

Alternative routes and solvents in polymer chemistry : microwave irradiation and ionic liquids

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Alternative routes and solvents in polymer chemistry

- Microwave irradiation and ionic liquids -

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op dinsdag 1 september 2009 om 16.00 uur

door

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geboren te Erfurt, Duitsland

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Chapter 1

Introduction to alternative green solvents and energy sources in polymer chemistry

Abstract

The usage of solvents produces the largest amount of auxiliary wastes. Since the idea of sustainable chemistry becomes more and more important in polymer research, alternative reaction media are investigated in order to reduce or replace organic solvents. The most widely used green solvents in polymer chemistry are ionic liquids, supercritical CO₂ and water. The progress of utilizing these green solvents in polymerization processes is highlighted in this chapter mainly on the basis of results published in the last five years.

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1.1 Introduction

Polymers are an important part of our daily life and over 30 million tons of synthetic polymers are produced every year.¹ Polymers have many advantages over traditional materials, such as *e.g.* less weight, higher energy efficiency, performance and durability, and more flexibility in design and processing. Several materials such as wood and glass can be replaced by polymers.^{1,2} Nowadays, sustainable chemistry becomes increasingly significant in polymer research, since nearly all aspects of polymerizations such as the synthetic pathway, the chemical feedstock, the reaction medium and the nature of the final polymer are related to its inherent toxicity or non-biodegradability.^{3,4}

Polymer modeling, new methods for polymer processing and synthesis, and the utilization of alternative reaction media are needed to improve the synthesis of polymers and/or to develop new polymers.¹ Advanced modeling of polymeric processes could result in reduced waste and energy use. New methods for polymer processing and synthesis could reduce or eliminate the environmental problems that are associated with polymer manufacturing as well as increase energy efficiency and decrease waste generation. Product recycling and recyclability is a potentially large area in which alternative processing and polymer synthesis could have a substantial impact. Alternative reaction media could reduce or replace solvents that are currently in use for polymer synthesis and processing.⁴ As environmental standards increase, methods to produce polymers in ways that either decrease the amounts of organic solvents being used or increase their recyclability will become more important, since the usage of solvents produces the largest amount of auxiliary wastes. The most widely used green solvents for polymer production are ionic liquids, supercritical CO₂ and water.⁵

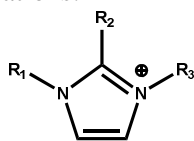
Microwave heating is an alternative for conductive heating systems, *e.g.* the oil bath. The first investigations, starting from the 1980s, were highly experimental, using domestic microwave ovens. Nearly a decade ago, the first scientific microwave ovens, dedicated and designed to perform chemical syntheses, were commercially available. The major advantage of this microwave synthesis equipment is the possibility of real-time monitoring of reaction temperature and pressure, which can be adjusted by controlling the microwave power. In addition, these reactors are designed to cope with violent explosions that might occur during runaway exothermic reactions. Nowadays, microwave dielectric heating is an established method in, *e.g.* synthetic organic⁶⁻¹⁰ and polymer chemistry¹¹⁻¹⁵ as well as bioscience (synthesis of peptides, and oligopeptides).¹⁶ The popularity of microwave irradiation for chemistry is based on the observed higher yields, faster reactions, reduced side-product formation, and in some cases even a changed selectivity was observed.¹⁷

In this regard, this chapter will provide an overview over alternative solvents and energy sources, namely ionic liquids and microwave irradiation, and their recent applications in polymer chemistry.

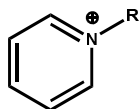
1.2 Ionic liquids

Ionic liquids are organic salts that are mainly composed of organic cations and inorganic anions (Figure 1.1), which are per definition liquid below 100 °C.^{18,19} In recent years, they have been proposed as ‘green’ solvents and as an attractive alternative to conventional volatile organic solvents due to their promising properties.^{20,21} The main advantages of ionic liquids are their negligible volatility, their non-flammability, the control of their properties due to their composition, their high compatibility with various organic compounds and other materials, and that they can easily be recycled and reused due to their immiscibility with a range of solvents.²⁰⁻²⁴ Ionic liquids have a broad range of applications²⁵⁻²⁷ and they have already been used as catalysts,^{28,29} reagents³⁰ or solvents^{31,32} in several chemical reactions. Further applications of ionic liquids can be found in separation processes³³ and as an electrolyte material in catalytic processes.^{34,35} However, for polymer chemistry, the utilization of ionic liquids as reaction medium was up to now less interesting, since organic solvents are mostly still needed for polymer purification. Nevertheless, the interest in utilizing ionic liquids as solvents,^{23,36} initiators,^{37,38} monomers,²³ catalysts³⁹ and for the preparation of ion gels⁴⁰ in polymer chemistry increased over the last years as can be concluded from Figure 1.2.⁴¹

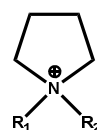
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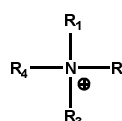
imidazolium



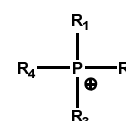
pyridinium



pyrrolidinium



ammonium



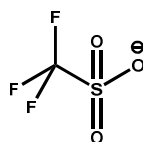
phosphonium

Anions:

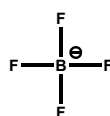
hydrophilic



chloride

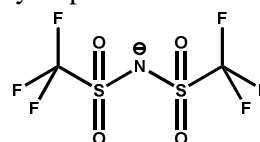


trifluoromethane-sulfonate

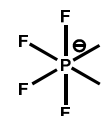


tetrafluoroborate

hydrophobic



bis(trifluoromethane-sulfonyl)amide



hexafluoro-phosphate

Figure 1.1 Schematic representation of selected structures of ionic liquid cations and anions utilized in polymer chemistry.

As described in the overview article from Kubisa,³⁶ the utilization of ionic liquids as solvents in polymerization processes can provide several advantages. For instance, the rate of propagation of free radical polymerizations conducted in ionic liquids increased, while the rate of termination decreased in comparison to conventional free radical polymerization. Besides radical polymerization processes, also coordination polymerization, polycondensation polymerization, electrochemical polymerization and enzymatic polymerization processes can benefit from the utilization of ionic liquids, *e.g.* mild reaction conditions, reuse of the catalytic system without loss of activity or even polymerization in the absence of catalyst, higher yields, high conductive polymer films and high enzyme activity were described.³⁶ In addition, when chiral ionic liquids

were used in stereoselective polymerizations (*e.g.* ATRP of acrylic monomer), the tacticity of the polymer was changed.⁴²

In the last years, the versatility of utilizing ionic liquids as reaction media in polymerization processes was enlarged by cationic ring-opening polymerizations (CROP), ring-opening polymerizations (ROP) and anionic polymerizations. In case of CROP, the polymerization rates were enhanced, which was explained by the presence of another ionic species, in this case the ionic liquid, modifying the association between the living polymer chain ends and their respective counter ions and thus reducing the reaction time. In addition, attention was also paid to the recycling of the applied ionic liquid after polymerization, showing that the ionic liquid can be recycled and reused. Comparable polymers with similar molar masses and polydispersity index (PDI) values can be achieved by using fresh or recycled ionic liquids under otherwise similar polymerization conditions. However, ionic liquids are still relatively expensive and their toxicity is still unknown limiting their application in polymerization processes at industrial scales.

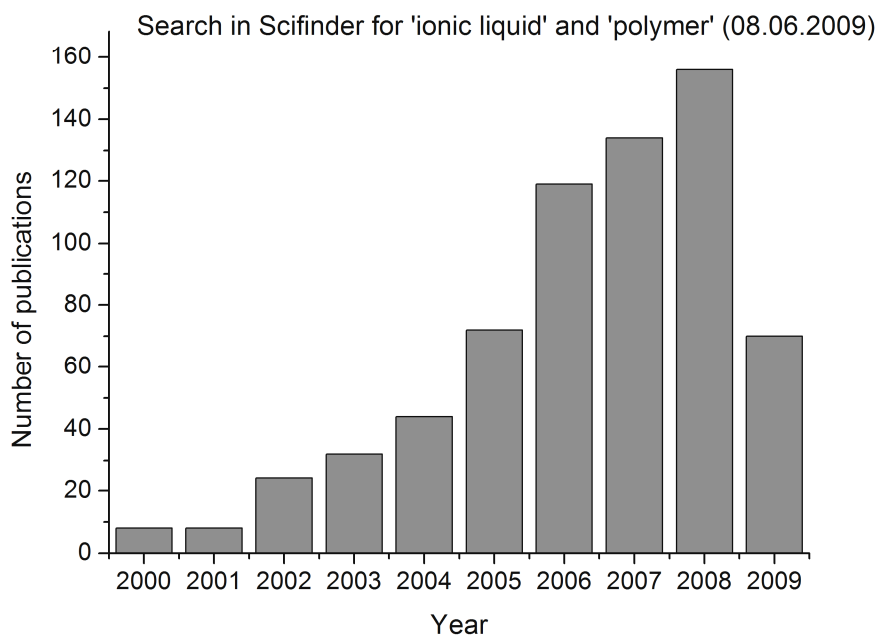


Figure 1.2 Schematic representation of the number of publications concerning ionic liquids and polymers starting from 2000.⁴¹

1.3 Supercritical carbon dioxide

Carbon dioxide (CO₂) is a sustainable solvent, due to its non-flammability and low toxicity. CO₂ is naturally abundant and relative inert, but it should be used judicious in order to improve the overall sustainability.⁴³⁻⁴⁶ An excellent and critical review about supercritical and near-critical CO₂ (scCO₂ and ncCO₂, respectively) in synthesis and processing, covering both organic and polymer chemistry, was written by Beckman.⁴³ More advantages of utilizing CO₂ are that it can be used as a solvent in oxidation processes, that it is an aprotic solvent, that the viscosity of the liquid state is only 1/10 of that of water and it is in general inert to free radical chemistry, just to name a few.⁴³ Carbon dioxide also exhibits some inherent disadvantages such as high critical

pressure and vapor pressure resulting in the need for specialized equipment, a low dielectric constant which limits the solubility, a low pH value (~ 3) upon contact with water and that it is not inert towards strong bases, metal alkoxides, metal alkyls, metal hybrids, and hydrogenation.⁴³ Beckman described in his review that in general polymers are poorly soluble in CO_2 , but they swell extensively under moderate CO_2 pressure.⁴³ In contrast, fluorinated polymers are soluble in CO_2 because of a specific interaction of the fluorine with the electron poor carbon on CO_2 and therefore, most publications in polymer chemistry are dealing with fluorinated polymers and block copolymers with at least one fluorophilic block.

1.3.1 Ring-opening and condensation polymerization

Carbon dioxide has been employed as solvent in cationic,⁴⁷ anionic,⁴⁷ metal-catalyzed⁴⁶ and metathesis ring-opening polymerizations⁴⁸ of various monomers.⁴³ In general, anionic polymerizations can not be performed in CO_2 due to the fact that CO_2 reacts with carbanions to form relatively unreactive carboxylates.⁴³ Surprisingly, poly(ϵ -caprolactone) was observed by anionic ring-opening polymerization in scCO_2 without incorporation of CO_2 .⁴⁷ It seems that the propagation of the polymerization occurs faster than the above described side reaction. In general, olefin polymerizations employing Ziegler catalysts are problematic in scCO_2 , because CO_2 will terminate and therefore inhibit polymerization.⁴³ In condensation polymerizations CO_2 has been applied as a dilute/plasticizer to enhance the removal of the small molecule byproducts, hence increasing the molar masses. In case of polyurethanes, scCO_2 was utilized as alternative 'blowing' agent to chlorofluorocarbon or methylene chloride.⁴³

1.3.2 Free radical polymerization

In homogeneous free radical polymerizations of fluoromonomers, mostly precipitation polymerization, scCO_2 can provide a chain-transfer free solvent and eliminate the need for surfactant.⁴³ In addition, dry, free-flowing, granular material can be generated, while emulsion or suspension polymerization conducted in, *e.g.*, hydrocarbon solvents are energy intensive and the removal of the alkane produces waste. On the other hand, specialized equipment is needed in order to handle the related high pressures. Heterogeneous free radical polymerization, such as emulsion, dispersion and suspension polymerizations were conducted in scCO_2 .⁴³ Only a few examples of emulsion polymerization were reported, including acrylamide, acrylic acid and *N*-vinyl formamide, due to the fact that it is difficult to identify a surfactant that is miscible with scCO_2 . Therefore, expensive fluorinated surfactants (nonionic and anionic) were employed resulting in fast polymerizations with high molar mass polymers. The less expensive silicone-functional surfactants revealed a rather good performance in comparison to the fluorinated surfactants. More extensive work has been done in the field of dispersion polymerization, where the monomers, *e.g.* vinyl monomers, are soluble in scCO_2 . Stabilization of particles was achieved by utilizing homo- and co-polymers of fluoroacrylate monomers, comb-type copolymers with an acrylate backbone and fluoroether side chains, or fluoroether carboxylic acid resulting in a rapid polymerization of MMA. In case of the suspension polymerization of

styrene/divinyl benzene in scCO₂ porous beads were obtained, where the pore size could be controlled by the pressure of the applied CO₂. In general, for heterogeneous polymerizations, the costs for the stabilizers are rather high, limiting the industrial application. During the last five years mainly heterogeneous radical polymerizations in scCO₂ were investigated utilizing random copolymers, both fluorous and non-fluorous, as stabilizers for the polymerization of various monomers in scCO₂. In particular non-fluorous stabilizers are of interest, since they can provide lower costs and enhance the biodegradability. In addition, controlled polymerizations were carried out in scCO₂.⁴³ It was shown, that living polymerizations can be conducted in scCO₂ resulting in polymers with high molar masses in high yields.

In conclusion, mostly heterogeneous radical polymerizations have been studied due to the fact that most polymers are not soluble in scCO₂. It was also shown that living polymerizations can be performed in scCO₂ yielding polymers with high molar masses and high yields. ScCO₂ has also the ability to act as a chain transfer free solvent, eliminating the need for surfactants. In addition, dry, free-flowing granular material can be obtained when polymerizations are conducted in scCO₂. On the other hand, specialized and expensive equipment is needed in order to handle the required high pressures limiting its applicability together with the rather expensive fluorinated stabilizers. In order to be able to compete with organic solvents low-cost stabilizers for scCO₂ are required.

1.4 Water

Polymerizations carried out in aqueous media receive more and more attention due to increased environmental concern and the growth of pharmaceutical and medical applications, where mostly hydrophilic polymers are required.⁴⁹ Water is the most environmentally friendly and inexpensive solvent of all.⁵⁰⁻⁵⁴ However, controlled/living radical polymerizations in aqueous media remain challenging due to compatibility problems of the radical mediator with water and the instability of the dormant species in the presence of water.⁴⁹

1.4.1 Homogeneous polymerization

The homogenous polymerization in aqueous media requires that the monomer, polymer and the radical mediator (in case of controlled radical polymerization) are water-soluble. In general, monomers with ionizable pendant groups polymerize much faster in water than in organic solvents or in bulk. This observed enhancement in the k_p/k_t ratio (k_p = propagation rate, k_t = termination rate; the ratio increases in the order of magnitude by 1.5–2) is attributed to (1) the higher reactivity of the monomers in water due to changes in electron density of the double bond caused by hydrogen bond formation between the monomer and water, (2) the greater electrostatic repulsion between two growing radicals as a result of the increased ionic dissociation of the pendant group and (3) the protection of the propagating radical center from termination by reason of polymer-water interactions that are able to produce a strong hydration shell.^{4,49} In general, reversible addition fragmentation chain transfer (RAFT) polymerizations are reported more often, while the literature for atom transfer radical polymerization (ATRP) is

limited to methacrylates and certain water-soluble styrenics;^{54,55} nitroxide mediated polymerization (NMP) of various water-soluble monomers^{6,7} are published too. The RAFT polymerization is the most versatile method, in terms of monomer choice and the ability to control the polymerization in a wide range of styrenic monomers in water, as well as neutral, anionic, and zwitterionic acrylamido monomers.⁵⁵⁻⁵⁷ In case of ATRP, the catalyst stability in aqueous media is problematic because of side reactions, such as dissociation, complexation and disproportionation.^{4,50,55,58} On the other hand, the aqueous ATRP benefits from rapid polymerization rates at ambient temperatures.^{4,55,59,60} The faster ATRP kinetics in aqueous media were mainly attributed to higher equilibrium concentrations of propagating radicals and to solvent effects on the rate of propagation.⁵⁸ In general, the addition of organic solvents to the water slows down the polymerization resulting in better-controlled polymerizations.⁴ In order to improve the control over the polymerization, catalysts with a large initial amount of deactivator or additional halide salts can be used in order to suppress the dissociation.⁴ Recently, ATRP of acrylic acid was described as well.⁶¹ The first aqueous NMP of sodium 4-styrenesulfonate (SSNa) utilizing a new carboxy functionalized water- and organo-soluble nitroxide based on 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy (TIPNO) was reported in 2007, yielding well-defined polymers at moderate temperatures (<100 °C).⁶ Furthermore, the utilization of tertiary SG-1 based alkoxyamine bearing a carboxyl acid function (MAMA-SG-1) as mediator in the NMP of acrylamide, acrylate and styrene based water-soluble monomers, lead to a controlled/living polymerizations with first-order kinetics up to high conversions.⁷

1.4.2 Heterogeneous polymerization

Heterogeneous polymerizations are applicable to a much wider range of monomers in comparison to homogenous polymerizations. Heterogeneous free-radical polymerization is a widely used polymerization technique in industry, in particular the emulsion polymerization.^{51,52,62,63} These aqueous dispersed systems are prior to homogenous processes, due to low viscosity, better control of heat transfer and faster rate of polymerization, just to mention a few.^{49,51,52,64} In order to obtain good polymerization results, the control agents have to be stable and efficient in aqueous media.⁴⁹ For controlled polymerizations, mainly 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and its derivatives, as well as acyclic nitroxides such as SG1 have been used in heterogeneous aqueous media as radical mediators in nitroxide mediated polymerizations.^{49,64} In case of ATRP the mediation with copper complexes have been studied most extensively.^{49,65} RAFT has been reported in miniemulsion polymerization utilizing nonionic surfactants, while cationic and anionic surfactants were unsuccessful.⁴⁹ In addition, transition-metal catalyzed polymerization of olefins,⁶⁶ as well as cationic^{53,67} and anionic heterogeneous polymerization in water were described.⁴⁹ In case of cationic polymerization, water-tolerant Lewis acids such as metal triflates^{53,67} or tetrafluoroborates⁵³ were employed. Recently, surfactant-free emulsion polymerizations were performed in aqueous media utilizing a cationic ionizable water-soluble initiator and cetyl alcohol as costabilizer,⁶⁸ a surface-active RAFT agent with low molar mass,⁶⁹ or a NMP macroinitiator.⁷⁰ In all cases fast

polymerizations, good control over the molar masses and smaller particles were obtained in comparison to a conventional emulsion polymerization. For a deeper insight into homogeneous^{49,50,55} and heterogeneous^{49,51,52,64} radical polymerizations in aqueous media several review articles are recommended. In the last years, controlled radical polymerizations in aqueous media were investigated in particular including NMP, ATRP and RAFT, showing that the control agents have to be carefully selected and further investigations are necessary in order to achieve comparable control as obtained in organic solvents.^{49,50,55,64} Besides controlled radical polymerizations, online-monitoring of emulsion polymerization processes, new heterophase polymerization processes (*e.g.* micro- and miniemulsion), synthesis of block copolymers and nanosized hybrid structures, new stabilizers and polymerization aids, model systems for latexes, and better understanding of the kinetics and mechanism were parts of the ongoing research in emulsion polymerizations.^{51,52}

In conclusion, water is already extensively used in emulsion polymerizations on industrial scale. In this case, a lower viscosity, a better control of heat transfer and faster polymerization rates are achieved in comparison to homogeneous polymerizations in water. Interestingly, homogeneous ATRP has shown rapid polymerization at low temperatures in aqueous media. The concept of near-critical water was introduced and applied in polymer chemistry. This concept seems quite promising due to the fact that two polymerization techniques (precipitation polymerization and the thermal polymerization) can be combined resulting in polymerization and precipitation in one step.

1.5 Microwave irradiation

The concept of sustainable chemistry represents an area of innovation which not only preserves resources, but also includes development processes in chemical industry. In this regard, alternative energy sources, such as photochemistry, microwave energy, electron beam and ultrasound, are investigated in order to replace conventional heat sources for *e.g.* polymer processing. The main goal of utilizing alternative energy sources is to improve the efficiency of the process by *e.g.* reducing the polymerization time. The main advantage utilizing microwaves as heating source is the rapid, instantaneous and selective heating compared to conventional heating. The microwaves penetrate the reaction mixture to a certain extend (depending on the penetration depth) providing volumetric heating, while the energy dissipation in an autoclave takes place by conduction and convection.³ In addition, microwave irradiation provides non-contact heating, circumventing decomposition of molecules close to the walls of the reaction vessel or the formation of undesired side products.⁷¹ Furthermore, increased reaction speeds and improvements in yield and selectivity have been observed for a large number of organic and inorganic reactions.⁷¹ Moreover, the usage of low boiling solvents is facilitated, since reactions can be performed in closed vessels. In polymer chemistry, a significant increase in reaction speed and therefore shorter reaction times were reported for most polymerizations (including step growth polymerization of polyamides, polyimides, polyethers, and polyesters, ring-opening polymerization of ϵ -caprolactams and ϵ -caprolactones, and free radical polymerization of styrene

and methyl methacrylate) resulting in an improved purity and, as a consequence, improved polymer properties.⁷¹

In general, microwaves are electromagnetic waves in the frequency range of 0.3 to 300 GHz, which corresponds to wavelengths of 100 to 1 cm, respectively. This region of the electromagnetic spectrum lies between the far infrared and radio frequencies (Figure 1.3). Out of the several frequency bands that are available for domestic and scientific applications, a frequency of 2.45 GHz (corresponding to a wavelength of 12.2 cm) is commonly used for kitchen microwave ovens and industrial microwave reactors. Radiation of this frequency only affects molecular rotation and is not strong enough to break chemical bonds, since a microwave photon has only an energy of 0.00001 eV in comparison to 5 eV for a covalent bond or 0.025 eV for the Brownian motion. As sources are available to efficiently generate microwaves at this frequency, it is a convenient method for heating microwave-absorbing substances. Microwaves, being of electromagnetic nature, consist of time-varying electric and magnetic fields, and propagate through space at the speed of light (Figure 1.4).

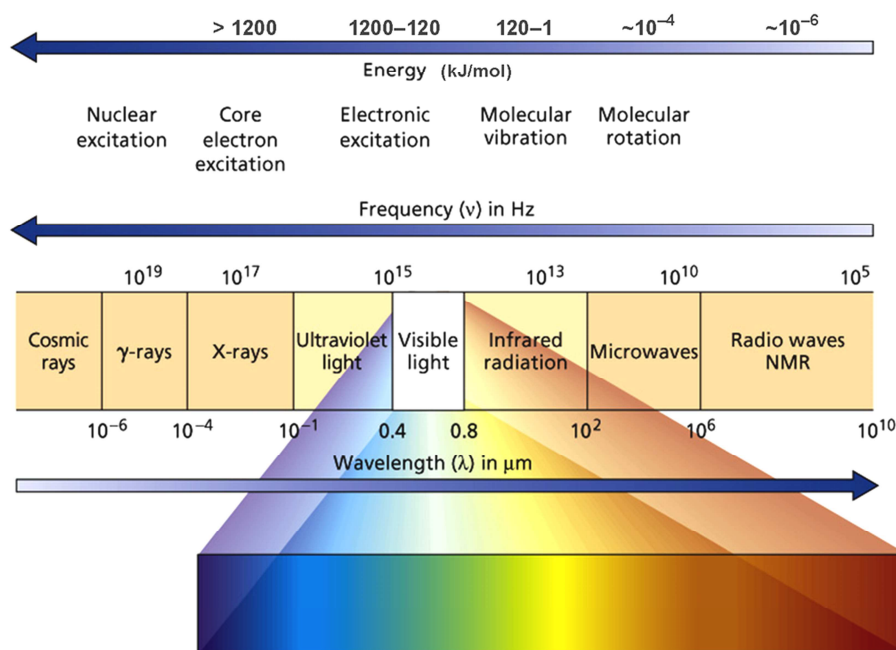


Figure 1.3 *Electromagnetic spectrum: wavelengths and frequencies (reprinted from reference 13).*

However, the magnetic part of the electromagnetic waves does not interact with organic media and, thus, will not participate in microwave heating for most chemical transformations. The capability of a compound to convert microwave irradiation to heat is given by the loss tangent (Equation 1.1).⁷³

$$\tan(\delta) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)} \quad \text{Equation 1.1}$$

ε_1 permittivity
 ε_2 dielectric loss factor
 ω electric field frequency

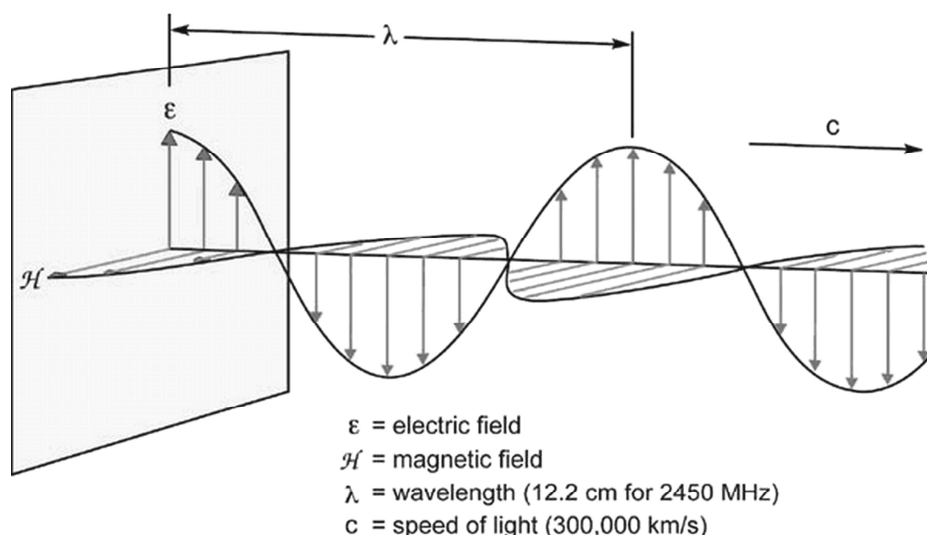


Figure 1.4 Schematic representation of a microwave at 2.45 GHz.⁷²

The higher the $\tan(\delta)$ is at 2.45 GHz, the better the compound will absorb microwaves, resulting in more efficient heating. Consequently, polar substances are expected to heat up more efficient than non- or less polar counterparts. In general, the dielectric loss factor of a solvent determines its ability to absorb microwave energy. The power dissipation by the dielectric material is proportional to this loss factor. However, dielectric properties are in general frequency and temperature dependent and, unfortunately, the optimal frequency for most efficient heating shifts further away from 2.45 GHz on heating.⁷⁴ Another important parameter depending on the dielectric constant is the penetration depth, which is quantitatively defined as the depth at which the intensity of the radiation inside the material falls to $1/e$ (~36.8%) of the original value at the surface. The penetration depth of microwaves is depending on the temperature and decreases for water with increasing temperature (Equation 1.2).⁷⁵ The dielectric properties of selected organic solvents and water are summarized in Table 1.1.

$$D_p = \frac{\lambda_0}{2\pi} \cdot \frac{\sqrt{\varepsilon_1}}{\varepsilon_2} \quad \text{Equation 1.2}$$

ε_1 permittivity
 ε_2 dielectric loss factor
 λ_0 wave length

Table 1.1 Dielectric parameters of different organic solvents and water.^{76,77}

Solvent	Boiling point [°C]	ϵ_1	$\tan \delta$	ϵ_2	Penetration depth [cm]
DMSO	189	45	0.83	37.13	0.75
Ethanol	78	243	0.94	22.89	0.91
Water	100	80.4	0.12	9.89	3.53
DMF	153	37.7	0.16	6.07	3.94
Chloroform	61	4.8	0.09	0.44	19.36
THF	66	7.4	0.05	0.35	30.19

Besides dielectric heating, ionic species can be heated under microwave irradiation by an ionic heating mechanism. When an ionic solution is placed in an electric field, the field causes an ionic current, which gives rise to joule heating of the solution, which is proportional to the ionic conductivity of the material. The ionic conductivity depends on the ion concentration and is, in general, also dependent on temperature and frequency. In general, ionic heating will occur in combination with dielectric heating of the surrounding solvent and the total average energy dissipation by a dielectric material in a microwave field can be given by Equation 1.3.⁷³

$$P = \frac{1}{2} \epsilon_0 \epsilon_2 (\omega) \omega E_0^2 + \frac{1}{2} \sigma_i (\omega) E_0^2 \quad \text{Equation 1.3}$$

ϵ_0	permittivity of vacuum
ϵ_2	dielectric loss factor
ω	electric field frequency
E_0	electric field amplitude
σ_i	ionic conductivity

The second term represents the power dissipation due to ionic currents, which depends on ion concentration, frequency, and temperature. For the temperature measurement in the microwave field, specialized equipment is necessary. Therefore, IR sensors, fiber-optic sensors, earthed and shielded thermocouple elements and gas thermometers are used for temperature measurements.⁷⁸⁻⁸¹ In case of an IR sensor, the temperature is measured on the surface of the reaction vessel and therefore large differences in temperature measurements can occur. Therefore, in most cases the temperature is calibrated by the pressure values obtained for distilled water, making the reported values more reliable. The fiber-optic sensors are rather expensive, but the accuracy of the temperature measurement is the best ($\pm 1-2$ K).⁷⁸ In general, there are four different types of fiber-optic sensors utilizing gallium-arsenide crystals, Fabry-Perot-Cavities, Bragg-Grids or luminescent/fluorescent substances.^{78,81} Earthed and shielded thermocouple elements are rather cheap in comparison to fiber-optic and IR, but they can only be used on larger scales (> 30 mL) with polar substances, otherwise they will heat up by themselves. In a gas thermometer the ability of gas to expand with increasing temperature is used to monitor the temperature. In general, two categories of equipment are used in microwave chemistry, based on different design requirements: single-mode and multi-mode microwave ovens. Both types cater to a specific market segment. Single-mode microwave equipment is

primarily used for chemical synthesis, whereas multi-mode microwave equipment is mainly used for chemical analysis. In single-mode microwave systems a homogenous microwave field is generating a standing wave (the wave guide has the length of the microwave). Unfortunately, the maximum power is limited (up to 400 W). In multi-mode microwave systems a 'homogenous' microwave field is created by a highly chaotic wave distribution (mode stirrer). In this case rather large quantities can be heated compared to the single-mode microwave systems.

1.6 Aim and outline of the thesis

As described above, alternative reaction media such as ionic liquids, water and scCO_2 are promising alternatives for organic solvents in polymerization processes. However, the variety of ionic liquids used in polymer chemistry is limited to a few examples up to now. In order to be able to obtain better results it is necessary to gain a deeper insight into the structure-property relationships. In Chapter 2, the synthesis of ionic liquids is described. The focus was on imidazolium based ionic liquids with different alkyl chain lengths as well as branched alkyl side chains resulting in a library of ionic liquids. During the synthesis microwave irradiation was used as a heating source, because ionic liquids can be synthesized in short times as a result of the elevated temperatures being applied. Moreover, the direct up-scaling of the microwave-assisted synthesis in batch and continuous flow reactors was investigated. In Chapter 3, the properties of the ionic liquids synthesized are addressed. In particular, the decomposition temperature, the thermal behavior and the water uptake were investigated in order to elucidate and compare first structure-property relationships of ionic liquids with linear and branched alkyl side chains. In cellulose chemistry, ionic liquids were found to be alternative solvents for dissolving cellulose. However, the ionic liquids used up to now are limited. In Chapter 4, the screening of the synthesized ionic liquids for their ability to dissolve cellulose is described. Selected ionic liquids, which dissolve cellulose in higher amounts, were utilized as reaction media for the homogenous tritylation reaction of cellulose in order to compare their performance. In Chapter 5, new imidazolium based polymers were synthesized by step growth polymerization. In order to control the molar masses, the application of molar imbalance and chain stoppers were investigated during the polymerization progress. The thermal behavior and the water uptake of these materials were investigated. In Chapter 6, alternative synthesis routes for synthetic polymers were investigated applying 'green solvents', such as near critical water and ethanol. In particular, the thermal auto-polymerization and precipitation polymerization of styrene were combined in order to develop an environmental friendly polymerization process. To improve the control on the thermal initiated polymerization of styrene in ethanol, the effect of the presence of a stable free nitroxide (SG-1) was examined. Furthermore, the hydrolytic ring-opening polymerization of polyamides at elevated temperatures under microwave irradiation was studied, since it could be expected that the utilization of microwave irradiation might lead to cleaner products with less side products.

1.7 References

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Chapter 2

Synthesis of ionic liquids

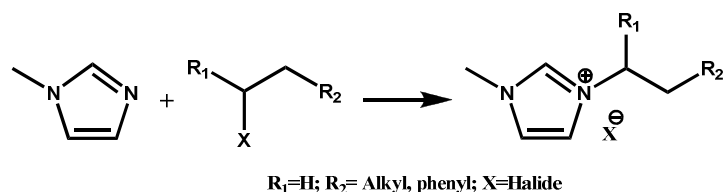
Abstract

Ionic liquids are considered to be ‘green’ solvents on account of their non-volatility and non-flammability – which are results of their negligible vapor pressure – as well as their reusability. On the basis of ecological concerns, ionic liquids seem to be an attractive alternative to conventional volatile organic solvents. Ionic liquids can be synthesized in a fast and efficient way by using microwave irradiation. In this thesis, various ionic liquids with linear and branched alkyl side chains were synthesized under microwave irradiation. The optimized reaction conditions for the synthesis of 1-butyl-3-methylimidazolium chloride were subsequently transferred to various microwave reactors. Batch and continuous flow, as well as mono-mode and multi-mode microwave reactors were used for the direct up-scaling from 0.01 to 1.15 mol. In addition, the homogeneous synthesis of 1-ethyl-3-methylimidazolium diethyl phosphate was performed in a continuous flow reactor as well.

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2.1 Introduction

Ionic liquids are in general synthesized by quarternization of amines, imidazoles, pyridines or phosphines through an alkylation reaction (Menshutkin reaction), as displayed in Scheme 2.1.



Scheme 2.1 Schematic representation of the general synthesis of 1-alkyl-3-methylimidazolium-based ionic liquids.

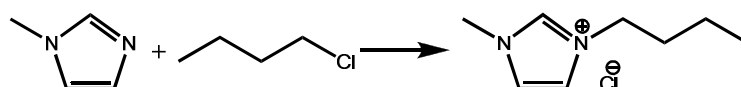
The reaction has been named after its discoverer, the chemist Nikolai Menshutkin, who described the procedure in 1890. The reaction between tertiary amines and alkyl halides is hard to control; however, when ionic liquids are the desired end product, this reaction becomes an interesting option, since the yields are good and the reaction is easily performed. Reactions can be accelerated by utilizing polar aprotic solvents, *e.g.* DMSO and THF, or higher reaction temperatures. Leaving groups facilitate the reaction in the order chlorine < bromine < iodine.

Typically, the synthesis of ionic liquids is time-consuming and requires reaction times up to several days.¹ However, in 2000, Personal Chemistry² synthesized for the first time ionic liquids by using single-mode microwave irradiation, and as a result, the reaction times were shortened from several hours to minutes. Varma and Nambodiri³ performed a solvent-free synthesis of ionic liquids in a household microwave oven in comparable time frames. This acceleration of the synthesis is believed to be a result of the increased reaction temperatures. The ability of ionic liquids to be efficiently heated by microwave irradiation arises from their ionic nature and is an appealing feature.^{4,6} The thermal stability and the low vapor pressure of ionic liquids also allows their use in high temperature reactions.

2.2 Ionic liquids with linear alkyl side chains

The microwave-assisted synthesis of ionic liquids with linear alkyl side chains in this thesis was optimized on a small scale (~ 2 mL) utilizing a single-mode microwave system (Biotage Emrys Liberator).⁷ The power can be either set to 150 or 300 W. The temperature was measured by an IR-sensor, located at the side of the microwave cavity. The maximum temperature and pressure were 250 °C and 20 bar, respectively. The reaction mixtures were stirred with a magnetic stirring bar. Reaction volumes of ~ 2 mL were used for the synthesis of the ionic liquids. The schematic representation of the synthesis of 1-butyl-3-methylimidazolium chloride is depicted in Scheme 2.2. In general, the synthesis of the ionic liquids was performed in the absence of an additional solvent and with a ratio of 1 to 1.3 of 1-methylimidazole to alkyl halide. Alkyl halides are non-polar substances, which are poorly absorbing microwave. Therefore, they are indirectly heated by the 1-methylimidazole and the arising ionic liquid, which are good microwave absorbers. The thermal overshoot, which mainly occurs due to the very fast heating of the

formed ionic liquids in the microwave field, could thus be reduced by the excess of the alkyl halides chloride preventing possible thermal runaways of the reactions. As a result of the very efficient microwave absorption of the ionic liquids, a power of 150 W was used and a temperature of 170 °C was chosen to stay within the safety-limitations of the microwave systems, also in case of a thermal runaway of the system. Nevertheless, a thermal overshoot of 8 °C was still observed under these conditions. The temperature/pressure profiles obtained during the reaction of 1-methylimidazole and butyl chloride are shown in Figure 2.1.



Scheme 2.2 Schematic representation of the synthesis of 1-butyl-3-methylimidazolium chloride.

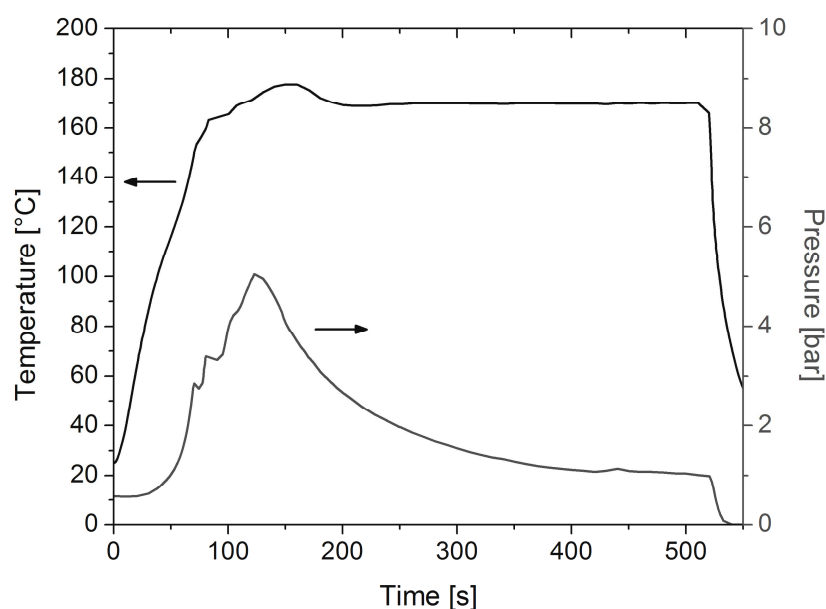


Figure 2.1 Microwave temperature and pressure profiles for the solvent-free synthesis of 1-butyl-3-methylimidazolium chloride on a small scale (0.01 mol) using a 1 to 1.3 ratio of 1-methylimidazole to butyl chloride (170 °C, 7 min, 150 W, IR sensor).

