{-1}$. Salts with imidazolium cations have generally the highest conductivities, typically in the order of 10 mS cm^{-1} . Ionic liquids based on ammonium, pyrrolidinium and piperidinium cations are characterized by considerably lower conductivities, between 0.1 and 5 mS cm^{-1} [10]. Higher conductivities of the imidazolium salts have been associated with planarity of the cation. The anions have also a remarkable effect on the conductivity as they influence viscosity of ionic liquids [11]. Although the conductivities of ionic liquids are commonly described as good, even the highest conductivities of these compounds are much lower than characteristic for conventional aqueous electrolyte solutions applied in electrochemistry. For example, the specific conductivity of aqueous KOH (29.4% w/w) solution, applied in alkaline batteries, is 540 mS cm^{-1} . The electrolyte applied in lead-acid batteries, 30% w/w aqueous H_2SO_4 , has the conductivity at about 730 mS cm^{-1} [10].

The conductivities of ionic liquids are lower than one might expect from ionic compounds due to high viscosities, which are about $30\text{--}50\text{ cP}$, but in some cases even as high as $500\text{--}600\text{ cP}$ [10]. To give a comparison – the viscosity of water is significantly lower ($\eta(\text{H}_2\text{O})=0.89\text{ cP}$ at 25°C). As mentioned previously, viscosities of ionic liquids are strongly dependent on the anions. More basic anions and those with hydrogen bond capability result in higher viscosities, whereas salts with TFSI[−] anion, for example, have low viscosities because of extensively delocalised charge [11]. Lower viscosities are preferable as it means also higher ionic conductivities. It is worth to mention that the viscosities of ionic liquids and therefore also the conductivities are strongly influenced by temperature.

Electrochemical window is defined as a voltage range where the substance does not get oxidized or reduced. For ionic liquids it is defined by the reduction of the cation and the oxidation of the anion [7]. Most ionic liquids have a wide electrochemical window, generally more than 4 V . Here imidazolium salts show lower stability (typically $4\text{--}4.5\text{ V}$) than ammonium or pyrrolidinium salts ($> 5\text{ V}$) [7,10].

1.1.2.3. Solvation in ionic liquids

Ionic liquids are recognized as polar solvents. Their polarity is similar to short-chain alcohols and other polar, aprotic solvents (DMSO, DMF, etc.) [4, 12]. By changing the nature of the ions, it is possible to change the properties of resulting ionic liquids, including their solubility and solvating abilities. The miscibility with water can be varied from complete miscibility to almost total immiscibility, by changing the anion, for example, from Cl^- to PF_6^- [9]. The solvent features of imidazolium based ionic liquids include the cations capability for hydrogen bond donation, hydrogen bond accepting functionality of the anion and π - π interactions which enhance solubility of aromatic compounds.

Ionic liquids can act as surfactants and are able to dissolve or disperse compounds, which dissolution is difficult to obtain in other solvents. Cellulose is a well known example. Using microwave heating a solution with cellulose content up to 25% in [BMIM][Cl] can be achieved [13]. Ionic liquids have also been successfully applied for dissolving other biomacromolecules like cyclodextrines, starch and chitin [14]. Ionic liquids capability to dissolve biomolecules has been explained by the ability to break intra and inter chain hydrogen bonds. Anions with high coordinating power like Cl^- are favourable for this process.

Ionic liquids even disperse carbon nanotubes (CNT). A phenomenon of gel formation by mixing CNTs and ionic liquid was first introduced by Fukushima and colleagues in 2003 [15]. Later the same authors showed that it is possible to prepare “bucky gels” with CNT content up to 24% in [BMIM][BF₄] simply by grinding the mixture in a mortar [16]. There is an on-going discussion about the mechanism of the process: is it caused either by π -cation [17] or π - π interactions [18]. Ionic liquids are also known to interact with transition metals, which make possible to stabilize metal nanoparticles in ionic liquids [19].

1.1.3. Synthesis of ionic liquids

Synthesis of ionic liquids is divided into two sections (Figure 3): (1) the formation of the desired cation and (2) the anion exchange when necessary. The following review of synthesis methods is not exhaustive and is focused only on ionic liquids based on 1,3-dialkylimidazolium cations, as these have dominated the field more than twenty years. Also, the aim of the current thesis was to synthesize different functionalized imidazolium based ionic liquids. However, discussed techniques are generally applicable for other cations as well.

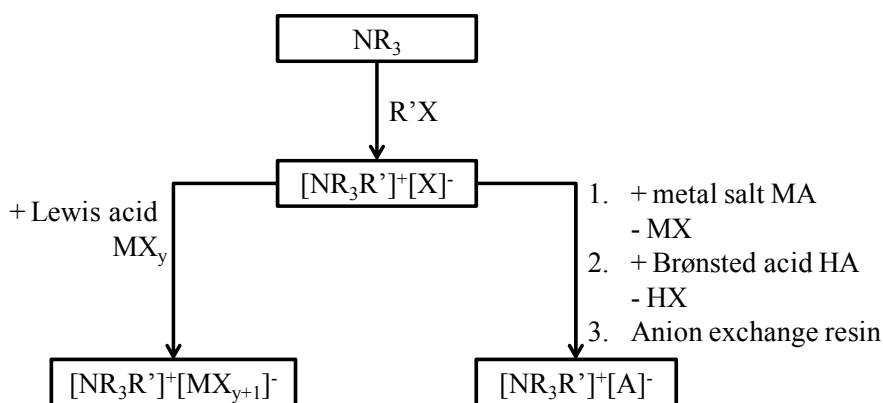
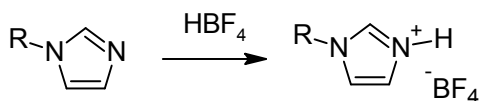


Figure 3. Typical synthesis routes for preparation of ionic liquids [20].

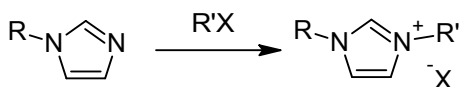
1.1.3.1. Synthesis of cations

Two common strategies are applied for formation of cations. First, the protonation of suitable starting materials with free acid (HHal, HNO₃, HBF₄) is the simplest method to obtain protic ionic liquids (Scheme 1) [7]. The same method was used by Walden for the synthesis of the first reported room temperature liquid salt, ethylammonium nitrate, which was prepared by mixing ethylamine with concentrated nitric acid [2]. Unfortunately, possible decomposition through deprotonation limits the usage of protic ionic liquids.



Scheme 1. Formation of ionic liquid by protonation.

Another more widely used method for preparation of cations is quaternization of amines or phosphines with suitable halogenoalkanes [7]. Quaternization has several advantages as a wide range of halogenoalkanes are available and formed halide salts can be easily converted into salts with other anions. Quaternization generally occurs smoothly at reasonable temperatures but it is important to note that the reaction is highly exothermic. Therefore cooling is advisable, especially in the large scale experiments. Beside safety concerns, the uncontrolled heat release may cause poor quality of the products (discussed in more detail in the section 1.1.3.3).



Scheme 2. Formation of ionic liquid by quaternization with halogenoalkane.
X= Cl, Br, I.

Different solvents are used in quaternization because the solvent can help to dissipate the heat generated during the substitution. However, the reactions can also be carried out without any solvent as the starting materials are often mutually miscible. Kinetic studies indicate that as expected for nucleophilic $\text{S}_{\text{N}}2$ reaction, polar aprotic solvents are more suitable for quaternization than protic polar solvents [21]. For suitable solvents the reaction rate decreases in the following order: DMSO >> ACN > cyclopentanone > acetone > 2-butanone > dichloromethane. When comparing the reaction rates with and without presence of the solvent, then only in DMSO and ACN the performance was enhanced.

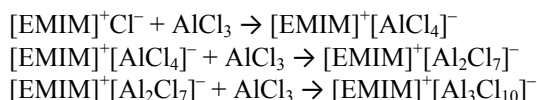
The reaction time of quaternization is dependent from the used halogenoalkane and the applied temperature. The rise of reaction rate follows the increase in electrophilicity of halogenoalkane in given order: Cl < Br < I. The quaternization of N-methylimidazole with chloroalkane takes 2–3 days at 80°C, with bromoalkanes 24 h at 50–60°C and with iodoalkanes less than 24 h at room temperature [7]. The reactions with iodoalkanes can be problematic as iodide salts are light sensitive. Quaternization can be accelerated using microwave approach. It has been demonstrated that in a domestic microwave oven the quaternization of N-alkylimidazole takes only a few minutes, whereas it may take several days for the general procedure, without microwave heating [22]. The reaction time and the temperature can also be decreased by using ultrasonication as it enables more efficient mixing. By applying ultrasonication, 1-alkyl-3-methylimidazolium bromides formed within a few hours with the yield of more than 90% [23].

Although the quaternization reactions may look very straightforward, there are many factors that can influence the results. The presence of moisture in the reaction mixture should be avoided, as ionic liquids are hygroscopic. It is not advisable to heat the halide salts to temperatures higher than 80°C because it can result in side reactions and lead to the formation of coloured by-products. However, the yield of quaternization is generally higher than 90% and the obtained product can be easily purified by recrystallization or vacuuming [7].

While quaternization is typically carried out in a classical batch reactor, the growing popularity of ionic liquids has led to development of new synthetic techniques. For example, continuously working microreactor systems have been used. A microreactor that enables to produce approximately 9.3 kg of [BMIM][Br] per day in a high yield and purity was reported quite recently [24]. The main advantages of microreactors are a high surface to volume ratio and efficient heat transfer. They are also suitable for industrial use due to the improved safety compared to the large scale batch reactors.

1.1.3.2. Anion exchange

Anion exchange reactions with ionic liquids can be divided into two distinct categories: direct treatment of halide salts with Lewis' acids (AlCl_3 , AlEtCl_2 , BCl_3 , CuCl , and SnCl_2 ; Scheme 3), and the formation of ionic liquids by anion metathesis [7]. Nowadays the latter is more widely used.

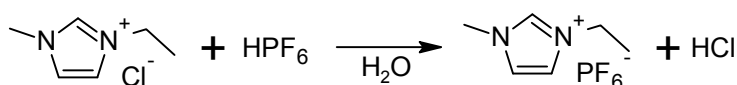


Scheme 3. Anion exchange with Lewis' acid.

Metathesis is a reaction where cations and anions from different salts are combined in a new way. The underlying principle is simple: the starting materials are dissolved and in the solution the solvated ions can combine in a new way. Driving force for the reaction is the formation of a more stable salt, which usually precipitates.

Anion metathesis reactions can be divided into two categories depending on the water solubility of the target ionic liquid. As there are numerous publications on the topic of anion metathesis, only the earliest examples are discussed here for the both categories.

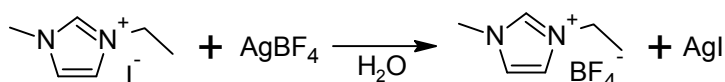
The synthesis of water-insoluble ionic liquids is very straightforward. The ionic liquid with halide anion is treated in aqueous solution with the free acid or salt of the desired anion. Both starting materials and reaction by-products (HCl , HBr , HI or simple halogenide salts) are soluble in water, whereas the resulting product (insoluble) forms a second phase and can be easily separated [7]. The preparation of $[\text{EMIM}][\text{PF}_6]$ in reaction between $[\text{EMIM}][\text{Cl}]$ and HPF_6 in aqueous solution was reported as the first water-insoluble ionic liquid obtained by anion metathesis [25].



Scheme 4. The synthesis of water-insoluble ionic liquids by metathesis.

The preparation of water-miscible ionic liquids involves the metathesis reaction between the ionic liquid with halide anion and the silver salt with the desired anion. This procedure was first described by Wilkes and Zaworotko in their groundbreaking publication in 1992 [3]. As already mentioned in the section 1.1.1, this was the first time when the air- and moisture-stable ionic liquids were synthesized and can be marked as the beginning of the field of modern ionic liquids. In the mentioned article $[\text{EMIM}][\text{I}]$ was treated with a range of silver salts (AgNO_3 , AgNO_2 , AgBF_4 , $\text{Ag}(\text{CO}_2\text{CH}_3)$, and Ag_2SO_4) in methanol or

aqueous methanol solution (Scheme 5). The almost negligible solubility of silver iodide in these solvents allowed its separation by filtration and after removing the solvent the desired ionic liquids were isolated in the high yields and purities. An obvious drawback of the method is the high cost of silver salts. Any other salt can be used as an alternative if it forms an insoluble by-product and a soluble product during the metathesis reaction.



Scheme 5. The synthesis of water-soluble ionic liquids by metathesis.

In addition to the above described water-based synthesis methods, several alternative procedures have been developed, which are carried out in organic solvents like dichloromethane or acetone. Several aspects need to be considered using organic solvents as reaction media for the metathesis. The starting materials are often not entirely soluble in organic solvents and therefore reactions should be carried out in suspension. The inorganic by-products may also have a limited solubility in organic media, which leads to the contamination of the desired ionic liquid. The precipitation of the inorganic salts can be slow [7]. Table 1 summarizes the anions that have often been incorporated into ionic liquids using the metathesis together with possible anion sources.

Table 1. Ionic liquids prepared by anion metathesis [7].