As depicted in Figure 2.1, the pressure increased upon heating due to vaporization of butyl chloride. As the reaction progressed, the pressure decreased as a consequence of the volatile educts being consumed and the formed 1-butyl-3-methylimidazolium chloride having no measurable vapor pressure at the applied reaction temperature. Consequently, the pressure decrease could be used to directly follow the conversion of the reaction. When the pressure inside the reaction vessel was stabilized, the reaction was completed. Subsequently, the mixture was cooled down by nitrogen, and a two phase system was obtained with the viscous ionic liquid at the bottom and the remaining excess of butyl chloride in the upper phase. The butyl chloride could be easily removed by decantation. The ^1H NMR spectrum of the crude product is depicted in Figure 2.2. For the first runs, a reaction time of 30 min was chosen. After this time, full conversion, as measured by ^1H NMR spectroscopy, was reached and the ionic liquid had a reddish brown color (Figure 2.3 A). The strong color was thought to originate from impurities of

the educts. Therefore, the experiment was conducted with freshly distilled 1-methylimidazole and butyl chloride. Unfortunately, only a small improvement in colorization was achieved (Figure 2.3 B). In a next step, the reaction time was decreased to only 5 minutes resulting in only slightly colored ionic liquid (Figure 2.3 C). After this short reaction time, still 7% of 1-methylimidazole were left (determined by ^1H NMR spectroscopy). However, the optimization of the reaction time, besides the reaction temperature, seems to be the main parameter to synthesize ionic liquids with only a slight coloration at elevated temperatures.

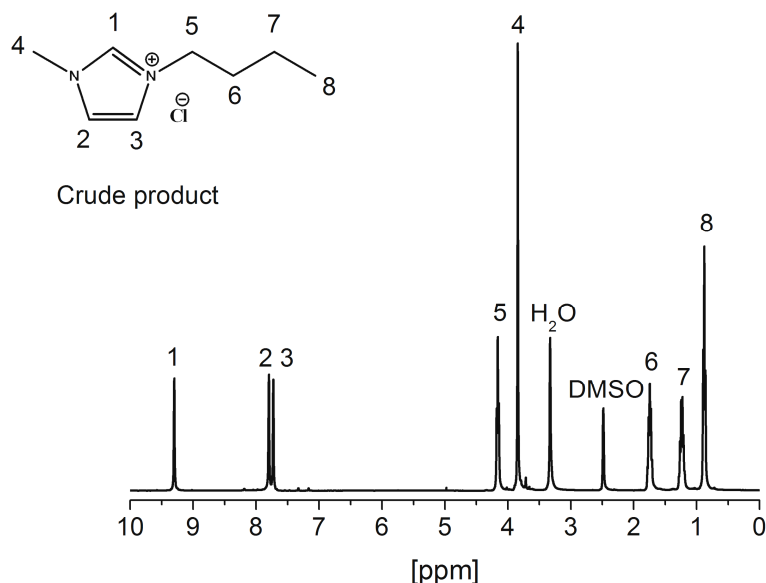


Figure 2.2 ^1H NMR spectrum of the 1-butyl-3-methylimidazolium chloride before purification (170 °C, 7 min, 150 W).

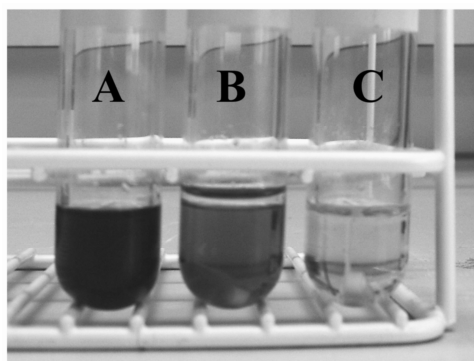


Figure 2.3 Synthesis of 1-butyl-3-methylimidazolium chloride at 170 °C: A) without purification of the educts, 30 min; B) with purified educts, 30 min; C) with purified educts, 5 min.

Based on the pressure diminution observed in Figure 2.3, the reaction time could be limited to a more specific time range for further optimization. In case of 1-butyl-3-methylimidazolium chloride, a reaction time of 7 minutes was found to be an optimum at 170 °C. Other ionic liquids with various alkyl chain lengths were synthesized and their reaction times optimized according to the above described procedure; the results are listed in Table 2.1. At these conditions full conversions were reached and the ionic liquids were only

slightly colored. Shorter reaction times resulted in lower conversions and longer reaction times in more strongly colored products. After decanting the remaining alkyl halide, the ionic liquids were extracted with ethyl acetate or acetone for further purification. The optimized reaction conditions found for the synthesis of 1-butyl-3-methylimidazolium chloride were employed to investigate the direct up-scaling utilizing various microwave systems, including both batch and continuous flow as well as mono-mode and multi-mode as described later in this chapter. In addition, ionic liquids with different chain lengths (from ethyl to decyl) utilizing alkyl bromides were synthesized under microwave irradiation. In these cases lower reaction temperatures (120 °C) were applied due to the higher reactivity of the alkyl bromides in comparison to the alkyl chlorides. The reaction times are summarized in Table 2.2. In case of the alkyl bromides, a large thermal overshoot (~55 °C) was obtained during the reaction, as depicted in the heating profile in Figure 2.4.

Table 2.1 *Optimized reaction conditions for the microwave-assisted synthesis of 1-alkyl/aryl-3-methylimidazolium based ionic liquids with chloride counter ion at 170 °C.*

Ionic liquid	Time [min]	Conversion ^b [%]	Yield [%]	Purity ^c [%]
[C ₃ MIM][Cl]	9	>99 ^b	95	96
[C ₄ MIM][Cl]	7	>99 ^b	99	95
[C ₅ MIM][Cl]	8	>99 ^b	98	94
[C ₁₀ MIM][Cl]	7	>99 ^b	98	98
[C ₁₆ MIM][Cl]	7	>99 ^b	97	95
[BnMIM][Cl]	1 ^a	>99 ^b	99	93

^a 100 °C, ^b no starting material detectable (determined by ¹H NMR spectroscopy), ^c purity determined by ¹H NMR spectroscopy.

Table 2.2 *Synthesized bromo containing ionic liquids with different alkyl side chain lengths.*

Ionic liquid	Time [min]	Conversion [%]
[C ₂ MIM][Br]	20	>99 ^a
[C ₃ MIM][Br]	30	>99 ^a
[C ₄ MIM][Br]	10	>99 ^a
[C ₅ MIM][Br]	20	99
[C ₆ MIM][Br]	10	>99 ^a
[C ₇ MIM][Br]	10	>99 ^a
[C ₈ MIM][Br]	10	>99 ^a
[C ₉ MIM][Br]	10	>99 ^a
[C ₁₀ MIM][Br]	10	>99 ^a

^a No starting material detectable (determined by ¹H NMR spectroscopy).

In addition, for the synthesis of 1-ethyl-3-methylimidazolium diethyl phosphate, full conversion was achieved after 5 hours reaction time at 150 °C. The educts were used in an equimolar amount, since no phase separation is taking place during the reaction making it more difficult to remove any excess of either 1-methylimidazole or triethyl phosphate.

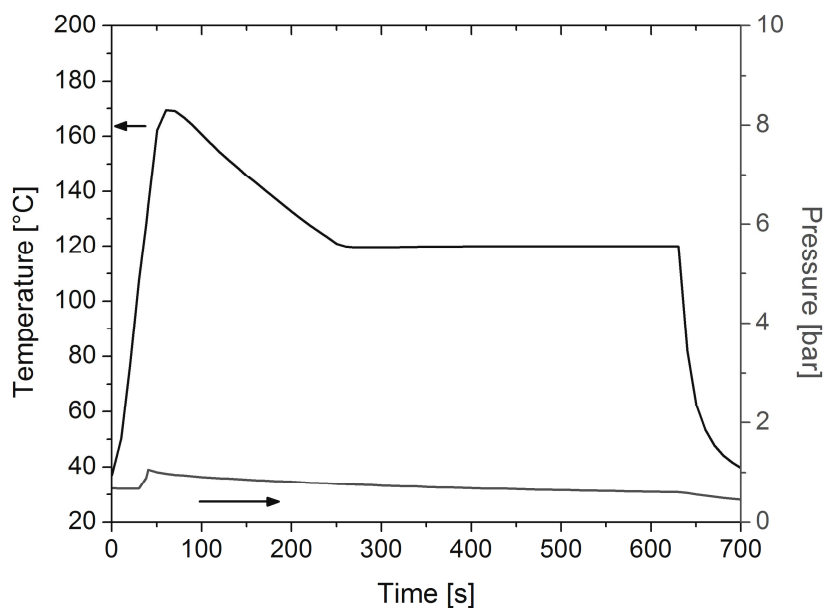
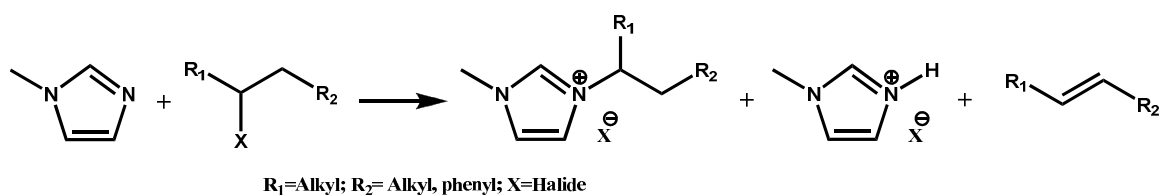


Figure 2.4 Microwave temperature and pressure profiles for the solvent-free synthesis of 1-methyl-3-pentylimidazolium bromide (120 °C, 10 min, 150 W, IR sensor).

2.3 Branched ionic liquids

When branched alkyl halides are used to synthesize ionic liquids not only a substitution, but also elimination takes place. Hydrogen chloride is produced as an elimination product, which reacts with the 1-methylimidazole to form 1-H-3-methylimidazolium chloride as side product, which could be identified by ^1H NMR spectroscopy for all branched ionic liquids, whereas the corresponding alkenes could not be detected due to their volatility. Thus, a mixture of two ionic liquids was obtained as depicted in Scheme 2.3.



Scheme 2.3 Schematic representation of the reaction scheme of 1-methylimidazole with branched alkyl chains yielding side products (1-H-3-methylimidazolium chloride and alkene).

Nevertheless, ionic liquids with branched alkyl side chains were synthesized under microwave irradiation at 170 °C. As depicted in Figure 2.5, the pressure increases during the synthesis of 1-(1-methylpropyl)-3-methylimidazolium chloride ([2-C₄MIM][Cl]) and even after cooling down to 40 °C, still a pressure of approximately 3 bar is detected for the system. In general, higher pressures were obtained as compared to the synthesis of [C₄MIM][Cl]. These findings support that a volatile compound, in this case most probably butene, arises during the reaction.

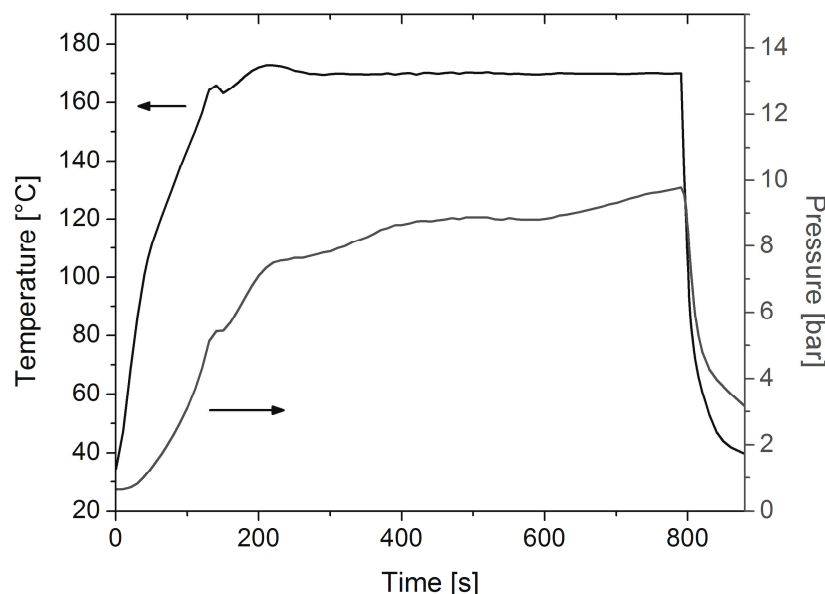


Figure 2.5 Synthesis of 1-(1-methylpropyl)-3-methylimidazolium chloride at 170 °C under microwave irradiation.

The conversions of the methylimidazole were quantitative (determined by ^1H NMR spectroscopy), but only 59% of the desired ionic liquid was produced in the best case due to the formation of the above described side product. The equilibrium between substitution and elimination could be shifted towards substitution by decreasing the reaction temperature to 80 °C. In this case, the side product could be decreased and 74% of the desired ionic liquid was obtained after 2 days reaction time. The optimized reaction conditions for the branched ionic liquids are summarized in Table 2.3.

Table 2.3 Optimized reaction conditions for the synthesis of different branched ionic liquids according to Scheme 2.1 under microwave irradiation at 170 °C and under conventional conditions at 80 °C.

Reaction type		Microwave-assisted (170 °C)			Conventional (80 °C)	
Ionic liquid	Time [min]	Conversion ^a [%]	Yield [%]	Purity ^c [%]	Time [h]	Conversion ^a [%]
[2-C ₃ MIM][Cl]	7	59	28	98	48	74
[2-C ₄ MIM][Cl]	11	35	31	96	48	68
[2-C ₅ MIM][Cl]	11	30	14	97	48	65
[3-C ₅ MIM][Br]	2	43	— ^b	— ^b		
[MBnMIM][Cl]	7	51	39	97		

^a Determined by ^1H NMR spectroscopy, ^b no separation/purification achieved, ^c purity determined by ^1H NMR spectroscopy.

In order to separate the 1-*H*-3-methylimidazolium chloride from the desired ionic liquid different solvents (*e.g.* tetrahydrofuran, methyl ethyl ketone, diethyl ether, and acetone) were investigated. This attempt was unfortunately unsuccessful as shown in Figure 2.6.

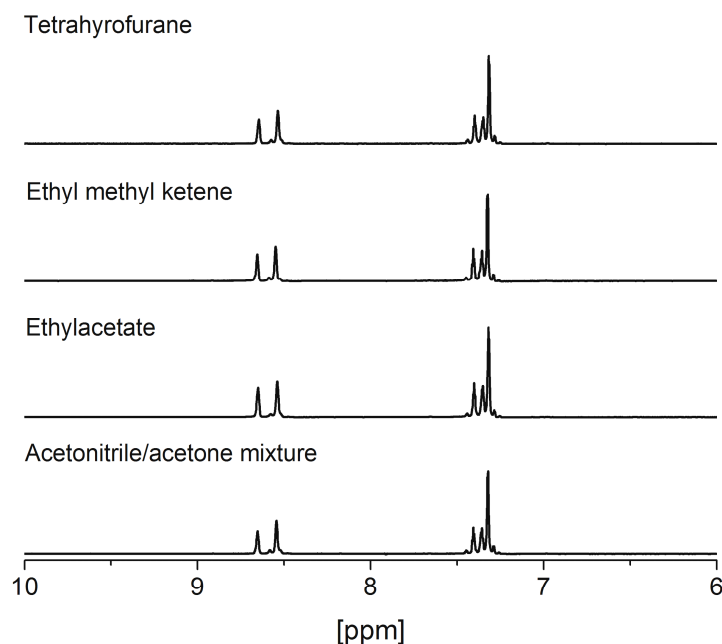


Figure 2.6 ^1H NMR spectra of a branched ionic liquid, containing 1-H-3-methylimidazolium chloride as side product, after extraction with different solvents and solvent mixtures.

The ^1H NMR spectra shows the two imidazolium rings of the branched ionic liquid and the side product in the aromatic region. Between 8 and 9 ppm still two peaks with the same ratios are obtained after extraction with different solvents and solvent mixtures in all cases. For this reason, an alternative purification procedure for the branched ionic liquids was developed, which consisted in drying the samples at 120 °C for two days under vacuum in an infrared-light evaporator (IR-Dancer). As depicted in Figure 2.7, the undesired side product was nearly removed after one day drying in the IR-dancer. For a complete removal of 1-H-3-methylimidazolium chloride the ionic liquid was dried an additional day.

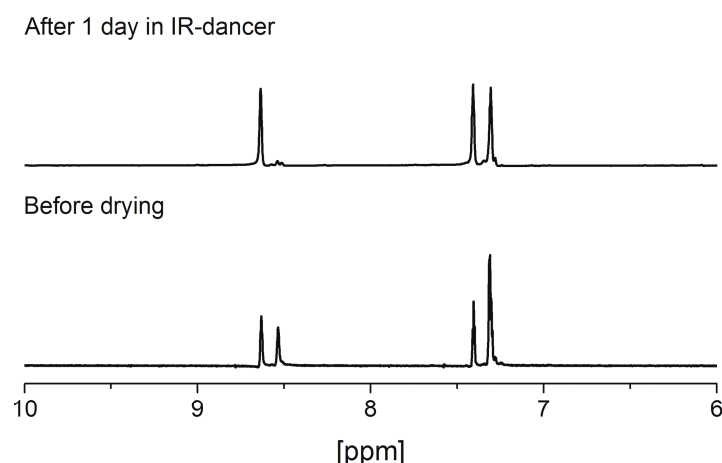
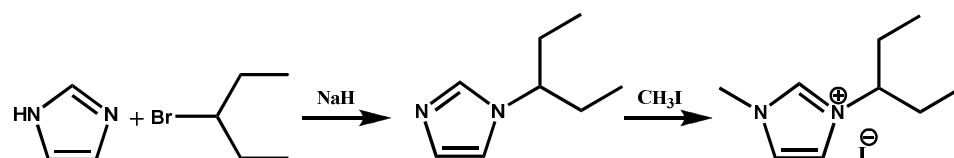


Figure 2.7 ^1H NMR spectra of a branched ionic liquid, containing 1-H-3-methylimidazolium chloride as side product, before and after one day drying in the IR-dancer.

It seems that the 1-*H*-3-methylimidazolium chloride decomposes to 1-methylimidazole and hydrogen chloride under the applied conditions. However, the side products could be successfully removed from the desired ionic liquid at high temperatures under vacuum. Subsequently, the remaining ionic liquid was finally purified by either filtration over silica gel or charcoal in order to remove traces of decomposed material. In the second case, the color of the ionic liquid is improving (slightly yellow).

In case of 1-(1-ethylpropyl)-3-methylimidazolium bromide the above described purification procedure was unsuccessful due to the fact that the 1-*H*-3-methylimidazolium bromide in contrast to the 1-*H*-3-methylimidazolium chloride could not be removed. A possible explanation for this finding is the higher stability of the 1-*H*-3-methylimidazolium bromide. The use of a higher temperature in the IR-Dancer is not possible and could, in general, also lead to a decomposition of the desired ionic liquid. As a consequence, an alternative synthesis route according to Scheme 2.4 was chosen.⁸



Scheme 2.4 Schematic representation of an alternative synthesis route for the synthesis of 1-(1-ethylpropyl)-3-methylimidazolium iodide.

In the first step of this new synthetic approach (Scheme 2.4), imidazole was alkylated with 3-bromopentane using sodium hydride as a deprotonating agent. The reaction was performed under conventional conditions and under microwave irradiation. The progress of the reaction was monitored by ¹H NMR spectroscopy as depicted in Figure 2.8.

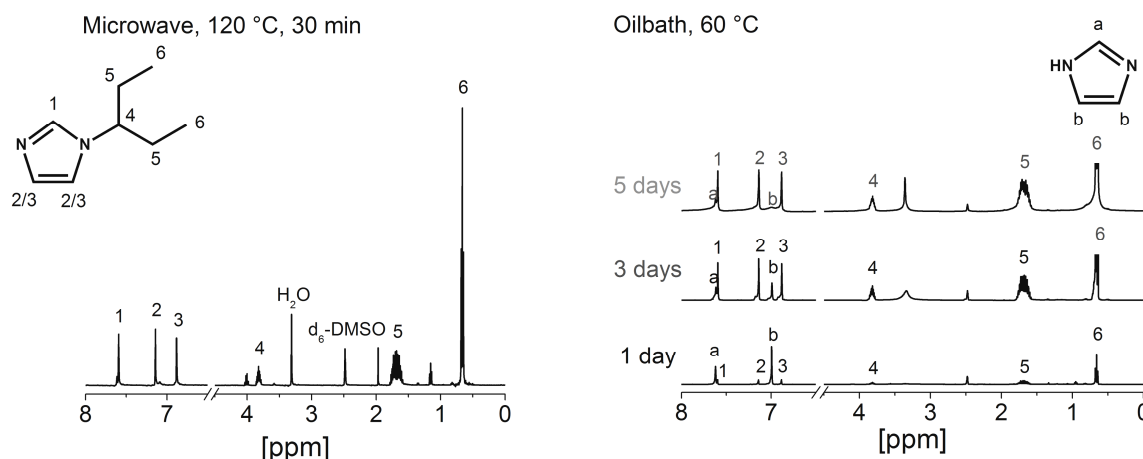


Figure 2.8 ¹H NMR spectra of the synthesis of 1-(1-ethylpropyl)imidazole under a) microwave irradiation (120 °C) and b) conventional conditions (60 °C).

The peak for the imidazole ring at 7.0 ppm (2) disappears, while two new signals at 7.14 (b) and 6.9 (c) arise for the alkylated imidazole ring. Nearly full conversions were obtained after 5 days under conventional heating (60 °C), while only 30 minutes were required under

microwave irradiation (120 °C). This acceleration in the reaction is caused by the applied higher temperature (120 °C instead of 60 °C), which is above the boiling point of the utilized solvent (THF). Thereafter, the obtained reaction mixture was purified by column chromatography and a yield of 48% was achieved. In the second reaction step methylene iodide was added to the alkylated imidazole at room temperature to yield 55% of the desired ionic liquid. The ^1H NMR spectrum of the desired ionic liquid is depicted in Figure 2.9. All peaks of the ^1H NMR spectrum could be assigned to the desired product. An overview of the ionic liquid cations with different branched side chains synthesized in this work is given in Figure 2.10.

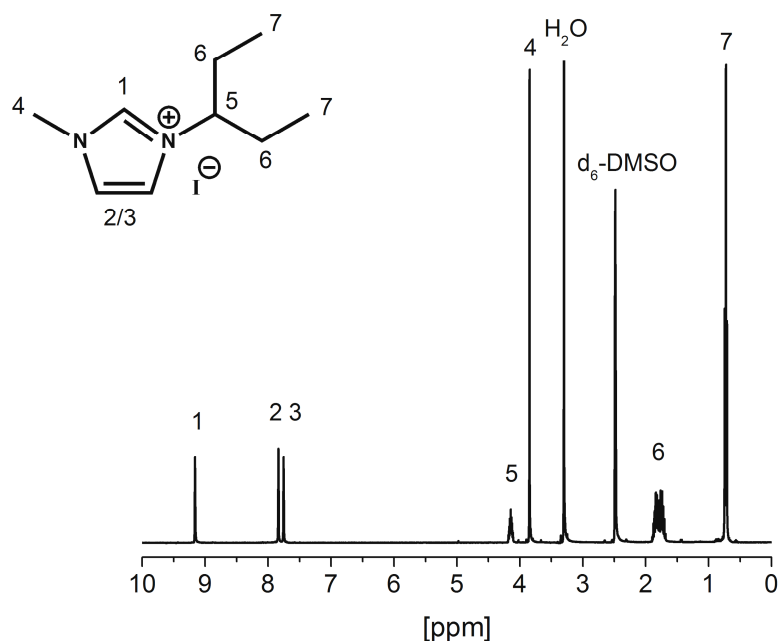


Figure 2.9 ^1H NMR spectrum of 1-(1-ethylpropyl)-3-methylimidazolium iodide.

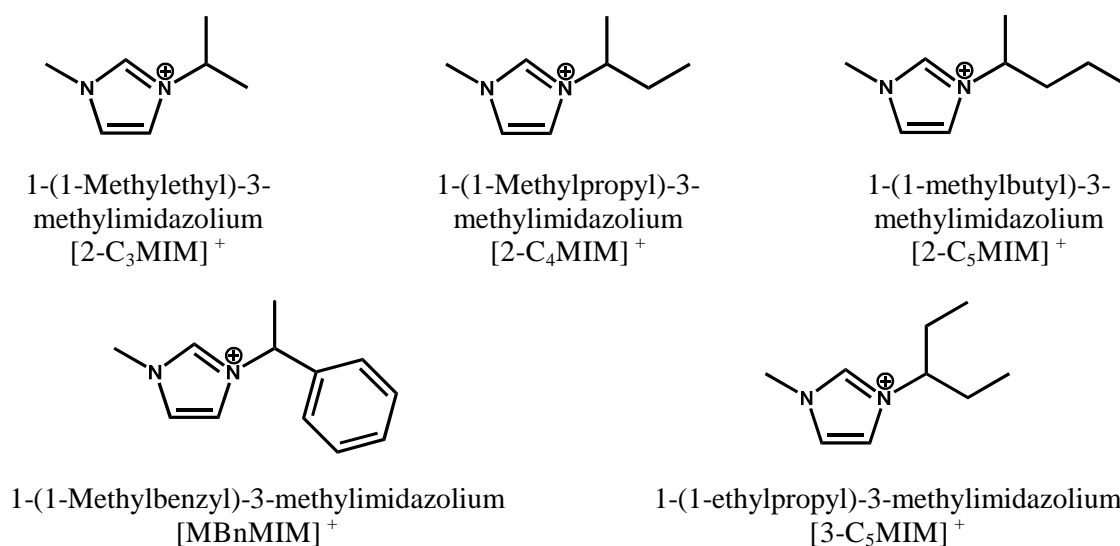


Figure 2.10 Overview of the chemical structures of the synthesized branched ionic liquid cations.

The synthesized ionic liquids were also characterized by matrix-assisted laser desorption/ionization – time of flight – mass spectrometry (MALDI-TOF-MS). Since the imidazolium rings of the ionic liquids are already charged and able to absorb the laser energy, no matrix or ionizing agents were required in order to measure the compounds (in this case the laser desorption/ionization approach (LDI-TOF-MS) was used). The ionic liquids were dissolved in methanol and directly spotted onto the target. The LDI-TOF-MS spectra were recorded in positive mode, measuring only the cations of the ionic liquids. The linear and branched ionic liquids have the same molar mass and therefore similar mass peaks and isotopic pattern were obtained as depicted in Figure 2.11. The measured spectra were fitting well to the calculated isotopic pattern.

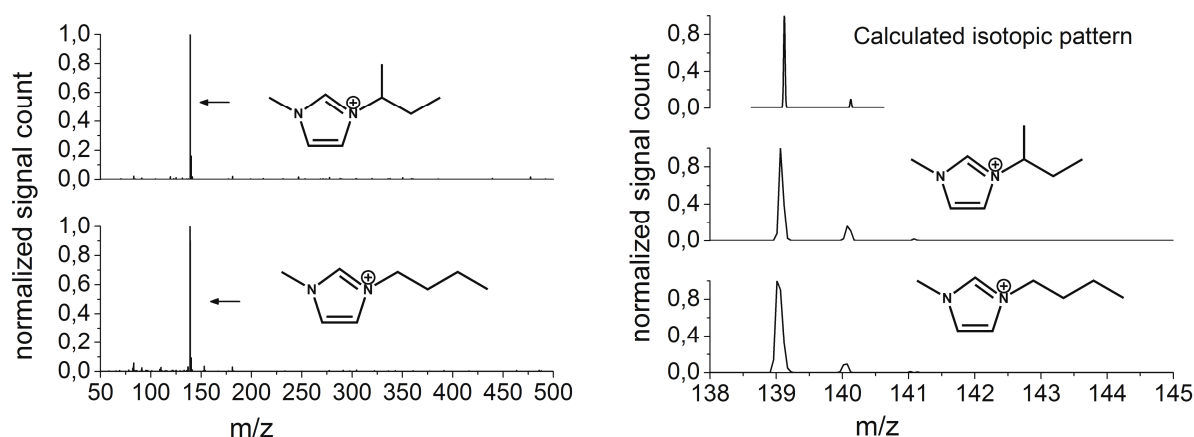


Figure 2.11 LDI-TOF-MS spectra (positive mode) of linear and branched ionic liquids with the same number of carbon atoms in the side chain. Left side, top: [2-C₄MIM][Cl]. Left side, bottom: [C₄MIM][Cl]. Right side: comparison of the theoretical (top) with the experimentally obtained isotopic pattern of the linear (bottom) and branched (middle) ionic liquid.

In order to get a better insight into the fragmentation behavior of linear and branched ionic liquids, LDI-TOF MS/MS was measured of 1-(1-methylpropyl)-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium chloride. In contrast to LDI-TOF-MS, a parent peak (in this case the ionic liquid cation) was selected by a precursor ion selector and the fragmentation of this parent peak was achieved by collision-induced dissociation (CID) resulting in an additional mass spectrum that allows the examination of cleavages and reaction pathways (Figure 2.12). In this case, better spectra were obtained when using a matrix (higher signal intensities, dithranol was used). For both ionic liquids, the MS spectra in Figure 2.12 showed that the dealkylation of the butyl side chain is the main fragmentation process (loss of the largest substituent is most favored). The spectrum illustrates the loss of the butyl carbocation (*n*-C₄H₈, or *sec*-C₄H₈) from the ionic liquid (*m/z* 139) and the resulting 1-methylimidazole ([MIMH]⁺, *m/z* 83 (100%)). A lower intensity for the molar peak (*m/z* 139) was found for the ionic liquid with branched butyl side chain (14%) as compared to the ionic liquid with linear butyl side chain (20%), which is in agreement for the findings observed with branched alkanes.⁹ In general, secondary carbocations are known to be more stable compared to primary carbocations (stability: tertiary > secondary > primary > methyl),⁹ which also might explain the overall lower fragment intensities for the ionic liquid with a branched butyl side chain (Figure 2.11, right side).

In addition, a difference in the fragmentation behavior was found in the region from 83 to 139 m/z . In case of 1-butyl-3-methylimidazolium chloride, fragments at 124, 110 and 96 m/z were found (typical for loss of CH_3 and CH_2), whereas the intensity increased with decreasing molar mass, as it would be expected. Since the cleavage of alkanes is favored at branching points,⁹ the fragment at 96 m/z found in the spectrum of 1-butyl-3-methylimidazolium chloride was not obtained in the spectrum of 1-(1-methylpropyl)-3-methylimidazolium chloride. In this case, the cleavage of C_2H_5 is favored as depicted in Figure 2.17 (left side).

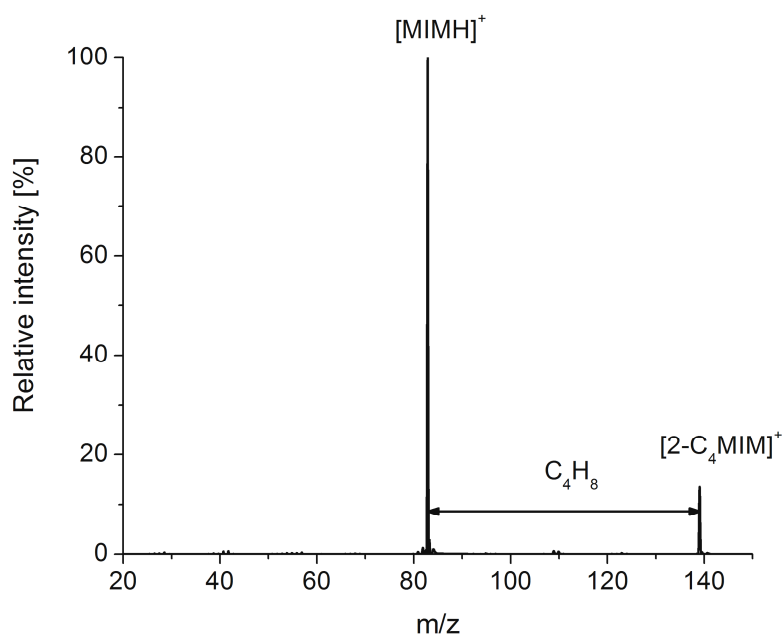


Figure 2.12 MALDI-TOF-MS/MS spectra of 1-(1-methylpropyl)-3-methylimidazolium cation.

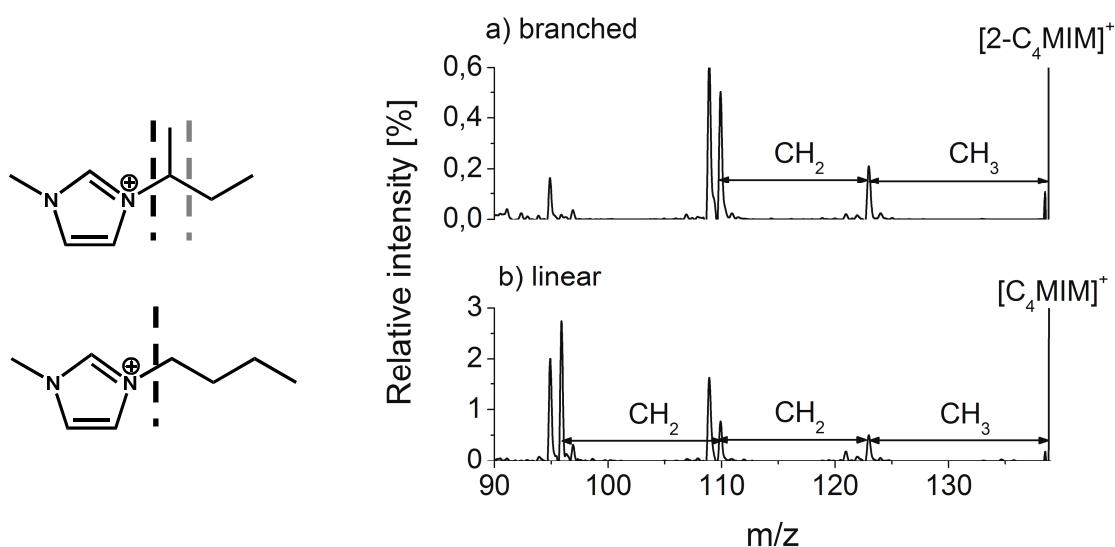
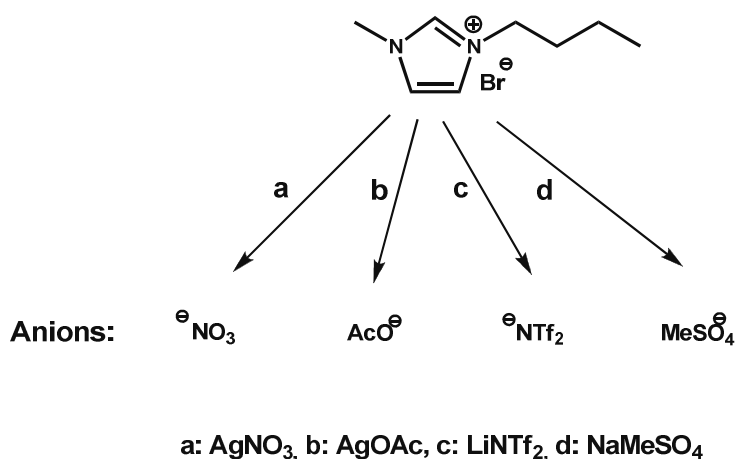


Figure 2.13 Left side: Schematic representation of the favored cleavage (--- more favored than ---) for 1-(1-methylpropyl)-3-methylimidazolium chloride ($[\text{C}_4\text{MIM}]$); Right side: MALDI-TOF-MS/MS spectra of $[\text{2-C}_4\text{MIM}]$ (top) and $[\text{C}_4\text{MIM}]$ (bottom) cation.

2.4 Anion exchange

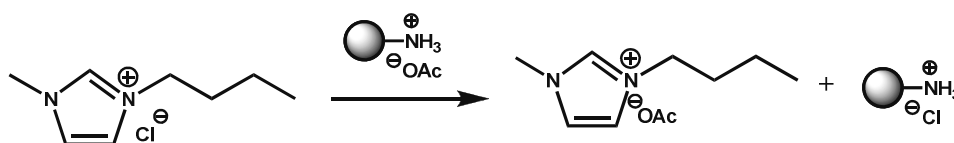
The bromide or chloride anions of the synthesized 1-alkyl-3-methylimidazolium based ionic liquids can be easily exchanged by various salts as depicted in Scheme 2.5. For some exchange reactions water was found to be the best solvent,¹⁰ other exchange reactions must be carried out in dichloromethane or acetonitrile.¹¹⁻¹³ In principle, sodium salts are used for the anion exchange from hydrophilic to hydrophobic anions, *e.g.* from $[\text{Cl}]^-$ to $[\text{PF}_6]^-$. In this case the ionic liquid separates from the aqueous phase, while the anion exchange salt stays in solution.

The completeness of the anion exchange was checked by adding a silver nitrate solution to a solution of the ionic liquid in water.¹⁰



Scheme 2.5 Schematic representation of the anion exchange of 1-alkyl-3-methylimidazolium based ionic liquids with halide counter ion.

In addition, an anion exchange resin *e.g.* Amberlite IRA-400¹⁴ can be used for the preparation of 1-alkyl-3-methylimidazolium acetate (Scheme 2.6).



Scheme 2.6 Schematic representation of the anion exchange with “Amberlite IRA-400”.

The advantage of using an exchange resin is the higher exchange efficiency and the minimized risk of contaminating the ionic liquid. Unfortunately, the use of the exchange resin is limited due to the fact that the exchange potential increases with increasing atomic number and that the solubility of the ionic liquid in the used solvent should stay the same. Therefore, the anion exchange from hydrophilic to hydrophobic anions is problematic and also for the synthesis of fluoride containing ionic liquids the exchange resin can not be used. Therefore silver fluoride (AgF) was used to synthesize 1-ethyl-3-methylimidazolium fluoride ($[\text{C}_2\text{MIM}][\text{F}]$) and 1-butyl-3-methylimidazolium fluoride ($[\text{C}_4\text{MIM}][\text{F}]$). During the exchange, the poorly soluble silver chloride precipitates from the solution.¹⁰ Unfortunately, some excess of silver fluoride remained in $[\text{C}_4\text{MIM}][\text{F}]$. The results for the anion exchange of selected ionic liquids are summarized in

Table 2.4. In case of the branched ionic liquids the anion of the chloride containing ionic liquids was exchanged according to a literature procedure.¹⁰ The ionic liquids were dissolved in water and the anion exchange salt was added in a ratio of 1.0 to 1.06 of ionic liquid to sodium tetrafluoroborate. The reaction mixture was stirred for 15 min and then methylene chloride was added. The aqueous phase was extracted with additional methylene chloride and the combined phases were washed with water containing sodium tetrafluoroborate. The methylene chloride was removed by evaporation under reduced pressure and the ionic liquid was freeze dried to remove remaining water. The completeness of the anion exchange was checked with silver nitrate. In addition, the OH stretching vibrations, which are very sensitive to hydrogen bonding, are shifted to higher wavenumbers and instead of broad absorption bands for the chloride and iodide containing ionic liquids, two narrow bands typical for symmetric 1:2 H-bonded complexes (anion-HOH-anion) were found as depicted in Figure 2.14.¹⁵

Table 2.4 Anion exchange of selected imidazolium based ionic liquids.

Ionic liquid	Conversion [%]	Purity ^b [%]
[C ₂ MIM][F]	>99 ^a	98
[C ₂ MIM][OAc]	>99 ^a	95
[C ₄ MIM][I]	>99 ^a	92
[C ₄ MIM][F]	>99 ^a	98
[C ₄ MIM][OAc]	95	95
[C ₄ MIM][NO ₃]	>99 ^a	99
[C ₄ MIM][NTf ₂]	99	95

^a No starting material detectable (determined by ¹H NMR spectroscopy),

^b purity determined by ¹H NMR spectroscopy.

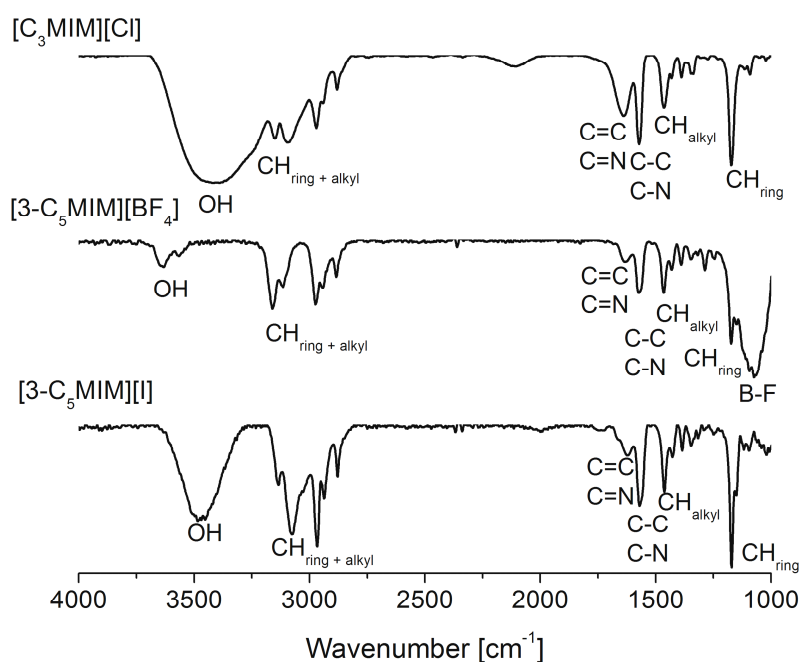


Figure 2.14 IR spectra of 1-alkyl-3-methylimidazolium based ionic liquids (linear and branched alkyl side chain) with different counter ions.

Furthermore, the anion exchange can be followed by LDI-TOF-MS. When measuring in the negative mode, in principle the anions of the ionic liquids can be measured (Figure 2.15). Unfortunately, in case of the chloride anion a large number of other peaks next to the chloride were detected. In case of tetrafluoroborate, only one peak was observed, but we can not conclude if the exchange was complete, since the chloride anion could not be easily detected.

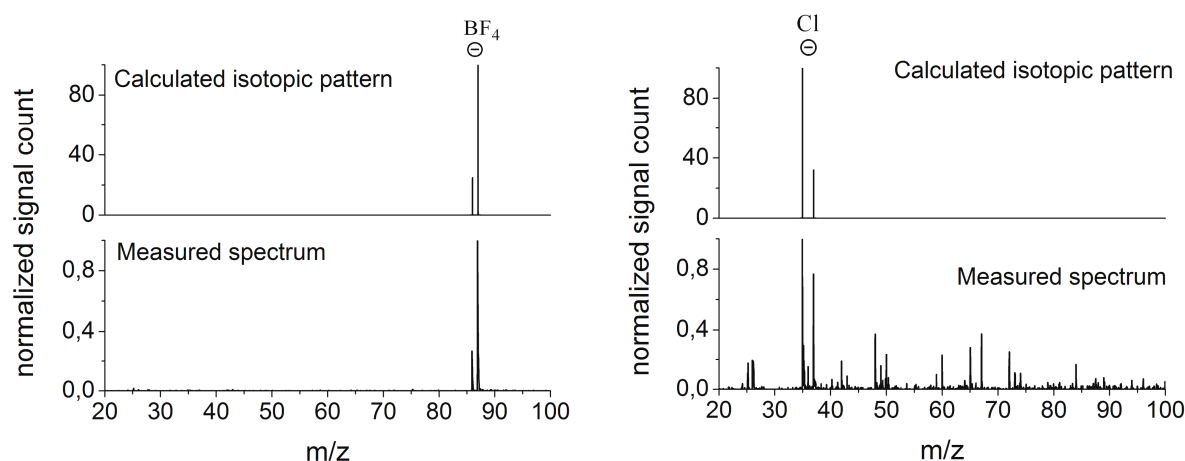


Figure 2.15 LDI-TOF-MS spectra (negative mode) of ionic liquids with different anions. Left side: comparison of the theoretical (top) with the experimentally obtained (bottom) isotopic pattern of [2-C₄MIM][BF₄]. Right side: comparison of the theoretical (top) with the experimentally obtained (bottom) isotopic pattern of [2-C₄MIM][Cl].

The anion of 1-(1-ethylpropyl)-3-methylimidazolium iodide was exchanged by using silver tetrafluoroborate as exchange salt. The ionic liquid was dissolved in water and the anion exchange salt was added in a ratio of 1.0 to 1.06 of ionic liquid to silver tetrafluoroborate. The precipitated silver iodide was filtered off the solution and the aqueous phase was extracted three times with methylene chloride. The solvent was removed by evaporation under reduced pressure and the ionic liquid was freeze dried to remove remaining water. The completeness of the anion exchange was checked with silver nitrate. The results of this anion exchange process are summarized in Table 2.5.

Table 2.5 Results for the anion exchange process of the investigated ionic liquids with linear and branched alkyl side chains.

Ionic liquid	Anion exchange salt	Yield [%]
[C ₃ MIM][Cl]	NaBF ₄	27
[C ₄ MIM][Cl]	NaBF ₄	62
[C ₅ MIM][Cl]	NaBF ₄	83
[BnMIM][Cl]	NaBF ₄	72
[2-C ₃ MIM][Cl]	NaBF ₄	19
[2-C ₄ MIM][Cl]	NaBF ₄	30
[2-C ₅ MIM][Cl]	NaBF ₄	71
[MBnMIM][Cl]	NaBF ₄	73
[3-C ₅ MIM][I]	AgBF ₄	50

2.5 Microwave-assisted up-scaling

In order to be able to take advantage of the promising properties and broad range of applications of ionic liquids, scale-up possibilities for their synthesis are of significant importance. The first attempts for large scale preparations of ionic liquids (from 0.3 to 2.0 mol) under microwave-assisted heating were performed in 2002 by Chan and coworkers,¹⁶ who carried out the synthesis in the absence of solvent and in an open vessel. In 2003, Deetlefs and Seddon¹ used a closed system for their medium scale synthesis (0.15 to 0.3 mol). The difficulty encountered during scale-up, particularly for continuous flow experiments, is the handling of a two-phase system with rather high viscosities. A too high viscosity can cause blockades in the tubes of the reactor. In this thesis, the reaction conditions for the synthesis of 1-butyl-3-methylimidazolium chloride were optimized on a small scale in a batch microwave reactor. Due to homogenous heating by microwave irradiation a direct up-scaling without heat and mass issues was expected,² and the obtained optimal reaction conditions could therefore be transferred to a variety of microwave reactors, both batch and continuous flow, for scale-up of the ionic liquid synthesis under pressurized conditions. In the current study, we investigated the scale-up of the synthesis of 1-butyl-3-methylimidazolium chloride under pressurized microwave conditions in order to produce large quantities of this ionic liquid in a short time. Special requirements for the microwave systems were necessary for this purpose. As a result of the rapid heating of the ionic liquid, a sufficient temperature control was required to avoid thermal runaway of the reaction. In addition, for the continuous flow synthesis, the microwave system must be able to handle a two phase reaction system and the high viscosity of the product. The microwave systems used in the current study for the synthesis of 1-butyl-3-methylimidazolium chloride are shown in Figure 2.16.

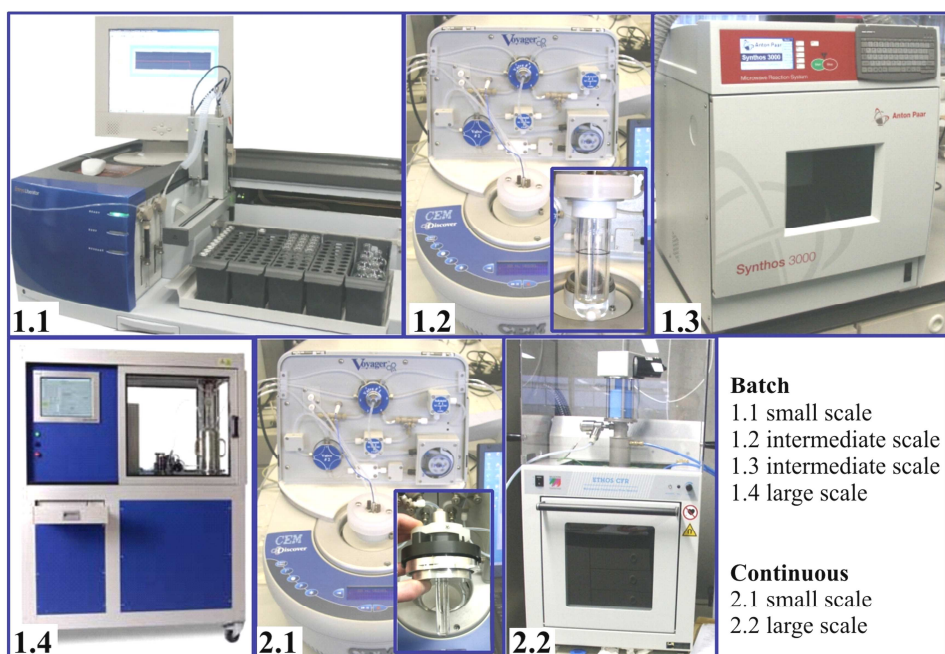
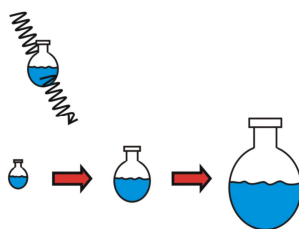


Figure 2.16 Pictures of the employed microwave systems. 1.1: Biotage Emrys Liberator, 1.2 & 2.1: CEM Discover®, 1.3: Anton Paar Synthos 3000, 1.4: Biotage Advancer™, 2.2: Milestone ETHOS CFR.

2.5.1 Batch reactor



The optimization of the synthesis of 1-butyl-3-methylimidazolium chloride on a small scale in a batch reactor under microwave irradiation is described in Chapter 2.2. The optimum conditions were found to be a 1 to 1.3 ratio of 1-methylimidazole to butyl chloride, a reaction temperature of 170 °C, a reaction time of 7 min and a power of 150 W. For up-scaling the reaction temperature, reaction time and ratio of 1-methylimidazole to butyl chloride were kept constant. In addition, the applied microwave power was fixed for the single-mode microwave systems.

2.5.1.1 Intermediate scale batch synthesis with single-mode microwave irradiation

At first, an intermediate up-scaling was investigated in a CEM Discover¹⁷ microwave system with a large reactor upgrade (up to 50 mL fill volume). In the single-mode microwave system the power could be set in intervals of 1 up to 300 W. The safety-limit for the temperature, which was measured by a fiber optic sensor, was 250 °C and the maximum pressure was 17 bar. The reaction mixture was stirred with a magnetic stirring bar. During the reaction, an additional simultaneous air cooling was possible, which allowed the use of higher microwave power while maintaining the internal reaction temperatures. The experiments were carried out on a reaction volume of 40.8 mL (0.19 mol) and the temperature was kept at 170 °C for 7 min without simultaneous cooling. Subsequently, the system was cooled with a compressed nitrogen flow and a slightly yellow colored ionic liquid was obtained. Under these conditions, conversions of 66% and 84% were reached for two reactions: with and without simultaneous cooling, respectively. This indicates that the reaction time was too short to reach full conversions. The differences between the two systems can be explained by the higher thermal overshoot of 19 °C in the system without cooling compared to 9 °C with cooling. In other words, a higher conversion could be reached for the reaction without simultaneous cooling (Figure 2.17). During the reaction, the temperature fluctuated around its target value. This was due to a gradual increase/decrease of the microwave power being applied. When the target temperature was reached, the applied microwave power was slowly reduced. In the mean time, the reaction mixture was heated further thus causing a thermal overshoot of around 3 °C. This occurred for both processes whether simultaneous cooling was employed or not. Subsequently, the temperature decreased as a result of the lower power supply. When the temperature fell below the set value, the system slowly increased the microwave power again. During this time, the temperature of the reaction mixture dropped around 3 °C below the set point. In addition, more power was necessary in order to reach the preset temperature value when simultaneous cooling was used.

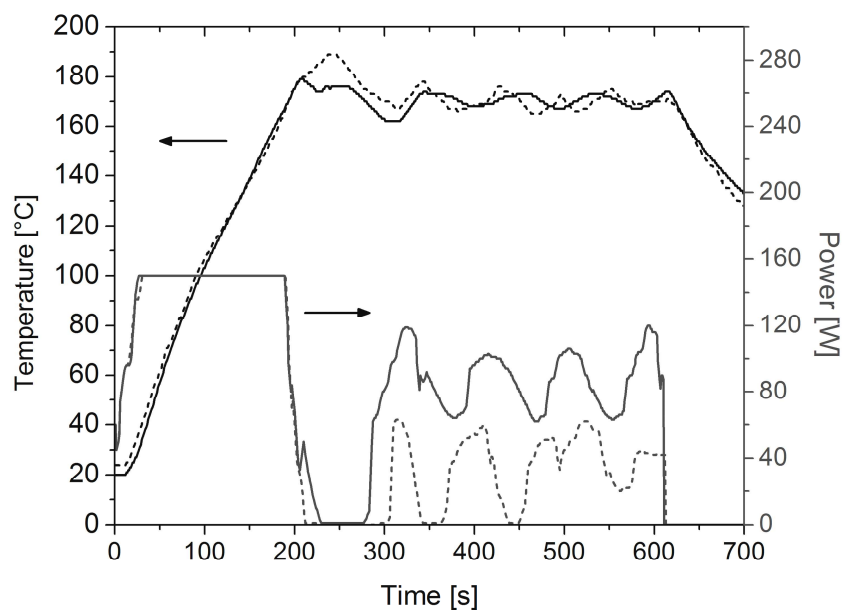


Figure 2.17 Microwave temperature and power profiles for the solvent-free synthesis of $[C_4MIM][Cl]$ with (line) and without (dash) simultaneous cooling on an intermediate scale (0.19 mol) using a 1 to 1.3 ratio of 1-methylimidazole to butyl chloride (170 °C, 7 min, 150 W, fiber optic sensor).

The lower conversions as compared to the 2 mL reactions might be explained by the observed fluctuations in reaction temperature or the different means of measuring the temperature of the two devices. To improve the conversion, the reaction time was increased to 10 min, and for these experiments, the difference between the thermal overshoots and the heating rates were found to be even larger. The experiment without cooling showed a thermal overshoot of 30 °C, while the experiment with cooling revealed almost no thermal overshoot at all. The reaction solution with cooling was heated more slowly in this experiment, which can be the result of a difference in air-flow as compared with the experiments where the reaction time was 7 min. The decreased heating rate might be a possible explanation why only a small thermal overshoot was observed. The conversions were found to be very similar, attaining values of 96% for the reaction without cooling and 98% for the one with. The color of the ionic liquid was similar to the product which was obtained in the 7 min reaction. In conclusion, the up-scaling of the synthesis of 1-butyl-3-methylimidazolium chloride could be performed in a single-mode CEM microwave system. However, a direct up-scaling resulted in lower conversions, probably due to temperature fluctuations, the different temperature measurement methods or inefficient stirring. For a reaction time of 10 min, nearly quantitative conversions were obtained.

2.5.1.2 Intermediate scale batch synthesis with multi-mode microwave irradiation

The up-scaling of the batch synthesis with multi-mode microwave irradiation was investigated in an Anton Paar Synthos 3000.¹⁸ In this multi-mode microwave system, the microwave power could be set in steps of 1 up to 1400 W. The maximum reaction volume of the reactor was 60 mL. In one run 4, 6 or 8 of these quartz-glass reactors could be used in parallel. The temperature inside a reference vessel was measured by a gas thermometer and the temperature outside of all

the vessels was obtained with an IR-sensor at the bottom of the microwave cavity. This temperature control system implied that all parallel reactors should have similar microwave absorptions to ensure an accurate temperature control. A safety-limit of 300 °C was set for the inside and 280 °C for the outside temperature. The maximal pressure is 120 bar (safety-limit) and the system can be operated up to 80 bar. The system is able to hold 120 bar, but the maximum working pressure is 80 bar, than the system turns off the microwave irradiation. The combination of 300 °C and 80 bar allowed reactions in near-critical water (temperature range of 250 to 350 °C). The reaction mixtures were stirred with magnetic stirring bars. The system could be cooled by three levels of air-flow, and the cooling could be independently set, both during heating and for the subsequent reaction. One run corresponded to four parallel reactions, each with a volume of 27.2 mL, resulting in a total reaction volume of 108.8 mL (0.50 mol). The volume could be further increased to 480 mL by using 8 times 60 mL per vessel. The targeted reaction temperature of 170 °C was reached *via* a temperature ramp of 5 min with the lowest level of cooling. The attained temperature was then held for 7 min under maximum cooling. No thermal overshoot was observed for this microwave system, which was probably a result of the well-controlled heating of the reaction mixture due to the selected temperature ramp (Figure 2.18).

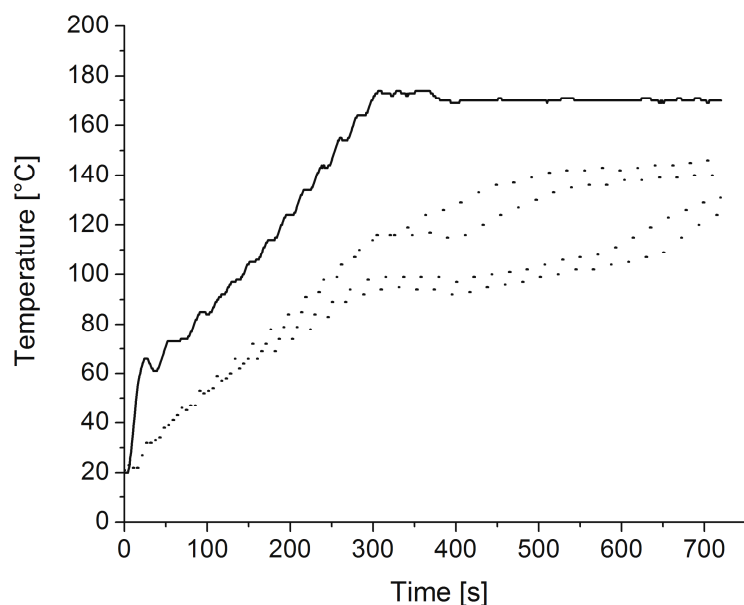


Figure 2.18 Microwave temperature profile for the solvent-free synthesis of $[C_4MIM][Cl]$ on an intermediate scale (0.50 mol) using a 1 to 1.3 ratio of 1-methylimidazole to butyl chloride (170 °C, $t_{ramp} = 3$ min, $t_{hold} = 7$ min, power adjusted automatically to control the temperature ramp, gas thermometer (line), IR-sensor (dash)).

The temperature fluctuations during the heating process were caused by the power regulation employed by the microwave system to follow the temperature ramp. All reactors showed more or less identical IR-temperature profiles, which were lower than the temperature profile of the immersed temperature-probe. During the heating step, where the lowest level of cooling was used, almost no difference between the IR-temperatures was observed, whereas a difference of 10 °C was detected for the reaction step with maximum cooling. At the end of the reaction, the

system was cooled down for half an hour and a yellowish ionic liquid was obtained. All four reactions revealed conversions of ~96% demonstrating that the small scale synthetic protocol could be directly scaled to this multimode microwave synthesizer.

2.5.1.3 Large scale batch synthesis with multi-mode microwave irradiation

The scale-up of the large batch synthesis with multi-mode microwave irradiation was investigated in a Biotage AdvancerTM.⁷ In this system, the microwave power could be set in steps of 1 up to 1200 W. The maximum volume of the reactor was 250 mL. The temperature was measured with an internal temperature probe and safety-limits were set to 250 °C and 20 bar. The reaction mixture was stirred with an overhead mechanical stirrer. The experiments were carried out with the maximum reaction volume, *e.g.* 250 mL (1.15 mol), and a preset temperature value of 170 °C that was held for 7 min.

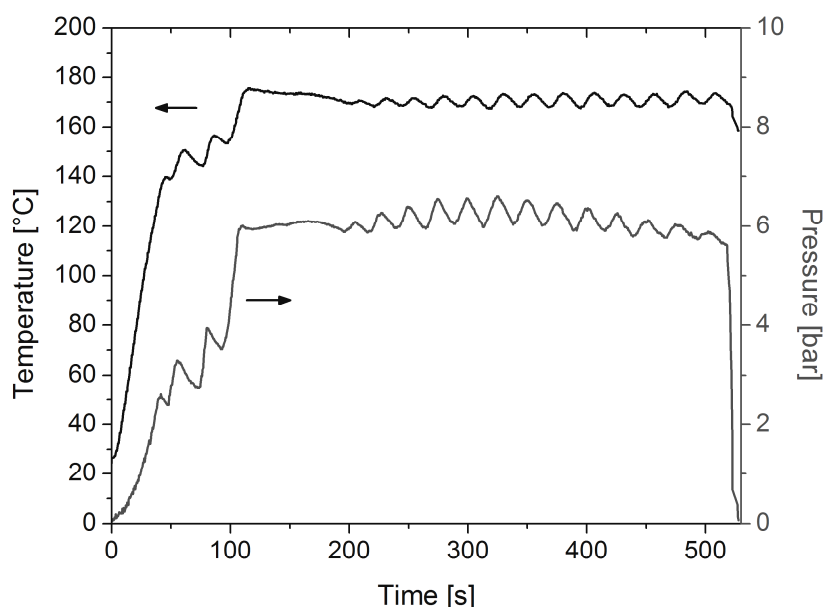
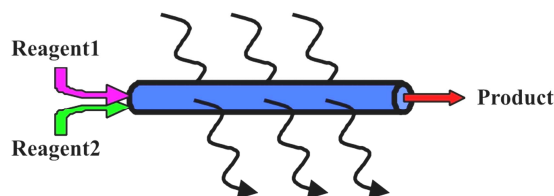


Figure 2.19 Microwave temperature and pressure profiles for the solvent-free synthesis of $[C_4MIM][Cl]$ with (line) and without (dash) simultaneous cooling on a large scale (1.15 mol) using a 1 to 1.3 ratio of 1-methylimidazole to butyl chloride (170 °C, 7 min, microwave power adjusted manually, internal temperature probe).

As shown in Figure 2.19, also this system revealed a thermal overshoot of approximately 6 °C. To prevent the occurrence of a larger thermal overshoot, the microwave power had to be carefully adjusted manually during the heating trajectory. After the 7 min hold time, the pressurized reaction mixture was released in a product vessel, which gave rise to an instantaneous adiabatic cooling. This procedure led to a conversion of 98%, which was comparable to what was obtained in the small scale synthesis. Surprisingly, the product obtained from this large scale synthesis was found to crystallize with time, whereas the small scale products remained viscous oils. A possible explanation for this behavior could be the rapid cooling. This parameter was the only difference between the methods, since the reaction temperature and the used chemicals were the same in all experiments.

2.5.2 Continuous flow reactor



2.5.2.1 Small scale continuous flow synthesis with single-mode microwave irradiation.

The single-mode microwave system from CEM could also be used in a continuous flow mode with the Voyager module. In this setup, the volume of the glass reactor was 10 mL. The flow rate could be varied from 0.01 to 20 mL/min, and the temperature was measured by an IR-sensor, located at the bottom of the microwave cavity. The system can be used with a maximum temperature of 250 °C and a maximum pressure of 17 bar. The reaction mixture flowed through a tube reactor without stirring. A residence time of 10 min, resulting in a flow rate of 1 mL/min (4.6 mmol/min), was chosen based on the batch experiments with this microwave system. Since the IR-sensor measured the temperature at the surface of the glass vessel, it was only possible to perform the experiment without simultaneous cooling. According to the temperature profile of the experiment there was no thermal overshoot. However, no ionic liquid was formed during the experiment using the above mentioned conditions. A possible explanation for this result was the fact that the temperature was measured with an IR-sensor. The temperature of the system was measured at the surface of the glass vessel, and during the early stages of the experiment, the reaction mixture was heated by absorbing microwave energy. This heat was then transferred to the colder glass vessel. During the experiment the measured temperature could thus be higher than the actual temperature of the reaction solution, since the glass vessel was heated by the exothermic reaction whereas the continuously added reaction mixture was much colder. As a result, the reaction solution was partially heated by the hot reaction vessel, since a microwave energy of only 1 W was applied to the system (continuous 10 mL vessel) throughout the duration of the reaction, whereas up to 60 W was required for the batch mode (50 mL vessel) in order to hold the temperature at the set value. To overcome the problem, the residence time was increased to 16 min by reducing the flow rate to 0.63 mL/min (2.9 mmol/min). The heating and conversion profiles of the experiment are shown in Figure 2.20. Under these conditions the reaction solution was heated very quickly giving rise to an enormous thermal overshoot of 33 °C. The average temperature was about 6 °C higher than the preset value of 170 °C and varied in a range of ± 3 °C. During the process, samples were collected for 1 min with 5 min intervals and the conversion was subsequently determined. As it can be seen in Figure 2.20, the conversion reached its maximum value of 64% after a reaction time (corresponding to the residence time) of 16 min. This indicated a narrow residence time distribution between 12 and 16 min. The conversion remained at a constant level until the completion of the reaction. The conversion value of 64 % was lower as compared to the small scale batch mode, even though the residence time was prolonged. A reasonable explanation is the temperature gradient in the flow

reactor. The IR-sensor measured the temperature at the bottom of the glass vessel, and the reaction mixture at the inlet of the flow reactor was at room temperature after which it was heated to the target value. It is unknown whether this value was reached at the point of temperature measurement or before. Due to the unknown heating profile inside the reactor, no conclusions about the residence time at the target temperature were possible. Additionally, the temperature profile inside the reactor was also unknown. The conversions might become higher with a lower flow rate, but such experiments would create a risk of clogging the system due to higher viscosities. The residence time distribution was checked by utilizing a methyl orange solution, which absorbs at 505 nm. Figure 2.21 shows the rather sharp increase in absorption maximum with increasing elution times, resulting in a relative narrow residence time distribution (1st derivative). Nevertheless, the residence time was increased further to 30 min, which corresponded to a flow rate of 0.33 mL/min (1.5 mmol/min). The heating and conversion profiles are shown in Figure 2.22.

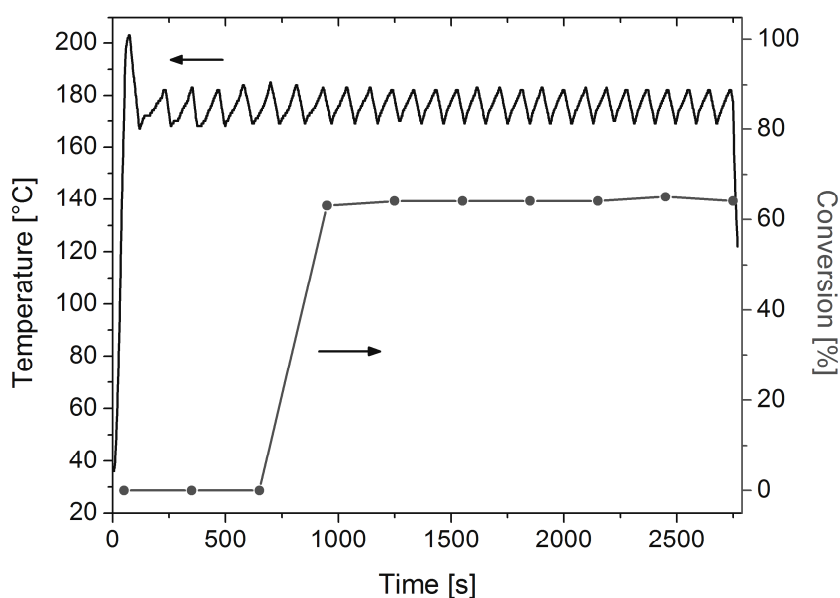


Figure 2.20 Microwave temperature and conversion profiles for the continuous flow solvent-free synthesis of $[C_4MIM][Cl]$ on a small scale (2.9 mmol/min) using a 1 to 1.3 ratio of 1-methylimidazole to butyl chloride (170 °C, 16 min residence time, 150 W, IR-sensor).

The heating profile was very similar to the experiment with a flow rate of 0.63 mL/min, as both the thermal overshoot and the temperature fluctuations were in the same range. In addition, the jump in conversion from 0 to 72% between 25 and 30 min was also rather sharp. However, the conversion only increased from 64 to 72% even though the residence time was prolonged from 16 to 30 min. In addition, more fluctuations in the conversions were observed, which might be explained by the irregular, pulse-wise release of product from the reaction vessel leading to differences in the residence times. The average conversion was $72\% \pm 5\%$, and this low value was most likely due to phase separation and the high viscosity of the reaction system. The 1-methylimidazole and the ionic liquid were miscible, whereas the butyl chloride was immiscible with the ionic liquid, thus giving rise to the phase separation. This phase separation and the

absence of stirring in combination with limited diffusion due to the high viscosity could explain the limited conversion observed.

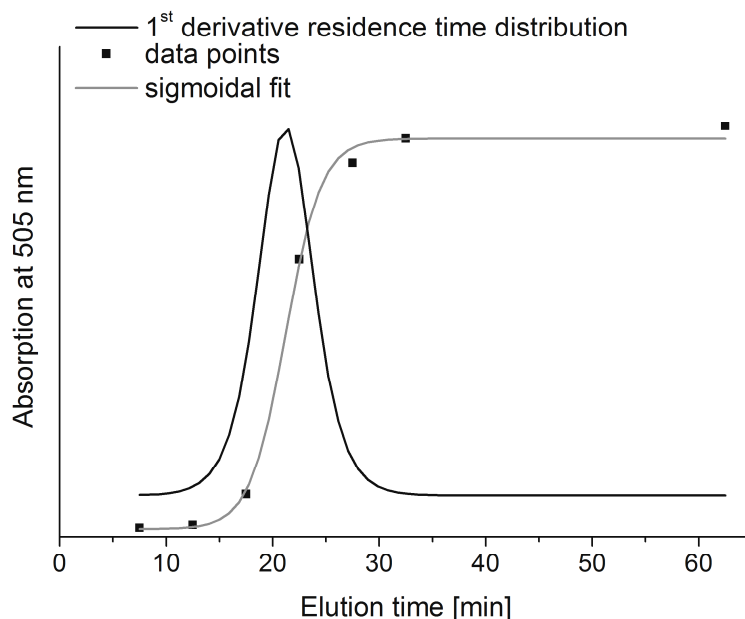


Figure 2.21 Residence time distribution of methyl orange for the CEM continuous flow reactor.

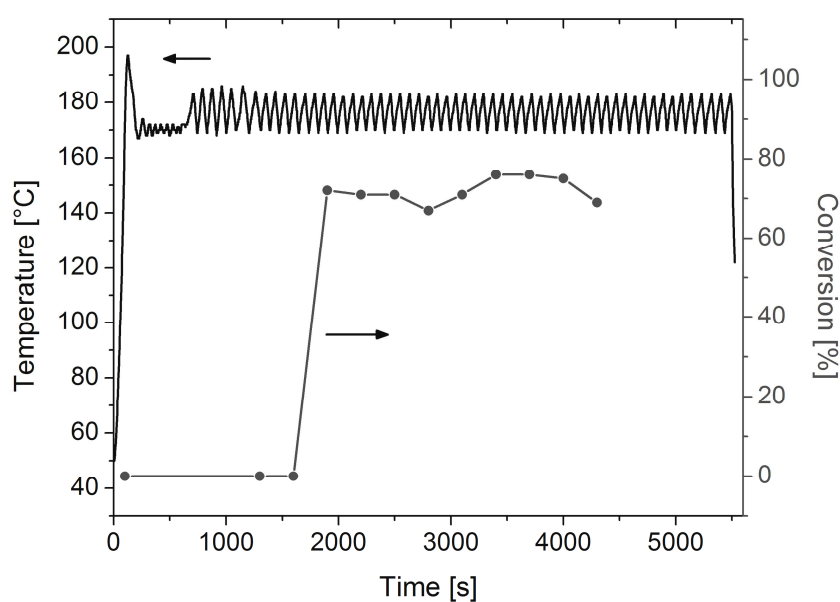


Figure 2.22 Microwave temperature and conversion profiles for the continuous flow solvent-free synthesis of $[C_4MIM][Cl]$ on a small scale (1.5 mmol/min) using a 1 to 1.3 ratio of 1-methylimidazole to butyl chloride (170 °C, 30 min residence time, 150 W, IR-sensor).

2.5.2.2 Large scale continuous flow synthesis with multi-mode microwave irradiation

Large scale synthesis in a continuous flow reactor with multi-mode microwave irradiation was investigated in a Milestone ETHOS CFR system.¹⁹ In this microwave system, the microwave power could be set in steps of 1 up to 1000 W. The volume of the continuous flow reactor was 200 mL. The flow rate could be varied from 12 to 130 mL/min resulting in residence times from

16 to 1.5 min. The residence times were thus determined by the pump speed. The temperature was measured in- and outside the reactor by a shielded thermocouple element. The system could endure a maximum temperature of 200 °C and a maximum pressure of 50 bar. The reaction solution was mixed with a mechanical screw stirrer located in the middle of the flow reactor as seen from top to bottom. At least 1 L of reaction medium was required in order to obtain a stable running system. A residence time corresponding to that of the small scale continuous flow synthesis (16 min) was chosen, which was obtained by setting the flow rate to 12.5 mL/min (58 mmol/min). No thermal overshoot occurred during the heating of the reaction solution, due to the controlled heating rate (Figure 2.23). The observed increase and decrease of temperature during the holding time were related to a sudden diminution of the pump pressure, which led to a lower flow of the reaction solution resulting in a longer heating period and, consequently, a higher reaction temperature. This behavior also occurred for the outlet temperature. After 18 min running time, which was close to the chosen residence time of 16 min, full conversion was not reached. This indicated a broad distribution of the residence time, which has also been observed for methyl orange as depicted in Figure 2.24.

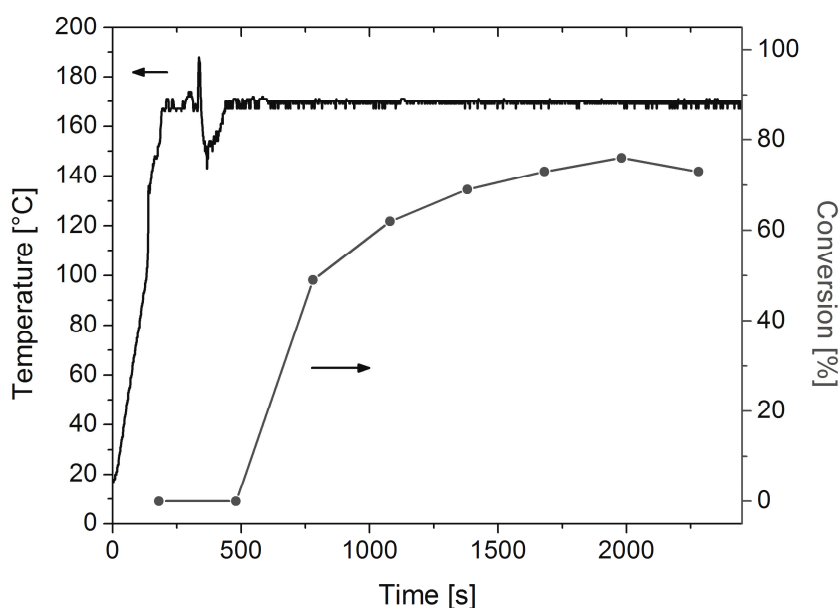


Figure 2.23 Microwave temperature and conversion profiles for the continuous flow solvent-free synthesis of $[C_4MIM][Cl]$ on a large scale (58 mmol/min, 170 °C, 16 min residence time).

The broad distribution with respect to the small scale continuous flow synthesis can be a result of the reactor size and the different flow profiles inside the reactors (Figure 2.24). The conversion of approximately 75% was lower than that obtained for the small scale batch mode, but higher than for the small scale continuous flow synthesis. These differences may have been caused by the temperature profile in the reactor. A longer residence time was not possible, due to the limitations of the pump. In addition, the synthesis of $[C_2MIM][Et_2PO_4]$ was performed in the Milestone ETHOS continuous flow reactor. In contrast to $[C_4MIM][Cl]$, no phase separation occurs, which should improve the conversion. A temperature of 140 °C was chosen, and the reaction solution was pumped in cycles through the microwave reactor. Samples were taken

every hour in order to check the conversion. In the batch experiments, nearly full conversion was reached after 5 h at 150 °C. For the continuous flow experiments, the conversion increased relative rapidly within the first 2 hours (up to 80%) as depicted in Figure 2.25. Afterwards, the conversion increased only slightly and reached a maximum of 97% after 10 hours. Unfortunately, the ionic liquid became relative rapidly dark under the applied conditions, which might be caused by hot spots due to insufficient stirring during the reaction (also under conventional conditions). In order to decrease the viscosity of the system and to avoid the strong colorization, 40 v% acetone was added to the reaction mixture. In this case, the reaction was slowed down and lower conversions (~30%) were obtained compared to the solvent-free synthesis as a result of the lower educt concentration. The addition of acetone did not have a significant influence on the color and a dark reaction mixture was obtained.

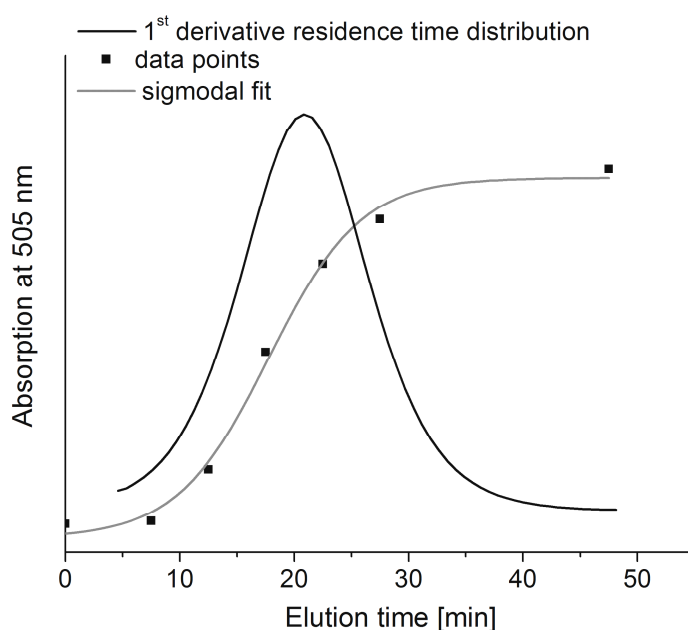


Figure 2.24 Residence time distribution of methyl orange for the Milestone continuous flow reactor.