Ionic liquid	Anion Source
[Cation][PF ₆]	HPF ₆
[Cation][BF ₄]	HBF ₄ , NH ₄ BF ₄ , NaBF ₄
[Cation][TFSI]	LiTFSI
[Cation][CF ₃ SO ₃]	CF ₃ SO ₃ CH ₃ , NH ₄ (CF ₃ SO ₃)
[Cation][NO ₃]	AgNO ₃ , NaNO ₃

1.1.3.3. Purification of ionic liquids

Although the synthesis of ionic liquids is quite straightforward, purification of the compounds is not an easy task to achieve. The lack of significant vapour pressure prevents distillation of ionic liquids. This also means that any volatile impurity can, in principle, be separated from an ionic liquid by distillation. It has been widely recognized that although ionic liquids should be colourless, they are frequently yellow or even dark brown. The colouring is caused by impurities present in very small amounts. The so called chromophores are present at ppm level as they are not detectable by spectroscopic analysis. The

nature of chromophores is still unclear but they are associated with side reactions occurring at higher temperatures ($> 80^{\circ}\text{C}$) during the synthesis [7, 26]. In literature there is no evidence that the chromophoric impurities affect either the chemical or the physical properties (except optical) of ionic liquids. However, in many applications the colouring is still a hindrance. There are some aspects, which if accounted during the synthesis, help to prevent the colourization of the product. For example, purification and usage of starting materials with highest possible quality is recommended. Advisable is to avoid high temperatures during the synthesis. It is also necessary to avoid the exposure of ionic liquids to oxygen and moisture. When the product still has a colour, passing through active charcoal column has been established as an efficient way to decolourize ionic liquids [26].

Water is the most common impurity in ionic liquids. Even the hydrophobic ionic liquids can contain some moisture. Unfortunately, already a small amount of water can significantly influence the properties of ionic liquids (for example the ionic conductivity) and the molar concentration of water can be remarkable due to its low molecular mass. It is also worth to mention that BF_4^- and PF_6^- , which are common anions for ionic liquids, can form highly corrosive HF in the presence of water [27].

1.1.4. Applications of ionic liquids

Ionic liquids have been in the focus of intense research due to their extraordinary physico-chemical properties such as low vapour pressure, good electrochemical performance and extraordinary solvating properties.

Since the early days of the field ionic liquids have been considered as environmental friendly alternatives to the conventional organic solvents because of their assumed non-volatility. Nowadays the „greenness“ of ionic liquids is being debated [27–30]. Nevertheless, this does not diminish their popularity as the alternative reaction media. It is hard to name any reaction, which could not be successfully carried out in ionic liquids [7, 31]. Ionic liquids can play different roles in chemical reactions. They can act as solvents, catalysts, phase transfer agents and stabilizing agents for catalysts or intermediates [32]. However, the scientific community has recognized ionic liquids also as tuneable, multipurpose materials for a variety of applications rather than only organic synthesis.

The unique solvating properties of ionic liquids are also beneficial in different separation techniques and analytical chemistry [33]. Ionic liquids have been successfully applied for extracting various organic and metal contaminations from environmental samples such as water and soil. Furthermore, they have been found efficient for extracting bioactive compounds from plants [34]. In chromatography ionic liquids can play different roles as a mobile phase additives in high performance liquid chromatography to improve the resolution

or as a stationary phase in gas chromatography. The behaviour of ionic liquids, when applied as the stationary phase, is unique because they are able to separate both polar and non-polar compounds [35].

There are several applications where the electrochemical properties of ionic liquids are exploited. Energy devices, such as fuel cells, dye-sensitized solar cells, lithium batteries and supercapacitors can greatly benefit from ionic liquids as the low vapour pressure and non-flammable electrolytes [36]. Safety is the key aspect in the development of electrochemical devices using ionic liquids.

Electrodeposition of metals or semiconductors is another field where the electrochemical properties of ionic liquids are applied. Due to the wide electrochemical window a large variety of metals and alloys, which cannot be electrodeposited in aqueous or organic solvents, can be produced in ionic liquids. Moreover, the choice of cation and anion in ionic liquid has influence to the morphology and the crystal size of the product [37].

In tribology ionic liquids have gained attention since the pioneering study by Liu in 2001 [38]. Thermal stability, non-flammability and negligible vapour pressure make ionic liquids suitable lubricants for the usage at extreme temperatures and in high vacuum where common oils and greases fail. Moreover, ionic liquids adsorb strongly on metal surfaces thus enhancing the tribological performance even more. Recently published reviews on the tribological applications of ionic liquids witness the great potential of ionic liquids as the advanced lubricants [39–41].

As the number of applications for ionic liquids is growing the previous overview is far from being exhaustive. However, for some applications the fluidity of ionic liquids may be disadvantageous as it may cause problems with leakage of the liquid and difficulties in obtaining or maintaining a predefined physical shape. So there is a challenging need to immobilize ionic liquids into solid phase, while keeping their special properties intact.

1.2. Immobilization of ionic liquids

The preparation of ionogels enables to immobilize ionic liquids into solid phase. Ionogels are a new type of hybrid materials consisting from an ionic liquid and a solid three-dimensional network (gel) intermingled at nanometer scale. Gel can be organic (low molecular weight gelators or polymers) or inorganic (oxide nanoparticles, CNTs or oxide networks arising from sol-gel approach). Based on the interactions between the gel and the ionic liquid, ionogels can be classified as physical and chemical gels, which are held together respectively either by weak and reversible interactions like van der Waals forces and hydrogen bonding or by much stronger and stable chemical bonds [42].

The physico-chemical properties of organic and inorganic ionogels are different, which make them suitable for different applications. Organic ionogels, in which the matrix is typically a polymer, are in focus because of the unique

combination from the ionic conductivity of ionic liquids and the elasticity and flexibility of polymers. The conductivity of material is secondary in case of inorganic ionogels. In inorganic ionogels ionic liquids are frequently used as linkers to immobilize substances that can be used for functionalization of the inorganic matrix. Therefore the ionic liquids' ability to interact with the gel as well as with the used additives is important for the development of new materials. Mechanical strength of inorganic ionogels provided by inorganic matrixes, like oxides, can also be beneficial for practical applications.

1.3. Organic ionogels

Organic ionogels are polymer gels (section 1.3.1) and also materials that are prepared by dispersing low molecular weight gelators in ionic liquid. Both previously named materials are considered as physical ionogels. There are also chemical gels involved in the class of organic ionogels. For example, polymerized ionic liquids (section 1.3.2) belong to chemical organic ionogels.

1.3.1. Polymer gels

Polymers are widely investigated from the perspective of immobilizing ionic liquids. There are two different routes for the preparation of polymer gels (Figure 4). First, gelled systems can be obtained by swelling polymers in ionic liquids or mixing the polymer and the ionic liquid together by means of a co-solvent. The mixtures are cast to a predesigned shape and the solvent is removed to obtain the solid gelled structures. The other route is to polymerize various monomers in ionic liquid, used as a solvent, and to leave it into the prepared polymer [43].

The first method enables to use polymers with different architectures, like homopolymers, co-polymers and block co-polymers for the preparation of ionogels. Fluorinated polymers, like polytetrafluoroethylene and polyvinylidene-fluoride are often applied in ionogels because of their inertness and good thermal stability [43]. Beside fluorinated polymers, the conventional hydrocarbon polymers have also been utilized with ionic liquids. The choice of polymer matrix depends on the planned applications. For example, poly(ethylene oxide) (PEO) based electrolytes are promising for lithium batteries due to the ability of PEO to coordinate ionic species and local flexibility that promotes ion mobility [44].

By choosing a polymer for the preparation of ionogels, polymer compatibility with ionic liquid is important. As the primary application for polymer gels are polymer electrolytes, the ionic conductivity is a crucial parameter for the material [43]. The conductivity of polymer gels depends on the amount of ionic liquid in the gel. The conductivity can be enhanced by increasing the content of ionic liquid, but only to a certain limit, as higher ionic liquid

concentration may result in poor mechanical stability and leaching. Decisive amount of ionic liquid is determined by the compatibility of materials. Several examples have been reported, where polymers can take up more than 100% w/w of ionic liquid by swelling, which can enhance the conductivities of materials to the level of neat ionic liquids. For example, [BMIM][Tf] uptake for Nafion membranes can be up to 120% (ionic liquid content in the resulting material 54% w/w). The obtained self-supporting membranes had the ionic conductivity of 110 mS cm^{-1} at 180°C [45].

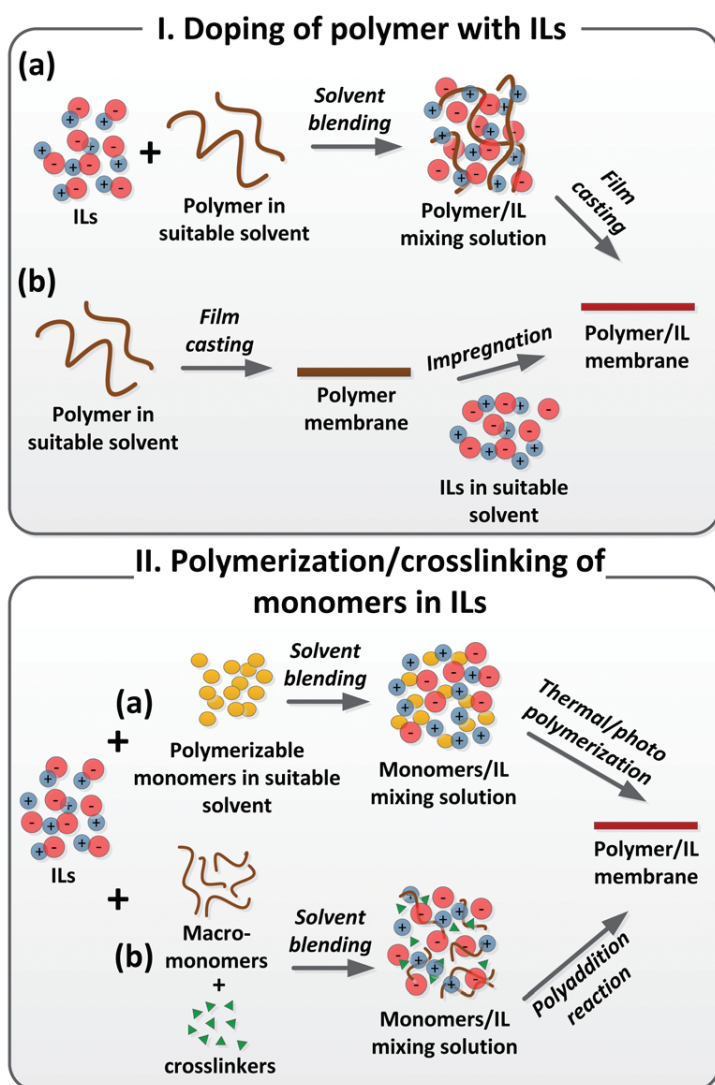


Figure 4. Schematic representation of methods for the preparation of polymer ionogels; IL – ionic liquid (adapted from ref. [43]).

Due to the extraordinary solvating properties of ionic liquids, the polymerization reactions, where ionic liquids are applied as solvents, have been investigated widely. There is a large variety of vinyl monomers, which are soluble in ionic liquids, especially in imidazolium salts. In order to obtain polymer gels, in which ionic liquid remains in polymer after the reaction, the compatibility of polymer and ionic liquid is also required in order to avoid the phase separation. Free radical polymerization of different monomers, such as methyl methacrylate, acrylonitrile, vinyl acetate, styrene, 2-hydroxyethyl methacrylate, methyl acrylate and acrylamide, have been investigated by Watanabe's group [46]. Although all investigated vinyl monomers were miscible with chosen ionic liquid [EMIM][TFSI], phase separation occurred in several cases due to incompatibility between the resulting vinyl polymers and the ionic liquid. In the critical review by Winterton it was concluded that there are several factors responsible for polymer solubility in ionic liquids and therefore further in-depth investigations are required to predict the behaviour of polymer-ionic liquid mixtures [47]. When phase separation is successfully avoided, ionogels with quite high ionic conductivity, about 1 mS cm^{-1} at ambient temperature, can be prepared by polymerization of vinyl monomers in ionic liquids [43].

There is very intense research going on in the field of polymer gels. However, the preparation of physical gels from ionic liquids and polymers remains outside of the focus of the current thesis and therefore the topic is not discussed here in more details.

I.3.2. Polymerized ionic liquids

Polymerized ionic liquids (PILs) belong to the class of chemical organic ionogels, where ionic liquid moiety is covalently bound to polymer matrix. According to the definition, PILs can be described as polymers containing at least one covalently bound ionic centre in the monomer unit. Whereby, the structure of the ionic centre is similar to ionic liquids [48].

Although PILs have gained a lot of attention since the milestone papers by Ohno and co-workers in beginning of 2000's [49–51], the initial research in the area of ionic vinyl monomers dates back to the 1970's [52].

PILs are generally prepared by polymerization of polymerizable ionic liquids, which are task-specific ionic liquids having a polymerizable functional group incorporated into the molecular structure. The post-polymerization modifications of suitable polymers to add the ionic liquid moieties are also possible [53].

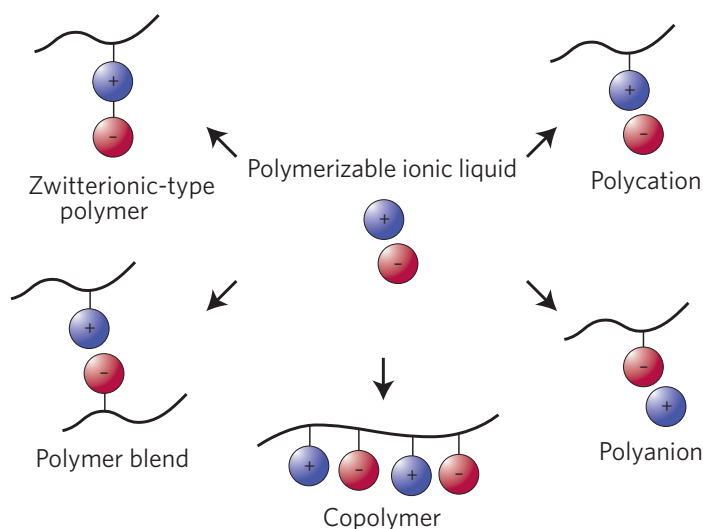
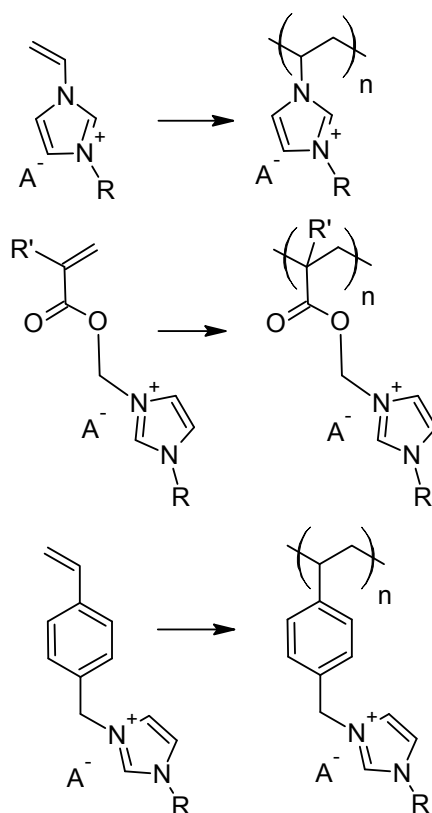


Figure 5. Various types of polymerized ionic liquids (adapted from ref. [36]).