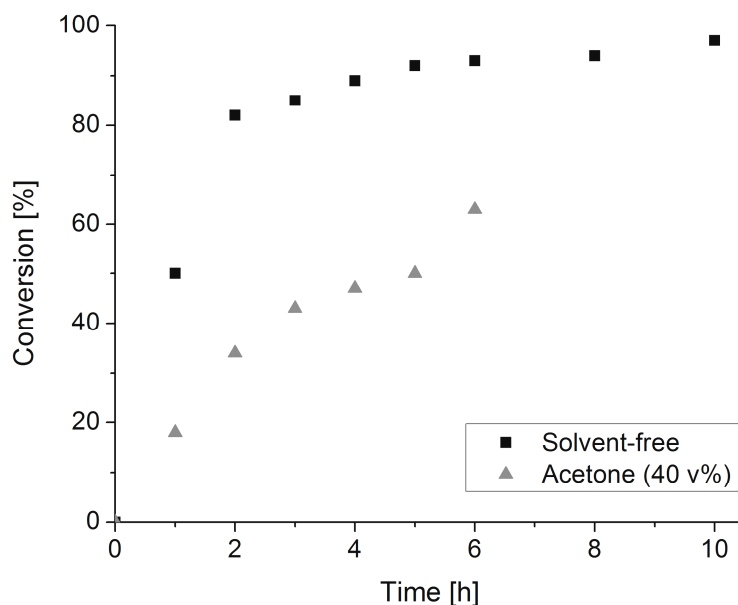


Figure 2.25 Microwave temperature and conversion profiles for the continuous flow synthesis of $[C_2MIM][Et_2PO_4]$ on a large scale (58 mmol/min, 170 °C, 16 min residence time) solvent-free and with 40 v% acetone.

2.6 Conclusions

Ionic liquids with a linear alkyl side chain can be synthesized in a fast and efficient way by using microwave irradiation (solvent-free, within 11 minutes). In general, the reaction times can be decreased from several hours to a few minutes. This acceleration is mainly a result of the elevated temperatures applied during the reaction. In case of the ionic liquids with branched alkyl side chain, the synthesis could be accelerated at elevated temperatures (170 °C) as well, but the equilibrium was shifting towards the undesired side product compared to the synthesis at lower temperatures (80 °C). In this regard, several new branched ionic liquids, *e.g.* 1-(1-ethylpropyl)-3-methylimidazolium iodide and 1-(1-methylbenzyl)-3-methylimidazolium chloride and their tetrafluoroborate containing analogues, were synthesized applying two different synthetic approaches. In principle, a direct scaling for the synthesis of ionic liquids with linear alkyl side chains from small scale (0.01 mol) to large scale (1.15 mol) was possible, although lower conversions were observed when using the CEM microwave system. Possible reasons for these differences include the temperature fluctuations, the different temperature measurement methods or inefficient stirring. However, almost complete conversions could be obtained in this system by increasing the reaction time to 10 min thus making it comparable with the other microwave systems. The details for all batch experiments are summarized in Table 2.6. The results of the continuous flow experiments indicated that 1-butyl-3-methylimidazolium chloride can be synthesized with short reaction times by using continuous flow microwave systems. However, direct scaling from the batch experiments was not possible. Even when employing a residence time of 16 min, a complete conversion could not be obtained. Further difficulties include the unknown temperature profile inside the reactor, the handling of a two-phase system during the reaction and a highly viscous product at the outlet of the reactor.

Nonetheless, for the first time, the synthesis of ionic liquids in continuous flow reactors was achieved. After optimization, the ionic liquid could be successfully synthesized in continuous flow reactors up to 58 mmol/min, corresponding to a pure product flow of ~ 460 g/h. The details for all continuous flow experiments for the synthesis of $[C_4MIM][Cl]$ are summarized in Table 2.7. In case of $[C_2MIM][Et_2PO_4]$, higher conversions were achieved, since the reaction proceeds in a homogeneous phase, but unfortunately only a strongly colored ionic liquid could be obtained under the applied conditions.

Table 2.6 Details of the synthesis of $[C_4MIM][Cl]$ at 170 °C with various batch microwave systems.

System	Volume [mL]	n [mol]	t _{hold} [min]	T _{overshoot} [°C]	Cooling	Conversion [%]
1.1	2.2	0.01	7	8	off	95
1.2	40.8	0.19	7	9	on	66
1.2	40.8	0.19	7	19	off	84
1.2	40.8	0.19	10	3	on	98
1.2	40.8	0.19	10	30	off	96
1.3	108.8	0.50	7	4	on	96
1.4	250	1.15	7	5	off	98

Table 2.7 Details of the synthesis of $[C_4MIM][Cl]$ at 170 °C with different continuous flow microwave systems.

System	Flow rate [mL/min]	Mass transport [mmol/min]	Residence time [min]	T _{overshoot} [°C]	Conversion (t _{hold} =30 min) [%]	Calcd. product throughput [g/h]
2.1	1.00	4.6	10	— ^a	— ^a	— ^a
2.1	0.63	2.9	16	33	64	19.5
2.1	0.33	1.5	30	27	72	11.3
2.2	12.50	58.0	16	4	76	462.0

^a No ionic liquid formed.

2.7 Experimental details

Materials

1-Methylimidazole (Aldrich) was distilled under reduced pressure prior to use and stored at room temperature. 1-Chloro-1-phenyl-ethane, 2-chloropropane and benzyl chloride (Acros Organics), iodomethane (Riedel–de Haën), all other alkyl halides (Aldrich), sodium hydride, sodium tetrafluoroborate and silver tetrafluoroborate (Aldrich) were used as received. THF (Biosolve) was dried and deoxygenated using a solvent purification system (PURE SOLV 400-4-MD, Innovative Technology). 1-Ethyl-3-methylimidazolium chloride and 1-methyl-3-octylimidazolium chloride were donated by Merck.

The synthesis of the ionic liquids was performed in a single-mode microwave reactor (Emrys Liberator, Biotage, Sweden).⁷ The reactions were performed in glass vials (2 to 5 mL) sealed

with a septum. The pressure of the system was controlled by a load cell connected to the vessel and the temperature of the reaction mixture was monitored using a calibrated infrared sensor which is located at the side of the reaction vessel. All experiments were performed using a Teflon[®]-coated magnetic stirring bar. In all microwave-assisted reactions a maximum microwave power of 150 W was used. The batch and continuous flow synthesis of the ionic liquids were performed using mono-mode microwave systems from Biotage (Emrys Liberator) and CEM (Discover[®]) as well as multi-mode microwave systems from Anton Paar (Synthos 3000), Biotage (AdvancerTM) and Milestone (ETHOS CFR).

An Infra-Red Vortex-Evaporator connected to a PoleStar Coldtrap System, both from HETTLAB, was used for drying the ionic liquids under vacuum. In this system the samples and a steel rack holder are heated by infrared light. The drying temperature was measured with a sensor connected to the steel rack. The maximum temperature for this system is 120 °C. To remove water after the anion exchange process the freeze dryer Alpha 1-2 LD from Christ was used. The dried ionic liquids were stored under dry conditions in an exsiccator.

¹H NMR spectra were recorded on Varian spectrometers (300 or 400 MHz) at 25 °C. Chemical shifts are given in ppm downfield from TMS. For FT-IR spectroscopy a TENSOR 37TM from Bruker was used. The device is equipped with a HTS-XT (High Throughput Screening eXTension) compartment to perform an automatic measurement of the samples in transmission and/or diffuse reflection mode. For all measurements with this compartment the transmission mode was used. In addition, the FT-IR spectrometer is equipped with a microscope (HYPERIONTM 3000), which was also used in transmission mode to characterize the samples. The samples were dissolved in methanol and spotted on a silica microtiter plate (96 well format). The background was measured on an empty spot on the microtiter plate. All MALDI-TOF-MS experiments (in this case LDI-TOF-MS experiments) were performed on a Voyager-DE PRO Biospectrometry Workstation (Applied Biosystems, Foster City, CA) time-of-flight mass spectrometer in reflector mode. All spectra were obtained in the positive ion mode. Ionization was performed with a 337-nm pulsed nitrogen laser. Samples were dissolved in methanol and spotted on the target without using any matrix. All spectra are averaged over 500 laser shots over the complete sample area. All data were processed using the Data Explorer software package (Applied Biosystems).

General synthesis for ionic liquids

A similar synthetic procedure as described in literature was used (new ionic liquids are marked with *).^{1,3,20} A mixture of 1-methylimidazole (5 to 13 mmol) and alkyl halide (6 to 16.9 mmol) was placed in a sealed reaction vessel (2 to 5 mL) with a magnetic stirrer. A 1.0 to 1.3 ratio of 1-methylimidazole to alkyl halide was used for all experiments. The reaction mixture was heated up to the desired temperature (120 to 170 °C) at 150 W and then hold at this temperature for the required reaction times (1 to 11 minutes). The reaction mixture was cooled down to 40 °C in the microwave system and after that to room temperature. Not reacted alkyl halide was decanted from the reaction mixture and the conversion was determined by ¹H NMR spectroscopy.

Purification of the ionic liquids with linear alkyl side chain

The high viscous product was dissolved in methylene chloride or in a mixture of methylene chloride and methanol (95:5) and subsequently filtered over silica gel.

Purification of the ionic liquids with branched alkyl side chain

The raw product was dried under vacuum in the IR-Dancer at 120 °C until complete removal of 1-*H*-3-methylimidazolium chloride. The high viscous product was dissolved in methylene chloride or in a mixture of methylene chloride and methanol (95:5) and subsequently filtered over silica gel.

Characterization of linear and branched ionic liquids

The pure product was characterized by ¹H NMR and FT-IR spectroscopy, as well as and LDI-TOF-MS.

1-Methyl-3-propylimidazolium chloride

Yield: 1.8 g (9.5 mmol, 95%), T_g: -44 °C.

¹H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.85 (3 H, t, *J* = 7.4 Hz, CH₃), 1.80 (2 H, m, CH₂), 3.86 (3 H, s, *N*-CH₃), 4.14 (2 H, t, *J* = 7.1 Hz, *N*-CH₂), 7.75 (1 H, s), 7.81 (1 H, s), 9.32 (1 H, s); IR (neat): 3414 (OH), 3150 (CH ring), 3096 (CH alkyl), 2970 (CH alkyl), 2880 (CH alkyl), 1638 (C=C, C=N), 1574 (C-C, C-N), 1462 (CH alkyl deform.), 1173 (CH ring deform.) cm⁻¹; LDI-TOF-MS for C₇H₁₃N₂⁺(125.1073): *m/z* 125 (100), 126 (5) g/mol.

1-Butyl-3-methylimidazolium chloride

Yield: 1.7 g (9.9 mmol, 99%), T_g: -41 °C.

¹H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.89 (3 H, t, *J* = 7.4 Hz, CH₃), 1.25 (2 H, m, CH₂), 1.76 (2 H, m, CH₂), 3.86 (3 H, s, *N*-CH₃), 4.18 (2 H, t, *J* = 7.1 Hz, *N*-CH₂), 7.74 (1 H, s), 7.82 (1 H, s), 9.33 (0.9(1) H, s); IR (neat): 3410 (OH), 3148 (CH ring), 3088 (CH alkyl), 2963 (CH alkyl), 2876 (CH alkyl), 2112 (N=C), 1640 (C=C, C=N), 1572 (C-C, C-N), 1466 (CH alkyl deform.), 1171 (CH ring deform.) cm⁻¹; LDI-TOF-MS for C₈H₁₅N₂⁺(139.1230): *m/z* 139 (100), 140 (10) g/mol.

1-Methyl-3-pentylimidazolium chloride

Yield: 1.8 g (9.8 mmol, 98%), T_g: -47 °C.

¹H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.86 (3 H, t, *J* = 7.1 Hz, CH₃), 1.14–1.38 (4 H, m, CH₂), 1.78 (2 H, m, CH₂), 3.86 (3 H, s, *N*-CH₃), 4.17 (2 H, t, *J* = 7.2 Hz, *N*-CH₂), 7.74 (1 H, s), 7.81 (1 H, s), 9.31 (1 H, s); IR (neat): 3408 (OH), 3148 (CH ring), 3086 (CH alkyl), 2959 (CH alkyl), 2864 (CH alkyl), 2108 (N=C), 1638 (C=C, C=N), 1572 (C-C, C-N), 1466 (CH alkyl deform.), 1171 (CH ring deform.) cm⁻¹; LDI-TOF-MS for C₉H₁₇N₂⁺(153.1386): *m/z* 153 (100), 154 (15) g/mol.

1-Benzyl-3-methylimidazolium chloride

Yield: 2.0 g (9.9 mmol, 99%), T_g : 2 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 3.85 (3 H, s, $N\text{-CH}_3$), 5.42 (2 H, s, $N\text{-CH}_2$), 7.38–7.45 (5 H, m, H_{aryl}), 7.72 (1 H, s), 7.79 (1 H, s), 9.24 (1 H, s); IR (neat): 3406 (OH), 3146 (CH ring), 3082 (CH alkyl), 2855 (CH alkyl), 2114 (N=C), 1634 (C=C, C=N), 1574 (C-C, C-N), 1456 (CH alkyl deform.), 1163 (CH ring deform.) cm^{-1} ; LDI-TOF-MS for $\text{C}_{12}\text{H}_{15}\text{N}_2^+$ (187.1230): m/z 173 (100), 174 (20) g/mol.

1-(1-Methylethyl)-3-methylimidazolium chloride

Yield: 0.4 g (2.8 mmol, 28%), T_g : –34 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 1.46 (6 H, d, J = 6.7 Hz, CH_3), 3.85 (3 H, s, $N\text{-CH}_3$), 4.64 (1 H, m, $N\text{-CH}$), 7.75 (1 H, s), 7.92 (1 H, s), 9.39 (1 H, s); IR (neat): 3416 (OH), 3148 (CH ring), 3090 (CH alkyl), 2986 (CH alkyl), 2884 (CH alkyl), 2112 (N=C), 1638 (C=C, C=N), 1574 (C-C, C-N), 1468 (CH alkyl deform.), 1186 (CH ring deform.) cm^{-1} ; LDI-TOF-MS for $\text{C}_7\text{H}_{13}\text{N}_2^+$ (125.1073): m/z 125 (100), 126 (25) g/mol.

1-(1-Methylpropyl)-3-methylimidazolium chloride

Yield: 0.6 g (3.1 mmol, 31%), T_g : –31 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.76 (3 H, t, J = 7.3 Hz, CH_3), 1.45 (3 H, d, J = 6.8 Hz, CH_3), 1.79 (2 H, m, CH_2), 3.86 (3 H, s, $N\text{-CH}_3$), 4.43 (1 H, m, $N\text{-CH}$), 7.78 (1 H, s), 7.92 (1 H, s), 9.43 (1 H, s); IR (neat): 3404 (OH), 3148 (CH ring), 3084 (CH alkyl), 2974 (CH alkyl), 2882 (CH alkyl), 2122 (N=C), 1640 (C=C, C=N), 1574 (C-C, C-N), 1464 (CH alkyl deform.), 1179 (CH ring deform.) cm^{-1} ; LDI-TOF-MS for $\text{C}_8\text{H}_{15}\text{N}_2^+$ (139.1230): m/z 139 (100), 140 (15) g/mol.

1-(1-Methylbutyl)-3-methylimidazolium chloride

Yield: 0.3 g (1.4 mmol, 14%), T_g : –19 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.85 (3 H, t, J = 7.3 Hz, CH_3), 0.92–1.32 (2 H, m, CH_2), 1.43 (3 H, d, J = 6.7 Hz, CH_3), 1.65–1.81 (2 H, m, CH_2), 3.83 (3 H, s, $N\text{-CH}_3$), 4.48 (1 H, m, $N\text{-CH}$), 7.72 (1 H, s), 7.87 (1 H, s), 9.26 (1 H, s); IR (neat): 3424 (OH), 3144 (CH ring), 3078 (CH alkyl), 2963 (CH alkyl), 2876 (CH alkyl), 2116 (N=C), 1636 (C=C, C=N), 1572 (C-C, C-N), 1466 (CH alkyl deform.), 1175 (CH ring deform.) cm^{-1} ; LDI-TOF-MS for $\text{C}_9\text{H}_{17}\text{N}_2^+$ (153.1386): m/z 153 (100), 154 (10) g/mol.

1-(1-Methylbenzyl)-3-methylimidazolium chloride*

Yield: 0.9 g (3.9 mmol, 39%), T_g : 10 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 1.87 (3 H, d, J = 7.1 Hz, CH_3), 3.86 (3 H, s, $N\text{-CH}_3$), 5.83 (1 H, m, $N\text{-CH}$), 7.33–7.48 (5 H, m, H_{aryl}), 7.76 (1 H, s), 7.91 (1 H, s), 9.56 (1 H, s); IR (neat): 3406 (OH), 3146 (CH ring), 3078 (CH alkyl), 2990 (CH alkyl), 2118 (N=C), 1638 (C=C, C=N), 1574 (C-C, C-N), 1456 (CH alkyl deform.), 1165 (CH ring deform.) cm^{-1} ; LDI-TOF-MS for $\text{C}_{12}\text{H}_{15}\text{N}_2^+$ (187.1230): m/z 187 (100), 188 (10) g/mol.

1-Ethyl-3-methylimidazolium bromide

T_m : 65 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 1.39 (3 H, t, J = 7.4 Hz, CH_3), 3.83 (3 H, s, $N\text{-CH}_3$), 4.18 (2 H, q, J = 7.4 Hz, $N\text{-CH}_2$), 7.69 (1 H, s), 7.78 (1 H, s), 9.15 (1 H, s). IR (neat): 3420 (OH), 3144 (CH ring), 3071 (CH alkyl), 2983 (CH alkyl), 1628 (C=C, N=C), 1570 (C-C, C-N), 1452 (CH alkyl deform.), 1336, 1167 (CH ring deform.), 1089, 829, 753 cm^{-1} .

1-Methyl-3-propylimidazolium bromide

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.84 (3 H, t, J = 7.4 Hz, CH_3), 1.79 (3 H, m, CH_2), 3.86 (3 H, s, $N\text{-CH}_3$), 4.14 (2 H, t, J = 7.1 Hz, $N\text{-CH}_2$), 7.74 (1 H, s), 7.81 (1 H, s), 9.23 (1 H, s). IR (neat): 3137 (CH ring), 3058 (CH alkyl), 2964 (CH alkyl), 2876 (CH alkyl), 1568 (C-C, C-N), 1458 (CH alkyl deform.), 1386, 1336, 1169 (CH ring deform.), 1090, 753 cm^{-1} .

1-Butyl-3-methylimidazolium bromide

Yield: 12.3 g (53.1 mmol, 44%)

^1H NMR: (300 MHz, DMSO, 25 °C): δ (ppm) = 0.89 (3 H, t, J = 7.3 Hz, CH_3), 1.25 (2 H, m, CH_2), 1.76 (2 H, m, CH_2), 3.86 (3 H, s, $N\text{-CH}_3$), 4.18 (2 H, t, J = 7.2 Hz, $N\text{-CH}_2$), 7.74 (1 H, s), 7.82 (1 H, s), 9.25 (1 H, s).

1-Methyl-3-pentylimidazolium bromide

Yield: 8.0 g (34.3 mmol, 56%)

^1H NMR (300 MHz, CDCl_3 , 25 °C): δ (ppm) = 0.74 (3 H, t, J = 6.8 Hz, CH_3), 1.20 (4 H, m, CH_2), 1.78 (2 H, m, CH_2), 4.00 (3 H, s, $N\text{-CH}_3$), 4.20 (2 H, t, J = 7.3 Hz, $N\text{-CH}_2$), 7.47 (1 H, s), 7.62 (1 H, s), 10.18 (1 H, s).

1-Hexyl-3-methylimidazolium bromide

Yield: 12.4 g (50.3 mmol, 83%)

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.85 (3 H, bs, CH_3), 1.25 (6 H, s, CH_2), 1.76 (2 H, s, CH_2), 3.85 (3 H, s, $N\text{-CH}_3$), 4.16 (2 H, s, $N\text{-CH}_2$), 7.72 (1 H, s), 7.79 (1 H, s), 9.19 (1 H, s).

1-Heptyl-3-methylimidazolium bromide

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.84 (3 H, bs, CH_3), 1.24 (8 H, s, CH_2), 1.77 (2 H, s, CH_2), 3.85 (3 H, s, $N\text{-CH}_3$), 4.16 (2 H, t, J = 7.2 Hz, $N\text{-CH}_2$), 7.73 (1 H, s), 7.80 (1 H, s), 9.20 (1 H, s).

1-Methyl-3-octylimidazolium bromide

T_m : 2 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.84 (3 H, t, J = 6.7 Hz, CH_3), 1.24 (10 H, s, CH_2), 1.76 (2 H, s, CH_2), 3.84 (3 H, s, $N\text{-CH}_3$), 4.15 (2 H, t, J = 7.2 Hz, $N\text{-CH}_2$), 7.72 (1 H, s), 7.78 (1 H, s), 9.17 (1 H, s).

1-Methyl-3-nonylimidazolium bromide T_m : 1 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.84 (3 H, t, J = 6.7 Hz, CH_3), 1.23 (12 H, s, CH_2), 1.76 (2 H, s, CH_2), 3.84 (3 H, s, $N\text{-CH}_3$), 4.15 (2 H, t, J = 7.2 Hz, $N\text{-CH}_2$), 7.72 (1 H, s), 7.79 (1 H, s), 9.19 (1 H, s).

1-Decyl-3-methylimidazolium bromide T_m : 10 °C.

^1H NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.83 (3 H, s, CH_3), 1.23 (14 H, s, CH_2), 1.76 (2 H, s, CH_2), 3.85 (3 H, s, $N\text{-CH}_3$), 4.15 (2 H, s, $N\text{-CH}_2$), 7.72 (1 H, s), 7.79 (1 H, s), 9.20 (1 H, s).

1-Allyl-3-methylimidazolium bromide T_g : -59 °C.

^1H NMR (300 MHz, CDCl_3 , 25 °C): δ (ppm) = 4.08 (3 H, s, $N\text{-CH}_3$), 4.98 (2 H, d, J = 6.3 Hz, $N\text{-CH}_2$), 5.43 (2 H, t, J = 13.0 Hz, $=\text{CH}_2$), 5.99 (1 H, d, J = 6.5 Hz, $=\text{CH}$), 7.48 (1 H, s), 7.67 (1 H, s), 10.19 (1 H, s). IR (neat): $\nu_{\text{max}}/\text{cm}^{-1}$ 3050 (CH ring), 2959 (CH alkyl), 2934, 2874, 1568 (C-C, C-N), 1465 (CH alkyl deform.), 1382, 1253, 1170 (CH ring deform.), 742, 657 cm^{-1} .

1,3-Dimethylimidazolium iodide

^1H NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 3.84 (6 H, s, $N\text{-CH}_3$), 7.66 (2 H, s), 9.02 (1 H, s).

1-Butyl-3-methylimidazolium iodide T_g : -59 °C.

^1H NMR (300 MHz, CDCl_3 , 25 °C): δ (ppm) = 0.91 (3 H, t, J = 8.2 Hz, CH_3), 1.43–1.27 (2 H, m, CH_2), 1.83–1.93 (2 H, m, CH_2), 4.05 (3 H, s, $N\text{-CH}_3$), 4.30 (2 H, t, J = 7.4 Hz, $N\text{-CH}_2$), 7.51 (1 H, s), 7.59 (1 H, s), 9.92 (1 H, s). IR (neat): 3468 (OH), 3140 (CH ring), 3077 (CH alkyl), 2958 (CH alkyl), 2933, 2872 (CH alkyl), 1568 (C-C, C-N), 1462 (CH alkyl deform.), 1382, 1337, 1165 (CH ring deform.), 820, 749 cm^{-1} .

1,3-Dimethylimidazolium dimethyl phosphate

^1H NMR (400 MHz, CDCl_3 , 25 °C): δ (ppm) = 3.24 (3 H, s, CH_3), 3.26 (3 H, s, CH_3), 3.83 (6 H, s, $N\text{-CH}_3$), 7.70 (2 H, d, J = 1.6 Hz), 9.31 (1 H, s). IR (neat): 3153 (CH ring), 3068 (CH alkyl), 2945 (CH alkyl), 2838 (CH alkyl), 1575 (C-C, C-N), 1462 (CH alkyl deform.), 1241, 1179 (CH ring deform.), 1091, 1036, 850, 770, 731 cm^{-1} .

1-Ethyl-3-methylimidazolium diethyl phosphate

Yield: 99 g (360 mmol, 48%)

^1H NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 1.04 (6 H, t, J = 7.1 Hz, CH_3), 1.39 (3 H, t, J = 7.3 Hz, CH_3), 3.59 (4 H, p, J = 7.0 Hz, CH_2), 3.84 (3 H, s, $N\text{-CH}_3$), 4.18 (2 H, q, J = 7.3 Hz, $N\text{-CH}_2$), 7.71 (1 H, s), 7.80 (1 H, s), 9.38 (1 H, s). IR (neat): 3375 (OH), 3073 (CH alkyl), 2974

(CH alkyl), 2934, 2893 (CH alkyl), 1572 (C-C, C-N), 1232, 1173, 1107 (CH ring deform.), 1082, 1043, 935, 779, 733 cm^{-1} .

1-Butyl-3-methylimidazolium dibutyl phosphate

T_g : $-71\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 0.85 (9 H, m, CH_3), 1.18–1.50 (10 H, m, CH_2), 1.69–1.82 (2 H, m, CH_2), 3.54–3.67 (4 H, m, CH_2), 3.84 (3 H, s, $N\text{-CH}_3$), 4.15 (2 H, t, $J = 7.2$, $N\text{-CH}_2$), 7.71 (1 H, s), 7.78 (1 H, s), 9.36 (1 H, s). IR (neat): 3387 (OH), 3078 (CH alkyl), 2959 (CH alkyl), 2936, 2874 (CH alkyl), 1570 (C-C, C-N), 1464 (CH alkyl deform.), 1236, 1173 (CH ring deform.), 1067, 1026, 1005, 974, 889, 820, 797, 733 cm^{-1} .

Synthesis of 1-(1-ethylpropyl)-3-methylimidazolium iodide*

1-(1-Ethylpropyl)-3-methylimidazolium iodide was synthesized according to a similar procedure described in literature.⁸

1-(1-Ethylpropyl)imidazole

A solution of imidazole (6 g, 88.2 mmol) in THF (80 mL) was slowly added into a solution of sodium hydride (2.46 g, 102.6 mmol) in THF (60 mL) at $0\text{ }^{\circ}\text{C}$. The mixture was stirred for 1 h at room temperature and subsequently 3-bromopentane (13.3 g, 11 mL, 88.2 mmol) was added slowly into this solution. The mixture was stirred for 5 d at $60\text{ }^{\circ}\text{C}$ to obtain nearly quantitative conversion. This can be also achieved by heating the same mixture for 30 min at $120\text{ }^{\circ}\text{C}$ in closed reaction vessels using microwave irradiation. Water was added to the mixture (100 mL) and the water phase was extracted three times with ethyl acetate (40 mL). The collected ethyl acetate phases were washed with a saturated solution of sodium chloride. The remaining ethyl acetate solution was dried over MgSO_4 and subsequently filtered. Ethyl acetate was removed under reduced pressure and the reaction mixture was separated by column chromatography on silica gel (methylene chloride: methanol = 95:5). The pure product was obtained as a slightly yellow liquid (5.9 g, 42.3 mmol, 48%).

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 0.66 (6 H, t, $J = 7.4\text{ Hz}$, CH_3), 1.57–1.79 (4 H, m, CH_2), 3.82 (1 H, m, $N\text{-CH}$), 6.88 (1 H, s), 7.14 (1 H, s), 7.60 (1 H, s).

1-(1-Ethylpropyl)-3-methylimidazolium iodide

Iodomethane (6.4 g, 44.7 mmol, 2.8 mL) was slowly added to 1-(1-ethylpropyl)imidazole (5.9 g, 42.3 mmol) in a pressure reaction tube at $0\text{ }^{\circ}\text{C}$. The reaction mixture was stirred until room temperature was reached. Subsequently water was added, and the aqueous phase was extracted three times with methylene chloride. The product was recovered by evaporation of the aqueous phase followed by freeze drying (6.59 g, 23.3 mmol, 55%). T_m : $124\text{ }^{\circ}\text{C}$, T_g : $45\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 0.73 (6 H, t, $J = 7.4\text{ Hz}$, CH_3), 1.67–1.90 (4 H, m, CH_2), 3.85 (3 H, s, $N\text{-CH}_3$), 4.15 (1 H, m, $N\text{-CH}$), 7.75 (1 H, s), 7.84 (1 H, s), 9.16 (1 H, s); IR (neat): 3474 (OH), 3134 (CH ring), 3077 (CH alkyl), 2967 (CH alkyl), 2878 (CH alkyl), 1624

(C=C, C=N), 1572 (C-C, C-N), 1462 (CH alkyl deform.), 1171 (CH ring deform.) cm^{-1} ; MALDI-TOF-MS for $\text{C}_9\text{H}_{17}\text{N}_2^+$ (153.1386): m/z 153 (100), 154 (15) g/mol.

Anion exchange

The anions could be exchanged by various sodium and ammonium salts to yield different 1-alkyl-3-methylimidazolium based ionic liquids. Whereas for some exchange reactions water was found to be the best solvent,¹⁰ other exchange reactions must be carried out in dichloromethane or acetonitrile.¹¹⁻¹³ The completeness was checked by adding a silver nitrate solution to a solution of the ionic liquid in water.¹⁰ An Amberlite IRA-400 exchange resin¹⁴ could be used for the preparation of 1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium acetate. Silver fluoride and silver tetrafluoroborate were used to synthesize fluoride and tetrafluoroborate containing ionic liquids, when the common approach of utilizing an anion exchange salt based on sodium or ammonium was unsuccessful.

1-Ethyl-3-methylimidazolium bromide

^1H NMR (300 MHz, DMSO, 25 °C) δ (ppm) = 1.37 (3 H, t, J = 7.2 Hz, CH_3), 3.81 (3 H, s, $N\text{-CH}_3$), 4.14 (2 H, q, J = 7.2 Hz, $N\text{-CH}_2$), 7.65 (2 H, bs), 10.14 (1 H, s).

1-Ethyl-3-methylimidazolium acetate

^1H NMR (400 MHz, DMSO, 25 °C) δ (ppm) = 1.39 (5 H, t, J = 7.3 Hz, CH_3), 3.84 (3 H, s, CH_3), 4.19 (3 H, q, J = 7.3 Hz, $N\text{-CH}_3$), 7.72 (1 H, d, J = 1.6 Hz), 7.81 (1 H, s), 9.73–9.81 (1 H, m). FT-IR (neat): 3362 (OH), 3073 (CH alkyl), 2981 (CH alkyl), 1562 (C-C, C-N), 1451 (CH alkyl deform.), 1427, 1384, 1331, 1172 (CH ring deform.), 907, 759, 701, 667 cm^{-1} .

1-Butyl-3-methylimidazolium acetate

T_g : -70 °C.

^1H NMR (400 MHz, DMSO, 25 °C) δ (ppm) = 0.87 (3 H, t, J = 8.4 Hz, CH_3), 1.23 (2 H, dq, J = 7.4 Hz, 14.6 Hz, CH_2), 1.56 (3 H, s, CH_3), 1.74 (2 H, dt, J = 7.4 Hz, 14.6 Hz, $N\text{-CH}_2$), 3.85 (4 H, s), 4.11–4.23 (2 H, m), 7.73 (1 H, s), 7.79 (1 H, s), 9.72 (1 H, s).

1-Butyl-3-methylimidazolium nitrate

T_g : -70 °C.

^1H NMR (300 MHz, DMSO, 25 °C) δ (ppm) = 0.90 (3H, t, J = 7.3 Hz, CH_3), 1.26 (2 H, dq, J = 7.3, 14.6 Hz, CH_2), 1.66–1.84 (2 H, m), 3.85 (3 H, s), 4.16 (2 H, t, J = 7.2 Hz), 7.71 (1 H, pt, J = 1.7 Hz), 7.78 (1 H, pt, J = 1.8 Hz), 9.13 (1 H, s).

1-Butyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide

T_g : -77 °C.

^1H NMR (400 MHz, DMSO, 25 °C) δ (ppm) = 0.78–0.96 (3 H, m), 1.23 (2 H, m), 1.75 (2 H,

m), 3.82 (3 H, s), 4.14 (2 H, q, $J = 3.6$ Hz), 7.68 (1 H, s), 7.75 (1 H, s), 9.08 (1 H, s). FT-IR (neat): 3457 (OH), 3017, 2971 (CH alkyl), 2946, 1738, 1729, 1456 (CH alkyl deform.), 1435, 1365, 1353, 1229, 1217, 1204, 1183 (CH ring deform.), 1132, 1053, 741, 654 cm^{-1} .

1-Methyl-3-propylimidazolium tetrafluoroborate

Yield: 0.5 g (27%), T_g : -84 °C.

^1H NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.84 (3 H, t, $J = 7.4$ Hz, CH_3), 1.78 (2 H, m, CH_2), 3.83 (3 H, s, $N\text{-CH}_3$), 4.10 (2 H, t, $J = 7.1$ Hz, $N\text{-CH}_2$), 7.68 (1 H, s), 7.74 (1 H, s), 9.06 (1 H, s); IR (neat): 3642 (OH), 3563 (OH), 3161 (CH ring), 3125 (CH ring), 2972 (CH alkyl), 2943 (CH alkyl), 2884 (CH alkyl), 2116 ($\text{N}=\text{C}$), 1636 ($\text{C}=\text{C}$, $\text{C}=\text{N}$), 1576 ($\text{C}-\text{C}$, $\text{C}-\text{N}$), 1468 (CH deform. alkyl), 1175 (CH deform. ring), 1076 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_7\text{H}_{13}\text{N}_2^+$ (125.1073): m/z 125 (100), 126 (10) g/mol.

1-(1-Methylethyl)-3-methylimidazolium tetrafluoroborate

Yield: 0.1 g (19%), T_m : 67 °C, T_g : -74 °C.

^1H NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 1.45 (6 H, d, $J = 6.7$ Hz, CH_3), 3.82 (3 H, s, $N\text{-CH}_3$), 4.60 (1 H, m, $N\text{-CH}$), 7.69 (1 H, s), 7.85 (1 H, s), 9.14 (1 H, s); IR (neat): 3632 (OH), 3167 (OH), 3115 (CH ring), 2990 (CH alkyl), 2945 (CH alkyl), 1626 ($\text{C}=\text{C}$, $\text{C}=\text{N}$), 1572 ($\text{C}-\text{C}$, $\text{C}-\text{N}$), 1470 (CH deform. alkyl), 1188 (CH deform. ring), 1059 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_7\text{H}_{13}\text{N}_2^+$ (125.1073): m/z 125 (100), 126 (20) g/mol.

1-Butyl-3-methylimidazolium tetrafluoroborate

Yield: 1.0 g (62%), T_g : -80 °C.

^1H NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.88 (3 H, t, $J = 7.4$ Hz, CH_3), 1.24 (2 H, m, CH_2), 1.74 (2 H, m, CH_2), 3.83 (3 H, s, $N\text{-CH}_3$), 4.14 (2 H, t, $J = 7.2$ Hz, $N\text{-CH}_2$), 7.67 (1 H, s), 7.74 (1 H, s), 9.06 (1 H, s); IR (neat): 3644 (OH), 3559 (OH), 3165 (CH ring), 3125 (CH ring), 2967 (CH alkyl), 2940 (CH alkyl), 2880 (CH alkyl), 1630 ($\text{C}=\text{C}$, $\text{C}=\text{N}$), 1576 ($\text{C}-\text{C}$, $\text{C}-\text{N}$), 1470 (CH deform. alkyl), 1173 (CH deform. ring), 1069 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_8\text{H}_{15}\text{N}_2^+$ (139.1230): m/z 139 (100), 140 (15) g/mol.

1-(1-Methylpropyl)-3-methylimidazolium tetrafluoroborate

Yield: 0.2 g (30%), T_g : -68 °C.

^1H NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.75 (3 H, t, $J = 7.4$ Hz, CH_3), 1.44 (3 H, d, $J = 6.8$ Hz, CH_3), 1.72–1.82 (2 H, m, CH_2), 3.83 (3 H, s, $N\text{-CH}_3$), 4.38 (1 H, m, $N\text{-CH}$), 7.70 (1 H, s), 7.83 (1 H, s), 9.13 (1 H, s); IR (neat): 3636 (OH), 3561 (OH), 3159 (CH ring), 3117 (CH ring), 2976 (CH alkyl), 2945 (CH alkyl), 2886 (CH alkyl), 2118 ($\text{N}=\text{C}$), 1630 ($\text{C}=\text{C}$, $\text{C}=\text{N}$), 1576 ($\text{C}-\text{C}$, $\text{C}-\text{N}$), 1466 (CH deform. alkyl), 1179 (CH deform. ring), 1069 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_8\text{H}_{15}\text{N}_2^+$ (139.1230): m/z 139 (100), 140 (10) g/mol.

1-Methyl-3-pentylimidazolium tetrafluoroborate

Yield: 1.5 g (83%), T_g : $-77\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 0.86 (3 H, t, $J = 7.2\text{ Hz}$, CH_3), 1.16–1.35 (4 H, m, CH_2), 1.77 (2 H, m, CH_2), 3.83 (3 H, s, $N\text{-CH}_3$), 4.13 (2 H, t, $J = 7.2\text{ Hz}$, $N\text{-CH}_2$), 7.67 (1 H, s), 7.74 (1 H, s), 9.06 (1 H, s); IR (neat): 3642 (OH), 3563 (OH), 3163 (CH ring), 3123 (CH ring), 2963 (CH alkyl), 2936 (CH alkyl), 2874 (CH alkyl), 1631 (C=C, C=N), 1576 (C-C, C-N), 1468 (CH deform. alkyl), 1175 (CH deform. ring), 1072 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_9\text{H}_{17}\text{N}_2^+$ (153.1386): m/z 153 (100), 154 (15) g/mol.

1-(1-Methylbutyl)-3-methylimidazolium tetrafluoroborate

Yield: 0.2 g (71%), T_g : $-66\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 0.85 (3 H, t, $J = 7.4\text{ Hz}$, CH_3), 0.99–1.29 (2 H, m, CH_2), 1.44 (3 H, d, $J = 6.7\text{ Hz}$, CH_3), 1.65–1.81 (2 H, m, CH_2), 3.82 (3 H, s, $N\text{-CH}_3$), 4.47 (1 H, m, $N\text{-CH}$), 7.69 (1 H, s), 7.84 (1 H, s), 9.13 (1 H, s); IR (neat): 3638 (OH), 3565 (OH), 3161 (CH ring), 3117 (CH ring), 2967 (CH alkyl), 2940 (CH alkyl), 2878 (CH alkyl), 2120 (N=C), 1628 (C=C, C=N), 1576 (C-C, C-N), 1468 (CH deform. alkyl), 1175 (CH deform. ring), 1065 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_9\text{H}_{17}\text{N}_2^+$ (153.1386): m/z 153 (100), 154 (10) g/mol.

1-(1-Ethylpropyl)-3-methylimidazolium tetrafluoroborate*

Yield: 3.3 g (50%), T_m : $68\text{ }^{\circ}\text{C}$, T_g : $-56\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 0.73 (6 H, t, $J = 7.4\text{ Hz}$, CH_3), 1.78 (4 H, m, CH_2), 3.84 (3 H, s, $N\text{-CH}_3$), 4.14 (1 H, m, $N\text{-CH}$), 7.74 (1 H, s), 7.83 (1 H, s), 9.14 (1 H, s); IR (neat): 3634 (OH), 3570 (OH), 3161 (CH ring), 3115 (CH ring), 2974 (CH alkyl), 2943 (CH alkyl), 2884 (CH alkyl), 1632 (C=C, C=N), 1576 (C-C, C-N), 1466 (CH deform. alkyl), 1173 (CH deform. ring), 1065 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_9\text{H}_{17}\text{N}_2^+$ (153.1386): m/z 153 (100), 154 (5) g/mol.

1-Benzyl-3-methylimidazolium tetrafluoroborate

Yield: 1.4 g (72%), T_g : $-33\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 3.84 (3 H, s, $N\text{-CH}_3$), 5.39 (2 H, s, $N\text{-CH}_2$), 7.37–7.43 (5 H, m, H_{aryl}), 7.69 (1 H, s), 7.76 (1 H, s), 9.17 (1 H, s); IR (neat): 3642 (OH), 3559 (OH), 3159 (CH ring), 3111 (CH ring), 3040 (CH alkyl), 2963 (CH alkyl), 1626 (C=C, C=N), 1576 (C-C, C-N), 1458 (CH deform. alkyl), 1167 (CH deform. ring), 1072 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_{12}\text{H}_{15}\text{N}_2^+$ (187.1230): m/z 173 (100), 174 (15) g/mol.

1-(1-Methylbenzyl)-3-methylimidazolium tetrafluoroborate*

Yield: 0.6 g (73%), T_m : $73\text{ }^{\circ}\text{C}$, T_g : $-22\text{ }^{\circ}\text{C}$.

^1H NMR (400 MHz, DMSO, $25\text{ }^{\circ}\text{C}$): δ (ppm) = 1.85 (3 H, d, $J = 7.1\text{ Hz}$, CH_3), 3.83 (3 H, s, $N\text{-CH}_3$), 5.75 (1 H, m, $N\text{-CH}$), 7.33–7.44 (5 H, m, H_{aryl}), 7.70 (1 H, s), 7.82 (1 H, s), 9.26 (1 H, s); IR (neat): 3644 (OH), 3561 (OH)*, 3161 (CH ring), 3125 (CH ring), 3038 (CH alkyl), 2965 (CH alkyl), 2110 (N=C), 1628 (C=C, C=N), 1578 (C-C, C-N), 1454 (CH deform. alkyl), 1167 (CH

deform. ring), 1051 (B-F) cm^{-1} ; LDI-TOF-MS for $\text{C}_{12}\text{H}_{15}\text{N}_2^+$ (187.1230): m/z 187 (100), 188 (20) g/mol.

Up-scaling the synthesis of 1-butyl-3-methylimidazolium chloride

A mixture of 1-methylimidazole and butyl chloride at a ratio of 1:1.3 was used for all experiments. The reaction mixture was heated to 170 °C and maintained at this temperature for 7 to 16 min. Non-reacted butyl chloride was decanted from the reaction mixture. An additional extraction step was required when the conversion was not quantitative. The ionic liquid was in this case extracted three times with ethyl acetate and dried in a vacuum oven at 40 °C to remove the remaining ethyl acetate. The highly viscous product was characterized by ^1H NMR spectroscopy before extraction to determine the conversions. In order to initiate crystallization of the highly viscous oil, the ionic liquid was frozen at -25 °C.

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Chapter 3

Properties of ionic liquids

Abstract

In order to elucidate structure–property relationships, several ionic liquids, both linear and branched, were investigated in detail. In particular, the influence of the branching on the thermophysical properties was of interest. Thermogravimetric analysis was utilized to investigate the decomposition behavior and differential scanning calorimetry was used to study the influence of the branching on the thermal behavior, *e.g.* the melting point, the glass transition temperature, the freezing point and the cold crystallization temperature. Moreover, the water uptake of selected ionic liquids was analyzed.

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3.1 Introduction

The properties of ionic liquids, such as melting point, density, viscosity, and hydrophobicity, can be adjusted by varying the composition of cation *vs.* anion.^{1,2} Therefore, this chapter describes the influence of different cations and anions on the properties of the investigated ionic liquids. In particular, the influence of the length and the branching of the alkyl side chain of imidazolium based ionic liquids were investigated. In general, a better understanding of the structure-property relationships is a crucial aspect for designing ionic liquids with tailor-made properties for a specific application. It is already known from alkanes that the length and the degree of branching have an influence on the chemical and physical properties, such as heat of combustion, boiling point and melting point.³ Moreover, it was already reported that compact, highly branched chains decrease the viscosity when introduced into ionic liquids, which might improve *e.g.* extraction processes.⁴ In order to understand the effect of branched alkyl chains on the properties of ionic liquids, new ionic liquids based on 1-(1-ethylpropyl)-3-methylimidazolium and 1-(1-methylbenzyl)-3-methylimidazolium cations were synthesized as described in Chapter 2 and, compared for a systematical investigation with known ionic liquids, both branched and linear ones. In particular the thermophysical properties, such as decomposition and glass transition temperatures, and selected additional properties, such as the water uptake, are discussed as an attempt to elucidate first structure-property relationships. Furthermore, some of the described branched ionic liquids contain a chiral center: these ionic liquids could be used as chiral ligands in asymmetric reactions or as stationary phases for chromatography applications, as addressed elsewhere.⁵

3.2 Decomposition temperature

3.2.1 Influence of the cations

The influence of the alkyl chain length on the decomposition temperature of 1-alkyl-3-methylimidazolium bromide was investigated. It was found, that the decomposition temperature is decreasing with increasing alkyl chain length. A minimum in decomposition temperature is reached for octyl as side chain and subsequently the decomposition temperature is increasing with the alkyl chain length as depicted in Figure 3.1. This behavior was also described by Seddon *et al.* for the melting points of 1-alkyl-3-methylimidazolium hexafluorophosphate.⁶ The increase in melting point for alkyl side chains longer than octyl was explained by the increasing van der Waals interactions (hydrophobic region, Figure 3.2). The heat of combustion is one of the chemical properties that is influenced by branching. Branched alkanes have a slightly lower heat of combustion and therefore they are more stable than their linear analogues.⁷ The interactions between the attractive forces are increasing in comparison to the repulsive forces, when the structure becomes more complex leading to a higher stability of the branched alkanes. Therefore it is expected that the decomposition temperatures, which are related to the stability of the ionic liquids, are higher

for branched ionic liquids than for their linear analogues. On the other hand, Awad *et al.* proposed a S_N1 reaction as the decomposition mechanism for imidazolium-based ionic liquids with an *iso*-butyl group and tetrafluoroborate as counter ion, leading to lower decomposition temperatures in comparison to the linear analogues.⁸

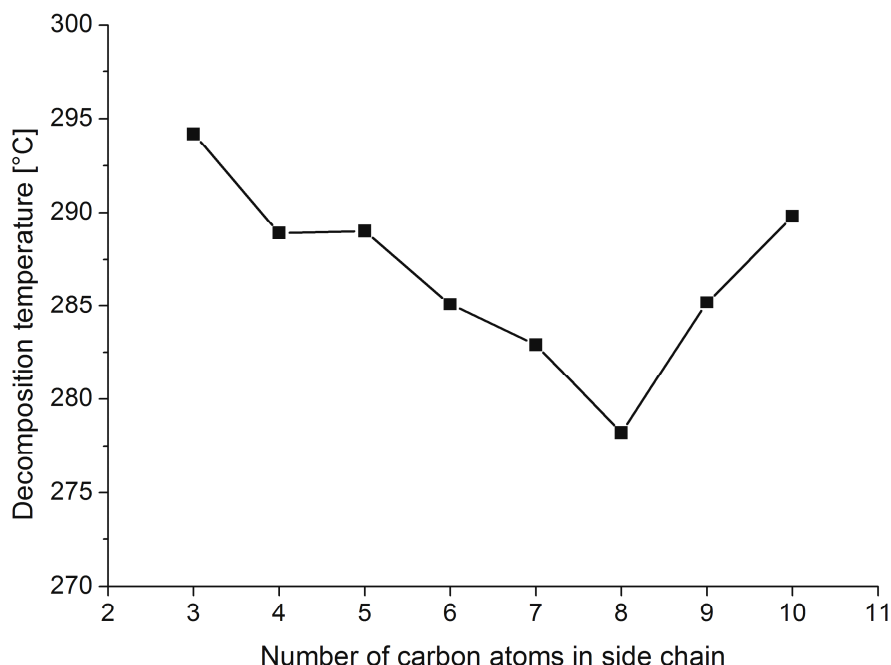


Figure 3.1 Decomposition temperatures of 1-alkyl-3-methylimidazolium bromide.

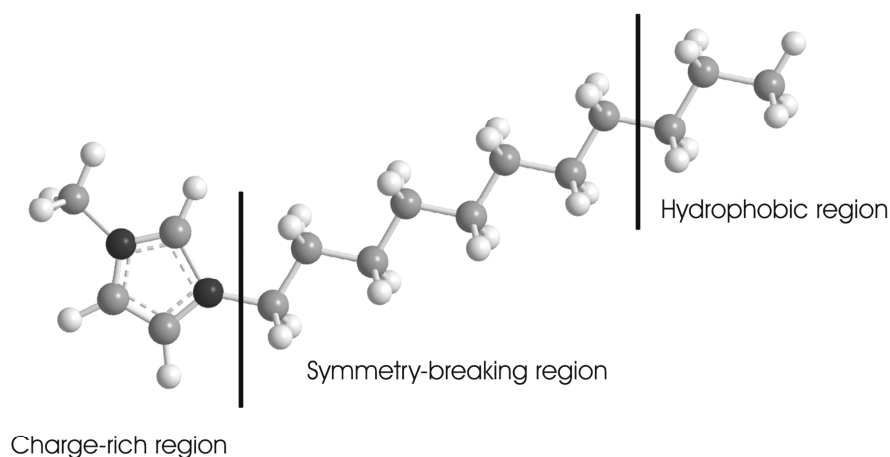


Figure 3.2 Structure of the $[C_{11}MIM]^+$ cation showing the structural regions that can influence the properties.

The results of the thermogravimetric analysis (TGA), depicted in Figure 3.3, revealed that the degree of branching has a small, but no significant influence on the decomposition temperature of the chloride containing ionic liquids, although the branched ionic liquids were found to be on average 10 °C more stable than their linear analogues. In literature, the decomposition of chloride containing ionic liquids has been ascribed to a dealkylation of the *N*-alkyl substituents

of the cation *via* a S_N2 mechanism⁹ (also see the LDI-TOF MS/MS spectra in Chapter 2). The findings described in this thesis support this decomposition pathway. The lower decomposition temperatures for linear ionic liquids might be explained by the more readily attack either of the *N*-alkyl substituents of the cation *via* the chloride anion in comparison to the branched analogues, where the dealkylation most likely occurs at the methyl group. As a result, the ionic liquids with linear alkyl chains degrade at lower temperatures. An exception to this finding were the aromatic ionic liquids, which displayed an inverse behavior, for instance the ionic liquid with the non-branched aromatic group was around 30 °C more stable than with the branched aromatic side group. The benzyl analogues seems to degrade *via* a dissociative mechanism (S_N1) leading to a more easily degradation of the branched analogues, which would also explain the lower decomposition temperatures in comparison to the alkyl chains.

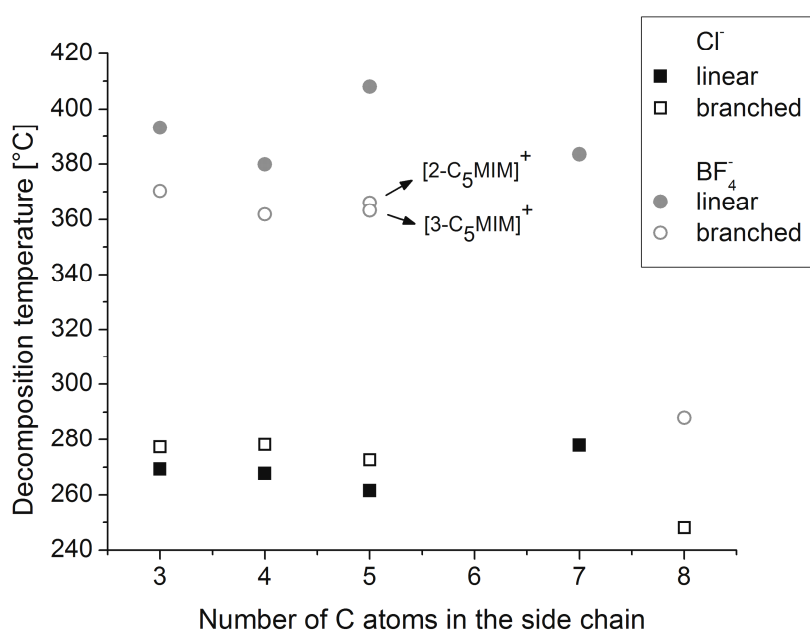


Figure 3.3 Decomposition temperatures of the different branched and linear imidazolium-based ionic liquids, bearing chloride and tetrafluoroborate as counter ions.

Regarding tetrafluoroborate containing ionic liquids, these ionic liquids are more stable than the corresponding halide containing ionic liquids and less hygroscopic as well. For instance, the ionic liquid bearing chloride as counter ion lost around 20 wt.-% of water during heating, whereas only a weight loss of around 3% was observed for the analogues with tetrafluoroborate as counter ion as displayed in Figure 3.4. Some ionic liquids show a hygroscopic character and they absorb water during their handling under atmospheric conditions. The minus values of the the mass of the chloride containing ionic liquid obtained by TGA is coming from the absorbed water. The ionic liquids are more or less dry when they are weight in and absorb water while standing in the auto-sampler. Therefore the minus values obtained are more or less in the same range like the water loss up to 150 °C.

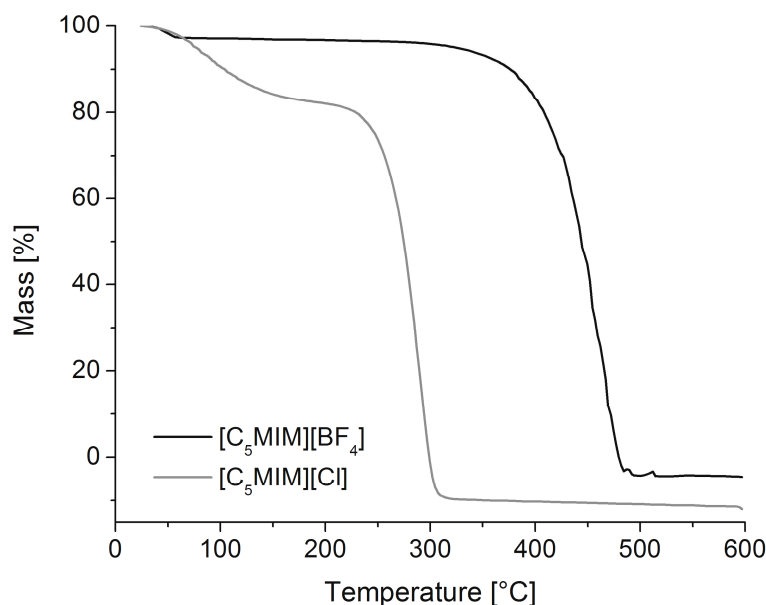


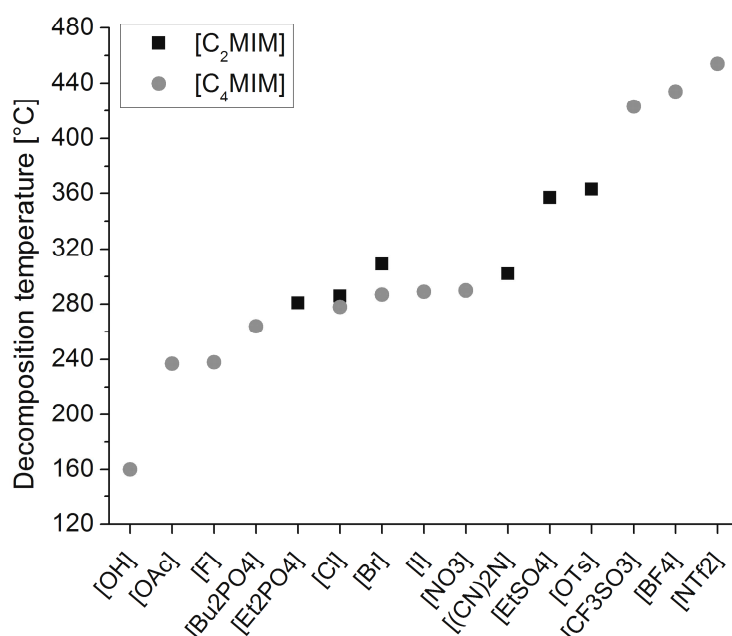
Figure 3.4 Characteristic decomposition behavior (TGA) for imidazolium-based ionic liquids, bearing chloride and tetrafluoroborate as counter ion.

3.2.2 Influence of the anions

The average decomposition temperature is mainly controlled by the anions. For instance, the average decomposition temperature for ionic liquids containing chloride and iodide was found to be around 270 °C, whereas an average value of 370 °C was observed for tetrafluoroborate containing ionic liquids. In all cases the linear ionic liquids bearing tetrafluoroborate as counter ion were more stable than their branched analogues, on average 30 °C for alkyl groups and 100 °C for aromatic side groups. This result is contrary to the behavior reported for alkanes and contrary to the observed behavior of ionic liquids with chloride as counter ion. On the other hand, these findings are similar to those reported by Awad *et al.* where the ionic liquids with *iso*-butyl alkyl side chains showed an around 50 °C lower decomposition temperature than their linear analogues.⁸ The differences between the chloride and tetrafluoroborate containing ionic liquids might be caused by a different decomposition mechanism. The degradation of tetrafluoroborate containing ionic liquids most probably leads to the formation of alkylimidazole, alkyl fluoride and BF₃ as described in literature. In addition, the formation of alcohol and HF is possible when water is present.⁹ Nevertheless, the degradation mechanism is less clear for tetrafluoroborate containing ionic liquids and more understanding would be required. Currently, we have no explanation for this different behavior. In general, more hydrophobic ionic liquids show a higher stability than hydrophilic ionic liquids. In Figure 3.5 the decomposition temperatures of 1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium based ionic liquids are plotted against the increasing hydrophobicity of their counter ions, showing that the decomposition temperature is mainly controlled by the anion, while the cation only has a small influence on the decomposition temperature.

Table 3.1 Decomposition temperatures (onset) for imidazolium-based ionic liquids with branched and non-branched alkyl (or aryl) side groups.

Cation	Anion	T _{dc} [°C]	Anion	T _{dc} [°C]
[C ₃ MIM] ⁺	[Cl] ⁻	269	[BF ₄] ⁻	393
[C ₄ MIM] ⁺	[Cl] ⁻	268	[BF ₄] ⁻	380
[C ₅ MIM] ⁺	[Cl] ⁻	262	[BF ₄] ⁻	408
[BnMIM] ⁺	[Cl] ⁻	278	[BF ₄] ⁻	384
[2-C ₃ MIM] ⁺	[Cl] ⁻	277	[BF ₄] ⁻	370
[2-C ₄ MIM] ⁺	[Cl] ⁻	278	[BF ₄] ⁻	362
[2-C ₅ MIM] ⁺	[Cl] ⁻	273	[BF ₄] ⁻	366
[3-C ₅ MIM] ⁺	[I] ⁻	284	[BF ₄] ⁻	363
[MBnMIM] ⁺	[Cl] ⁻	248	[BF ₄] ⁻	288

**Figure 3.5** Decomposition temperature (onset) for imidazolium based ionic liquids with different counter ions.

3.3 Thermal behavior

3.3.1 Influence of the cations

The boiling points of alkanes is another physical property affected by the degree of branching and increases with increasing length of the molecules. Branched alkanes with the same number of carbon atoms as their linear analogues show in general lower boiling points. The same trend is visible for the melting points of the alkanes.⁷ The intermolecular interactions, in this case induced-dipole/induced-dipole attractions, increase for longer chains and decrease for branched alkanes as a result of a smaller surface area, which causes

less contact for intermolecular associations. Based on this conclusion, a similar behavior is also expected for the melting points of dialkyl-imidazolium-based ionic liquids. Another property, related to the melting point, is the glass transition temperature of a molecule. From literature it is known, that the glass transition temperature is approximately two third of the value of the melting point.¹⁰ The range of values for T_g/T_m was found to vary from 0.58 to 0.78 for different molecules and polymers.¹¹ The same ratio is also expected for the melting points and glass transition temperatures of the prepared ionic liquids. Fredlake *et al.*¹² have described three different types of thermal behaviors for imidazolium-based ionic liquids. These different types were also observed while measuring the synthesized ionic liquids using a differential scanning calorimetry (DSC). As shown in Figure 3.6, ionic liquids with visible melting and freezing points (Figure 3.6 a) or with only a glass transition temperature (Figure 3.6 b) could be found. However, Figure 3.6 c displays a case of more complex thermal behavior; this ionic liquid revealed a glassy transition at a subcooled liquid state upon heating, followed by a cold crystallization and a melting point. Nevertheless, for most of the investigated ionic liquids only a glass transition temperature (T_g) could be detected.

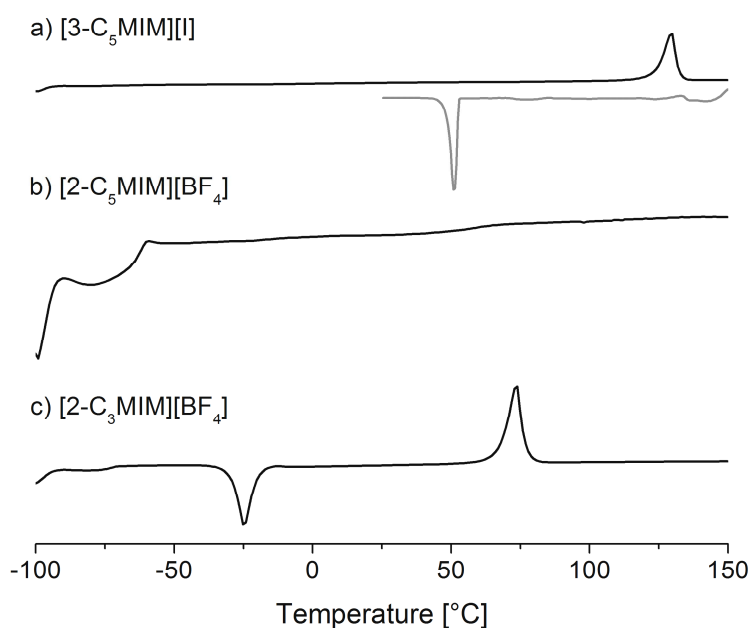


Figure 3.6 Three different kinds of thermal behavior of imidazolium-based ionic liquids as determined by DSC.

In general, the glass transition temperature was found to be higher for ionic liquids with branched alkyl side chains, which is an inverse behavior to the melting and boiling points of alkanes (Figure 3.7). The drop in T_g might be explained by the loss of the alkyl chain elasticity (as a result of the branching) and the reduced alkyl chain length for the same amount of carbon atoms in the alkyl side chain. The T_g for the tetrafluoroborate containing ionic liquids was in average 35 °C lower than for the chloride containing analogues. For both counter ions, the T_g of branched ionic liquids was around 15 °C higher than for the linear alkyl side chain cases, and around 10 °C higher for the aromatic side groups.

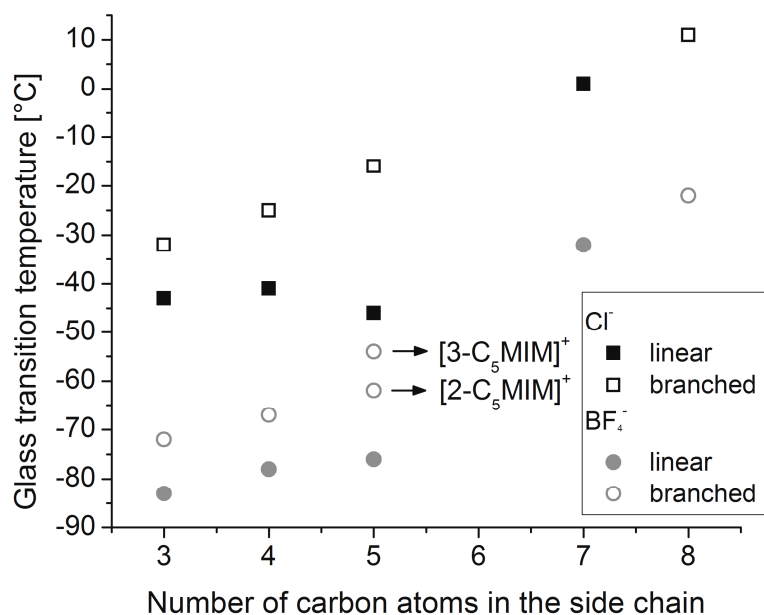


Figure 3.7 Glass transition temperatures of the different branched and linear imidazolium-based ionic liquids, bearing chloride and tetrafluoroborate as counter ion.

It was also found that the ionic liquids with an aromatic side group revealed higher T_g values (around 40 to 45 °C) than the investigated ionic liquids with an alkyl side chain. In this thesis, the T_g to T_m ratio was determined for the three cases where the ionic liquids revealed a melting point and a glass transition temperature. The values found were 0.59, 0.64 and 0.73 for [2-C₃MIM][BF₄], [3-C₅MIM][BF₄] and [MBnMIM][BF₄], respectively and they are fitting well to the values found for other molecules (inorganic and organic) and polymers in literature (from 0.58 to 0.78).¹¹ All results of the differential scanning calorimetry before and after the anion exchange are summarized in Table 3.2. In general, the tetrafluoroborate containing ionic liquids revealed a lower glass transition temperature than their chloride analogues (on average 38 °C). For the branched ionic liquids the T_g values found were 10 to 15 °C higher than for the linear analogues for both anions. The ionic liquids with an aromatic group showed the highest T_g value of all the investigated ionic liquids.

3.3.2 Influence of the anions

The thermal behavior was investigated for selected 1-butyl-3-methylimidazolium based ionic liquids with different counter ions. It was found, that the counter ion does not have a strong influence on the thermal behavior of the ionic liquids. The glass transition temperature was found to be between –50 and –80 °C, independent on the hydrophilicity of the counter ion. The results obtained are summarized in Table 3.3.

Table 3.2 Melting (T_m), freezing (T_f), cold crystallization (T_{cc}), and glass transition (T_g) temperatures for imidazolium-based ionic liquids with branched and non-branched alkyl (or aryl) side groups.

Cation	Anion	T_m [°C]	T_f [°C]	T_{cc} [°C]	T_g [°C]
[C ₃ MIM] ⁺	[Cl] ⁻				-44
[C ₄ MIM] ⁺	[Cl] ⁻				-41
[C ₅ MIM] ⁺	[Cl] ⁻				-47
[BnMIM] ⁺	[Cl] ⁻				2
[2-C ₃ MIM] ⁺	[Cl] ⁻				-34
[2-C ₄ MIM] ⁺	[Cl] ⁻				-31
[2-C ₅ MIM] ⁺	[Cl] ⁻				-19
[3-C ₅ MIM] ⁺	[I] ⁻	124	45		
[MBnMIM] ⁺	[Cl] ⁻				10
[C ₃ MIM] ⁺	[BF ₄] ⁻				-84
[C ₄ MIM] ⁺	[BF ₄] ⁻				-80
[C ₅ MIM] ⁺	[BF ₄] ⁻				-77
[BnMIM] ⁺	[BF ₄] ⁻				-33
[2-C ₃ MIM] ⁺	[BF ₄] ⁻	67		-30	-74
[2-C ₄ MIM] ⁺	[BF ₄] ⁻				-68
[2-C ₅ MIM] ⁺	[BF ₄] ⁻				-66
[3-C ₅ MIM] ⁺	[BF ₄] ⁻	68		-6	-56
[MBnMIM] ⁺	[BF ₄] ⁻	73		35	-22

Table 3.3 Melting (T_m), cold crystallization (T_{cc}), and glass transition (T_g) temperatures for 1-butyl-3-methylimidazolium based ionic liquids with different counter ions.

Ionic liquid	T_g [°C]	T_c [°C]	T_m [°C]
[C ₄ MIM][OH]	-54		
[C ₄ MIM][Oac]	-70		
[C ₄ MIM][F]			
[C ₄ MIM][Bu ₂ PO ₄]	-71		
[C ₄ MIM][Cl]	-41		
[C ₄ MIM][I]	-59		
[C ₄ MIM][NO ₃]	-70		
[C ₄ MIM][DCA]		-34	2
[C ₄ MIM][BF ₄]	-80		
[C ₄ MIM][NTf ₂]	-77		
[C ₄ MIM][PF ₆]		-20	-9

3.4 Water uptake

Another important property of ionic liquids is their ability to absorb water. The water uptake of the ionic liquids was investigated with a “Dynamic Vapor Sorption (DVS)” technique (Figure 3.8).

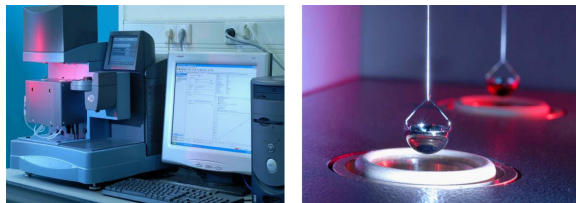


Figure 3.8 Photo of the TGA Q5000 SA thermo gravimetric analyzer used to study the water uptake (left). Sample and reference pan for the water uptake measurements (right).

Applying this measurement technique, a sample is subjected to varying conditions of humidity and temperature and the response of the sample is measured gravimetrically. In general, the weight of the sample decreases slightly during the drying step. The resulting weight (when the weight change is smaller than 0.05% for a period of 60 minutes) is used to set the weight change to zero at this point. After the saturation the temperature was adjusted to 25 °C and the relative humidity was subsequently increased stepwise to 20%, 50% and 80% relative humidity (RH, Figure 3.9). In the same manner, the humidity was decreased and an additional drying step was included to compare the initial and final sample weights. A typical water uptake plot for 1-ethyl-3-methylimidazolium chloride ($[\text{C}_2\text{MIM}][\text{Cl}]$) is depicted in Figure 3.9.

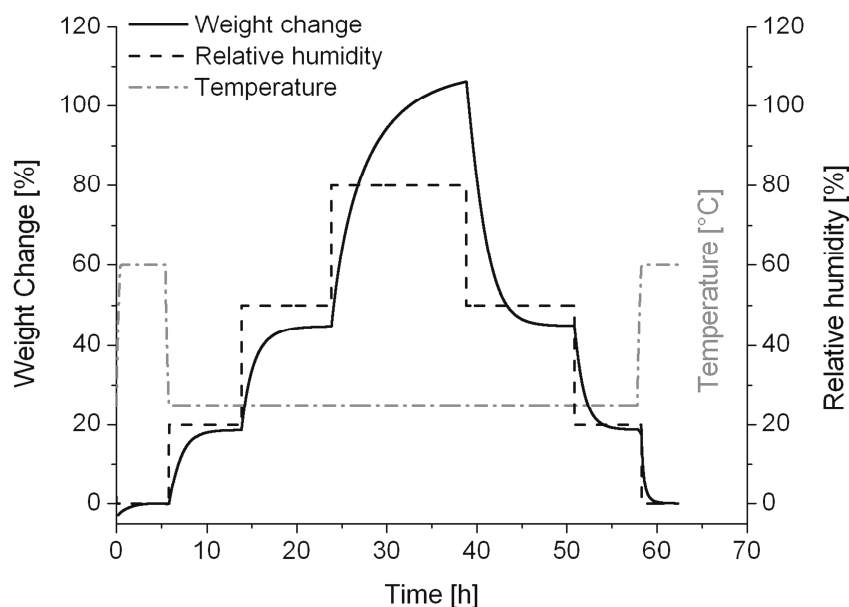


Figure 3.9 Representation for the water uptake measurement of $[\text{C}_2\text{MIM}][\text{Cl}]$ at 25 °C.

For an initial measurement, the standard heated vacuum oven was used to dry the ionic liquid. Subsequently, $[\text{C}_2\text{MIM}][\text{Cl}]$ was dried for 3 days in a freeze dryer. In Figure 3.9 it is visible for $[\text{C}_2\text{MIM}][\text{Cl}]$ that at the “drying-step” this freeze dried ionic liquid is very

hygroscopic and able to absorb 6 wt.-% of water at 60 °C in a 0% humidity atmosphere (dried N₂ flow). In contrast, the weight decreased in case of the vacuum oven dried IL. From these results we can assume that the normal vacuum oven is not sufficient to dry especially highly hygroscopic ionic liquids.

3.4.1 Different alkyl chain length & branching

Alkanes are known to be hydrophobic compounds; therefore, an influence on the ability to absorb water is expected for hydrophilic imidazolium-based ionic liquids bearing different alkyl chains as side groups. In case of water-soluble ionic liquids an increase in the alkyl chain length of their cations should lead to a lower water uptake.¹² From alkanes it is known, that branching results in a more compact structure and therefore a smaller surface area.⁷ Thus, we expected the branched ionic liquids to absorb more water than their linear analogues, because the branching allows the water molecules to penetrate the ionic liquid more easily. Furthermore, the hydrogen bonds of water molecules are less locally ordered around the branched alkyl chains,⁷ and therefore it is thought that alkyl branched ionic liquids might become more hydrophilic than their linear analogues. In addition, for ammonium based ionic liquids the water content for branched ionic liquids was reported to be ~ 0.4% higher than for their linear analogues, which is in line with our expectation.¹³

As mentioned before, the cation of the ionic liquid only has a slight influence on the hydrophobicity, while the anion mainly dictates the water miscibility. The water uptake is expected to be larger for ionic liquids containing a chloride counter ion than for tetrafluoroborate containing ionic liquids, because the van der Waals volume for a chloride anion is 28 Å³, whereas for tetrafluoroborate it is 48 Å³ as determined elsewhere.¹⁴ This results in a higher charge density for the chloride anion and it is believed that smaller anions will absorb more water.¹⁵ For these reasons, the chloride containing ionic liquids were chosen to investigate the influence of the cation structure on the water uptake due to their well-known hydrophilic nature. Thus, the water uptake of the ionic liquids was investigated at three different relative humidities (20, 50 and 80%) at 25 °C. The measurement procedure used is similar to that one described in literature.^{14,16} The results of the water uptake measurements of the investigated chloride containing ionic liquids are depicted in Figure 3.10. As observed for the investigated ionic liquids in Figure 3.10 the water absorption decreases as the length of the alkyl side chain for both linear and branched side chains increases, which is in agreement with previous observations.^{13,15} Figure 3.10 shows that [C₂MIM][Cl] had the highest water uptake values of all the investigated ionic liquids (up to 106 wt.-%). In addition, it was found, that the introduction of a branching point increases the water uptake. According to Figure 3.10 the branching seems to improve the penetration of water, which might be a result of decreased hydrocarbon-water interactions resulting in less amphiphilic self-assembly in branched ionic liquids due to their lower surface tension as reported for ammonium based ionic liquids.¹⁷ Thus, the amount of water uptake for branched alkyl side chains is more similar to the amount for the shorter linear

alkyl chains than compared to the linear alkyl chains with the same amount of carbon atoms. This effect is more pronounced in case of $[2\text{-C}_4\text{MIM}][\text{Cl}]$, which water uptake behavior is more similar to $[\text{C}_3\text{MIM}][\text{Cl}]$ than to $[\text{C}_4\text{MIM}][\text{Cl}]$. As expected, ionic liquids with aromatic groups absorbed less water than ionic liquids with alkyl side chains due to the higher hydrophobicity of aromatic substituents. The introduction of a methyl group to the benzyl group did not significantly change the absorption of water and only a marginal decrease was measured.

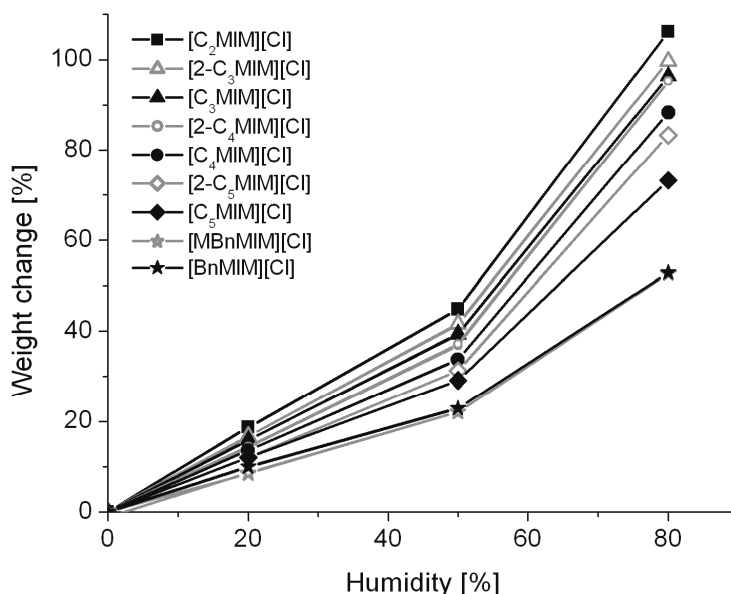


Figure 3.10 Water uptake of different linear and branched imidazolium-based ionic liquids containing chloride as counter ion (at 25 °C).

The water uptake was plotted against the number of carbon atoms in the alkyl and aryl side groups (Figure 3.11) to investigate if the difference in the water uptake between the alkyl and the aryl group is due to their nature (alkyl or aryl). A linear trend was found, which shows, that the water uptake is mainly depending on the number of carbon atoms in the side group and not on the nature of the group (alkyl or aryl). In addition, the water uptake of $[\text{C}_8\text{MIM}][\text{Cl}]$ was measured, which is fitting perfectly to the observed linear trend and the values obtained are lower compared to the branched ionic liquid with the same number of carbon atoms in the side chain ($[\text{MBnMIM}][\text{Cl}]$). From the plot in Figure 3.11 we can conclude, that the water uptake within the series of linear or branched ionic liquids is mainly controlled by the hydrophobicity of the alkyl side chains, whereas the higher water uptake of branched ionic liquids is a result of the decreased ability to self-assembly.

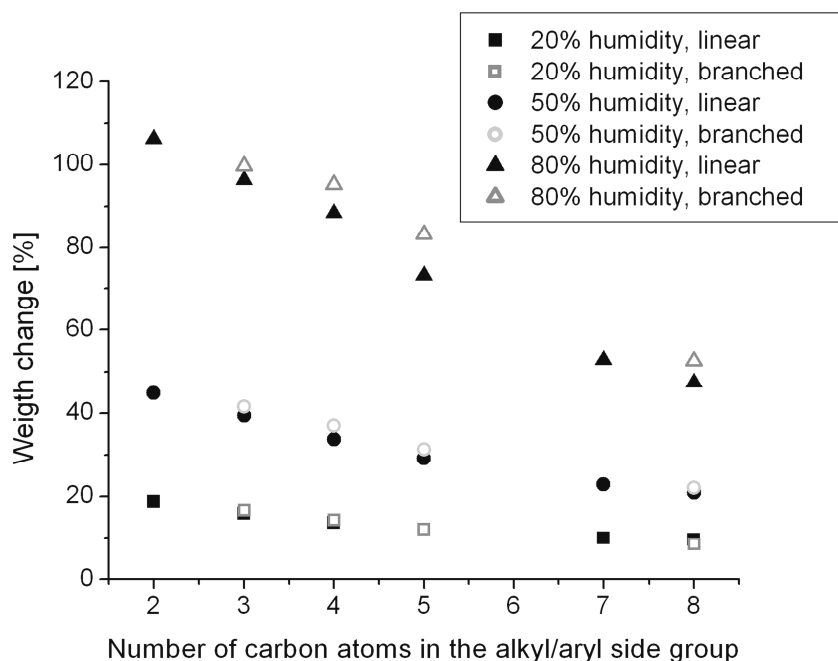


Figure 3.11 Dependence of the number of C atoms in the side chain on the water uptake of different linear imidazolium-based ionic liquids containing chloride as counter ion.