PILs can be classified as polycations and polyanions bearing corresponding ions in the macromolecular backbone or as zwitterions having both cation and anion covalently bound to the polymer structure (Figure 5) [54]. Special polymerization techniques also enable to prepare various co-polymers and polymer blends from polymerizable ionic liquids (section 1.3.2.2). So far the research has been mainly focused on introduction of a polymerizable functional group (vinyl, (meth)acrylate or styrene) into cation. Scheme 6 gives an overview about commonly used structures of polycationic PILs with imidazolium cation.

While imidazolium is the most popular choice as cation for PILs, the use of other cations, such as tetraalkyl ammonium [55], pyridinium [56], pyrrolidonium or piperidinium [57], have also been reported together with a wide variety of counter anions like halides, BF_4^- , PF_6^- , Tf^- , NO_3^- , TFSI^- and alkylsulphonates. At the same time, only few articles have been published about polyanions [58–60].

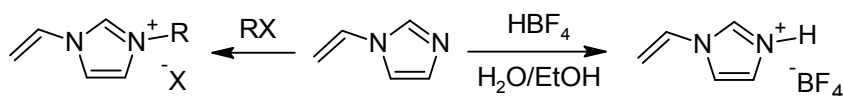


Scheme 6. Structural variabilities of polycationic polymerized ionic liquids. A^- – anion, R – alkyl, R' – CH_3 , H .

1.3.2.1. Synthesis of polymerizable ionic liquids

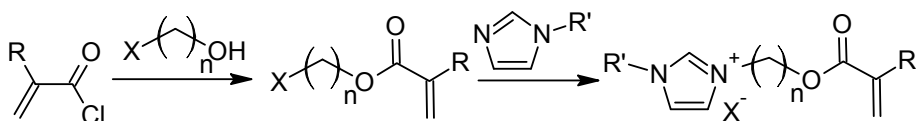
According to the focus of the current thesis only the synthesis of polymerizable ionic liquids with imidazolium cations is reviewed.

The synthesis of N-vinylimidazolium based PIL monomers is the most straightforward. Commercially available N-vinylimidazole is quaternized with halogenoalkane (Scheme 7) [51, 54]. An alternative “halide-free” approach involves quaternization of N-vinylimidazole with free acids, for example with tetrafluoroboric acid (HBF_4) or hexafluorophosphoric acid (HPF_6) [61] (Scheme 7). Quaternization with halogenoalkanes is more favourable due to the opportunity to influence the material properties by choice of alkyl substituent. Usually, non-halide anions are more preferable for different applications, so the main advantage of free acid approach is the possibility to synthesize ionic liquids with the desired anion by using only one step. On the contrary, the anion exchange as a second synthetic step is generally required in case of halogenoalkanes. The least possible number of steps is preferred considering the instability of polymerizable ionic liquids and risk for premature polymerization.



Scheme 7. Synthesis of N-vinylimidazolium salts. R – alkyl, X[–] – halide.

General approach for preparing acrylate or methacrylate containing PIL monomers is usually accomplished in a two-step synthesis route (Scheme 8). In the first step, α,ω -halogenoalcohol is treated with (meth)acryloyl chloride, which results in formation of a corresponding ester. As the next step, N-alkylimidazole is quaternized with the formed ester [62, 63]. Methacrylate based polymerizable ionic liquids are the most diverse class among polymerizable ionic liquids. The selection of starting materials enables to prepare different structures. The choice of α,ω -halogenoalcohol allows to modify the length of the linker between the cation and the polymerizable functional group. Imidazoles with different alkyl substituent (typically methyl and butyl but not limited to these) can be used as starting material for quaternization. Also, the polymerizable functional group offers the choice between acryloyl or methacryloyl moieties.



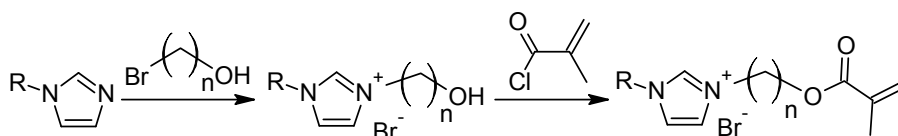
Scheme 8. Synthesis of methacryloyl or acryloyl imidazolium salts.
R – CH₃, H; R' – alkyl; X[–] – halide.

In the first step of synthesis, the formation of (meth)acrylate ester occurs in high yields (approximately 80%). The reaction is exothermic, therefore cooling and slow addition of (meth)acryloyl chloride is recommended. During the reaction HCl as a side product is neutralized using triethylamine to protect C=C bond for electrophilic attack. α,ω -bromoalcohols are preferred over different halogenoalcohols because the rate of quaternization depends on the electrophilicity of applied halogeno compounds (section 1.1.3.1). Quaternization with bromides occurs at moderate temperatures in reasonable time (40°C, 48 h). Although 2-chloroethyl methacrylate has been used for the synthesis of 1-[2-(methacryloyloxy)ethyl]-3-ethylimidazolium chloride [64], the extended heating at higher temperatures (60°C, 120 h) is required for the reaction, and this is not advisable due to the instability of (meth)acrylate esters. Quaternization is reported to occur with quantitative yields, like in similar reactions to prepare conventional ionic liquids, although often the yield for the given reaction is lower or is not reported in the literature. Again, the main reason for this is the instability of (meth)acrylate esters and synthesized polymerizable ionic liquids.

Both tend to autopolymerize and even a moderate heating may accelerate the polymerization reaction. The reason for autopolymerization is not well understood but it is often hypothesized to be caused by peroxide accumulation during the exposure to air. Therefore, all synthetic steps should be carried out in inert atmosphere. The addition of radical scavengers, like 2,6-di-*tert*-butyl-4-methylphenol (BHT), also helps to avoid the polymerization.

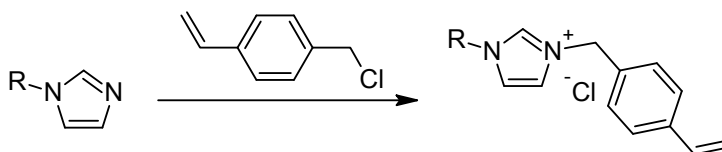
Similar approach was with some modification applied for the preparation of methacrylate functional ionic liquids in which a poly(ethyleneoxide) (PEO) linker is between the cation and the polymerizable functional group. In the first step poly(ethylene oxide) monomethacrylate was terminally chlorinated with thionyl chloride in the presence of pyridine and the obtained compound was used for quaternization of N-ethylimidazole [49].

Alternative synthesis strategies have also been reported for the preparation of polymerizable ionic liquids with (meth)acrylate functionality. A very efficient route was proposed by Shaplov and co-workers in which the order of synthetic steps was reversed and the polymerizable functionality was added in the last step (Scheme 9) [65]. This helps to avoid premature polymerization during the quaternization reaction. 1-[3-(methacryloyloxy)propyl]-3-methylimidazolium TFSI⁻ and 1-[11-(methacryloyloxy)undecyl]-3-methylimidazolium TFSI⁻ were obtained in high yields (more than 80%) using this approach. Even though holding a great potential, the described method has not gained any further attention and has not been studied systematically.



Scheme 9. Reversed synthesis of PIL monomers with methacryloyl group. R – alkyl.

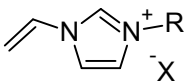
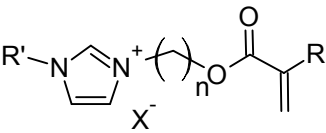
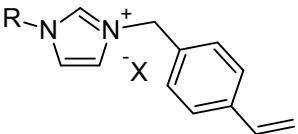
Styrenic PIL monomers are generally prepared by quaternization of N-alkyl-imidazole with 4-chloromethyl styrene, which is widely used in polymer industry (Scheme 10) [53]. The reaction proceeds in high yield (approximately 80%).



Scheme 10. Synthesis of imidazolium salts with styrene group. R – alkyl.

Possible structural variations of previously discussed polymerizable ionic liquids are summarized in Table 2. A suitable counter anion can be introduced to the polymerizable ionic liquids using anion metathesis either before or after polymerization [66]. Both methods have advantages as well as disadvantages. Exchange of the anion before polymerization adds at least one synthetic and purification step at the monomer level, which is not favourable due to instability of the compounds. Contrarily, anion exchange with the polymerized material may not result in quantitative conversion.

Table 2. Structural variation of polymerizable ionic liquids

Polymerizable ionic liquid	Structural variations
	<ul style="list-style-type: none"> Alkyl substituent R Anion X⁻
	<ul style="list-style-type: none"> R: H or CH₃ Alkyl substituent R' Linker between cation and polymerizable functional group Anion X⁻
	<ul style="list-style-type: none"> Alkyl substituent R Anion X⁻

I.3.2.2. Polymerization of polymerizable ionic liquids

Free radical polymerization is the most widely used method for the preparation of PILs. Polymerization is generally thermally initiated using azobisisobutyronitrile (AIBN) and carried out in bulk [67] or in solution, only infrequently in emulsion or dispersion [68].

The main advantage of free radical polymerization is the great tolerance towards functional groups, moisture and impurities, as the difficulties in purification, like removing moisture, is well known for ionic liquids. Beside this, free radical polymerization results in high molecular weights. For methacrylate type PILs with various cations (imidazolium, pyrrolidinium) molecular weights between $0.5\text{--}2.5 \times 10^6$ have been reported [69]. Polymerization was carried out in different solvents (ratio monomer:solvent 1:1) at 60°C during 16 h using AIBN (0.5% w/w) as the initiator.

The fast development of controlled/living radical polymerization techniques during the last decades has had a strong impact on polymer science and on preparation of PILs as well. For example, atom transfer radical polymerization (ATRP) using copper(I)bromide/2,2'-bipyridine based catalyst system was successfully applied for a very fast polymerization of different PILs [63]. In this

report solidification of 1-[2-(methacryloyloxy)ethyl]-3-butylimidazolium tetrafluoroborate was achieved at 60°C in 5 minutes with 72% of conversion. Number-average molecular weight for the obtained PIL was 10,800 and polydispersity index 1.93. Reversible addition-fragmentation transfer polymerization (RAFT) has been found versatile for the preparation of PIL block co-polymers [70,71]. RAFT polymerization is suitable for the preparation of polymers with complex architecture, controlled molecular weight and low polydispersity. Co-polymerization enables to modify the properties of PILs, for example, co-polymerization with non-ionic monomers can be used to decrease the concentration of ionic liquid moieties in the polymer backbone. Using cationic and anionic PIL monomers together as starting materials, co-polymer with opposite charges in the backbone can be prepared. Ring-opening metathesis polymerization [72] and cyclopolymerization [73] of PIL monomers has also been reported in literature.

Beside thermally initiated radical polymerization, the usage of photopolymerization of vinyl monomers is being widely used in the polymer industry. The process is solvent free, energy efficient and cost-effective. Photopolymerization has found extensive applications for example in coatings industry [74]. So far, the photopolymerization method has not been widely applied for preparing PILs. In the literature only a few studies have been reported regardless of the great potential of the method [75–77].

1.3.2.3. Properties and applications of polymerized ionic liquids

Typical PILs are transparent non-crystalline amorphous solids. Mechanical properties of PILs can vary from sticky gels to rubber-like materials. Below T_g PILs can be glassy and brittle. T_g of PILs depends on the chemical nature of the polymer backbone but even more on the anion. The reported T_g -s for polymerized 1-[2-(methacryloyloxy)ethyl]-3-butylimidazolium salts illustrate clearly the relationship between T_g and anion plasticizing effect. T_g was 7°C with TFSI⁻ anion, but increased to 102°C for Br⁻ [78]. Mechanical properties of PILs are not so widely studied as some other characteristics, like ionic conductivity for example. Mechanical properties of multiple PILs were systematically studied by Shaplov and co-workers [79]. Methacrylate type polymerizable ionic liquids with different cations (ammonium, imidazolium, pyrrolidinium) were co-polymerized together with poly(ethylene glycol) dimethacrylate (PEGDM) in ratio PIL monomer:PEGDM 2:1. From investigated polymers the ammonium based PIL had the highest tensile strength – 2200 kPa and also the highest measured elongation (99%). The tensile strengths for the PILs with imidazolium and pyrrolidinium cations were 300 kPa and 180 kPa and the elongation 23% and 14% respectively. For comparison, the tensile strength of poly(methyl methacrylate) is 48–76 MPa and elongation 2–10% [80]. The same study also illustrates the difference between linear and

crosslinked PILs. Some of the investigated PILs did not form self-supporting materials when polymerized without crosslinker.

One of the most important characteristics of PILs is ionic conductivity due to their potential as polymer electrolytes in electrochemical devices. Ionic conductivity is reviewed in more detail in the section 1.3.2.4. In applications of PILs, ion transport, besides ionic conductivity, plays also an important role. For example, zwitterionic PILs can be successfully applied as target ion transport membranes (single ion conductors) [81]. Zwitterionic PILs contain no charge carrier as all ions are fixed. Migration of component ions along the potential gradient is impossible, but they provide ionic environment, which promote transport of added target ions (for example Li^+) in the material. Same effect can be obtained in PILs where polycations are combined with polyanions [82].

Alongside with the electrochemical properties, PILs' ability to absorb different gases has gained much attention. The mentioned property in combination with solid state and non-volatility makes PILs attractive as a safe medium for gas storage. Gas absorption is also important for gas capture and separation from waste streams. PILs, especially with ammonium cation, exhibit high CO_2 absorption capacity [55, 83]. Beside absorption, the gas permeability (CO_2 , N_2 , and CH_4) of PIL membranes has been investigated [77]. However, the field is still in its infancy and additional research is needed to understand gas absorption mechanism in PILs and also the relationships between gas permeability and PILs structure.

Similarly to other ionic liquids, PILs monomers have extraordinary solvating properties. Their ability to dissolve cellulose or carbon nanotubes (CNTs) enables to prepare composites with unique characteristics and improve the mechanical properties of PILs. Fukushima and co-workers have demonstrated that polymerization of single-walled CNT dispersion in polymerizable ionic liquids (1-vinyl-3-ethylimidazolium TFSI^- and different acrylate and methacrylate based imidazolium salts) leads to hybrid materials in which electron conductivity of CNTs and ionic conductivity of PILs are combined [84]. The resulting conductivities for the materials were reported to range from 0.1 to 1.3 S cm^{-1} . Enhanced mechanical properties were observed next to increased conductivities. Only 7% of CNTs in PIL increased the Young's modulus of polymerized material 120 times, from 0.38 MPa to 46 MPa.

PIL have high thermal stability when compared to conventional polymers. As an example the decomposition temperatures (T_d) for polymerized 1-[2-(methacryloyloxy)ethyl]-3-butylimidazolium salts are above 300°C , depending on anion (313°C with BF_4^- , 306°C with PF_6^- , 363°C with TFSI^-) [78] but for poly(methyl methacrylate) T_d is 272°C [62]. T_d of PILs is higher because thermal decomposition of methacrylic polymers starts from backbone scission and imidazolium cations may stabilize it. For different anions T_d of PILs follows the same order as for conventional ionic liquids (section 1.1.2.1).

1.3.2.4. Ionic conductivity of polymerized ionic liquids

Although polymerizable ionic liquid monomers show similar ionic conductivities to common ionic liquids (about 10^{-3} S cm $^{-1}$), the conductivities of polymerized materials are several orders of magnitude lower (10^{-6} – 10^{-8} S cm $^{-1}$) [85]. Ionic conductivity depends on the number of carrier ions and their mobility. Polymerization results in decrease of both, because in the polymerized material cations or anions (or both in case of zwitterionic PILs) are fixed to polymer backbone and although counter ions can move along the potential gradient, their mobility is lower due to high viscosity of the material.

Ohno and co-workers investigated a variety of PILs and concluded that the conductivity of PILs is influenced by polymer architecture, molecular weight, glass transition temperature (T_g) and chemical nature of polymer and ionic liquid moiety. Two strategies can be applied to increase the ionic conductivity of PILs: (1) add carrier ions; (2) lower T_g through modifying the material structure [85].

T_g can be lowered through structural modifications, which add more freedom for segmental motion. As mentioned previously in the section 1.3.2.3, T_g of PILs is influenced by the anion and decrease when the size of the anion and the extent of charge delocalization increase. T_g values for methacrylate [78] and vinyl type PILs [86] decrease in the following order: Br $^-$ > PF $_6^-$ > BF $_4^-$ > Tf $^-$ > TFSI $^-$; and the ionic conductivities increase in the same order.

T_g of PILs can be also influenced by addition of flexible spacer between the ionic liquid moiety and the polymerizable functional group. The spacer helps to retain mobility of the covalently fixed cations and adds free volume, which is necessary to promote segmental motion of macromolecular chain. Ohno and co-workers synthesized a variety of PIL monomers with poly(ethylene oxide) (PEO) or a hydrocarbon spacer between (meth)acrylate group and imidazolium cation and investigated the effect of spacer length to the ionic conductivity and thermal properties [87]. With the both types of spacer the conductivities around 10^{-4} S cm $^{-1}$ were achieved after polymerization, which are several orders of magnitude higher than without spacer. The conductivities with hydrocarbon spacer were slightly better than with PEO: 3.62×10^{-4} S cm $^{-1}$ and 1.49×10^{-4} S cm $^{-1}$ respectively (at 30°C). The difference was explained with a much weaker interaction force of alkyl chain towards anion compared to PEO chain. In case of PEO spacer there was also significant difference between the conductivities with Cl $^-$ and TFSI $^-$ anion, the latter had 20 times higher conductivity. Addition to general anion effect, this difference can be attributed to weaker interaction force of ether oxygen towards TFSI $^-$ than Cl $^-$. Unfortunately PILs with flexible spacers appeared to be sticky and difficult to handle, therefore addition of a small amount of crosslinker was suggested. It was found that already 1 mol% of crosslinker enabled to prepare of self-supporting PIL films without considerable decrease in ionic conductivity after polymerization [88]. As crosslinkers poly(ethylene glycol)divinyl ethers, poly(ethylene glycol)diacrylates and poly(ethylene glycol)dimethacrylates were used.

Besides using the spacer, co-polymerization of PIL monomer together with analogous non-charged monomers is another way to add free volume to PIL system. For example, polymerization of 1-[2-(methacryloyloxy)ethyl]-3-butyl imidazolium salts together with hexyl methacrylate (HMA) led to co-polymers with higher conductivity than original PILs [62]. Surprisingly it was shown in the same study that the conductivity of co-polymers increases with increasing content of non-ionic component, which decreases the overall charge content. This means that the increase of segmental motion (decrease of T_g) has a more significant positive effect on the ionic conductivity than the reduction in charge content, which should decrease the conductivity. Of course, there is a critical concentration of non-ionic polymer, from which point further addition of it leads to the conductivity drop.

Ohno and co-workers also suggested that ionic conductivity can be enhanced by increasing the number of carrier ions. This can simply be achieved through the addition of ionic compounds, like different Li-salts, to PILs. The addition of 20% of LiBF_4 increased the conductivity of poly(vinylimidazolium) from 10^{-8} to $10^{-4} \text{ S cm}^{-1}$. Surprisingly, after the addition of LiCl no improvement was found [85]. From this can be concluded that the number of carrier ions is not the only factor, which leads to the higher conductivity when LiBF_4 is added. The dissociation degree of added salt as well as changes in viscosity may play an important role.

I.4. Inorganic ionogels

This group of ionogels include materials, in which ionic liquids are combined with inorganic networks. Inorganic network can be different nanoparticles (metals, oxides) or carbon nanomaterials (carbon nanotubes, graphene). A convenient method for preparation of inorganic matrix is sol-gel process. Overview about ionogels prepared by sol-gel method is given in the section 1.4.1. Analogous to polymerizable ionic liquids, functionalization of ionic liquids with alkoxysilyl moiety allows covalent binding of ionic liquid with inorganic network and the obtained materials can therefore be classified as chemical ionogels (section 1.4.2).

I.4.1. Inorganic gels by sol-gel process

Sol-gel method is defined as a method for preparing ceramic materials from organometallic precursors (metal or silicon alkoxides) through following stages: (1) preparation of sol, (2) gelation of sol and (3) solvent removal [89].

The essence of sol-gel chemistry is simple: the molecular precursors are transformed into an oxide network by hydrolysis and condensation reactions. Acid or base catalysed hydrolysis of alkoxides and following condensation produces a sol, which is a dispersion of colloidal particles (oligomeric

hydrolysis and condensation products). When condensation proceeds further the colloidal particles link together and form a three-dimensional network, named gel. Next, aging and drying of the gel is carried out in order to increase the strength of the material. Hydrolysis and condensation reactions are schematically presented in Figure 6 [89].

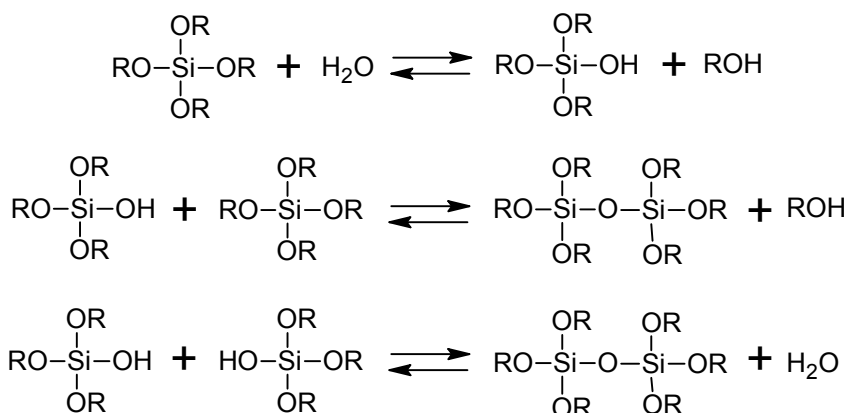


Figure 6. Hydrolysis and condensation reactions in sol-gel process.

Advantages that differentiate sol-gel method from conventional oxide preparation strategies is the usage of relatively low temperature and the synthesis of ceramic materials directly in a designed shape, excluding energy consuming melting and sintering steps. The structures producible by sol-gel techniques are monoliths, fibers, films, membranes, nanoparticles and powders [89].

Combining the sol-gel approach with ionic liquids results in a new interesting class of ionogels. Ionic liquids can play different roles in sol-gel process. They can act as solvents (or co-solvents), drying control chemical additives, catalysts and even as structure directing agents [90]. Using ionic liquids as drying control chemicals helps to avoid cracking and formation of other defects in the sol-gel materials. Reason for this is the negligible volatility of ionic liquids. When using conventional organic solvents, the cracking is related to interface strains associated with formation of a meniscus during evaporation. Whereas ionic liquids form a non-volatile film on the walls of the pores and prevent the formation of surface strains [91].

The first sol-gel synthesis in an ionic liquid solvent was reported in 2000 by Dai and colleagues [92]. In this study 1-alkyl-3-methylimidazolium salts were used as solvents for preparation of aerogel-like silica monoliths from tetramethoxysilane. Stable aerogels were produced without supercritical drying process, which is usually applied for synthesis of aerogels. This pioneering work initiated intensive investigations of the influence of ionic liquids on the structure of the sol-gel material. Porosity of synthesized oxide materials can be

controlled by varying the ratio of ionic liquid and sol-gel precursor or by anion [93]. Different anions lead to distinct morphologies, as it was demonstrated in the synthesis of silica xerogels using 1-methyl-3-(2-methoxyethyl)imidazolium based ionic liquids. Depending on the counter anion, the prepared gels were lamellar monoliths (mesylate anion), powder of aggregated spherical particles (BF_4^-) or porcelain-like honeycomb shape aggregates (PF_6^-) [94].

In early days of the field, ionic liquids were applied as structure directing templates in sol-gel process and were subsequently removed after the gelation step by extraction with acetonitrile or acetone. Only later it was realized that ionic liquids in gel network can be beneficial for several applications as ionic liquids enable to immobilize different functional additives into inorganic matrix. Silica based ionogels containing ionic liquids have been recognized as nanoreactor systems as ionic liquids enable to encapsulate different catalytically active compounds. For example, catalytically active metal complexes ($\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$) were dissolved in 1,3-dialkylimidazolium salts and confined in silica matrix together with ionic liquids [95]. The obtained nanoliquid catalyst was successfully applied for various reactions, for example carbonylation of nitrobenzene and aniline to diphenyl urea. Pd complexes encapsulated in ionogels were also applied as catalysts for C-C coupling reactions like Heck [96] and Suzuki reaction [97].

Due to biocompatibility, biodegradability and resistance to microbial attack, silica matrixes have been considered as drug carriers. Imidazolium salts with very long alkyl substituents (more than 10 carbon atoms) have anti-bacterial properties. Encapsulating such ionic liquids in silica matrix resulted in ionogels, which are applicable as antibacterial controlled release delivery devices [98]. Ionogels containing imidazolium ibuprofenate were also prepared and demonstrated as an efficient drug releasing system [99].

Beside silica-based ionogels, gels from various metal alkoxides have also been investigated. Among them TiO_2 structures are the most studied ones due to their photoactivity and potential applications in solar cells and opto-electronics. As the physical and chemical properties of TiO_2 are dependent on its structure, synthesis in ionic liquids to modify the structure of TiO_2 can be advantageous [90]. Moreover, TiO_2 based ionogels containing 1-methyl-3-propylimidazolium iodide were successfully applied as electrolytes in dye-sensitized solar cells [100].

Other metal oxides, which have been used for preparation of ionogels are tin dioxide, alumina, vanadia and there are also some examples about mixed oxides [90]. All of them have some special characteristics and potential applications, but the in-depth review of these remains outside the focus of the current thesis.

1.4.2. Chemical inorganic ionogels

In addition to previously described ionogels in which ionic liquid is encapsulated into solid inorganic network, there are also hybrid materials in which ionic liquid moiety is covalently bound to inorganic matrix. This type of materials can be classified as chemical inorganic gels. Covalent immobilization is usually achieved through silyl functional groups incorporated in ionic liquid structure. In context of ionic liquids and ionogels, these materials first gained attention in early 2000's but there is also strong analogy with silanization and preparation of ORMOSILs (Organically Modified Silica) which are known already for decades [101]. Therefore silyl functionalized ionic liquids can also be classified as silanization reagents with ionic liquid moiety.

Silanization is a sol-gel method for preparation of organic thin films on a surface (Figure 7). In most cases silanization is used to give specific properties to a substrate.