3.4.2 Different anions

Finally, the water uptake was measured for selected ionic liquids with different anions. From literature it is known that hydrophobic ionic liquids are able to absorb water to a certain extent. Examples from literature show that after 24 h exposure to air the water content of $[\text{C}_4\text{MIM}][\text{BF}_4]$ is 0.32 M (~5 wt.-%).¹⁸ Even more hydrophobic ionic liquids, *e.g.* $[\text{C}_4\text{MIM}][\text{PF}_6]$ and $[\text{C}_4\text{MIM}][\text{Tf}_2\text{N}]$, were reported to have a water content of 0.08 M,¹⁸ 1.8% (v/v)¹⁹ and 0.10 M,¹⁸ 1.4 wt.-%,²⁰ respectively. These values are depending on the impurities and the humidity in the air. Most values reported in literature are given without the present humidity and therefore differences in the saturated water content are possible. As depicted in Figure 3.12, the ionic liquids bearing a chloride anion approximately absorb ten times more water than ionic liquids with a tetrafluoroborate anion. It is worth to note that the amount of absorbed water can be up to 10 wt.-% for a hydrophobic ionic liquid under high humidity (80% RH). In addition, remarkable abilities for the absorption of water were observed for ionic liquids with $[\text{OAc}]$, $[\text{Et}_2\text{PO}_4]$ and $[\text{Cl}]$ anions. From the data obtained, a sorption isotherm was contracted revealing that the absorption and desorption of water is completely reversible.

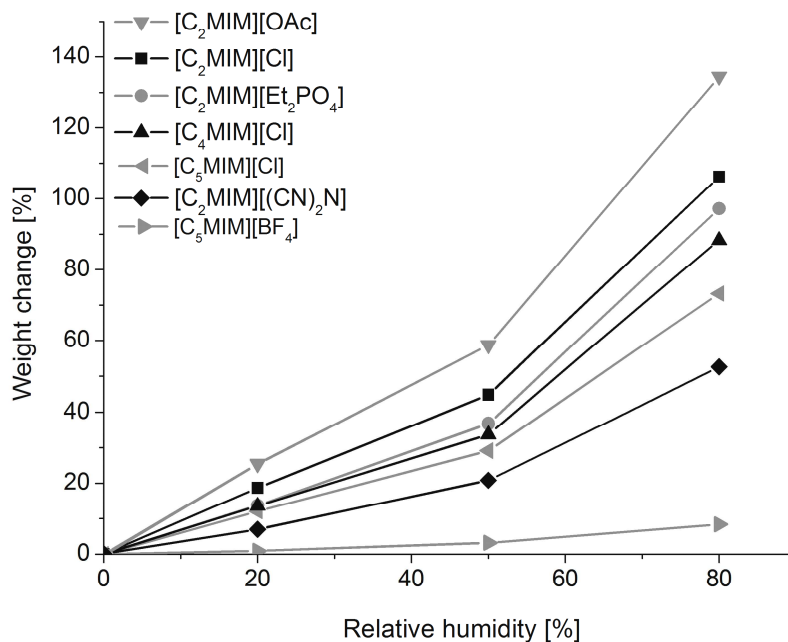


Figure 3.12 Water uptake of 1-alkyl-3-methylimidazolium based ionic liquids containing various anions (acetate, chloride, diethyl phosphate, (dicyanide)amide and tetrafluoroborate) at 25 °C.

3.5 Viscosity

IL's have a very high viscosity, which makes it extremely difficult to measure the viscosity of a pure IL. For the first trials methylene chloride was used to dilute the ionic liquids, because all synthesized IL's were soluble in this solvent making a comparison possible. For the determination of the kinematic viscosity a Mikro-Ubbelohde viscometer was used. Five different concentrations and the pure solvent were measured at $25\text{ °C} \pm 0.01\text{ °C}$. The first results for 1-propyl-3-methylimidazolium chloride ([C₃MIM][Cl]), 1-butyl-3-methylimidazolium chloride ([C₄MIM][Cl]) and 1-pentyl-3-methylimidazolium chloride ([C₅MIM][Cl]) are shown in Figure 3.13. For low ionic liquid concentrations the kinematic viscosities of the three IL's are similar. At higher concentrations ($>1\text{ mol/L}$) an increase in viscosity for longer alkyl side chains is obtained as a result of the increasing van der Waals interactions. Furthermore, the dynamic viscosity behavior of [C₂MIM][Et₂PO₄] was investigated. The viscosity was measured on an automated microviscometer by Anton Paar (AMVn) based on the approved and acknowledged rolling/falling ball principle according to DIN 53015 and ISO 12058, respectively. Figure 3.14 shows the plots of the dynamic viscosity against the temperature for different measuring angles. Assuming that the viscosity is independent from the measuring angle, it can be deduced that the ionic liquid used behaves like a Newtonian liquid. This result is similar to the already described behavior of imidazolium dialkylphosphates.²¹ The viscosity is reduced to approximately the half of its earlier value only by heating up for 10 °C (Figure 3.14). Since water can influence the viscosity of ionic liquids dramatically, it is essential that the ionic liquids are severely dried before their use. In addition, only a closed viscometer should be used because ionic liquids can absorb a high amount of water as visible from the before discussed water uptake measurements.

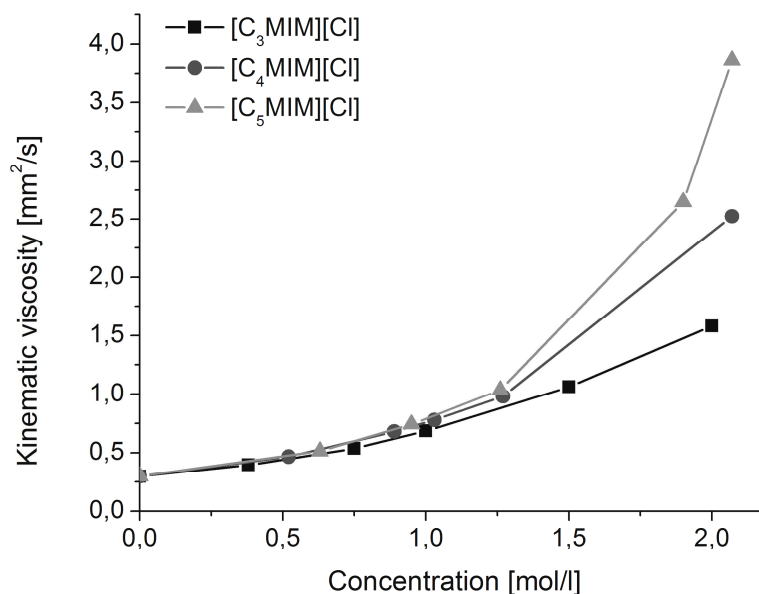


Figure 3.13 Determination of the kinematic viscosities of $[C_3MIM][Cl]$, $[C_4MIM][Cl]$ and $[C_5MIM][Cl]$ in methylene chloride with a Mikro-Ubbelohde viscometer at 25 °C.

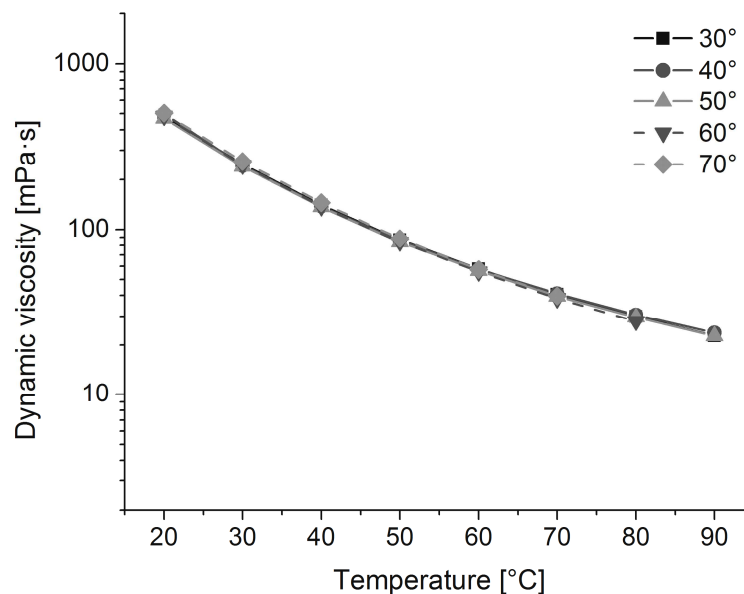


Figure 3.14 Dynamic viscosity measurement of $[C_2MIM][Et_2PO_4]$ at 30°, 40°, 50°, 60°, and 70°, respectively.

3.6 Conclusions

A series of linear and branched ionic liquids were synthesized under microwave irradiation to elucidate first structure-property relationships. In this regard, new ionic liquids were synthesized, *e.g.* 1-(1-ethylpropyl)-3-methylimidazolium iodide and 1-(1-methylbenzyl)-3-methylimidazolium chloride and their tetrafluoroborate containing analogues. Apart from these new ionic liquids, a series of known linear and branched ionic liquids were also

synthesized to allow a first systematical study of the thermophysical properties of these substances.

It was found that branched ionic liquids containing chloride were slightly more stable (10 °C) than their linear analogues supporting a S_N2 decomposition pathway. However, the tetrafluoroborate containing ionic liquids revealed a 30 °C higher thermal stability for the cases with linear alkyl chains, which might be due to a different decomposition mechanism initiated by the anion. For both investigated anions the ionic liquid with the non-branched aromatic group was more stable assuming a more dissociative decomposition mechanism (S_N1).

The tetrafluoroborate containing ionic liquids revealed a lower glass transition temperature than the chloride analogues. For the branched ionic liquids the T_g values found were 10 to 15 °C higher than for the linear analogues for both anions. The ionic liquids with an aromatic group showed the highest T_g values of all the investigated ionic liquids.

Moreover, the water uptake of the ionic liquids was measured and revealed a systematic dependency on the length of the alkyl side chain and on the branching. It was found, that the water absorption decreases when the alkyl chain length for linear and branched alkyl groups increases, due to the increasing hydrophobicity of the alkyl/aryl group. The ionic liquids with branched alkyl chains showed a higher water uptake than their linear analogues as a result of their decreased ability for amphiphilic self-assembly. In general, the water uptake for branched ionic liquids was lower than for ionic liquids with a shorter alkyl side chain ($C_n < C_{n-1}$).

The described results allow a better insight into the structure-property relationship of ionic liquids. The introduction of branches to the side chain of ionic liquids will allow the synthesis of tailor-made ionic liquids and the fine-tuning of the chemical and physical properties, such as stability, water uptake, glass transition temperature and other.

3.7 Experimental details

Materials

The synthesis of the ionic liquids and the origin of the commercial available ionic liquids is described in Chapter 2.

Melting points (onset of an endothermic peak on heating), freezing points (onset of an exothermic peak on cooling), cold crystallization temperatures (onset of an exothermic peak on heating) and glass transition temperatures (midpoint of a small endothermic heat capacity change) were determined on a DSC 204 F1 Phoenix by Netzsch under a nitrogen atmosphere from -100 to 150 °C with a heating rate of 20 K min⁻¹ (a first heating cycle to 150 °C was not considered for the calculations). Thermogravimetric analyses were performed in a TG 209 F1 Iris by Netzsch under a nitrogen atmosphere in the range from 25 to 600 °C with a heating rate of 20 K/min. The water uptake measurements of the ionic liquids were performed on a Q5000 SA thermo gravimetric analyzer from TA Instruments containing a microbalance in which the sample and reference pans were enclosed in a humidity and

temperature controlled chamber. The temperature in the Q5000 SA was controlled by Peltier elements. A dried N₂ gas flow (200 mL/min) was split into two parts, of which one part was humidified by passing it through a water-saturated chamber. The desired relative humidity (RH) for the measurements could subsequently be obtained by mixing proper proportions (regulated by mass flow controllers) of dry and wet stream. The standard isotherm measurement consisted of a number of subsequent steps. First, the sample was dried at 60 °C and 0% RH for a specific time until the weight change was stabilized to be less than 0.05% for a time period of 60 minutes. In the second step, the temperature was decreased to 25 °C and the relative humidity increased to 20%. The humidity was then increased step-wise (with steps of 30% RH) to a maximum of 80% RH. The weight change of the sample was stabilized after each step until it was smaller than 0.05% for a time period of 60 minutes. In addition, the reverse isotherm was also measured. In this case the humidity was decreased down to 0% (in steps of 30% RH) and the samples were allowed to stabilize after each step. In order to finalize the isotherm and to compare the results with the initial weight of the sample, an additional drying step was included (60 °C at 0% RH). The differences between absorption and desorption was less than 0.4% for 50% humidity and less than 0.15% for 20% humidity. The accuracy of the measurement was checked by a second run. It was found, that the variation of the two runs was within the range of the variation between absorption and desorption. Dynamic and kinetic viscosities were measured on a AMVn microviscometer by Anton Paar which is based on the approved and acknowledged rolling/falling ball principle according to DIN 53015 and ISO 12058. The system allows a variable inclination angle of the measurement capillary and, therefore, both the variation of shear stress and shear rate and the easy repetition of measurements on a wide viscosity range (0.3–2500 mPa·s). A Peltier thermostat allowed to measure over a large temperature range (+5 to 135 °C).

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Chapter 4

Applications of ionic liquids in cellulose chemistry

Abstract

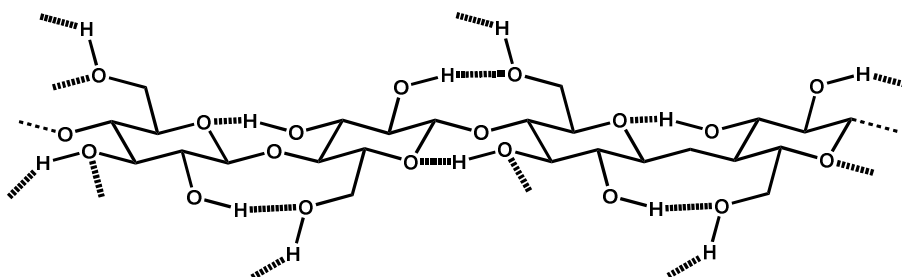
Several 1-alkyl-3-methylimidazolium based ionic liquids were screened in order to investigate their ability to dissolve cellulose. In particular, the influence of different alkyl chain lengths, branched alkyl side chains and the anion on the dissolution of cellulose was investigated. The alkyl chain length was varied from ethyl to decyl, including both even and odd numbered chains, to elucidate structure-dissolution properties revealing a remarkable odd-even effect. In addition, ionic liquids with branched alkyl side chains varied from propyl to pentyl were tested, showing a reverse odd-even effect with overall lower dissolution ability in comparison to their linear analogues. The tritylation of cellulose was performed in selected ionic liquids using pyridine as base in order to compare their performance. The influence of the reaction time and the ratio of trityl chloride per cellulose monomer unit on the degree of substitution were investigated in detail for 1-butyl-3-methylimidazolium chloride and the optimized reaction conditions were applied for the other ionic liquids as well.

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4.1 Introduction

Cellulose is the most abundant natural polymer in nature and its derivative products have many important applications in fiber, paper, membrane, polymer and paint industries.¹⁻⁴ However, cellulose is insoluble in water and most common organic solvents, because of its fibril structure and the pronounced presence of inter- and intermolecular hydrogen bonding as depicted in Scheme 4.1.^{5,6}



Scheme 4.1 Schematic representation of the structure of cellulose (with hydrogen bonds).

The most commonly applied industrial process to obtain regenerated, processible cellulose is the xanthogenate process during which cellulose is swollen with aqueous sodium hydroxide and subsequently treated with carbon disulfide (CS_2) leading to a highly viscous sodium-xanthogenate solution. This solution is later treated with acidic solution to reform the cellulose and CS_2 . The main drawbacks of this process are the degradation of the cellulose backbone and the formation of toxic H_2S as byproduct.⁷⁻⁹ Other derivatizing solvents like trifluoro acetic acid, formic acid, or *N,N*-dimethylformamide/nitrogen peroxide could also be applied for the functionalization of cellulose with or without isolation of the intermediate. Newer examples for non-derivatizing solvents with aqueous inorganic complexes are, *e.g.*, cuprammonium hydroxide (Cuoxam, Cuam), cupriethylene diamine (Cuen) and cadmiumd oxide/ethylenediamine (Cadoxen), or non-aqueous solvents together with inorganic salts or gases, *e.g.* dimethylacetamide/lithium chloride (DMA/LiCl), dimethylsulfoxide/sulphur dioxide (DMSO/SO_2), or dimethylacetamide/tetrabutylammonium fluoride (DMSO/TBAF).^{5,10-12} More environmentally friendly solvents for the derivatization of cellulose continue to be developed.

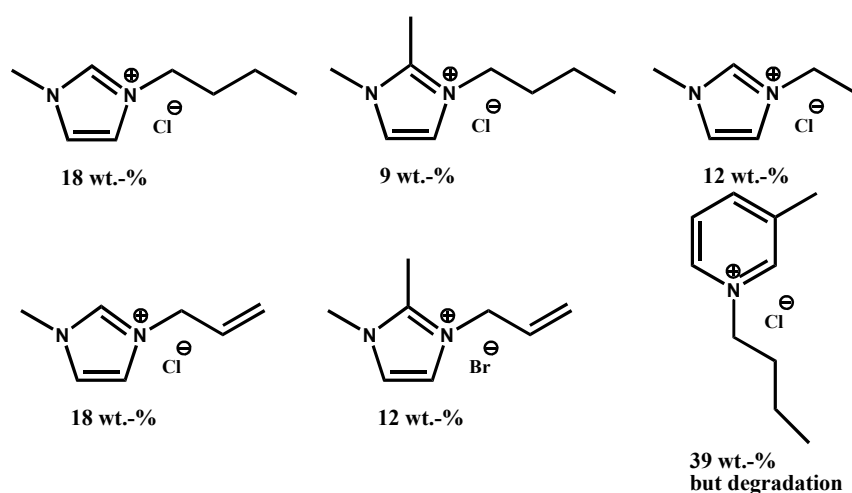
4.2 Dissolution studies

Recently, ionic liquids were found to dissolve cellulose and they are considered to be ‘green’ solvents on account of their non-volatility and non-flammability, which is a result of their negligible vapor pressure at ambient temperature.¹³⁻¹⁸ On the basis of ecological and economic concerns ionic liquids seem to be an attractive alternative to conventional volatile organic solvents.^{13,14,19} The most studied ionic liquids are highly solvating, non-coordinating and possess a high compatibility with various organic compounds.²⁰ They are recyclable and reusable because of their immiscibility with a range of organic solvents.^{14,19,21} Ionic liquids consist of an organic cation and an inorganic anion; their properties such as melting point, density, viscosity and hydrophobicity can be adjusted by varying their composition.^{18,22,23} In 1934 Graenacher discovered that cellulose can be dissolved in molten salts, such as allyl-, ethyl- and

benzylpyridinium chloride.²⁴ However, this finding was thought to be of little practical value at the time. In 2002, the idea of using ionic liquids for the dissolution of cellulose was revived by Roger *et al.*^{16,17} In their work different ionic liquids containing 1-butyl-3-methylimidazolium cations were tested, with the most efficient solubility being obtained when chloride was used as the anion. The chloride ions are nonhydrated and can disrupt and break the intramolecular hydrogen bonds of the cellulose network without derivatizing it.²⁵⁻²⁷

4.2.1 Screening

In order to extend the potential application of IL's for cellulose processing, we screened other ionic liquids for their ability to dissolve cellulose. Although there are already some ionic liquids described in literature (Scheme 4.2) which are able to dissolve cellulose in high amounts, they all show some disadvantages.



Scheme 4.2 Schematic representation of commonly known ionic liquids with the ability to dissolve cellulose.²⁸⁻³⁰

For example the ionic liquid 1-butyl-3-methylimidazolium chloride can dissolve up to 25 wt.-% of cellulose (as reported by Rogers *et al.*).¹⁶ However, a melting point above 70 °C, the high viscosity of the [C₄MIM][Cl] solution and the high hygroscopicity – in general valid for all imidazolium based ionic liquids with a chloride counter anion – makes the handling difficult. New ionic liquids might be better suitable for the dissolution and processing of cellulose possibly circumventing the mentioned drawbacks. Therefore, the newly synthesized ionic liquids as well as commercially available ionic liquids were subsequently used in this chapter for the dissolution studies of cellulose. In this context, also a correlation between the water content and the solubility was found. When using non-dried ionic liquids, the solubility of cellulose was reduced. Therefore, it was necessary to dry all ionic liquids carefully before use. It is noteworthy that the vacuum oven (at 40 °C) was not sufficient to dry the ionic liquids; only a freeze dryer was able to remove the last percentages of water. For the dissolution studies we used either 0.5 to 2 mL microwave vials (Figure 4.1 left side) or small 2 mL vials (Figure 4.1 right side). After the ionic liquid was filled in, the cellulose was added and the vial was heated to about 100 °C

utilizing an oil bath or a metal holder. After approximately 15 min to 1 h, the dissolution of cellulose was checked visually. During these screening tests, a different behavior of the cellulose in the dissolution experiments was observed. Whereas the solutions of cellulose in compatible ionic liquids like $[C_4MIM][Cl]$ and $[C_6MIM][Cl]$ became clear and stayed dissolved at room temperature (whereby, in particular, the pure chlorides are solids; see Figure 4.2 A), other solutions tend to crystallize back at room temperature, *e.g.* $[C_3MIM][Cl]$ (Figure 4.2 B). If no dissolution can be observed, the cellulose is either only “suspended” in the ionic liquid as shown in Figure 4.2 C, or is rapidly degraded as evidenced by a deep coloration of the solution seen in Figure 4.2 D. This effect was observed very often in particular when using higher amounts of cellulose.

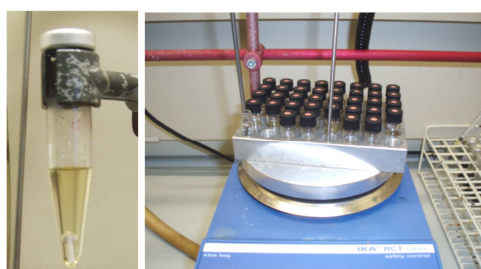


Figure 4.1 Dissolution of cellulose: a) microwave vial; b) parallel setup.

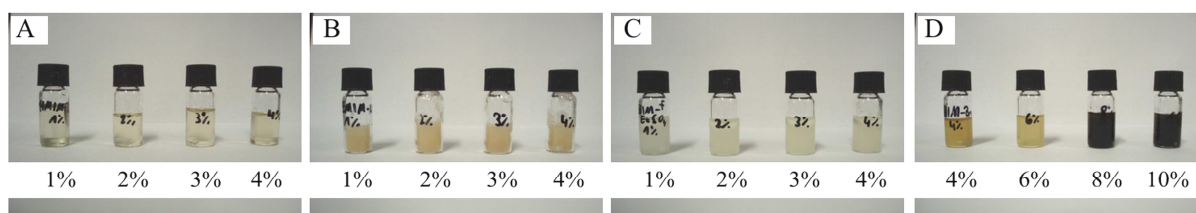


Figure 4.2 Cellulose dissolved in $[C_6MIM][Cl]$ (A), $[C_2MIM][Cl]$ (B), $[C_2MIM][EtSO_4]$ (C), and $[C_4MIM][Br]$ (D), respectively.

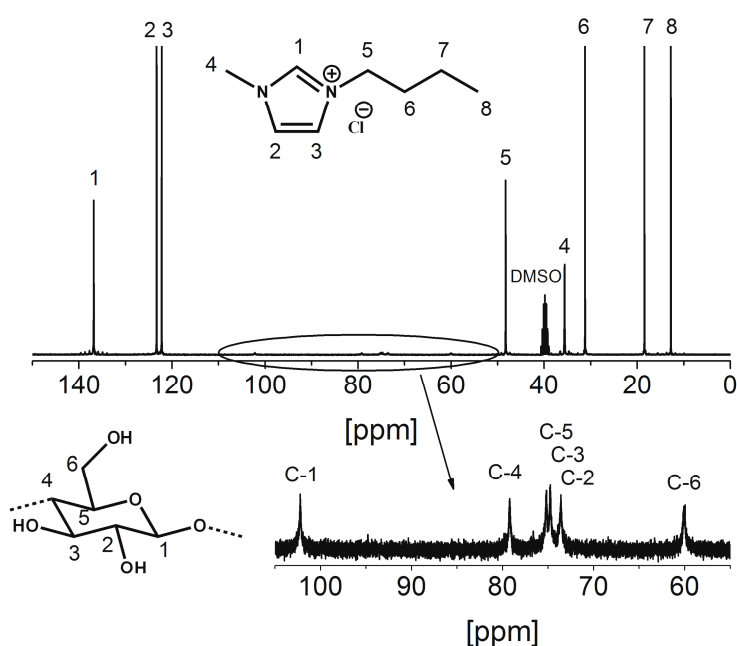


Figure 4.3 ^{13}C NMR spectrum of cellulose (10wt.-%) in 1-butyl-3-methylimidazolium chloride (100 MHz, d_6 -DMSO (25 wt.-%), 100 °C).

^{13}C NMR spectroscopy was used to prove the structure of the dissolved cellulose. Specifically, 10 wt.-% of cellulose was dissolved in 1-butyl-3-methylimidazolium chloride, and 25 wt.-% DMSO- d_6 was added. The addition of DMSO decreased the viscosity of the solution without precipitating the dissolved cellulose.²⁸ The ^{13}C NMR spectrum was recorded at 100 °C (Figure 4.3). For the ionic liquid, namely 1-butyl-3-methylimidazolium chloride, three signals were found at 136.8 (1), 123.3 (2) and 122.2 ppm (3) for the imidazolium ring. The chemical shift at 35.3 ppm can be assigned for the methyl group (4) and the signals for the butyl group were obtained at 48.3 (5), 31.2 (6), 18.5 (7) and 12.8 ppm (8). The signals for the dissolved cellulose are located in the region between 120 and 60 ppm. Six signals for cellulose were found at 102.2 (C-1), 79.2 (C-4), 75.2 (C-5), 74.8 (C-3), 73.6 (C-2) and 60.1 ppm (C-6) in the ^{13}C NMR spectrum. These chemical shifts are comparable to the values reported in literature.^{25,28} For the degradation experiments, we used the ILs $[\text{C}_4\text{MIM}][\text{Cl}]$, $[\text{C}_2\text{MIM}][\text{Cl}]$ and $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ to dissolve cellulose. As a general procedure the solution contained 8 wt.-% of cellulose and the mixture was heated up to 100 °C and left at this temperature for 2 hours. The automated ChemSpeed A100 AutoPlant robot with its internal anchor stirrers was used to ensure an efficient heating, stirring and cooling. Then, the DP values of both the starting cellulose and the regenerated samples were determined by capillary viscometry in Cuen utilizing Equations 4.1–4.4.²⁸

$$[\eta_{rel}] = \frac{t}{t_0} \quad \text{Equation 4.1}$$

$$[\eta] = \frac{(\eta_{rel} - 1)}{1 + K_n(\eta_{rel} - 1)} \quad \text{Equation 4.2}$$

$$M_w = \left(\frac{[\eta]}{0.0116} \right)^{\frac{1}{0.83}} \quad \text{Equation 4.3}$$

$$DP = \frac{M_w}{162} \quad \text{Equation 4.4}$$

$[\eta]$	<i>intrinsic (limit) viscosity ($\text{mL} \cdot \text{g}^{-1}$)</i>
t	<i>flow rate of the solution(s)</i>
t_0	<i>flow rate of the solvent(s)</i>
c	<i>concentration of the solution ($\text{g} \cdot \text{mL}^{-1}$)</i>
K_n	<i>instrument constant $K_n=0.29$</i>

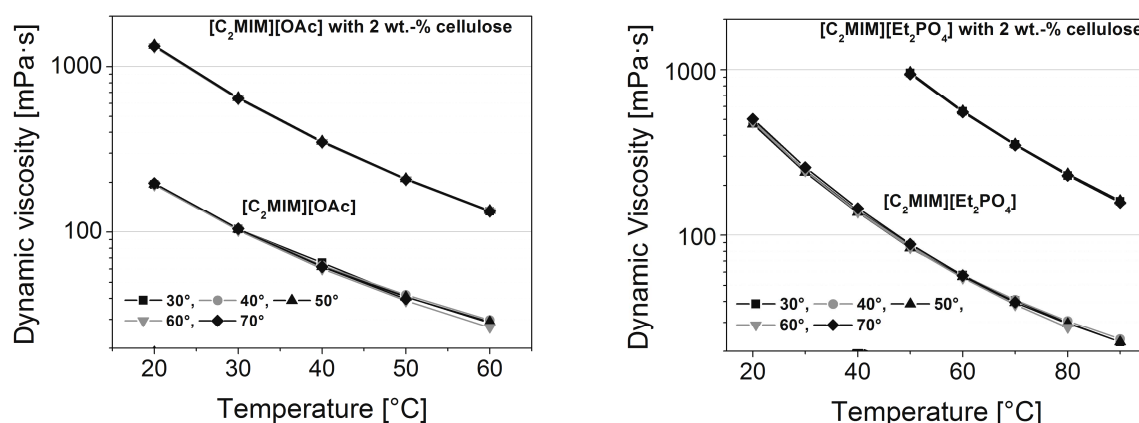
The obtained values for the degree of polymerization before and after dissolution of cellulose in ionic liquid are depicted in Table 4.1.

Table 4.1 Comparison of the degree of polymerization of cellulose before and after dissolution in selected ionic liquids.

IL	Temperature [°C]	Time [min]	Yield [%]	DP
Avicel PH-101	—	—	—	398 ^a
[C ₄ MIM][Cl]	100	120	79	311 ^b
[C ₂ MIM][Cl]	100	120	86	358 ^b
[C ₂ MIM][Et ₂ PO ₄]	100	120	96	378 ^b

^a Before processing, ^b after regeneration.

These values indicate that the highest degradation of cellulose appears in [C₄MIM][Cl] and a slightly lower degradation in [C₂MIM][Cl]. The lowest degradation after 2 hours of heating at 100 °C was found in [C₂MIM][Et₂PO₄]. The high yield of cellulose with 96% after the regeneration shows a significant benefit for the use of this ionic liquid. Furthermore, the low melting point at about 25 °C supports the handling of that ionic liquid. It must be noted that the melting point can only be observed visually since it could not be determined by DSC because this ionic liquid – like many others – behaves like a supercooled melt.³¹

**Figure 4.4** Dynamic viscosity for [C₂MIM][OAc] (left) and [C₂MIM][Et₂PO₄] (right) with and without 2 wt.-% cellulose at different angles (30–70°) and temperatures (20–90 °C).

In order to show the stability of cellulose in ionic liquid solutions, the ionic liquids [C₂MIM][OAc] and [C₂MIM][Et₂PO₄] were selected and the viscosities of the pure ionic liquids and the 2 wt.-% cellulose solutions were measured with an automated microviscometer based on the rolling/falling ball principle. Figure 4.4 shows the plots of the dynamic viscosity *versus* the temperature for different measuring angles. As a rule of thumb, the viscosity is reduced to approximately the half of its starting value only by increasing the temperature by 10 °C. Since water can influence the viscosity of ionic liquids significantly, it is essential that the ionic liquids are severely dried before their use. In addition, the viscosity is independent from the measuring angle and the ionic liquids used behave like Newtonian liquids.³¹ On the other hand, the use of ILs as cellulose solvents requires advanced equipment due to their high dynamic viscosity. For example, only adding 2 wt.-% of cellulose to [C₂MIM][OAc] leads to an increase from 200 mPa·s to 1100 mPa·s, in case of [C₂MIM][Et₂PO₄] from 480 mPa·s to 6900 mPa·s at room

temperature as determined by rheometry. In general, the viscosity can be significantly decreased by diluting a cellulose/IL solution with an organic solvent, like for instance pyridine. However, a possible precipitation of cellulose must be avoided. Furthermore, a solution of [C₂MIM][Et₂PO₄]/cellulose/pyridine was stored and the dynamic viscosity was measured after 3 months again. The viscosities did not change significantly and it can be concluded that the cellulose is stable in these solvent mixtures over a long period of time at room temperature.

4.2.1.1 Influence of the alkyl chain length and branching

Lately, the solubility of cellulose in various ionic liquids has been reported and it was found that ionic liquids with chloride as their anion are the most effective for dissolving cellulose.^{16,17,27,28,32} So far, 1-butyl-3-methylimidazolium chloride gave the best results, with a yield of 18 to 25 wt.-% dissolved cellulose. However, only 1-alkyl-3-methylimidazolium chlorides with even-numbered alkyl chains (butyl, hexyl and octyl) have been reported.^{16,17,28} In our work we investigated the influence of the alkyl chain length from C₂ to C₁₀ of 1-alkyl-3-methylimidazolium chlorides on the solubility of cellulose. All experiments were carried out at 100 °C, and the results are presented in Figure 4.5.

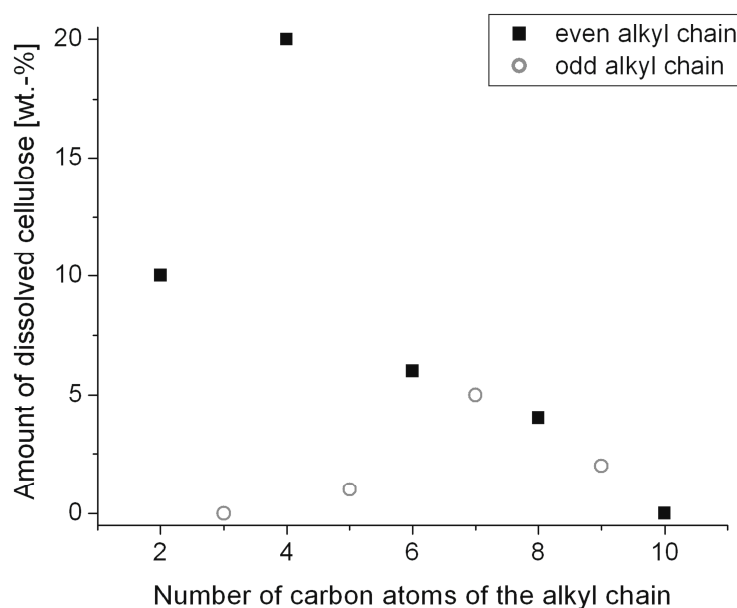


Figure 4.5 Dependency of the alkyl chain length of 1-alkyl-3-methylimidazolium chloride on the solubility of cellulose at 100 °C.

Surprisingly, the solubility of cellulose in 1-alkyl-3-methylimidazolium based ionic liquids does not regularly decrease with increasing length of the alkyl chain. In fact, a strong odd-even effect was observed for the small alkyl chains; pentyl and shorter. Cellulose was more soluble in 1-alkyl-3-methylimidazolium based ionic liquids with even-numbered alkyl chains compared to odd-numbered alkyl chains, below six carbon units. 1-Butyl-3-methylimidazolium chloride gave the best performance of the even-numbered alkyl chains, dissolving 20 wt.-% of cellulose, whereas 1-heptyl-3-methylimidazolium chloride was the most efficient odd-numbered ionic

liquid dissolving up to 5 wt.-% of cellulose. In general, the first odd-even effect was discovered for the melting temperature of *n*-alkanes and thereafter it was found that most series containing alkyl chains show odd-even effects for, *e.g.*, transition temperature, volume changes, chiral properties, dielectric properties, and dipole moments.³³ The reason for this odd-even effect and the large difference in optimal chain length for the cellulose dissolution is not fully understood at this moment. A possible explanation might be differences in the range of conformation for odd and even alkyl chains.³³ As described in literature, the mesogenic units of the alkyl chains are oriented differently for odd and even alkyl chains in the all trans-conformation. In case of an even number of CH₂ repeating units, the mesogenic units are parallel to each other, while in case of an odd number of CH₂ repeating units they are oriented inclined to each other, as depicted in Figure 4.6.



Figure 4.6 Schematic representation of the orientation of the mesogenic units of odd/even alkyl chains in all trans-conformation. Left: odd n of $(\text{CH}_2)_n$ units (inclined mesogenic units). Right: even n of $(\text{CH}_2)_n$ units (parallel mesogenic units).

This difference in orientation leads to significantly different packing of the alkyl chains (Figure 4.7). Alkyl chains with inclined mesogenic groups are packed less efficient (disordered structure with two alternating conformations), leading to a bent alkyl chain.^{33,34} In case of parallel mesogenic groups, the packing is more efficient and the molecules closely align in pairs resulting in a linear chain (well-ordered structure).

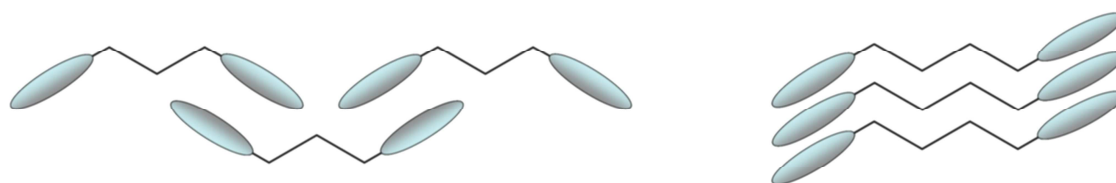


Figure 4.7 Schematic representation of the packing of odd/even alkyl chains in all trans-conformation. Left: odd n of $(\text{CH}_2)_n$ units. Right: even n of $(\text{CH}_2)_n$ units.

Therefore, alkyl chains with inclined mesogenic units have a greater propensity to distort from the all trans-configuration with little disruption of the intermolecular packing resulting in a greater range of conformations in comparison to alkyl chains with parallel mesogenic units.³³ In general, the range of conformation affects melting point, hydrogen bonds, enthalpies and entropies of aliphatic hydrocarbons.³⁴

In case of ionic liquids, the mesogenic units are the imidazolium ring and the methyl group. The ionic liquids with even alkyl chains showing good cellulose dissolving properties have inclined mesogenic groups (disordered alkyl chain), while the odd alkyl side chains showing no or only bad cellulose dissolving properties have parallel mesogenic groups (ordered alkyl chains). Based

on this knowledge, we have tried to predict the ability of branched ionic liquids to dissolve cellulose. In general, the alkyl chains in the branched ionic liquids are one CH_2 unit shorter than in their linear analogues. Therefore better cellulose solubility is expected for $[2\text{-C}_3\text{MIM}][\text{Cl}]$ and $[2\text{-C}_5\text{MIM}][\text{Cl}]$, while $[2\text{-C}_4\text{MIM}][\text{Cl}]$ should show no or only bad cellulose solubility. In order to predict if the branched ionic liquids will be able to dissolve more/less cellulose than the ionic liquids with linear alkyl side chains, the conformational energy was calculated by ChemBio3D Ultra 11.0 for the C-N bond at different angles. Figure 4.8 shows that the conformational energy increases with longer side chains. Furthermore, in case of $[2\text{-C}_n\text{MIM}][\text{Cl}]$ ($n > 3$), the overall conformational energy is much higher than for $[2\text{-C}_3\text{MIM}][\text{Cl}]$ or $[\text{C}_n\text{MIM}][\text{Cl}]$ ($n > 1$), thus for $[2\text{-C}_n\text{MIM}][\text{Cl}]$ ($n > 3$) the distortion from the trans-configuration is greater compared to $[2\text{-C}_3\text{MIM}][\text{Cl}]$ or $[\text{C}_n\text{MIM}][\text{Cl}]$ ($n > 1$) limiting the range of conformation. Therefore, lower cellulose solubility is expected for ionic liquids with branched alkyl side chains compared to linear alkyl side chains, as well as for $[2\text{-C}_5\text{MIM}][\text{Cl}]$ compared to $[2\text{-C}_3\text{MIM}][\text{Cl}]$.

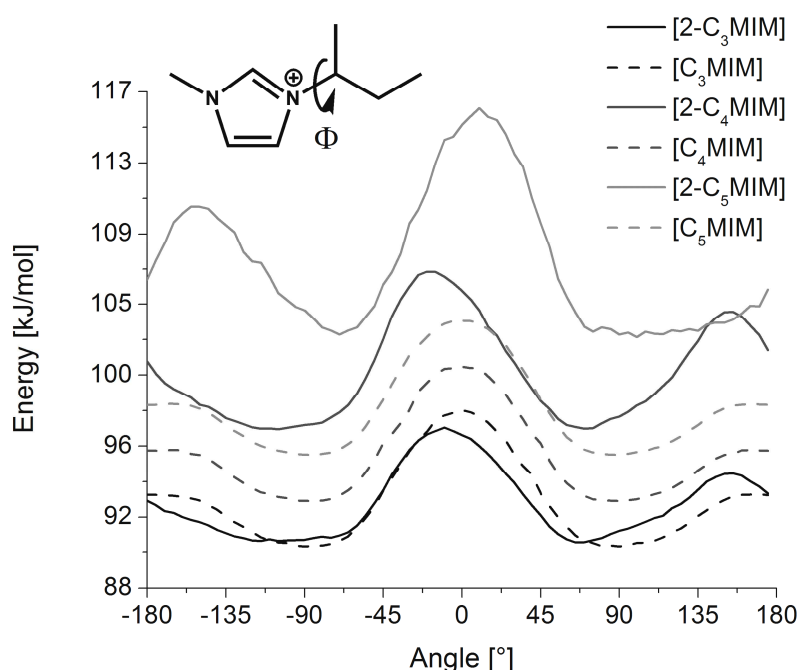


Figure 4.8 Dihedral angle distribution of the C-N bond (Φ) in the ionic liquids with linear and branched alkyl side chains calculated by ChemBio3D Ultra 11.0 with minimized energy.

The dissolution experiments of cellulose (1 wt.-%) in the ionic liquids with branched alkyl side chains ($[2\text{-C}_n\text{MIM}][\text{Cl}]$ ($n = 3$ to 5)) revealed that cellulose was not soluble in $[2\text{-C}_4\text{MIM}][\text{Cl}]$, while $[2\text{-C}_3\text{MIM}][\text{Cl}]$ and $[2\text{-C}_5\text{MIM}][\text{Cl}]$ in general were able to dissolve cellulose, as it was predicted from the results obtained with the linear analogues. A strong degradation of cellulose in $[2\text{-C}_4\text{MIM}][\text{Cl}]$ was observed, since the ionic liquid turned dark brown in relative short time, while the cellulose solution in $[2\text{-C}_3\text{MIM}][\text{Cl}]$ and $[2\text{-C}_5\text{MIM}][\text{Cl}]$ did not show any change in color (Figure 4.9). However, the dissolution of cellulose in the ionic liquid with branched alkyl side chains needed longer dissolution times (sometimes more than 1 h) in comparison to the linear analogues. It was found that $[2\text{-C}_5\text{MIM}][\text{Cl}]$ was able to dissolve up to 6 wt.% cellulose, but also a slight degradation was observed, since the color of the solution became slightly

brownish. In case of [2-C₃MIM][Cl], up to 9 wt.% of cellulose could be dissolved and no color change was observed. The observed results are nicely fitting to the above described expectations.

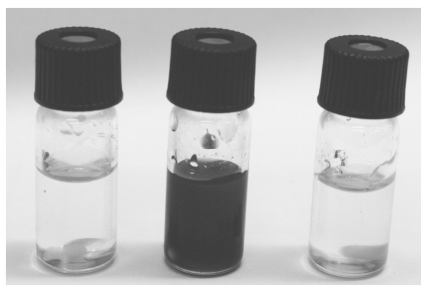


Figure 4.9 Dissolution of 1 wt.-% cellulose in ionic liquids with branched alkyl side chains: [2-C₃MIM][Cl] (left), [2-C₄MIM][Cl] (middle) and [2-C₅MIM][Cl] (right).

In addition, the synthesis of 1-alkyl-3-methylimidazolium based ionic liquids with bromide anions was envisioned to support the above described odd-even effect. Unfortunately, the earlier recognized effect for the chlorides was not observed for the bromides. Maybe due to the overall lower solubility of cellulose (1–3 wt.-%) in these ionic liquids containing bromide as the counter anion, a response to different side chain lengths is not clearly visible. The results of the dissolution experiments are summarized in Table 4.2.

Table 4.2 Overview – dissolution studies of imidazolium based ionic liquids with different alkyl chain lengths and branching.

Alkyl side chain of MIM cation	Anion	
	[Cl] [−]	[Br] [−]
C ₂	10–14%	1–2%
C ₃	not soluble	1–2%
C ₄	20%	2–3%
C ₅	1%	1–2%
C ₆	6%	1–2%
C ₇	5%	1%
C ₈	4%	1%
C ₉	2%	1%
C ₁₀	not soluble	not soluble
2-C ₃	9%	
2-C ₄	not soluble	
2-C ₅	6%	

In addition, the synthesis of 1-alkyl-3-methylimidazolium based ionic liquids with bromide anions was envisioned to support the above described odd-even effect. Unfortunately, the earlier recognized effect for the chlorides was not observed for the bromides. Maybe due to the overall lower solubility of cellulose (1–3 wt.-%) in these ionic liquids containing bromide as the counter anion, a response to different side chain lengths is not clearly visible. The results of the dissolution experiments are summarized in Table 4.2.

4.2.1.2 Influence of the anion

In order to investigate the influence of different anions on their ability to dissolve cellulose, the bromide or chloride anions could be exchanged to yield 1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium based ionic liquids with different anions. The procedures used for the anion exchange are described in Chapter 1. In general, the chlorides showed very good dissolving properties, mostly all other ionic liquids show less or no dissolution of cellulose ($[F]^-$, $[Br]^-$, $[I]^-$, $[BF_4]^-$, $[PF_6]^-$, $[NO_3]^-$, $[NTf_2]^-$, $[F_3CSO_3]^-$, $[EtSO_4]^-$, $[(CN)_2N]^-$). From literature it is known that ionic liquids with non-hydrated anions such as chloride and high hydrogen bonding basicity interact with the hydroxyl protons of cellulose and thereby breaking the hydrogen bonding network. Ionic liquids with weaker hydrogen bond acceptors or non-coordinating groups are poor cellulose solvents.²⁶ Additionally to the ionic liquids with chloride as counter ion, only the ILs with thiocyanate, acetate and phosphate counter anions revealed good dissolving properties for cellulose. For instance, 8 wt.-% of cellulose could be dissolved in $[C_2MIM][OAc]$ and 12 wt.-% in $[C_4MIM][OAc]$, whereby the solutions became colored, indicating degradation of cellulose. Surprisingly, $[C_2MIM][Et_2PO_4]$ has the ability to dissolve up to 14 wt.-% of cellulose and $[DiMIM][Me_2PO_4]$ up to 10 wt.-%, whereas $[C_4MIM][Bu_2PO_4]$ could not dissolve cellulose at all. The results are summarized in Table 4.3.

Table 4.3 Overview – dissolution studies of imidazolium based ionic liquids with different anions.

Anion	Cation			
	$[DiMIM]^+$	$[C_2MIM]^+$	$[C_4MIM]^+$	$[AllylMIM]^+$
$[F]^-$		2%		
$[Cl]^-$		10–14%	20% ^a	15% ^c
$[Br]^-$		1–2%	2–3%	not soluble
$[I]^-$	not soluble		1–2%	
$[SCN]^-$			5–7% ^b	
$[BF_4]^-$			not soluble ^b	
$[PF_6]^-$			not soluble ^b	
$[NO_3]^-$			not soluble	
$[NTf_2]^-$			not soluble	
$[F_3CSO_3]^-$			not soluble	
$[EtSO_4]^-$		not soluble		
$[(CN)_2N]^-$		not soluble		
$[TsO]^-$		1%		
$[OAc]^-$		8%	12%	
$[R_2PO_4]^-$	10% ^d	12–14% ^e	not soluble ^f	

^a 25% under microwave irradiation according to Rogers *et al.*,¹⁶ ^b Results of Rogers *et al.*,¹⁶

^c Results of Wu *et al.*,^{27,30} ^d R = Me, ^e R = Et, ^f R = Bu.

4.2.2 Microwave-assisted dissolution of cellulose

A selection of ionic liquids was studied for the dissolution of cellulose under microwave irradiation in the Biotage “Emrys Liberator” and “Initiator” microwave synthesizers. First tests

were less successful and showed mostly brownish solutions after heating. This suggests a strong degradation of the cellulose under these conditions. However, with the “Initiator” or “Swave” microwave it is possible to set the maximum power introduced into the solvent. By using different power/temperature settings, we found a relationship between the colorization of the cellulose solution and the maximum power introduced. Typical heating and power profiles for the dissolution of cellulose under microwave irradiation are depicted in Figure 4.10. This figure shows similar temperature and power profiles for different concentrations of cellulose in $[C_2MIM][Cl]$. Although a reduced maximum power was chosen, a thermal overshoot could not be avoided when using concentrations above 4 wt.-%. In addition, the maximum power of 60 Watt was reduced automatically after the final temperature was reached. Since the dissolution was performed in the absence of additional solvent and the ionic liquid used shows no significant vapor pressure, the pressure is negligible.

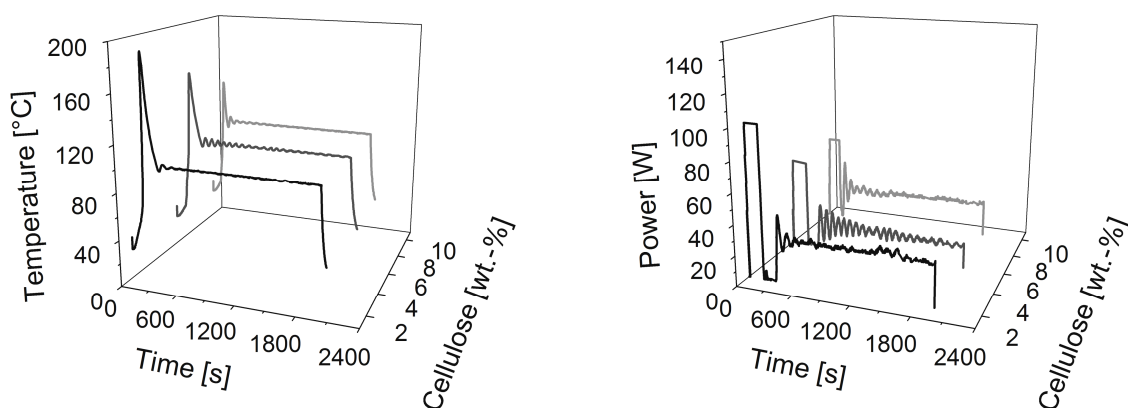


Figure 4.10 Heating (left) and power (right) profiles for the dissolution of cellulose in $[C_2MIM][Cl]$ at different concentrations under microwave irradiation.

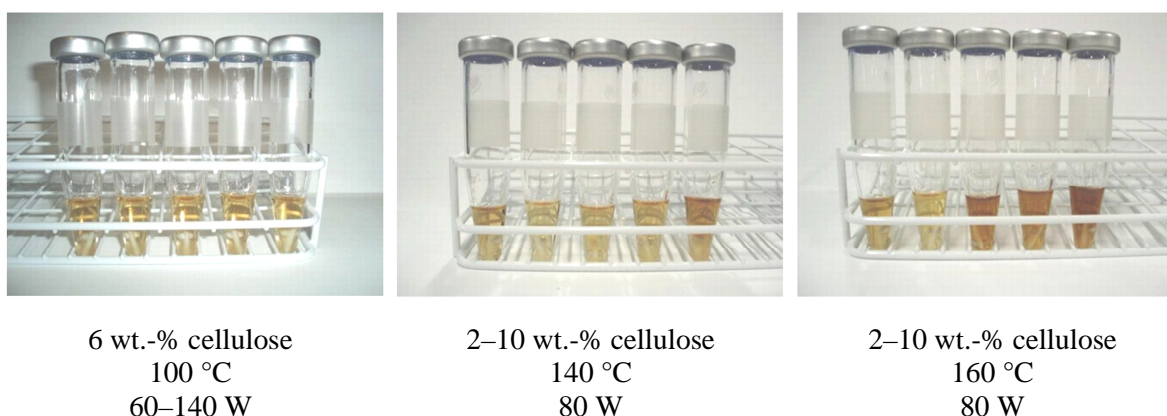


Figure 4.11 Dissolution of cellulose in $[C_2MIM]Cl$ under microwave irradiation.

For example by dissolving 6 wt.-% of cellulose in $[C_2MIM][Cl]$, the power could be varied between 60 and 140 Watt without any color change at 100 °C (Figure 4.11, A). By using a higher concentration of cellulose (up to 10 wt.-%), a color change was clearly visible at 140 and 160 °C (constant temperature/power). In addition, between both test series, a deeper

color was visible for the higher temperature (Figure 4.11, B and C). Not only the power/temperature/concentration settings are important, but also the ionic liquid used has an influence. In addition, the degradation was investigated for the microwave-assisted dissolution of cellulose. The results are shown in Table 4.4. Four samples were heated between 30 and 120 min at 100 °C. The degradation under microwave irradiation seems to be higher than under classical heating conditions. However, there is no real correlation between the DP values and the heating time. Therefore, we assumed that a “stirring problem” caused the higher degradation of cellulose in this case. In the “Initiator” microwave only magnetic stirring bars can be used.

Table 4.4 Comparison of the degree of polymerization of cellulose before and after dissolution in selected ionic liquids under microwave irradiation.

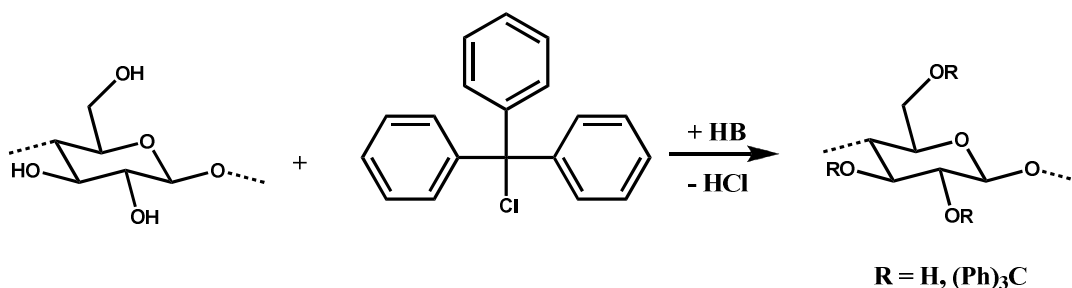
IL	Temperature [°C]	Time [min]	DP
Avicel PH-101	–	–	398 ^a
[C ₄ MIM][Cl]	100	30	172 ^b
	100	60	255 ^b
	100	90	300 ^b
	100	120	230 ^b

^a Before processing, ^b after regeneration.

4.3 Tritylation of cellulose in ionic liquid

Ionic liquids have been used for the homogenous derivation, like etherification³⁵ and esterification of cellulose, *e.g.* acetylation^{28,30} and carboxymethylation.²⁸ The acetylation of cellulose in ionic liquids can be performed catalyst-free, in a short time with a controllable degree of substitution (DS). Furthermore, the ionic liquid can be recycled. Another important reaction for the derivatization of cellulose is the tritylation, which is a well-known and common method for the regioselective protection of the 6-*O* position of the cellulose backbone. Trityl cellulose was first synthesized in 1924 by Helferich and Köster from generated cellulose under heterogeneous reaction conditions.³⁶ The free hydroxyl groups at 2- and 3-position can be subsequently substituted and afterwards the protecting group can be removed easily under mild conditions. The 6-*O*-protected trityl cellulose can be functionalized *e.g.* with methyl groups at the 2- and 3-positions to prepare uniform 2,3-substituted methoxy cellulose derivatives.³⁷ The 2,3-substituted methoxy cellulose synthesized under homogenous conditions has different properties in comparison to statistical functionalized derivatives.³⁸ Trityl cellulose was also used as the starting material to synthesize a hetero-substituted cellulose with carbamate substitutes at the 2- and 3-position and a benzoate substitute at the 6-position. This regioselective substituted cellulose was used as a chiral stationary phase for chromatography.³⁹ Finally, 4-methoxy trityl chlorides have also been used for different synthesis in the field of nucleotide and nucleoside chemistry.³⁷ The selectivity regarding the primary hydroxyl group can be adjusted by varying reaction time and ratio of trityl chloride per cellulose monomer unit.⁴⁰ To overcome the

problems concerning the synthesis under heterogeneous reaction conditions Camacho Gómez *et al.* demonstrated the synthesis of trityl and 4-methoxy substituted trityl cellulose under homogenous conditions in a DMA/LiCl solvent system, where cellulose is completely soluble.^{37,41,42} The homogenous dissolution of cellulose in ionic liquid can be used to introduce functionalities to the cellulose backbone. Therefore, the tritylation reaction was chosen as a model reaction, since the more reactive primary hydroxyl group can be protected selectively. The general reaction scheme of the tritylation is shown in Scheme 4.3.



Scheme 4.3 Schematic representation of the general synthesis of trityl cellulose.

4.3.1 Optimization of the tritylation of cellulose in ionic liquid

The homogenous tritylation of cellulose was performed utilizing ionic liquids as solvents and pyridine as base. To obtain a degree of substitution of 1 the reaction time, the ratio of trityl chloride and pyridine per cellulose monomer unit was varied. In addition, the recycling of the ionic liquid used for the tritylation of cellulose was investigated. However, the use of a base during the reaction complicates the recycling since the ionic liquid and the base are completely miscible.

Initial attempts to perform the tritylation in pure ionic liquid and in an ionic liquid/DMSO mixture were carried out at 100 °C for 24 hours. Unfortunately, only a black mixture was obtained and no product precipitated in methanol, ethanol, 2-propanol, acetone or diethyl ether, which indicates a decomposition of the cellulose. It is assumed that the black color is caused by a combination of the released hydrogen chloride and the decomposition products of cellulose.³⁶ Therefore, the tritylation was repeated with pyridine as a base for capturing the released hydrogen chloride. Unfortunately, again black reaction mixtures containing only small amounts of cellulose were obtained after 24 hours at 100 °C. However, after reducing the reaction time to 14 hours, the expected brown color was obtained.³⁶ Subsequently, the trityl cellulose was precipitated in methanol to isolate the product and was washed three times with methanol. For the resulting trityl cellulose a carbon content of 69.98% and a hydrogen content of 6.41% was found using elemental analysis, which corresponds to a degree of substitution of 0.71. The degree of substitution was also determined by ¹H NMR spectroscopy after perpropionylation,⁴³ giving a DS of 0.88. These values are comparable to the previously reported DS which was obtained when a DMA/LiCl mixture was used.³⁷ The elemental analysis also revealed that up to 0.5% of ionic liquid were still present. Figure 4.12 shows the IR spectrum of the trityl cellulose where the valence vibration for the OH group is visible at 3345 cm⁻¹. The asymmetric and

symmetric vibrations for the =CH and CH groups are between 3100 to 2800 cm^{-1} and above 1000 cm^{-1} . The peaks for the aromatic system are located at 1625, 1448 and 1490 cm^{-1} . The strong absorption peak for the C-O-C can be found at 1028 cm^{-1} . The structure was also proven by ^{13}C NMR spectroscopy (Figure 4.13). The peaks for the cellulose backbone are between 62.9 ppm and 101.5 ppm. Between 125.5 to 130.6 ppm and 144.2 ppm the signals for the aromatic carbon atoms are found. The quaternary C-7 atom is assigned at 86.5 ppm. The obtained spectrum matches literature data.^{25,26}

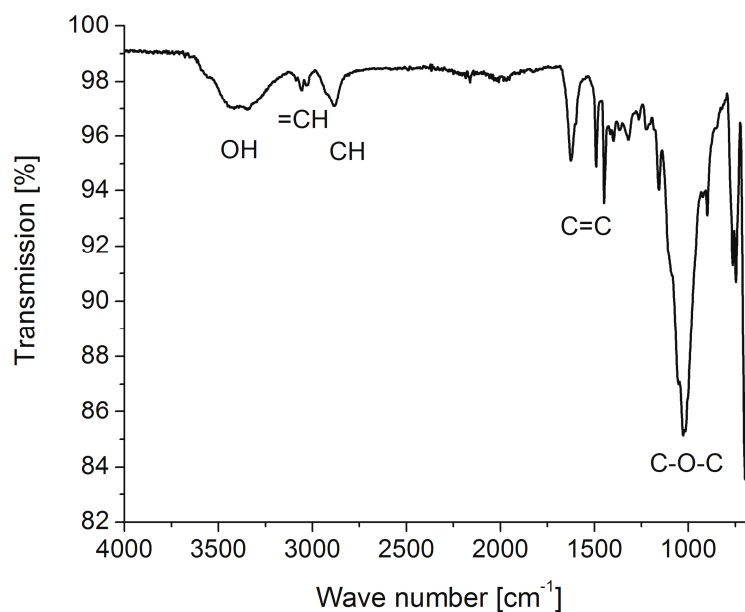


Figure 4.12 IR spectrum of trityl cellulose.

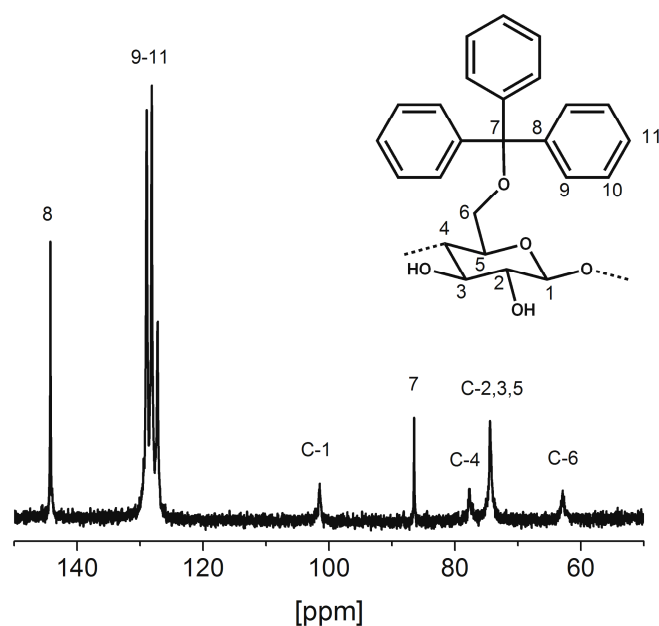


Figure 4.13 ^{13}C NMR spectrum of trityl cellulose (100 MHz, d_6 -DMSO, 80 °C).

In order to increase the degree of substitution larger amounts of trityl chloride were used (Table 4.5). In general, it is expected that the degree of substitution will increase with increasing ratios of trityl chloride to cellulose monomer unit. This trend was also observed for the synthesis of trityl cellulose using 1-butyl-3-methylimidazolium chloride as solvent. For a four and five fold excess of trityl chloride a DS of nearly 1 was obtained. Higher amounts of trityl chloride resulted in a DS of 1.22 and 1.30 for a six fold excess and a DS of 1.26 and 1.37 for a nine fold excess.

Table 4.5 *Tritylation of cellulose in 1-butyl-3-methylimidazolium chloride for 14 h at 100 °C.*

Molar equivalents		DS	
Cellulose : trityl chloride	Pyridine	EA ^a	NMR ^b
1 : 3	5	0.71	0.88
1 : 4	6.7	1.14	0.96
1 : 5	8.3	0.98	1.17
1 : 6	10	1.22	1.30
1 : 9	15	1.26	1.37

^a Determined by elemental analysis; ^b determined by ¹H NMR spectroscopy.

Further investigation on the influence of the amount of pyridine was carried out keeping the ratio of trityl chloride to cellulose at six molar equivalents. With 6.8 molar equivalents pyridine, trityl cellulose with a DS of ~0.8 was obtained (Table 4.6). In comparison with the results presented in Table 4.5 the lower excess of base might result in a slower reaction. When the molar equivalents of pyridine were increased to 8.4 or 10, the resulting DS was higher than 1 after 14 hours reaction time. When the reaction time was reduced from 14 to 5 hours, the degree of substitution was surprisingly roughly unchanged, when using 10 molar equivalents of pyridine. A DS of 1.22 and 1.30 (determined by elemental analysis and ¹H NMR spectroscopy, respectively) was obtained for 14 h and for 5 h a DS of 1.24 and 1.11 was found, indicating that it is not necessary to use such long reaction times. After 3 hours reaction time a DS of 1.09 and 0.97 was obtained. The reaction time was decreased even further to 1 hour and a DS of 0.91 and 0.96 was found. For the solvent system DMA/LiCl 24 hours are required to obtain trityl cellulose with a comparable degree of substitution.

Table 4.6 *Tritylation of cellulose with 6 fold excess of trityl chloride per cellulose monomer unit in 1-butyl-3-methylimidazolium chloride at 100 °C.*

Molar equivalents pyridine	Time [h]	DS ^a	DS ^b
6.8	14	0.76	0.83
8.4	14	1.49	1.32
10	14	1.22	1.30
10	5	1.24	1.11
10	3	1.09	0.97
10	1	0.91	0.96

^a Determined by elemental analysis; ^b determined by ¹H NMR spectroscopy.

4.3.2 Tritylation of cellulose in ionic liquid – recycling issues

As stated earlier, one of the benefits of ionic liquids is that they can be recycled and subsequently reused. Therefore, the methanol solution that contains the ionic liquid was collected after filtration of the cellulose and the methanol was evaporated. The ^1H NMR spectrum of the crude mixture is shown in Figure 4.16.

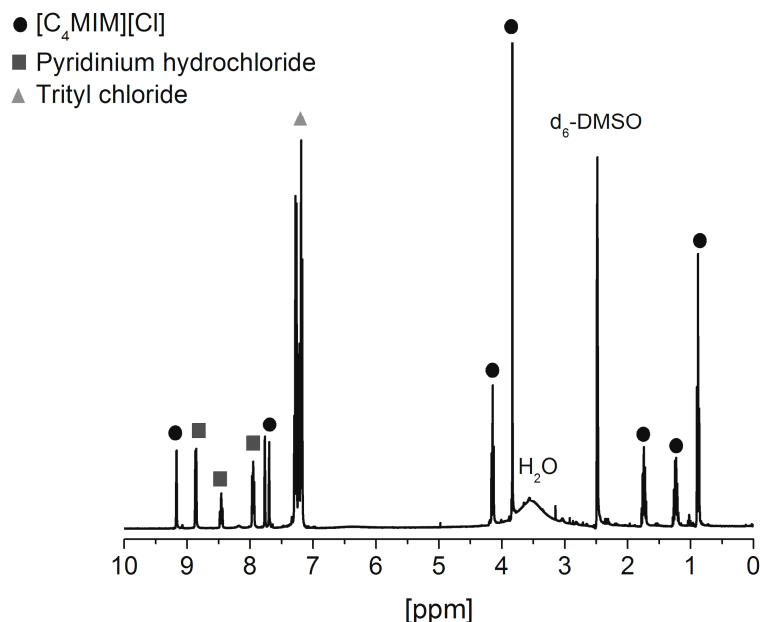


Figure 4.16 ^1H NMR spectrum of the crude ionic liquid after tritylation containing remaining trityl chloride and the side product pyridinium hydrochloride (400 MHz, d_6 -DMSO, 25 °C).

The peaks in the ^1H NMR spectrum are separated and can be assigned to the ionic liquid, the remaining tritylchloride and the pyridinium hydrochloride, produced as a result of the reaction of pyridine with the arising hydrogen chloride during the tritylation. In general, two ways are possible to remove the remaining trityl chloride. When the mixture is treated with water, trityl chloride is converted to triphenyl methanol, which is water insoluble and can easily be removed by filtration. The obtained triphenyl methanol was brownish and the water solution was yellowish after filtration, indicating that the main impurities were removed. A second possibility is the use of acetonitrile, where trityl chloride is not soluble. After the acetonitrile purification, dichloromethane was used in a second step to remove further insoluble impurities. After this procedure the dichloromethane solution was brownish, indicating the presence of remaining impurities. Therefore, the treatment with water seems to be the better alternative. Additionally, water is also preferable in contrast to volatile organic compounds, because it does not harm the environment. The ^1H NMR spectrum in Figure 4.17 clearly shows (ring) that the multiplet signal for trityl chloride between 7 and 7.5 ppm disappeared after applying the purification step described above. Just the signals for pyridinium hydrochloride and 1-butyl-3-methylimidazolium chloride were still visible. In a first attempt we tried to remove the remaining pyridinium hydrochloride by extraction with ethyl acetate using also acetonitrile and dichloromethane as co-solvents; however, this procedure was not efficient. After several extraction steps 30% of the pyridinium hydrochloride was still left. Extracting pyridinium

hydrochloride from 1-butyl-3-methylimidazolium chloride is not a viable purification route since a lot of extraction steps and associated solvents are required. In a second step, the ionic liquid and the remaining pyridinium hydrochloride were heated at 120 °C under vacuum overnight. Pyridinium hydrochloride could be removed by decomposition, but a dark colored ionic liquid was obtained after this treatment. The dark color of the ionic liquid proves its partial decomposition under these conditions. At lower temperatures, *e.g.* 70 °C, the pyridinium hydrochloride could not be removed. Obviously, pyridinium hydrochloride is too similar to 1-butyl-3-methylimidazolium chloride and can not be separated easily.

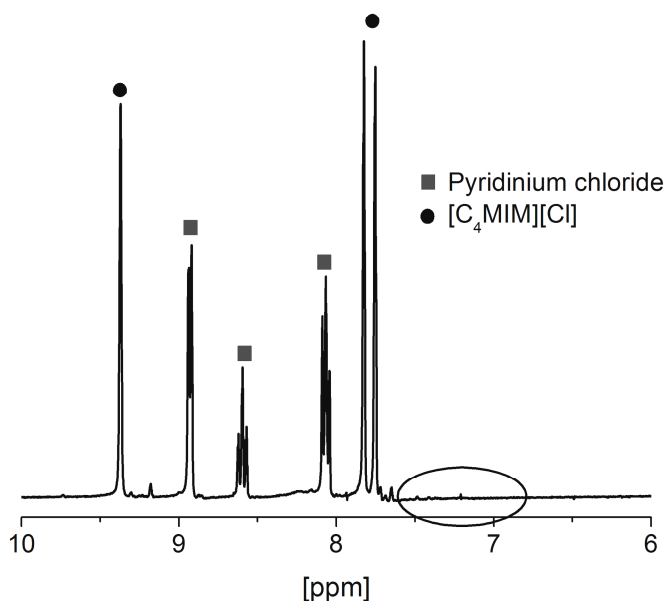


Figure 4.17 ^1H NMR spectrum of the crude ionic liquid after trityl chloride removal via water (ring: no aromatic signals detected anymore for the trityl chloride) containing the remaining side product pyridinium hydrochloride (400 MHz, d_6 -DMSO, 25 °C).

To circumvent this problem, we performed the tritylation using triethylamine instead of pyridine as a base. Triethylamine was reported to be less toxic than pyridine, easy to remove from the product mixtures and lead to trityl cellulose in good yield.⁴⁴ Triethylamine is not completely miscible with the ionic liquid and the reaction solution turned black after 1.5 hours. Nevertheless, trityl cellulose was precipitating in methanol and the degree of substitution of the white product was 0.98. Trityl chloride was removed from the ionic liquid by adding water and filtration as described before. Again, the main impurities were removed together with triphenyl methanol resulting in a yellow aqueous solution. After removal of the remaining water and triethylamine by evaporation, ethyl acetate was added to the mixture of 1-butyl-3-methylimidazolium chloride and triethylammonium chloride. Both are not soluble in the solvent, but the addition of ethyl acetate led to a mixture containing triethylammonium chloride as a solid, while 1-butyl-3-methylimidazolium chloride was present as a high viscous oil. The system was separated by filtration and washed with ethyl acetate. This procedure was repeated two times and resulted in nearly pure 1-butyl-3-methylimidazolium chloride containing only 0.5 wt.-% of triethylammonium chloride (determined by ^1H NMR spectroscopy, Figure 4.18).

The color of the recycled ionic liquid was only slightly yellow after this purification procedure, similar to the starting ionic liquid.

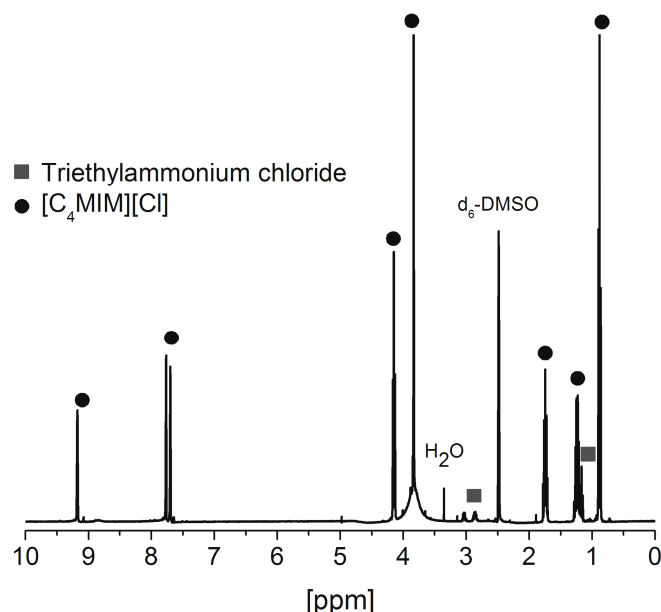


Figure 4.18 ^1H NMR spectrum of the recycled ionic liquid after tritylation with triethylamine (400 MHz, d_6 -DMSO, 25 °C).

4.3.3 Tritylation of cellulose in ionic liquid – comparison with other ionic liquids

As a result of the dissolution studies, it was found that $[\text{C}_2\text{MIM}][\text{Cl}]$, $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ and $[\text{AllylMIM}][\text{Cl}]$ are also promising candidates for the dissolution of cellulose. To show their applicability as a reaction medium in a homogeneous functionalization reaction, the tritylation of cellulose was performed by using pyridine as base according to the method described above. From elemental analysis a degree of substitution of 1.17 for $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ was obtained for the product after 2.5 h reaction time using a six fold excess of trityl chloride. This result was checked by ^1H NMR measurements of the acetylated and propionylated trityl cellulose samples showing DS values of 1.10 and 1.12, respectively. The completeness of the esterifications were proven by IR measurement. The elemental analysis also revealed that small amounts of ionic liquid (~0.4%) were still present after the purification procedure. In comparison to $[\text{C}_4\text{MIM}][\text{Cl}]$, $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ showed a higher DS after a shorter reaction time additionally to a lower degradation of the cellulose, while the tritylation in $[\text{C}_2\text{MIM}][\text{Cl}]$ resulted in tritylcellulose with lower DS than for the tritylation in $[\text{C}_4\text{MIM}][\text{Cl}]$. In addition, the ionic liquid $[\text{AllylMIM}][\text{Cl}]$ showed comparable results to $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$. The values obtained for $[\text{C}_4\text{MIM}][\text{Cl}]$, $[\text{C}_2\text{MIM}][\text{Cl}]$, $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ and $[\text{AllylMIM}][\text{Cl}]$ are summarized in Table 4.7. The obtained trityl cellulose samples were also characterized by size exclusion chromatography utilizing DMA/LiCl as eluent and polystyrene as standard. The SEC's of $[\text{C}_4\text{MIM}][\text{Cl}]$, $[\text{C}_2\text{MIM}][\text{Cl}]$ and $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ are depicted in Figure 4.19. The curves for $[\text{C}_4\text{MIM}][\text{Cl}]$ and $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ are shifted to higher molar masses, since the DS of these samples were

~ 1 , whereas the sample of $[\text{C}_2\text{MIM}][\text{Cl}]$ only showed a DS of ~ 0.5 . In general, the degradation of cellulose is lower in $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$ than in $[\text{C}_4\text{MIM}][\text{Cl}]$, which might be an explanation for the shift to higher molar masses for $[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$. Overall, the samples showed low molar mass shoulders resulting in a broad molar mass distribution ($\text{PDI} > 2$), except for $[\text{C}_2\text{MIM}][\text{Cl}]$ where the PDI was found to be 1.63 resulting in a higher calculated molar mass. In order to evaluate if the styrene calibration is suitable for the trityl cellulose samples, a viscosity detector was applied to obtain absolute molar mass values. Table 4.8 shows the measured values and it can be concluded, that in this case the values obtained by the RI detector and a polystyrene standard are comparable to the results obtained with the viscosity detector.

Table 4.7 DS values after tritylation of cellulose in different ionic liquids.

Ionic liquid	DS (EA)	DS (Acetylation)	DS (Propionylation)
$[\text{C}_4\text{MIM}][\text{Cl}]$	1.09	0.92	1.06
$[\text{C}_2\text{MIM}][\text{Cl}]$	0.51	0.63	0.83
$[\text{C}_2\text{MIM}][\text{Et}_2\text{PO}_4]$	1.17	1.10	1.12
$[\text{AllylMIM}][\text{Cl}]$	1.18	— ^a	— ^a

^a DS only determined by elemental analysis.

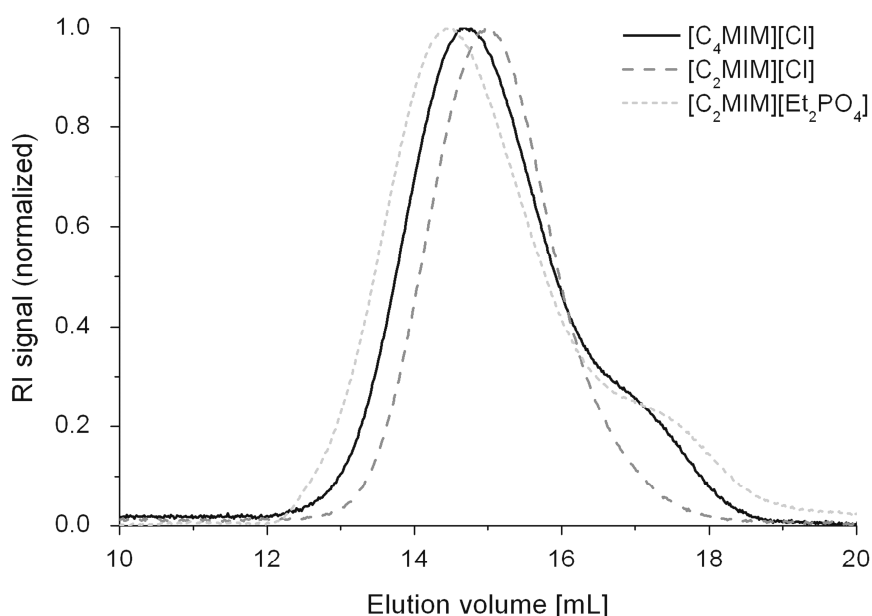


Figure 4.19 SEC curves (DMA/LiCl) of trityl cellulose synthesized in different ionic liquids for 2.5 h at 100 °C.

Table 4.8 Molar masses of trityl cellulose synthesized in different ionic liquids for 2.5 h at 100 °C determined by SEC (DMA/LiCl) utilizing a RI detector with PS calibration and a viscosity detector.