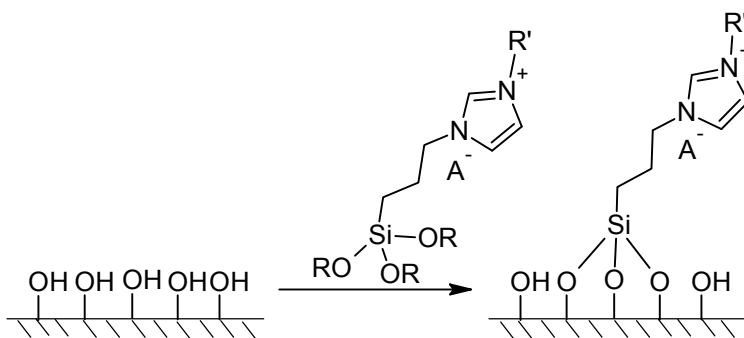


Figure 7. Surface silanization with silyl functionalized ionic liquid.
R, R' – alkyl, A⁻ – anion.

Silanization of a surface with ionic liquids functionalized reagents enables to prepare switchable surfaces. It is known that miscibility of alkylimidazolium salts with water depends on anion. 1-alkyl-3-(3'-triethoxysilylpropyl)-imidazolium salts were used to prepare surface coatings which wettability depends on the ionic liquid anion (in case of Cl⁻ hydrophilic, but with PF₆⁻ hydrophobic) [102]. In this study the properties of ionic liquids were successfully applied in solid phase: tuneable water miscibility of 1,3-di-alkylimidazolium salts was transformed into water wettability of surfaces having ionic liquid functionalized coating.

Another application for the ionic liquid functionalized surfaces is catalysis. Ionic liquids have been used as catalysts for different reactions [32]. Heterogeneous catalysts are frequently used in chemical industry, especially in continuous flow processes. Immobilization of catalyst also simplifies its separation from the reaction medium. Supported ionic liquids can itself be used as catalysts (SILC – supported ionic liquid catalysis) or as reaction media and

matrix for immobilization of the catalysts (SILP – supported ionic liquid phase). Several examples on the latter are also given in the section 1.4.1 but compared to these, covalent immobilization of ionic liquid significantly improves the stability of SILPs and reduces leaching of ionic liquid and catalytically active species out of silica matrix. Silica particles are generally favourable as solid support material due to their thermal and chemical stability.

In SILCs common ionic liquid cations are often combined with exotic anions like different catalytically active metal complexes. For example magnetic nanoparticles have been covalently functionalized with 1-methyl-3-[3'-(triethoxysilyl)propyl]imidazolium polyoxometalates ($[W_2O_{11}]^{2-}$) [103]. Metal-oxygen clusters have attracted attention as active species in oxidation reactions. Magnetic particles with $[W_2O_{11}]^{2-}$ ionic liquid coating were successfully tested for epoxidation of alkenes. The main advantage for such particles is magnetic separation. Another example on catalytically active metal complexes as ionic liquid anion is a study, where treatment of 1-methyl-3-[3'-(triethoxysilyl)propyl]imidazolium chloride impregnated silica particles with $NiCl_2$ leads to formation of $NiCl_4^{2-}$ as a new ionic liquid anion. The functionalized particles were used as a catalyst for oxidation of styrene [104].

However, there are more studies where ionic liquid is used as a linker for immobilizing a catalyst not as the catalyst itself. SILPs containing various covalently bound or physically adsorbed metal particles or ions have been used to catalyse various reactions. Ru-complexes are highly efficient catalysts for olefin metathesis. Typically, they contain N-heterocyclic carbene ligands generated from imidazolium salts. Therefore it is beneficial to use ionic liquids for covalent immobilization of Ru-catalysts [105]. Using SILP with immobilized Ru-complex, similar catalytic activity to corresponding homogenous catalysts and recyclability were witnessed in ring-closing metathesis. Synthesis methods for preparation of C-C bond are under intense investigation. Therefore an analogous approach has been employed for grafting Pd-catalysts on surface of SiO_2 by the means of ionic liquid. The obtained heterogeneous catalyst was successfully applied in Heck reaction [106].

Although in the previously mentioned studies the covalent linking did not affect the catalytic activity, it may become hindrance in some cases. For example, by immobilization of catalytically active enzymes the covalent bond could form at the active site of the enzyme and decrease the catalytic activity. Therefore ionic liquid functionalized SiO_2 nanoparticles were applied for immobilization of an enzyme, Penicillin G acylase, through physical adsorption [107]. Penicillin G acylase is used as a catalyst in manufacture of semisynthetic antibiotics.

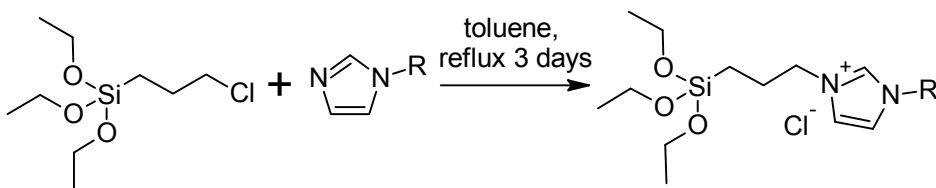
Beside catalysis ionic liquid functionalized SiO_2 particles have been applied in analytical chemistry and separation sciences. The usage of neat ionic liquids in chromatography is limited due to possible leakage. Immobilization of ionic liquids seems to solve this problem, as it can be concluded from testing ionic liquid functionalized SiO_2 particles as stationary phase for high performance

liquid chromatography [108]. Ionic liquids' ability to interact with transition metals have been found beneficial not only for immobilization of catalysts but also to absorb metal ions, for example to remove hazardous pollutants like Cr(VI) from wastewater [109].

Although ionogels with imidazolium cations are prevalent in literature, there are also a lot of studies based on silyl functionalized ammonium salts. Such ionic liquids can be easily prepared from (3-aminopropyl)trimethoxysilane (APTES) which is a widely used surface silanization reagent. With the help of N-trimethoxysilylpropyl-N,N,N-trimethylammonium salt cylindrical helical stacking of porphyrins was achieved. This chiral mesostructured porphyrin-silica hybrids are promising as heterogeneous asymmetric catalysts for small chiral molecules [110]. Silyl functionalized ammonium iodide impregnated silica particles have been used as electrolytes in dye-sensitised solar cells [111]. Immobilized ammonium salts have been found effective as antibacterial coatings [112]. In order to increase stability of the antibacterial coating, zwitterionic ionic liquids functionalized with silyl groups and having ammonium cation and sulphonium anion have also been prepared [113].

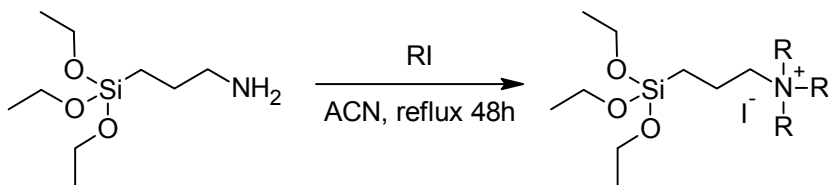
1.4.2.1. Synthesis of silyl functionalized ionic liquids

The synthesis of 1-[n-(trialkoxysilyl)alkyl]-3-alkylimidazolium salts is similar to the synthesis of conventional ionic liquids. The salt is formed through quaternization of N-alkylimidazole with suitable silyl functional reagent but significantly higher temperatures are necessary and because of that the yields are lower as possible side reactions can occur. Scheme 11 describes quaternization in synthesis of 1-[3'-(triethoxysilyl)alkyl]-3-methylimidazolium chloride. Interestingly, it has been shown that yields are better for reactions with N-alkylimidazole with longer alkyl substituents. For example, quaternization of N-butylimidazole occurred with a yield of 73% but with N-methylimidazole the yield was 58% [114]. Anion exchange can be done by anion metathesis if necessary. As with polymerized ionic liquids, anion exchange can be done with synthesized ionic liquid or after immobilization (polymerization or sol-gel reactions). As anion metathesis is often carried out in aqueous solution or water is used in separation steps, it is recommended to change anion after the sol-gel process.



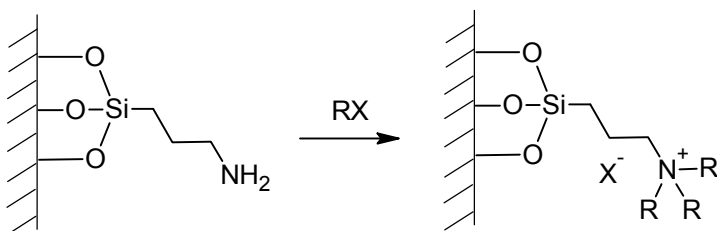
Scheme 11. Synthesis of 1-[(3'-triethoxysilyl)propyl]-3-methylimidazolium chloride.
R – alkyl.

Synthesis of silyl functionalized ionic liquids with other cations than imidazolium is rather rare in the literature. Synthesis of triethoxysilanes bearing quaternary ammonium alkyl iodides has been reported [115]. Salts were formed through quaternization of APTES with iodoalkanes with different alkyl chain lengths (R – ethyl, heptyl, dodecyl) in high yield (>88%) (Scheme 12). Obtained salts were liquids at room temperature and can be classified as ionic liquids.



Scheme 12. Synthesis of silyl functionalized ammonium salts. R – alkyl.

An alternative route for preparation of ammonium salt based covalent ionogels is to form ionic liquid like moiety already on the surface. First, the substrate is silanized with APTES and then its quaternization with halogenoalkanes leads to formation of immobilized ionic liquid like structure (Scheme 13) [111].



Scheme 13. Formation of ionic liquid like structure on surface.
R – alkyl; X- halide.

From comparison of the two methods can be conclude that preparation of ionic liquid first and then carrying out silanization is more efficient as quaternization of immobilized amine can result in an insufficient conversion [111].

2. AIMS OF THE STUDY

Two different types of ionogels were in the focus of the present study. According to definitions in the section 1.2, the prepared materials can be classified as chemical organic ionogels and chemical inorganic ionogels.

The purpose of developing the new type of organic ionogels was to prepare a transparent, flexible and conductive material with tuneable mechanical properties. As a self-supporting matrix, polymerized ionic liquids (PIL) prepared from 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium salts were chosen due to the high conductivity of imidazolium-based ionic liquids and the possible structural variations of this type of PILs. To modify the physico-chemical properties of PILs, the material was mixed with a conventional ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]). More specifically the objectives for the part of organic ionogels were set as follows:

1. To develop an improved method for synthesis of polymerizable ionic liquids with methacrylate or acrylate functional group as a polymerizable moiety. The aim of finding new ways for synthesis of polymerizable ionic liquids was to avoid the premature polymerization of the synthesized compounds.
2. To prepare 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium bromides with different alkyl chain lengths between the polymerizable functional group and the ionic liquid cation (n=2, 6, 7, 10), by applying the newly developed synthesis method.
3. To estimate suitability of the photopolymerization as a feasible technique for polymerizing the synthesized ionic liquids.
4. To prepare material with enhanced ionic conductivity by combining the prepared PILs with [EMIM][BF₄].

The main goal for the research in the field of inorganic ionogels was to develop a method for synthesis of hydrazinosilanes, like (3-hydrazinopropyl)-trimethoxysilane. Hydrazinosilanes can be used as silanization reagents similarly to aminofunctional silanes. Both aminosilanes and hydrazinosilanes can be applied as precursors for preparation of inorganic ionogels. Hydrazino-functional ionic liquid like structures on various substrates may have several advantages compared to ammonium salts. More specifically, the aims for this part of the thesis were set as follows:

1. To find selective reaction conditions for the synthesis of allyl hydrazine, which is a starting material for preparation of (3-hydrazinopropyl)-trimethoxysilane.
2. To develop a synthesis method for preparation of (3-hydrazinopropyl)-trimethoxysilane as a prototypic reagent for different hydrazinosilanes.

3. METHODS

3.1. Synthesis of ionic liquids

All reactions for preparing ionic liquids were carried out in inert atmosphere in carefully dried and vacuumed apparatus. All used solvents were previously dried using standard procedures.

3.2. Characterization of synthesized compounds

All synthesized compounds were characterized by NMR and IR spectroscopy. ^1H - and ^{13}C -NMR spectra were recorded at ambient temperature on a Bruker Avance II 200 spectrometer, using d_6 -DMSO or CDCl_3 as a solvent. The ^1H -NMR spectra were measured at 200 MHz and the ^{13}C -NMR spectra at 50 MHz. The chemical shifts were internally referenced by the residual solvent signals relative to tetramethylsilane. The IR spectra were obtained on a Perkin-Elmer Spectrum BXII FT-IR instrument. Purity of synthesised α,ω -bromo-alcohols was determined using GC-MS (Agilent Technologies 7890A GC System MSD 5975C, column HP-5 ms 30 m \times 0.25 mm).

During the course of this doctoral study following five compounds were synthesized for the first time:

- 1-(7-hydroxyheptyl)-3-methylimidazolium bromide
- 1-(10-hydroxydecyl)-3-methylimidazolium bromide
- 1-[(7-methacryloyloxy)heptyl]-3-methylimidazolium bromide
- 1-[(10-methacryloyloxy)decyl]-3-methylimidazolium bromide
- (3-hydrazinopropyl)trimethoxysilane.

For all new compounds HRMS was measured using a Thermo Electron LTQ Orbitrap ESI spectrometer.

3.3. Polymerization and *in situ* conductivity measurements

Photoinduced free radical polymerization of polymerizable ionic liquids and mixtures of polymerizable ionic liquids and $[\text{EMIM}][\text{BF}_4]$ were carried out in 2 mL eppendorf tubes; the volume of reaction mixtures was 1 mL. For *in situ* conductivity measurements during polymerization platinum electrodes were immersed in the mixtures to a certain depth (see Figure 8).

Samples were placed into a UV-chamber, consisting of an aluminium box with internal dimensions of 98 \times 260 \times 70 mm, equipped with four 8 W blacklight fluorescent lamps with a peak emission wavelength of 352 nm, symmetrically positioned around the samples. The samples were irradiated for 40 h.

The platinum electrodes were prepared from 0.5 mm diameter Pt wire (99.9%, Aldrich), separated by a distance of 4.9 mm using a Teflon spacer. The cell constant K , necessary for calculating resistivity from the measured resistance values, was determined using 0.1 M KCl aqueous solution with known conductivity of 12.64 mS/cm at 24°C. The platinum electrodes were cleaned with piranha solution and washed thoroughly with distilled water prior to the cell constant measurements.

The temperature inside the irradiation chamber was measured conjointly with the electrical resistance of the samples using Pt100 thermoresistor connected to a Keithley 2400 sourcemeter. The electrical resistance measurements were carried out at a 1 kHz frequency and current through a sample was set to 0.13 mA, which was kept constant during all the experiments. A Metrix3240 signal generator was used as a voltage source. Voltage and current were measured by Agilent 34410A multimeters and a relay card was used for measuring multiple objects simultaneously. The operation of all the devices was controlled by a PC.

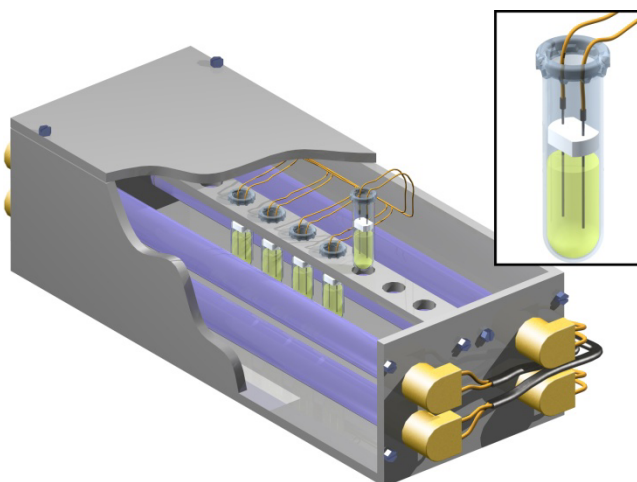


Figure 8. Set-up for polymerization of ionic liquid mixtures and *in situ* conductivity measurements.

4. RESULTS AND DISCUSSION

Experimental work and results in the present thesis are divided into two parts. The studies I and II are focused on preparation of organic ionogels from polymerizable ionic liquids and mixtures of polymerizable and conventional ionic liquids. The studies III and IV cover the development of synthesis method for preparing hydrazinosilanes.

4.1. Ionogels from polymerized ionic liquids

4.1.1. Synthesis of polymerizable ionic liquids

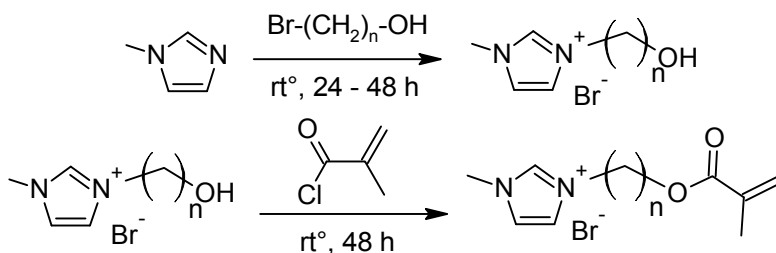
In the study I a new method for synthesis of polymerizable ionic liquid monomers with methacrylate moiety as the polymerizable functional group was developed. The aim for finding new synthesis routes was to avoid the premature polymerization of the synthesized compounds during preparation. Applying the developed method, 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium bromides with different alkyl chain lengths between the polymerizable functional group and the ionic liquid cation (n=2, 6, 7, 10) were synthesized in high yields (more than 80% over two steps).

The common synthesis route for preparing acrylate- and methacrylate functionalized ionic liquids involves formation of (meth)acrylate ester by acylation of α,ω -bromoalcohol with (meth)acrylic chloride and quaternization of N-alkylimidazole (or other substrate) with the corresponding ester. Although the described method has been widely used by many authors, it has several drawbacks related with stability and possible premature polymerization of compounds during the synthesis. To date, most of the studies in the field of polymerized ionic liquids have mainly been focused on the investigation of the properties and the potential applications of the material. In order to put these applications into practice, the synthesis of (meth)acrylate ionic liquids as starting materials requires further optimising.

As mentioned, the main disadvantage of the common synthesis method is premature polymerization during the synthesis. Both methacrylate esters as the starting materials and the forming ionic liquids may undergo polymerization. The polymerization occurs in the quaternization step, as this step is usually accelerated by moderate heating. Unfortunately, heating also increase the rate of polymerization reaction and compared to quaternization, polymerization using free radical mechanism is a significantly faster reaction and therefore prevalent.

To overcome the described drawback, in the present study the order of the synthetic steps were reversed so, that the polymerizable functional group was added in the last step and the reaction conditions were also chosen as mild as possible (Scheme 14). Being guided by the possible applications of polymerized ionic liquids, the alkyl chain length between the imidazolium cation and the polymerizable moiety was varied (from 2 to 10 carbon atoms) as it has been

shown to increase the ionic conductivity of the polymerized material (section 1.3.2.4). To vary the spacer length, different α,ω -bromoalcohols were synthesised from corresponding α,ω -diols and used for quaternization of N-methylimidazole. Obtained hydroxyl functionalized imidazolium salts were acylated with acryloyl chloride or methacryloyl chloride. Similar synthesis has been previously proposed by Shaplov [65] (section 1.3.2.1). Differently from Shaplov's procedure, in the present study all synthetic steps were successfully carried out at room temperature.



Scheme 14. Synthesis of polymerizable ionic liquids with methacrylate functional group; $n=2, 6, 7, 10$.

Table 3 summarizes the results of the synthesis. The first step, quaternization of N-methylimidazole to form 1-(n-hydroxyalkyl)-3-methylimidazolium bromides, occurred in all cases with quantitative yield. Physical state of the obtained products was dependent of the length of alkyl substituent. The resulting salt was solid with 2-hydroxyethyl chain, liquid with longer substituents but a solid state was obtained again in case of 10-hydroxydecyl. The trend is typical to ionic liquids. Solidification of ionic liquids with long alkyl chains can be explained with formation of a lamellar structure. It is worth to mention that hydroxy-functionalized ionic liquids prepared in the first step of the synthesis have gained attention in the context of task-specific ionic liquids [116]. For example, they can be applied in tribology [117], where the hydroxyl group provides strong adsorption with different metal surfaces. Another application for these ionic liquids is as catalysts for coupling reactions [118,119].

The next synthetic step, acylation with methacryloyl chloride was also successful with all starting compounds and 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium bromides were synthesised in high yields. The reaction was carried out in mild conditions at room temperature. Heating was avoided to prevent polymerization. Compared to conventional synthesis, acylation of 1-(n-hydroxyalkyl)-3-methylimidazolium bromides was considerably slower than the formation of methacrylate ester from methacryloyl chloride and α,ω -bromoalcohols. Also, the excess of methacryloyl chloride was needed to complete the reaction. The excessive reagent can be removed after reaction by extraction with diethyl ether. A correlation between the reaction time and the

length of hydroxyalkyl substituent on imidazolium cation was observed – with longer substituents extended time was needed to complete the reaction. Although the risk for premature polymerization was reduced using this synthetic route, BHT as polymerization inhibitor was still added to the reaction mixture and during the storage to the synthesized products as well.

Table 3. Results for synthesis of polymerizable ionic liquids.

Alkyl chain length n	I step, yield %	II step, yield %
2	99	95
6	99	97
7	89	93
10	94	92

Although the results for synthesis of 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium bromides were excellent, the method has limitation with acrylates. In acylation with methacryloyl chloride or acryloyl chloride HCl is formed as a side product and it can react with carbon-carbon double bond (C=C). The chemical nature of methacrylic and acrylic C=C bond is different and in case of methacrylates electrophilic addition to double bond is prevented. To the contrary, in acrylates the C=C bond readily reacts with HCl. To avoid the HCl addition, different scavengers can be used, but in this point the developed method needs further improvement as in current study all tested scavengers (TEA, molecular sieves, anionite Purolite A103S) were not particularly efficient.

To conclude, a new method for the synthesis of methacrylate functionalized ionic liquids was developed and applying the method 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium bromides with the alkyl chain length from 2 to 10 atoms were synthesized in high yields. Four compounds from the synthesized ionic liquids were prepared for the first time (see the section 3.2).

4.1.2. Preparation of ionogel with tuneable properties

In the study II a new type of organic ionogels with tuneable properties were developed. Polymerized ionic liquids (PILs) are known to have significantly lower ionic conductivity than corresponding ionic liquid monomers. In the present study the ionic conductivity of the material was increased by mixing PILs with a conventional ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]).

1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium bromides prepared in the study I were mixed with [EMIM][BF₄] in various proportions (up to 75% v/v of [EMIM][BF₄]). The obtained mixtures as well as the neat PIL monomers were polymerized as bulk using self-initiated photopolymerization carried out

as described in the section 3.3. During polymerization, the electrical resistivity of the polymerizing materials was measured to observe the progression of the polymerization reaction.

Hypothesis for the current study was that the addition of [EMIM][BF₄] improves the ionic conductivity of the materials because it increases the number of carrier ions and decreases the T_g and the viscosity of the materials due to the structural alteration.

A similar study has been previously carried out with 1-alkyl-3-vinylimidazolium salts by Marcilla and co-workers [120]. In the present study 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium salts were preferred because they allow more structural variations compared to other type of PILs. The spacer length between the cation and the polymerizable moiety can be varied and it plays an important role in increasing the conductivity. In Marcilla's study, already polymerized ionic liquids were dispersed in ionic liquid to prepare PIL/IL mixtures, whereas in the current study PIL monomers and ionic liquid were mixed before polymerization to achieve a more homogenous dispersion.

In situ measurements of resistivity of the polymerizing PILs and PIL/IL mixtures have not been carried out prior to the present study. The resistivity measurements provide information about changes in the conductivities of the materials during polymerization and also enable to observe the progression of the polymerization reactions. Figures 9–11 present changes in the resistivity of PIL/IL mixtures during the irradiation.

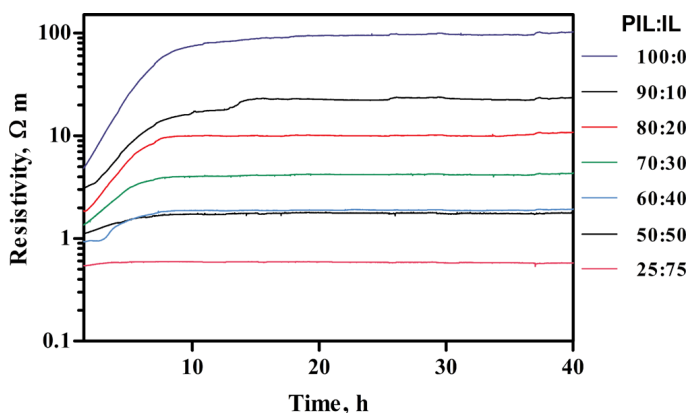


Figure 9. Resistivity of mixtures from 1-[6-(methacryloyloxy)hexyl]-3-methylimidazolium bromide and [EMIM][BF₄].

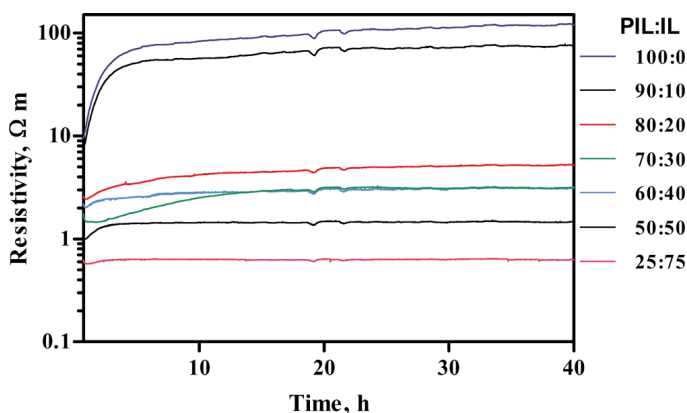


Figure 10. Resistivity of mixtures from 1-[7-(methacryloyloxy)heptyl]-3-methylimidazolium bromide and [EMIM][BF₄].

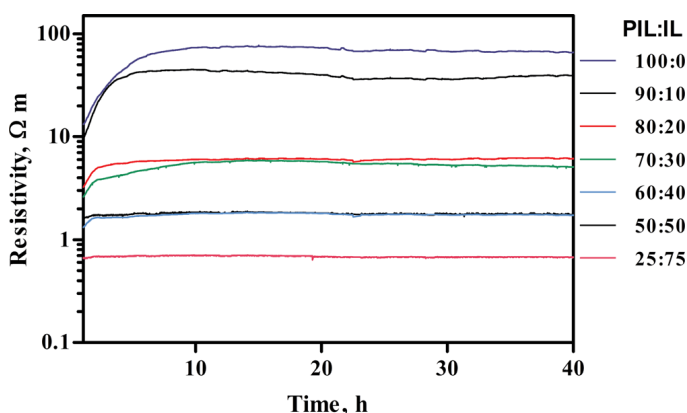


Figure 11. Resistivity of mixtures from 1-[(10-methacryloyloxy)decyl]-3-methylimidazolium bromide and [EMIM][BF₄].

From Figures 9–11 it can be concluded that the addition of [EMIM][BF₄] significantly decreases the resistivity of the material. From the polymerization curves follows also that although the PIL/IL mixtures were irradiated for 40 h, most of the changes in the resistivity occurred only within several hours and after that a plateau was reached. A conclusion can be made that the polymerization merely proceeds within few hours. ¹H-NMR spectra of the neat PILs confirmed the efficiency of photopolymerization as the full conversion of methacrylate group was observed during the polymerization.

From the resistivity measurements it is evident that PILs with different alkyl chain lengths reach the plateau in different times. This is caused by differences in the viscosities and the concentrations of the polymerizable functional groups in the materials. Comparison of the PIL/IL mixtures with different ratios

prepared from the same PIL monomer indicates that the mixtures with different ratios also reach the plateau in different times. Likewise, again both the viscosity and the concentration of the polymerizable functional group play a significant role.

A further aim of the present study was also to estimate, how the spacer length between the cation and polymerizable functional group influences the ionic conductivity of PILs. A linear correlation presented in Figure 12 was found between the conductivity of PILs and the alkyl chain length n . The longer spacer results in higher mobility of the covalently fixed cation and therefore also in higher conductivity of the material.

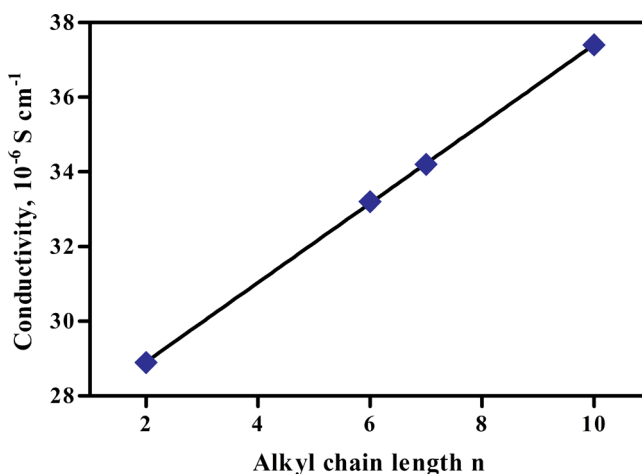


Figure 12. Correlation between the ionic conductivity of PIL and the spacer length between the cation and polymerizable moiety.

In the present study the content of $[\text{EMIM}][\text{BF}_4]$ in PILs was varied from 10 to 75% v/v. Figure 13 presents the exponential correlation between the ionic conductivity of the polymerized material and the content of $[\text{EMIM}][\text{BF}_4]$.

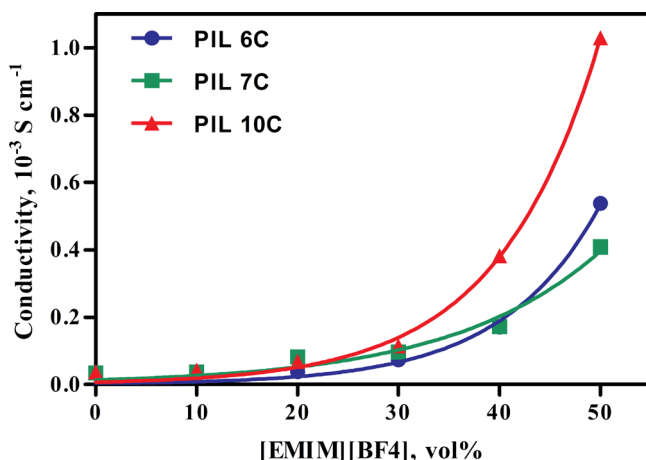


Figure 13. Correlation between the ionic conductivity and the content of [EMIM][BF₄] in PILs.

The final conductivities of all PIL/IL mixtures at room temperature after polymerization are summarized in Table 4. The conductivities for the neat PILs were around 10^{-5} S cm⁻¹ at room temperature. Among the neat PILs, the conductivity of PIL 10C was the highest. The addition of 10% v/v of [EMIM][BF₄] to PIL 10C resulted in material with 13% higher conductivity compared to the neat PIL. When the content of [EMIM][BF₄] reached 20% v/v, the conductivity rise of about 85% was obtained. The increase of the conductivities over an order of magnitude (from 10^{-5} S cm⁻¹ to 10^{-4} S cm⁻¹) were achieved for all PIL/IL mixtures with the [EMIM][BF₄] content about 40% v/v.

Table 4. Ionic conductivities for PIL:IL mixtures at room temperatures

[EMIM][BF ₄] % v/v	Ionic conductivity S/cm		
	PIL 6C	PIL 7C	PIL 10C
0	3.32×10^{-5}	3.42×10^{-5}	3.74×10^{-5}
10	3.71×10^{-5}	3.68×10^{-5}	4.23×10^{-5}
20	3.82×10^{-5}	8.17×10^{-5}	6.92×10^{-5}
30	7.35×10^{-5}	9.65×10^{-5}	1.15×10^{-4}
40	1.71×10^{-4}	1.73×10^{-4}	3.83×10^{-4}
50	5.38×10^{-4}	4.08×10^{-4}	1.03×10^{-3}
75	4.49×10^{-3}	3.41×10^{-3}	5.15×10^{-3}
100	1.32×10^{-2}	1.32×10^{-2}	1.32×10^{-2}

PIL 6C: poly(1-[6-(methacryloyloxy)hexyl]-3-methylimidazolium bromide)

PIL 7C: poly(1-[7-(methacryloyloxy)heptyl]-3-methylimidazolium bromide)

PIL 10C: poly(1-[10-(methacryloyloxy)decyl]-3-methylimidazolium bromide)

Besides the ionic conductivity, the mechanical properties of the materials are also influenced by the content of [EMIM][BF₄]. Physical state of the PIL/IL mixtures varied after polymerization from transparent self-supporting solids to viscous and sticky gels depending on the content of [EMIM][BF₄]. The increase of the amount of IL in PILs leads to the formation of gel-like materials instead of hard solids, which is characteristic to the neat PILs. When the content of [EMIM][BF₄] was higher than 50% v/v, the mixtures were liquid even after polymerization.

In preparation of polymer gels consisting of conventional polymers and ionic liquids, the main problems are associated with achieving a homogenous and stable material, because of the incompatibility of polymer and ionic liquid. Therefore it is important to note, that all PIL/IL mixtures prepared in the present study were homogenous and phase separation was not observed although the content of [EMIM][BF₄] was varied in wide range.

4.2. Hydrazino-functional precursor for inorganic ionogels

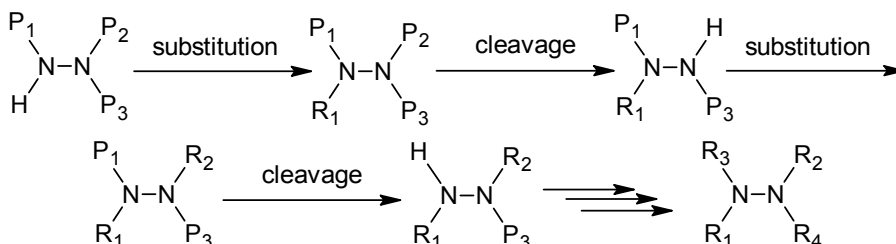
4.2.1. Different methods for synthesis of allyl hydrazine

In the study III synthesis of allyl hydrazine as a starting material for (3-hydrazinopropyl)trimethoxysilane was investigated. Different methods for synthesizing allyl hydrazine based on direct alkylation as well as protective group strategy were tested and compared on the basis of yield, efficiency and selectivity. The number of synthetic steps and overall cost-effectivity of synthesis were also considered.

Despite the simple structure of allyl hydrazine and other alkylsubstituted hydrazine derivatives the selective synthesis of these compounds is rather difficult task to achieve. Classical methods, like direct alkylation of hydrazine hydrate, generally result in a complex mixture of different polyalkylated and even quaternized products. Separation of the desired product from the mixture is usually complicated.

Due to difficulties with the classical method, the protective group strategy was applied for preparation of allyl hydrazine in the current study. The orthogonal protective group strategy was first introduced for hydrazine derivatives in 1996 by Mäeorg and co-workers [121]. They used triprotected hydrazine precursor, 1,1,2-tris-(*tert*-butoxycarbonyl)hydrazine (tri-Boc-hydrazine) for the synthesis of different alkylsubstituted hydrazines. Since that the given method has been widely used for the synthesis of substituted hydrazines. A variety of different hydrazine precursors have been synthesized by combining various protective groups (Z (benzyloxycarbonyl), Tos (para-toluenesulphonyl), Cbs (cyanobenzenesulphonyl)), which beside alkyl substitution also enable to synthesize aryl hydrazines [122–125].

Scheme 15 describes the general principle of the orthogonal protective group strategy. The concept of orthogonality means that different protective groups can be removed selectively one by one. Even when the protective groups are of the same type, like in tri-Boc-hydrazine, the different chemical properties of unequally substituted amino groups allow the selective cleavage.



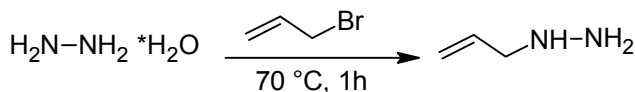
Scheme 15. Stepwise synthesis of substituted hydrazines by protective group strategy. P – protective group.

In the present study hydrazine hydrate and Boc-hydrazines with different substitution patterns were selected as precursors for the synthesis of allyl hydrazine. Boc was chosen as a protective group because it is easily and efficiently removable. Results for the different reactions are summarized in Table 5.

Table 5. Results for allylation of hydrazine hydrate and different protected precursors.

starting material	product	yield, %	selectivity
hydrazine hydrate	allyl hydrazine	13	no
Boc-hydrazine	1,1-diallyl-2-Boc-hydrazine	56	yes
1,2-bis-Boc-hydrazine	1-allyl-1,2-bis-Boc-hydrazine	50	no
1,1,2-tri-Boc-hydrazine	1-allyl-1,1,2-tri-Boc-hydrazine	82	yes

Direct alkylation of hydrazine hydrate with allyl bromide (Scheme 16), which was carried out according to the protocol developed by Ioffe and co-workers [126] gave a mixture of allyl hydrazine and 1,1-diallyl hydrazine.

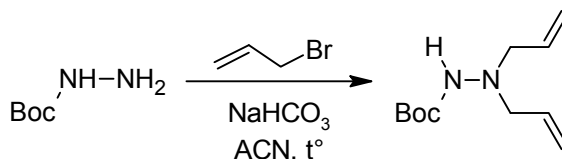


Scheme 16. Alkylation of hydrazine hydrate.

The main advantages of this method are simplicity as it involves only one synthetic step and a low price. Therefore the direct alkylation might be feasible when the desired product could be separated from the obtained mixture.

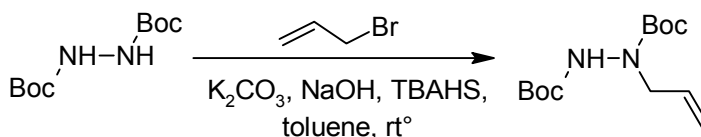
Unfortunately in the current study efficient isolation of allyl hydrazine was not observed due to similar physico-chemical properties of allyl hydrazine and 1,1-diallyl hydrazine.

Boc-hydrazine was found unsuitable for the synthesis of allyl hydrazine as its alkylation resulted in formation of only dialkylated product (Scheme 17). However, the obtained product can be applied as a useful building block for preparation of more sophisticated compounds.



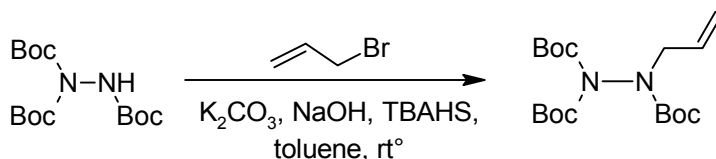
Scheme 17. Alkylation of Boc-hydrazine.

The feasibility of 1,2-bis-Boc-hydrazine as the parent compound for allyl hydrazine has been pointed out previously by other authors [127]. Although in the present study the conditions for a very fast allylation under the phase transfer catalysis were found (reaction was completed within 10 minutes), the selectivity of alkylation remained questionable (Scheme 18). In small scale the reaction was selective and only traces of dialkylated product were found. However, in larger scale a mixture of mono- and dialkylated product was obtained. Monoallylated product was separated by column chromatography with a satisfactory yield (50%) and the cleavage of Boc-groups succeeded with a very high yield (98%) by a well-known method with trifluoroacetic acid. The loss of selectivity in larger scale can be explained by the peculiarities of the phase transfer catalysis.



Scheme 18. Allylation of 1,2-bis-Boc-hydrazine.

Alkylation of tri-Boc-hydrazine in the same phase transfer catalysis conditions as were used for 1,2-bis-Boc-hydrazine resulted in allylated product with the yield of 82% (Scheme 19). The reaction also proceeded very fast and was completed within 15 minutes. Boc-groups were removed using trifluoroacetic acid (yield 97%).



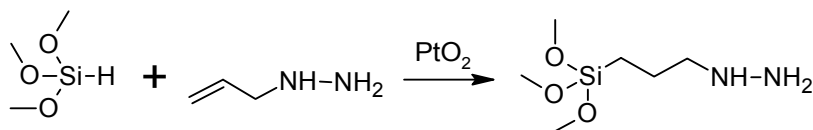
Scheme 19. Alkylation of tri-Boc-hydrazine.

Not surprisingly, tri-Boc-hydrazine was found to be the most selective starting material as the formation of the side products is prevented. However, from the economical perspective the use of this precursor is not rational, as it involves several additional steps, like preparation of hydrazine precursor and cleavage of protective groups, when compared to direct alkylation.

4.2.2. Synthesis of (3-hydrazinopropyl)trimethoxysilane

The main objective of the study IV was to develop a synthesis method for preparation of hydrazinosilanes. (3-hydrazinopropyl)trimethoxysilane (HPTMS) was prepared as a prototype reagent (Scheme 20). The applied synthetic strategy can be used for preparation of other hydrazinosilanes as well, for example alkoxy groups on silane can be varied or other hydrazine precursors beside allyl hydrazine can be used. Although structurally similar to aminosilanes, the preparation of hydrazinosilanes had not been reported prior to the study IV of the current thesis.

HPTMS is analogous to (3-aminopropyl)trimethoxysilane (APTES), which is a widely used silanization reagent for preparation of functionalized siloxane films on different substrates (glass, quartz, alumina). The main applications for APTES are in biotechnology and coating industries, as it can be applied as a linker for immobilizing different biomolecules and other compounds on surfaces. Quaternization of APTES enables the preparation of ionic liquid like structures that can be classified as inorganic chemical ionogels (sections 1.2 and 1.4.2).



Scheme 20. Synthesis of (3-hydrazinopropyl)trimethoxysilane.

The developed method for the synthesis of HPTMS is based on hydrosilylation like the synthesis of analogous aminosilanes. Trimethoxysilane was used for hydrosilylation of allyl hydrazine (Scheme 20). Hydrosilylation requires catalyst for C=C bond activation. Electron rich complexes of Co(I), Rh(I),

Ni(0), Pd(0) and Pt(0) are generally used. In the present study the reaction was catalysed by PtO₂, which has been found very efficient for hydrosilylation of various alkenes, especially aminoalkenes [128]. PtO₂ as a heterogeneous catalyst was due to its easy separation preferred to Speier catalyst (H₂PtCl₆*6H₂O/iPrOH), which is a routinely applied homogenous catalyst for hydrosilylation.

The main difficulty in the synthesis of HPTMS lies in the requirement to use anhydrous reagents in order to avoid hydrolysis of trimethoxysilane. Hydrazines, like amines, form strong hydrates due to the basicity of the compounds. From the various studies aiming to prepare anhydrous hydrazines can be concluded that hydrates of hydrazines are very stable and extremely strong drying agents are needed to obtain anhydrous compounds [129].

Hydrazines can also form azeotropes with water: for example, hydrazine at the mixture composition of 71.5% w/w of hydrazine and monomethyl hydrazine at 35% w/w [129]. No specific studies on hydrates and azeotropes of allyl hydrazine have been previously carried out. However, the data for boiling point of allyl hydrazine indicate some inconsistencies that may be caused either by the formation of an azeotrope or a hydrate. Namely, two substantially different temperatures have been reported for the boiling point of allyl hydrazine (at normal pressure): 122–124°C [126] and 102–112°C [130].

As already mentioned previously, anhydrous starting materials and reaction environment are necessary during the synthesis of HPTMS to avoid the potential hydrolysis of trimethoxysilane. Hydrolysis of trimethoxysilane and other alkoxy silanes results in formation of different polysiloxanes. Therefore preparation of anhydrous allyl hydrazine was in the focus of the current study. Allyl hydrazine used for the synthesis of HPTMS was prepared by using different synthesis methods, which all involved steps carried out in the presence of water (study III, section 4.2.1). Therefore obtained allyl hydrazine probably contained a significant amount of water. Also, allyl hydrazine as a commercial product is available as a hydrate only.

For preparation of anhydrous allyl hydrazine, the analogy with hydrazine hydrate was applied. There are two methods for removing water from hydrazine hydrate: by applying drying agents or by azeotropic distillation with aniline as an entrainer. Azeotropic distillation was discarded due to lack of information about azeotropes of allyl hydrazine. Several drying agents (NaOH, CaH₂, BaO and molecular sieves (3Å and 4Å)), which have been found efficient for preparation of anhydrous hydrazine [129], were applied for drying allyl hydrazine. However, after treatment with drying agents the hydrolysis still occurred during the reaction between allyl hydrazine and trimethoxysilane.

As applied drying agents turned out to be insufficient for preparation of anhydrous allyl hydrazine, excess of trimethoxysilane was used for preparation of HPTMS. It was found that in the case of dilution and great excess of silane, trimethoxysilane acts like a drying agent and generates anhydrous allyl hydrazine *in situ*, which then immediately reacts further with remaining

trimethoxy silane to form HPTMS in the presence of PtO_2 catalyst and heating. To suppress the polymerization of the hydrolysis products, the reaction was carried out in THF in great dilution. The formation of HPTMS was confirmed by spectroscopic analysis (NMR, IR, MS). The yield was considerably improved when compared to the usage of trimethoxysilane in stoichiometric amount when only traces of HPTMS were found [131]. However, excess of trimethoxysilane and formed polysiloxanes remained in the obtained product.

To conclude, HPTMS was synthesized using hydrosilylation approach, which can also be applied for preparation of various other hydrazinosilanes. Compared to aminosilanes, hydrazinosilanes have several advantages arising from the additional amino group. For example, immobilization of biomolecules via aldehyde linking is a traditional application of aminosilanes. Using hydrazinosilanes for aldehyde linking a hydrazone is formed from hydrazino group, which is hydrolytically more stable than imine obtained from amino group. The improved stability makes hydrazinosilanes applicable in a broader pH range. Another advantage may rise from the greater chemical versatility of hydrazines, as they can have larger number of substituents than amines.

Quaternization of hydrazinosilanes enables to prepare ionic liquid like structures on surfaces. Hydrazinium ionic liquids are previously known from the literature as hypergolic fuel-oxidizer systems for rocket and spacecraft propellants [132, 133]. Hydrazinium ionic liquid functionalized ionogels can be useful for development of safer solid-state propellants. Another potential application for such novel hybrid materials is the immobilization of catalysts analogically to inorganic ionogels based on imidazolium and ammonium ionic liquids. However, specific properties of hydrazino group may lead to novel and yet unconsidered applications of hydrazino-functional surfaces and immobilized hydrazinium ionic liquids.

5. SUMMARY AND CONCLUSIONS

In the present thesis the preparation of chemical organic and inorganic ionogels as a method for immobilizing ionic liquids into solid state was investigated. Immobilization of ionic liquids while retaining their extraordinary physico-chemical properties is needed for several practical applications, where the fluidity of ionic liquids leads to problems related to leakage and difficulties in obtaining or maintaining a predefined physical shape of the material.

The properties of ionogels are strongly influenced by the solid network chosen for immobilization of ionic liquid. Polymers are suitable matrixes for the preparation of organic ionogels, as both ionic liquids and polymers have virtually unlimited tuneability, which enables the preparation of ionogels with various properties. Beside this, the polymer-based technologies are already well established in the industry. The major driving force for the research in polymer-ionic liquid ionogels is their potential applications as polyelectrolytes in different electrochemical devices.

In the present thesis novel organic ionogels were prepared by mixing methacrylate type polymerized ionic liquids (PILs) with 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]; 10–75% v/v). The motivation of addition of [EMIM][BF₄] was to prepare transparent and flexible materials with higher conductivity than that of the neat PILs. The results of the current thesis show that by mixing PILs with the conventional ionic liquid, the conductivity increase about an order of magnitude can be achieved.

The sol-gel process is a convenient and flexible method for the preparation of inorganic ionogels, where ionic liquids are combined with oxide networks. The characteristic features for inorganic ionogels are mechanical strength and the possibility to immobilize different compounds, for example different catalytically active species. The starting materials for the preparation of chemical inorganic ionogels are different silyl functionalized ionic liquids, which can be classified also as ORMOSILs (Organically Modified Silica). The ORMOSIL-type functionalized surface silanization reagents are applicable for the preparation of various functionalized surface coatings.

In the current thesis hydrazinosilanes as an alternative for silyl functionalized imidazolium or ammonium ionic liquids were proposed as starting materials for the inorganic chemical ionogels. The preparation of hydrazinosilanes had not been reported prior to the synthesis of (3-hydrazinopropyl)trimethoxysilane carried out in the present thesis. The motivation for preparation of hydrazinosilanes were their potential advantages compared to aminosilanes, like stability in broader pH range and chemical versatility due to an additional amino group. The quaternization of prepared hydrazinosilane and the potential applications for the hydrazinium ionic liquids based ionogels need further investigations.

In more detail, following conclusions can be drawn from the present thesis:

1. 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium bromides (n=2, 6, 7, 10) were synthesized in high yields and purities (yields over two steps > 80%). The efficiency of synthesis can be increased by changing the order of synthetic steps compared to the common widely used synthesis route. Using the method developed in the current thesis, the polymerizable functional group is added in the last synthetic step, which helps to avoid the premature polymerization of obtained unstable methacrylic compounds during the preparation.
2. Photopolymerization as an energy efficient and cost-effective method is suitable for polymerization of 1-[n-(methacryloyloxy)alkyl]-3-methylimidazolium salts. This method helps to prepare PILs already in a predefined form, as films or layers, and opens new frontiers for broader practical applications of the material. For the first time the progress of the polymerization reaction was observed *in situ* by measuring resistivity of the polymerizing material.
3. The addition of [EMIM][BF₄] was found efficient for the preparation of PIL/IL composites with higher ionic conductivity than that of the neat PILs (conductivity increase from 10⁻⁵ to 10⁻⁴ S cm⁻¹). The influence of [EMIM][BF₄] is related to the higher number of charge carriers and the lower viscosities of the materials. Due to the chemical affinity of PILs and IL, the content of [EMIM][BF₄] in PILs can be varied in a wide range without phase separation.
4. The conductivity of PILs was found to be influenced by the length of alkyl chain between the polymerizable methacryl group and the imidazolium cation. The longer is the spacer, the higher is the mobility of cations and therefore also the higher the conductivity of the material.
5. The efficiency of different synthesis routes for the preparation of allyl hydrazine as a precursor for (3-hydrazinopropyl)trimethoxysilane was evaluated. From the used starting materials tri-Boc-hydrazine was found to be the most selective, but the preparation of tri-Boc-hydrazine adds several steps to the synthesis route towards (3-hydrazinopropyl)trimethoxysilane.
6. The hydrosilylation of allyl hydrazine with trimethoxysilane in the presence of PtO₂ catalyst was found a suitable method for the synthesis of (3-hydrazinopropyl)trimethoxysilane. The same procedure can also be applied for the preparation of other hydrazinosilanes.
7. It was found that allyl hydrazine can form very stable hydrates. Applying trimethoxysilane in excess allows first to use it as a drying agent to generate anhydrous allyl hydrazine *in situ* and then as the hydrosilylation reagent to prepare the desired hydrazinosilane.

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7. SUMMARY IN ESTONIAN

Uudsed orgaanilised ja anorgaanilised ionogeelid: valmistamine ja karakteriseerimine

Ioonsed vedelikud on pälvinud tähelepanu mitmesugustes rakendustes tänu unikaalsetele füüsiko-keemilistele omadustele, nagu madal aururõhk, termiline stabiilsus, küllaltki hea elektrijuhtivus ning mitmekülgsed solvateerivad omadused. Teatud rakendustes ei ole vedelikud voolavusest tingitud lekkimisohtu tõttu sobivad ning seega on vaja leida võimalusi, kuidas siduda ioonseid vedelikke tahkesse faasi, et nende omadused säiliks.

Ionogeelid on hübriidmaterjalid, milles ioonne vedelik on seotud kolme-dimensionaalse tahke võrgustikuga ehk geeliga. Vastavalt geelmatriksi omadustele eristatakse orgaanilisi ja anorgaanilisi ionogeele ning vastavalt interaktsioonidele ioonse vedeliku ja geeli vahel jaotatakse ionogeelid keemilisteks (kovaalentside) ja füüsikalisteks (van der Waalsi jõud). Käesolevas doktoritöös töötati välja kaks uutset hübriidmaterjali, mis liigituvad orgaaniliseks ja anorgaaniliseks keemiliseks ionogeeliks.

Polümeerid on levinud matriksid orgaaniliste ionogeelide valmistamiseks, sest nii polümeeride kui ioonsete vedelike omadusi on võimalik varieerida, valmistamaks mitmesuguste omadustega hübriidmaterjale. Antud doktoritöö üheks eesmärgiks oli välja töötada läbipaistev, painduv ja elektrit juhtiv materjal. Selleks valmistati polümeriseeritavatest ioonsetest vedelikest, 1-[n-(metakrüüloksü)alküül]-3-metüülimidasoolium bromiididest ($n = 2-10$) uudsed orgaanilised ionogeelid, mille omadusi saab varieerida lisades erineva hulga ioonset vedelikku, 1-etiül-3-metüülimidasooliumtetrafluoroboraati ([EMIM][BF₄]). Leiti, et valmistatud hübriidmaterjalide juhtivus sõltub eksponentsiaalselt lisatud ioonse vedeliku kontsentratsioonist. 40% v/v [EMIM][BF₄] lisamine tõstis materjali juhtivust suurusjärgu võrra ($10^{-5} \text{ S cm}^{-1}$ -lt $10^{-4} \text{ S cm}^{-1}$ -le). Tänu polümeriseeritud ja traditsioonilise ioonse vedeliku keemilisele affinsusele õnnestus [EMIM][BF₄] sisaldust materjalis varieerida laias vahemikus (10–75% v/v) säilitades materjali homogeensuse. Sõltuvalt [EMIM][BF₄] sisaldusest varieerus saadud hübriidmaterjalide olek tahkest geeljani.

Teine käesolevas töös välja pakutud uudne hübriidmaterjal on hüdrasiinium-ioonsel vedelikul baseeruv anorgaaniline ionogeel. Töötati välja sünteesimeetod hüdrasiinosilaanide valmistamiseks ja sünteesiti esimene prototüüpühend (3-hüdrasiinopropüül)trimetoksüsilaan. Analoogilisi aminosilaane, näiteks (3-aminopropüül)trietoksüsilaani, on laialdaselt kasutatud mitmesuguste funktsionaalsete pinnakatete valmistamisel ja biomolekulide immobiliseerimisel. Sarnaselt aminosilaanidele võimaldab hüdrasiinorühma kvaternerimine valmistada ioonseid vedelikke ja sool-geel protsessil ka vastavaid ionogeele. Hüdrasiinosilaanidel ja hüdrasiinium-ioonsetel vedelikel on võrreldes aminosilaanide ja ammooniumsooladega mitmeid struktuurist tulenevaid eeliseid, mille rakendusvõimalused vajavad täiendavat uurimist.

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