Ionic liquid	RI detector		Viscosity detector	
	M _n [g/mol]	PDI	M _v [g/mol]	PDI
[C ₄ MIM][Cl]	44,800	2.26	45,700	2.3
[C ₂ MIM][Cl]	52,800	1.63	60,300	1.61
[C ₂ MIM][Et ₂ PO ₄]	44,000	2.95	47,300	3.97
[AllylMIM][Cl]	29,400	2.02	30,400	2.24

4.4 Conclusions

Since ionic liquids became advantageous solvents for the dissolution of cellulose, they were used for a number of different reactions to process cellulose. To extend the range of suitable ionic liquids, we screened known but also new tailor-made ionic liquids. Savagely dried ionic liquids are indispensable for the dissolution of cellulose. 1-Alkyl-3-methylimidazolium based ionic liquids with alkyl chains from ethyl to decyl were investigated for their ability to dissolve cellulose. A strong odd-even effect of the alkyl chains on the solubility of cellulose in the ionic liquid was observed for chain lengths up to hexyl. The optimal even-numbered chain length was butyl (20 wt.-% cellulose) and the optimal odd-numbered chain length was heptyl (5 wt.-% cellulose). On the other hand, such an odd-even effect was not observed for the bromide containing ionic liquids, which might be due to the overall low solubility of cellulose in these ionic liquids. In case of branched alkyl side chains also the above described odd-even effect was found. The ionic liquids with 1-methylethyl and 1-methylbutyl side chain showed good cellulose dissolution, while the imidazolium based ionic liquid with 1-methylpropyl side chain did not dissolve cellulose at all. A possible explanation of these results is the different range of conformations for odd and even alkyl chains. The earlier found odd-even effect for the 1-alkyl-3-methylimidazolium chlorides was not observed for the bromides. Whereas all the even chlorides with shorter side chains showed good dissolving properties, mostly all other ionic liquids revealed less or no dissolution of cellulose. Only the ILs with chloride, acetate and phosphate counter anions showed good dissolving properties for cellulose. [C₂MIM][Et₂PO₄] was found to be a suitable candidate for the dissolution of cellulose because almost no color change and therefore a very low degradation of cellulose was observed. These visual results were supported by DP measurements from dissolved and precipitated cellulose showing a DP value of 378 after 2 h of heating when starting with a DS of 398 for the Avicel PH-101. In addition, the [C₂MIM][Et₂PO₄] melts at low temperatures just above room temperature (melting point could not be determined by DSC) which makes the handling easier. When using microwave irradiation for the dissolution of cellulose, a correlation of power, temperature, and concentration was found. By using low amounts of cellulose, the influence of the power introduced into the solution as well as the temperature is relatively low. With higher amounts of cellulose, a color

change indicating a degradation of the polymer backbone was clearly visible in the direction to higher concentrations.

For the homogeneous tritylation of cellulose in various imidazolium based ionic liquids, pyridine is required as a base to capture hydrogen chloride. The reaction time was reduced from 48 h to 3 h to obtain trityl cellulose with the desired DS of nearly 1.0 using a six fold excess of trityl chloride. When utilizing $[C_2MIM][Et_2PO_4]$, higher DS values could be reached in shorter reaction times in comparison with $[C_4MIM][Cl]$. Recycling of $[C_4MIM][Cl]$ was not achieved for the reaction with pyridine as base, since pyridinium hydrochloride and 1-butyl-3-methylimidazolium chloride seem to be too similar, which prevented separation by extraction. Pyridinium hydrochloride can be removed by decomposition, which resulted in a dark colored ionic liquid. As an alternative base, triethylamine was used instead of pyridine for the tritylation reaction. First experiments were carried out obtaining trityl cellulose with a DS of 0.98 after 1.5 hours. Furthermore, 1-butyl-3-methylimidazolium chloride could be successfully recycled (although 0.5 wt.-% triethylammonium chloride remained). After this promising preliminary result, future work will be done to improve the efficiency of the recycling procedure, for example by increasing the temperature during the filtration process to reduce the viscosity of the ionic liquid. We will also test different bases, which might allow an easier purification due to different solubilities to simplify the recycling process.

4.5 Experimental details

Materials

Avicel PH-101 cellulose (Fluka) and pyridine (Biosolve) were purchased commercially. The ionic liquids 1-ethyl-3-ethylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride, 1-octyl-3-methylimidazolium chloride, 1-decyl-3-methylimidazolium chloride, trihexyl(tetradecyl) phosphonium chloride and 1-ethyl-3-methylimidazolium ethylsulfate were donated by Merck. The ionic liquids 1-butyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium tosylate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-ethyl-3-methylimidazolium (dicyan)amide and 1-butyl-3-methylimidazolium trifluoromethanesulfonate were donated by Solvent Innovation. All other ionic liquids were synthesized according to Chapter 2 using microwave reactors (Emrys Liberator and Initiator, Biotage, Sweden, and Swave, Chemspeed, Switzerland) and anion exchange reactions.⁴⁵⁻⁵⁰ Triphenylchloromethane (Fluka), Avicel® PH-101 cellulose (Fluka), pyridine (Biosolve) and triethylamine (Merck) were purchased commercially. The ionic liquids 1-ethyl-3-methylimidazolium chloride, 1-hexyl-3-methylimidazolium chloride, 1-octyl-3-methylimidazolium chloride and 1-decyl-3-methylimidazolium chloride were donated by Merck. The Avicel cellulose was dried for 12 h at 100 °C under reduced pressure (10 mbar) before use.

1H NMR and ^{13}C NMR spectroscopy were recorded on a Varian Mercury spectrometer using a frequency of 400 MHz at 80 °C or on a Varian Gemini spectrometer at a frequency of 300 MHz at 100 °C. Chemical shifts are given in ppm downfield from TMS. IR spectra were recorded on a

Perkin Elmer 1600 FT-IR spectrometer. Elemental analyses were carried out on a EuroVector EuroEA3000 elemental analyzer for CHNS-O.

Dissolving of cellulose in ionic liquids

The ionic liquid was preheated at 100 °C and then the cellulose was added. This mixture was stirred with a magnetic stirrer at 100 °C for a maximum of 2 hours. The solubility of cellulose in the ionic liquid was checked visually.

Dissolving of cellulose in ionic liquids under microwave irradiation

The ionic liquid and cellulose was filled into a microwave vials (0.5–2 mL and 2–5 mL vials) and heated under microwave irradiation.

Degradation experiments

The examination for the degradation of cellulose was performed in an automated Chemspeed AutoPlant 100 robot (Augst, Switzerland) equipped with internal anchor stirrers to ensure efficient heating, stirring and cooling. Again, the cellulose was filled into the preheated ionic liquid and heated for 2.5 hours. Then dimethylsulfoxide was added (approximately 15 mL) and the dissolved cellulose was precipitated in methanol (500 mL).

The intrinsic viscosities of the cellulose samples were determined by capillary viscosimetry according to DIN 54270 applying copper(II)-ethylenediamine (Cuen) as solvent.²⁹ From the intrinsic viscosities, the DP can be calculated. A LAUDA PVS 1/4 with four measuring stands and an automatic cleaning set-up was used as a viscosimeter. It has an automatic flow time measurement and online cleaning. A maximum temperature stability (variation < 0.01 °C) over a large temperature range (–20 °C up to 200 °C) is possible. The system was fitted with a micro-Ubbelohde capillary with a filling volume of 2–3 mL and a total length of 290 mm (accuracy of $\pm 0.5\%$, calibrated for absolute and automatic measurements). The measurements were performed at 20 °C.

Representative synthesis of trityl cellulose

A mixture of cellulose (1 g, 6.15 mmol), 1-butyl-3-methylimidazolium chloride (9 g, 51.53 mmol), trityl chloride (5.14 to 15.4 g, 18.5 to 55.5 mmol) and 2.5 to 7 mL pyridine was heated in an oil bath to 100 °C and kept at this temperature. The reaction mixture was precipitated in 200 mL methanol. The trityl cellulose was filtered and washed several times with methanol. The polymer was dissolved in 200 mL THF and re-precipitated in 700 mL methanol. After filtration and washing several times with methanol the product was dried at 40 °C in vacuum.

Yield: 70%

¹³C NMR (100 MHz, d₆-DMSO, 80 °C): δ = 62.9 (C-6), 72.0–76.3 (C-2,3,5), 77.7 (C-4), 86.5 (7) 101.5 (C-1), 125.5–130.6 (9–11), 144.2 (8). IR (neat): 3345 (OH), 3056 (=C-H), 2886 (CH), 1625, 1490, 1448 (C-C_{arom}), 1156 (C-O-C), 1028 (C-O), 698 (=C-H) cm⁻¹. (C₂₅H₂₄O₅)_n (404.5)_n: Calcd. C 74.24, H 5.98, O 19.78, DS=1; Found C 69.98, H 6.41, DS=0.71.

Determination of DS by ^1H NMR spectroscopy

Propionylation

The propionylation of trityl cellulose was performed according to literature (263 mg, $\text{DS}_{\text{Trityl}} = 1.12$).⁴³

^1H NMR (400 MHz, CD_2Cl_2 , 25 °C) $\delta = 0.20\text{--}1.42$ (CH_3), $1.92\text{--}2.74$ (CH_2), $2.76\text{--}5.10$ ($\text{H}_{\text{Cellulose}}$), $6.35\text{--}8.69$ (H_{Trityl}). FT-IR(neat): 3059 (=CH), 3034, 2978 (CH), 2942, 2882 (CH), 1757, 1724 (CO_{Ester}), 1651, 1599, 1493, 1449 (C-C_{arom}), 1323, 1275, 1155 (C-O-C), 1078 (C-O), 1040, 764, 748, 706 (CH), 633 cm^{-1} .

Acetylation

For the acetylation, a modified procedure of the propionylation was used: A mixture of pyridine (6 mL, 74.2 mmol), acetic acid anhydride (6 mL, 63.5 mmol) and 4-(dimethylamino)pyridine (50 mg) was added to the trityl cellulose (225 mg, 0.56 mmol). The reaction mixture was heated for 24 h at 80 °C. After cooling to room temperature the product was precipitated in a ethanol/hexane mixture (1:2), filtered-off, washed with ethanol and dried in a vacuum oven at 45 °C (307 mg, $\text{DS}_{\text{Trityl}} = 1.10$).

^1H NMR: (400 MHz, CD_2Cl_2 , 25 °C) $\delta = 0.38\text{--}1.37$ (CH_3), $2.52\text{--}5.10$ ($\text{H}_{\text{Cellulose}}$), $6.18\text{--}8.33$ (H_{Trityl}). FT-IR: 3059 (=CH), 3032, 2938, 2882 (CH), 1761 (CO_{Ester}), 1665, 1491, 1449 (C-C_{arom}), 1370, 1221 (C-O-C), 1109 (C-O), 1063, 764, 748, 706 (CH), 635 cm^{-1} .

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Chapter 5

Synthesis, characterization, and properties of 4,4-imidazolium ionenes

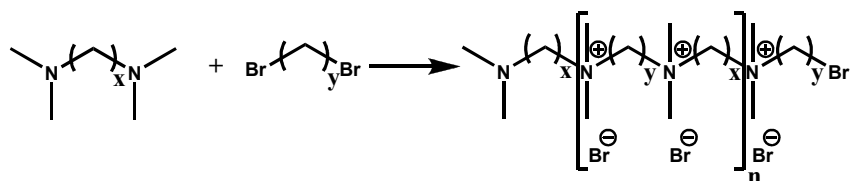
Abstract

New 4,4-imidazolium ionenes were synthesized under microwave irradiation. The polymerization times could be decreased from 24 to 1 h as a result of the applied elevated temperatures above the boiling points of the applied solvents. Moreover, higher molar masses were found for the polymers synthesized under microwave irradiation. Furthermore, the properties of the synthesized 4,4-imidazolium ionenes, such as thermal behavior, solubility behavior, water uptake and conductivity were investigated as well. The 4,4-imidazolium ionenes revealed a high water uptake and can be classified as humidity absorber.

Parts of this chapter will be published: T. Erdmenger, J. Vitz, U. S. Schubert, in preparation.

5.1 Introduction

Polyionenes, or ionenes, are ion-containing polymers that contain quaternary nitrogen atoms in the macromolecular main chain. In 1933, Gibbs and co-workers were the first to report the synthesis of ionenes from dimethylamino-*n*-alkyl halides *via* a step-growth polymerization process.¹ In general, step-growth polymerization is a process that involves a chemical reaction between multifunctional monomers. In case of ionenes, the polymerization between an alkyl dihalide and a ditertiary amine according to the Menshutkin reaction takes place, as depicted in Scheme 5.1.²



Scheme 5.1 Schematic representation of the synthesis of *x,y*-ammonium ionenes.

In a step-growth reaction, the growing chains may react with each other to form longer chains. This applies to chains of all lengths. Thus, a monomer or dimer may react in just the same way as a chain hundreds of monomer units long. A wide range of ionenes can be synthesized due to a large variety of ditertiary amines and dihalides.³⁻⁶ The polymer is commonly named from the number of methylene units, which correspond to the ditertiary amine and dihalide monomers, respectively (*x,y*-ionene).⁵

Ionenes are known to possess excellent mechanical properties and typically exhibit moduli and glass transition temperatures (T_g) which are significantly higher than for their nonionic counterparts.⁷⁻⁹ An ion-containing polymer has a higher apparent molar mass and possesses similar mechanical properties and thermal transitions as nonionic polymers of higher molar mass. Reversible cross-links, formed from ionic aggregates, allow an easier melt processability, higher melt stability, and lower melt viscosity than nonionic polymers.

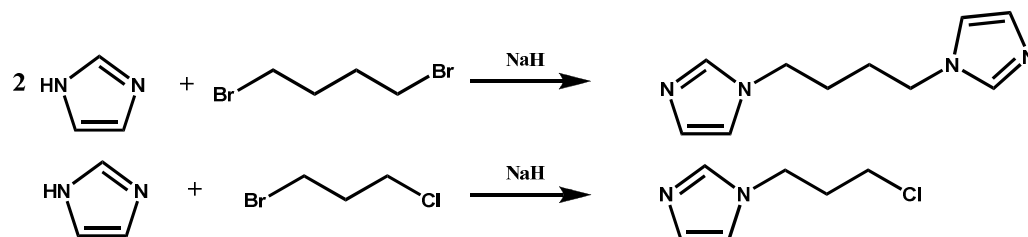
In addition, ionenes offer many potential applications in emerging biomedical fields, *e.g.* DNA delivery or antimicrobial applications.^{10,11} The concentration, charge density, hydrophobicity, and molar mass dictate whether an ionene is suitable for DNA delivery or antimicrobial applications.^{12,13} Recently, imidazolium ionenes were utilized as quasi-solid electrolytes for solar cells¹⁴ and as solid support for peptide synthesis.¹⁵

5.2 Synthesis and characterization of 4,4-imidazolium ionenes

5.2.1 Monomer synthesis

In order to obtain 1,4-di(1*H*-imidazol-1-yl)butane as a monomer 1*H*-imidazole was activated by sodium hydride and reacted with 1,4-dibromobutane according to Scheme 5.2 (top). Nearly full conversion was obtained after 2 days at 60 °C (determined by ¹H NMR spectroscopy). The crude reaction mixture was filtered and purified by precipitation into water. The monomer is

hygroscopic and was freeze dried in order to remove remaining water for further characterization, *e.g.* elemental analysis. MALDI-TOF-MS was measured without using any matrix (LDI-TOF-MS), since the imidazole ring is able to absorb the laser energy, avoiding possible interferences with the matrix. The LDI-TOF-MS spectrum in Figure 5.1 only showed the desired mass peak of the monomer (190 g/mol) charged by a proton (191 g/mol). In addition, the isotopic patterning is in good agreement with the calculated values (less than 0.1 g/mol difference). Furthermore, the ^1H NMR spectrum and the elemental analysis values were consistent with the desired product.



Scheme 5.2 Schematic representation of the general synthesis of 1,4-di(1H-imidazol-1-yl)butane (AA monomer, top) and of 1-(3-chloropropyl)-1H-imidazole (AB monomer, bottom).

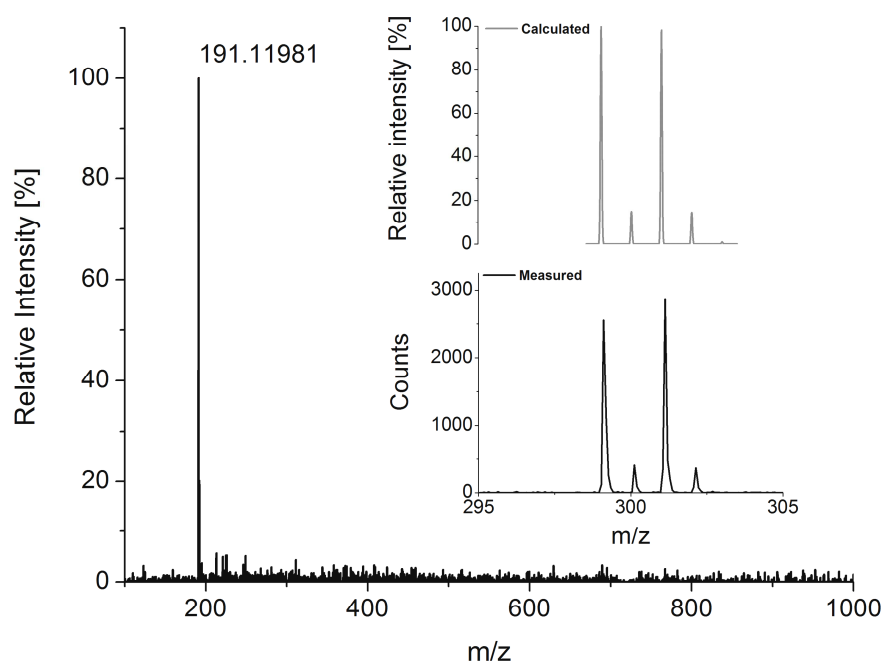
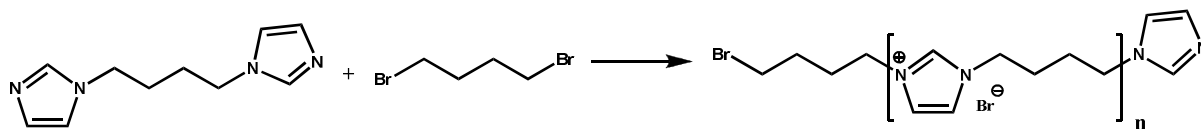


Figure 5.1 LDI-TOF-MS spectrum of 1,4-di(1H-imidazol-1-yl)butane.

The same approach can be used to synthesize AB monomers (*e.g.* 1-(3-chloropropyl)-1H-imidazole) utilizing bifunctional alkyl halides (*e.g.* 1-bromo-3-chloropropane) with a bromo and a chloro end group (Scheme 5.2, bottom). In this case, the more reactive bromo end group reacts with the imidazole, resulting in an alkylated imidazole with a chloro end group in the alkyl side chain. Unfortunately, the number of commercial available hetero dihalide compounds is limited. Therefore, this second route was not further explored.

5.2.2 Step growth polymerization

The synthesized 1,4-di(1*H*-imidazol-1-yl)butane was polymerized with an equimolar amount of 1,4-dibromobutane for 15 h at 60 °C to obtain the desired polymer poly(4,4-imidazolium bromide) as depicted in Scheme 5.3.



Scheme 5.3 Schematic representation of the polymerization of poly(4,4-imidazolium bromide) with equimolar amount of monomers.

The resulting polymer was only soluble in methanol and water at room temperature. In order to measure size exclusion chromatography (SEC) on the available systems, polymer solubility in dimethylformamide, dimethylacetamide or chloroform was required. From literature it is known that the anion of poly(ionic liquid)s (synthesized *via* free radical polymerization) strongly influences the solubility of the polymer and it was reported that hexafluorophosphate containing poly(ionic liquid)s were soluble in dimethylformamide.¹⁶ Therefore, the anions of poly(4,4-imidazolium bromide) were exchanged to hexafluorophosphate by adding sodium hexafluorophosphate to an aqueous solution of poly(4,4-imidazolium bromide). The polymers were precipitating from aqueous solution, since poly(4,4-imidazolium hexafluorophosphate)s are insoluble in water, while being soluble in acetone and dimethylformamide. The measured SEC trace is shown in Figure 5.2.

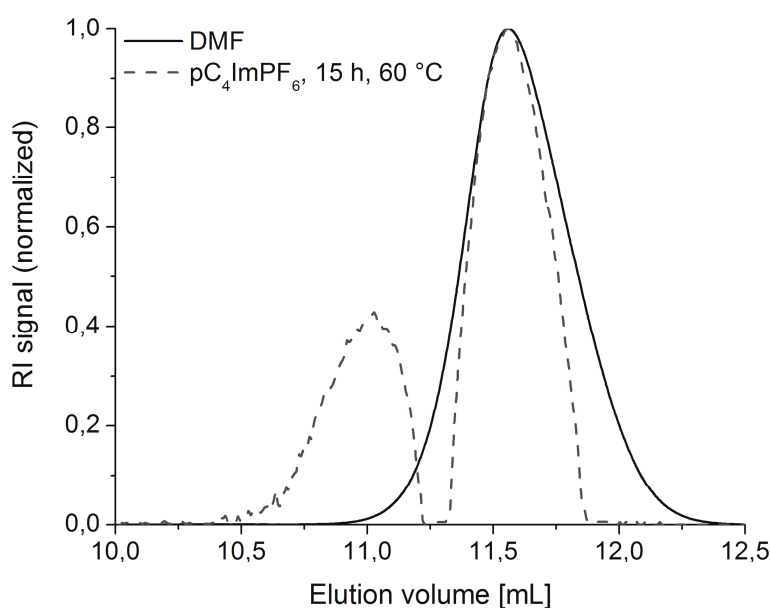
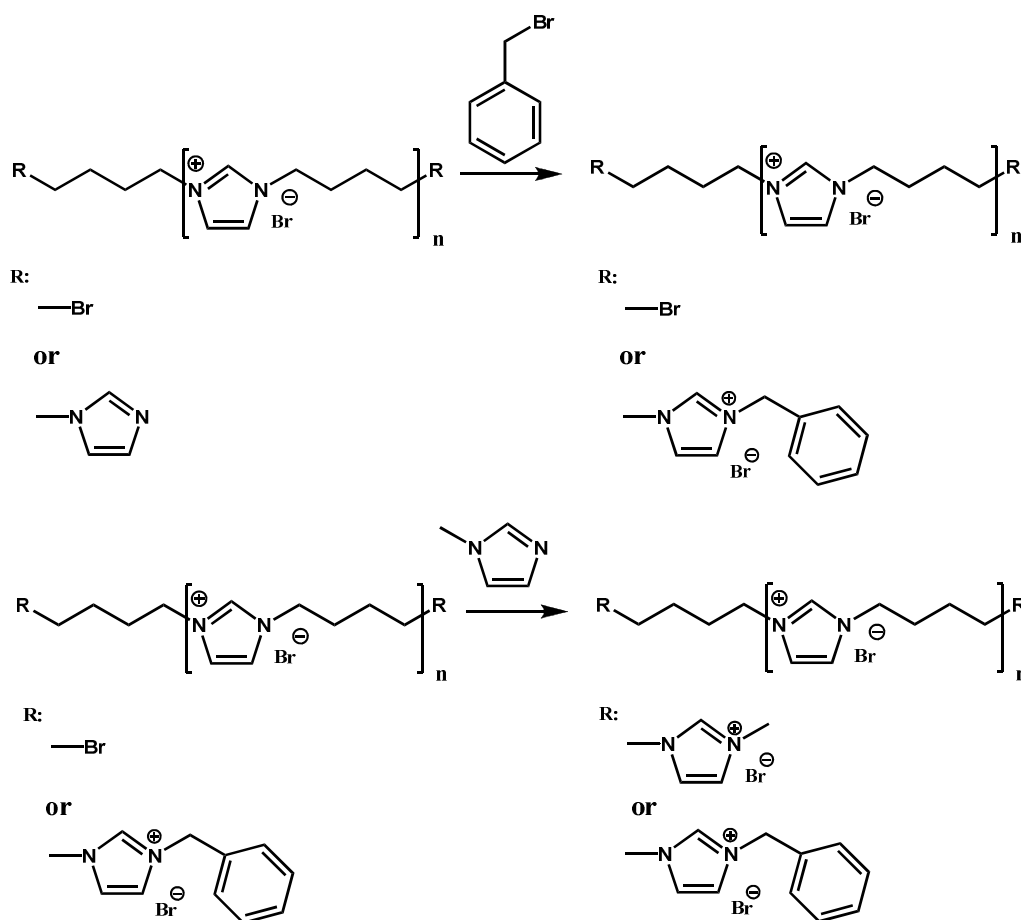


Figure 5.2 SEC curves of the eluent and poly(4,4-imidazolium hexafluorophosphate) polymerized for 15 h at 60 °C.

The obtained SEC curves were very noisy, maybe caused by the relative similar refractive indices of dimethylformamide and the ionenes. The peak at higher molar mass belongs to the polymer and different calibrations (PEG, PMMA and PS) were applied to calculate the molar mass and molar mass distribution (Table 5.1). As expected, all three calibrations resulted in different molar masses, since SEC is a relative technique. In order to find out which calibration is most suitable for the poly(4,4-imidazolium hexafluorophosphate), the molar mass was estimated by ^1H NMR spectroscopy. Therefore, both possible end groups, namely imidazole and the bromo end group, were functionalized using benzyl bromide and 1-methylimidazole, respectively as depicted in Scheme 5.4.

Table 5.1 Molar mass values for poly(4,4-imidazolium hexafluorophosphate) obtained utilizing different calibrations for SEC analysis.

Calibration	M_n [g/mol]	M_w [g/mol]	PDI
PEG	700	800	1.11
PMMA	1,900	2,200	1.12
PS	8,000	8,400	1.04



Scheme 5.4 Schematic representation of the end group functionalization of poly(4,4-imidazolium bromide) polymerized with equimolar amounts of monomers.

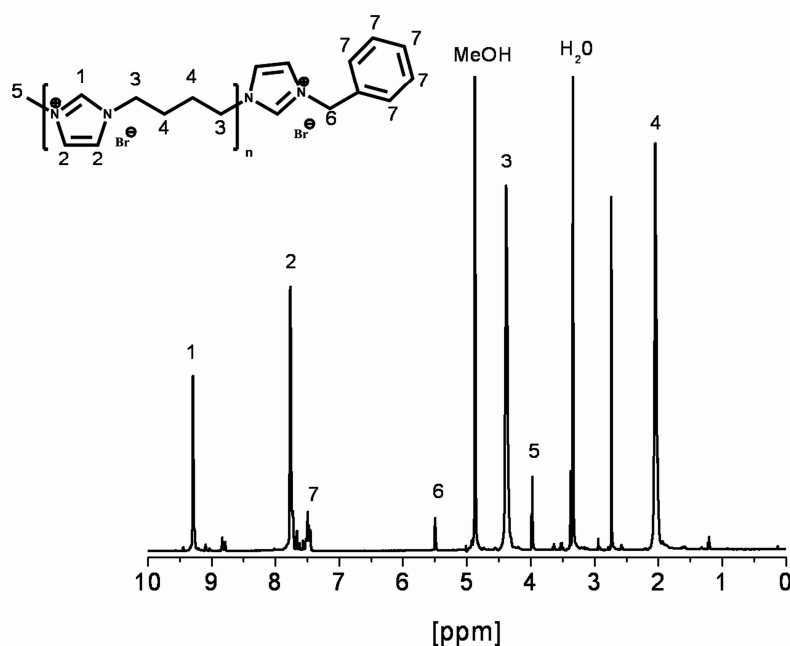


Figure 5.3 ^1H NMR spectrum of poly(4,4-imidazolium bromide) (polymerized for 15 h at 60 °C in MeOH/DMF) functionalized with 1-methylimidazole and benzylbromide in .

The ratio of the methyl group and benzyl group was found to be 1 to 1 as expected for an equimolar ratio of 1,4-di(1*H*-imidazol-1-yl)butane and 1,4-dibromobutane. The number average molar mass calculated from the ^1H NMR spectrum in Figure 5.3 was 3,000 g/mol before and 3,900 g/mol after the anion exchange, which is equal to an average of 15 imidazolium rings per polymer chain. Thus, no SEC calibration was matching to the number average molar masses obtained by ^1H NMR spectroscopy. The values obtained were larger than those with PEG or PMMA calibration and lower than the PS calibration. In general, the molar masses obtained by SEC are overestimated compared to neutral polymer standards, because the ionenes should be in a stretched conformation in a polar solvent as a result of their charges.²⁴ In addition, the M_n values obtained by ^1H NMR spectroscopy might be overestimated because of the possible presence of cycles. When the reaction time of the polymerization was increased from 15 to 24 h, only macrocycles were obtained, since no endgroups could be detected by ^1H NMR spectroscopy after end group functionalization. This formation of macrocycles is typical for a step growth polymerization at high conversions.¹⁷ Ring formation was also obtained by performing the polymerization at 120 °C for 1 h under microwave irradiation. From literature it is known that the molar mass can be controlled by either a nonstoichiometric imbalance of the bifunctional monomers or the utilization of monofunctional reagents as chain stoppers.^{18,19} Both approaches were explored in order to avoid the formation of macrocycles and to control the molar masses.

5.2.2.1 Application of monomer imbalance

In the first case, an excess of 1,4-di(1*H*-imidazol-1-yl)butane (1.03, 1.05 and 1.10 mol equivalent, respectively) was used during the polymerization of poly(4,4-imidazolium bromide). In general, ionenes with two imidazole end groups should be obtained, and higher ratios of 1,4-

di(1*H*-imidazol-1-yl)butane should result in ionenes with lower molar mass as depicted in Table 5.2. The expected molar mass was calculated using the Equations 5.1 to 5.3.

$$r = \frac{N_A}{N_B} \quad \text{Equation 5.1}$$

$$\overline{X}_n = \frac{1+r}{1-r} \quad \text{Equation 5.2}$$

$$\overline{M}_n = M_0 \times \overline{X}_n \quad \text{Equation 5.2}$$

N_A moles of functional group A

N_B moles of functional group B

$r < 1$

M_0 molar mass (monomer A + monomer B)

Table 5.2 Expected molar mass for the polymerization of poly(4,4-imidazolium bromide) utilizing monomer imbalance.

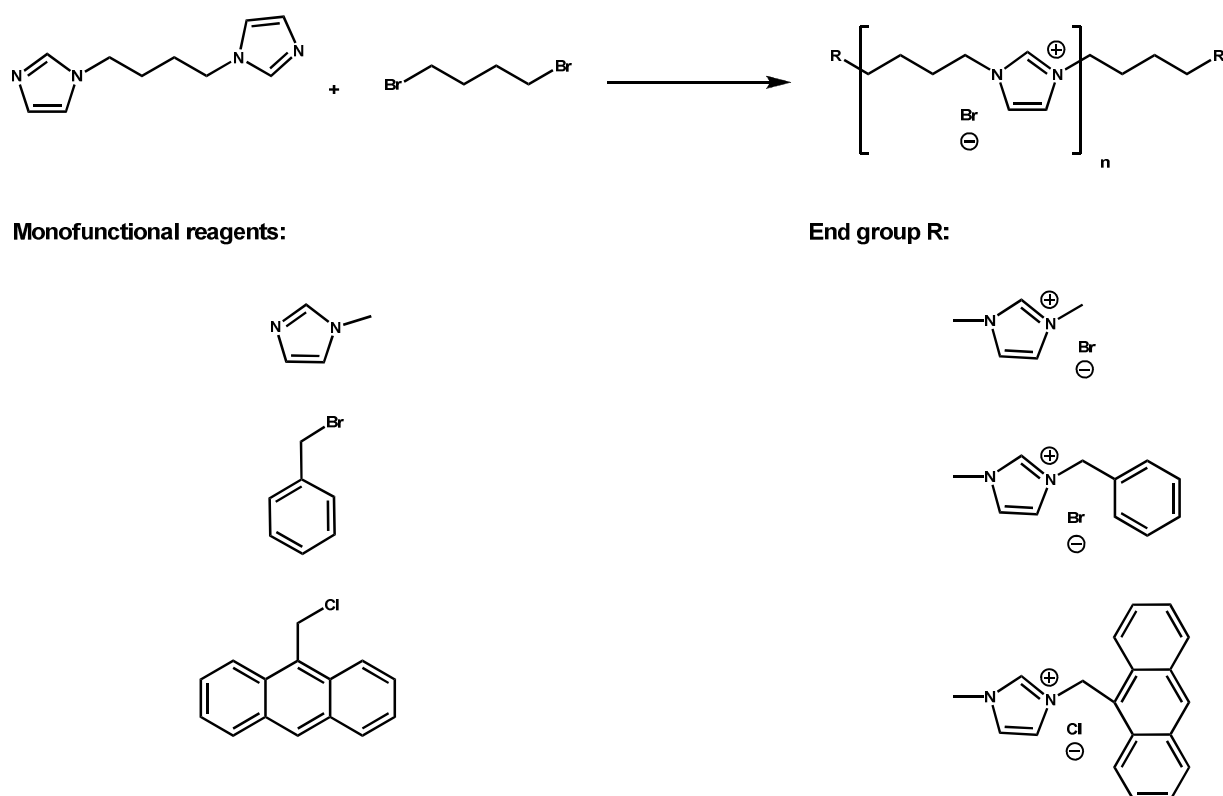
[Dibromide]/[Diimidazole]	M_n (calcd.) [g/mol]
1/1.03	27,600
1/1.05	16,500
1/1.10	8,500

The polymerizations were conducted for 1 h at 120 °C under microwave irradiation. In all cases, no end groups could be detected by ^1H NMR spectroscopy. Therefore, the polymers were treated with benzyl bromide in order to functionalize the imidazole endgroups. But also in this case, neither benzyl groups could be detected by ^1H NMR spectroscopy, nor the methyl group when treated with 1-methylimidazole. It seems like that only macrocycles were formed in all cases, since no end groups could be detected. Similar results were obtained for the polymerization in an oilbath (1 d, 80 °C). A possible explanation for the ring formation might be a too low monomer concentration (1 M) favoring ring formation. Therefore, the polymerization was conducted at a concentration of 4 M, but also in this case only macrocycles were formed. Up to know we do not have an explanation, why obviously only cycles are formed.

5.2.2.2 Application of monofunctional reagents

In the second case, different monofunctional reagents, namely benzyl bromide, 1-methylimidazole and 9-(chloromethyl)anthracene, were utilized in different concentrations in order to control the molar mass as depicted in Scheme 5.5. For the first trials, 10 mol% of the above mentioned monofunctional reagents were used during the microwave-assisted polymerizations (conducted for 1 h at 120 °C). In all cases a molar mass of 8,100 g/mol is expected assuming that no cycles are formed during the polymerization. The molar mass was estimated by ^1H NMR spectroscopy utilizing either the signals of the benzyl or of the methyl

group attached to the imidazolium ring. These signals are shifted to lower magnetic fields in comparison to the uncharged reagents. In general, the molar masses obtained by ^1H NMR spectroscopy might be overestimated due to the possible formation of cycles during the polymerization. The number average molar masses obtained by ^1H NMR spectroscopy are depicted in Table 5.3, showing that rather different molar masses were obtained for the different chain stoppers, which might be related to their different reactivity in comparison to the monomers, or to a limited solubility in the applied solvent (anthracene is insoluble in MeOH at room temperature). In this regard, the molar mass of the 4,4-imidazolium ionene obtained by utilizing benzyl bromide as chain stopper was in agreement with the expected molar mass. In addition, the 4,4-imidazolium ionenes were characterized by IR spectroscopy showing similar spectra as compared the synthesized ionic liquids in Chapter 2. Moreover the values obtained for elemental analysis were fitting rather well to the expected values.



Scheme 5.5 Schematic representation of the utilized monofunctional reagents during the polymerization of 4,4'-imidazolium ionenes and their resulting end groups.

Table 5.3 Expected and obtained molar masses for the polymerization of poly(4,4'-imidazolium bromide) utilizing different chain stoppers.

Chain stopper	M_n (calcd.) [g/mol]	M_n (^1H NMR) [g/mol]
1-Methylimidazole	9,700	4 700
Benzyl bromide	9,800	6 400
9-(Chloromethyl)anthracene	9,900	14 200

In case of 9-(chloromethyl)anthracene as chain stopper, different concentrations of the monofunctional reagent were applied during the polymerization of 1,4-di(1*H*-imidazol-1-yl)butane. In general, lower concentrations of chain stopper should lead to polymers with higher molar mass. As expected, the molar masses found by ^1H NMR spectroscopy were increasing with decreasing the chain stopper concentration (Table 5.4). As already described above, the molar masses found were much higher than the calculated molar masses, which is most likely due to the limited solubility of 9-(chloromethyl)anthracene in the reaction mixture. The polymers obtained were purified by precipitation into diethyl ether and the yields obtained were rather high (71 to 92%).

Table 5.4 Expected and obtained molar masses for the polymerization of poly(4,4-imidazolium bromide) utilizing 9-(chloromethyl)anthracene as chain stopper.

9-(Chloromethyl)anthracene [mol%]	M_n (calcd.) [g/mol]	M_n (^1H NMR) [g/mol]	Yield [%]
3	28,000	51,700	71
5	16,900	31,500	87
10	9,900	14,200	92

The polymers were also characterized by SEC after an anion exchange to PF_6^- . In this case, the PDA detector of the SEC system could be used, since 9-(chloromethyl)anthracene has a strong absorption at 376 nm. Figure 5.4 shows that the absorption peak for the 9-(chloromethyl)anthracene is shifting towards lower retention times after polymerization demonstrating that the rather bulky chain stopper is attached to the polymer chain, which was also supported by the above described signal shift in the ^1H NMR spectrum. Unfortunately, no separation of the different molar masses was achieved by the SEC system. Furthermore, the polymerizations were conducted under microwave irradiation for 1 h at 120 °C and in an oil bath for 24 h at 80 °C utilizing different benzyl bromide concentrations (Table 5.5). In both cases, the molar masses increased with a decreasing benzyl bromide concentration. In general, the molar masses obtained under microwave irradiation were found to be higher than for the polymerizations performed in the oil bath. For the polymerizations performed in the oil bath, the values for the molar mass were in a better agreement with the theoretical values compared to the experiments performed under microwave irradiation. It seems that at higher temperatures the ring formation is more favored resulting in higher molar masses as found by ^1H NMR spectroscopy. Additionally, the viscosity of the ionenes was investigated by capillary viscometry utilizing 0.2 M sodium bromide to suppress the polyelectrolyte effect (increasing viscosity with decreasing concentration). The viscosity values obtained (Table 5.5) were slightly decreasing with higher amounts of benzyl bromide, but these changes were not in the same order of magnitude as compared to the calculated and obtained molar masses (estimated by ^1H NMR spectroscopy). Therefore, the samples were also investigated by analytical ultracentrifugation (AUC), which is an absolute method for determination of molar masses, since no calibration standards are needed (Table 5.5). However, the specific partial volume of the compound has to be known. Significant differences in the molar masses between AUC and ^1H NMR

spectroscopy were found, which can only be explained by ring formation at a large scale. It seems that for the applied monomers the formation of cycles is favored. The use of chain stoppers leads to ionenes existing as a mixture of rings and linear chains (both with similar molar mass). For these cases, the amount of linear chains could be estimated to be in the range of 7 to 18% (content of linear chains increases with the amount of benzyl bromide) corresponding to a ring formation between 82 and 93%, respectively.

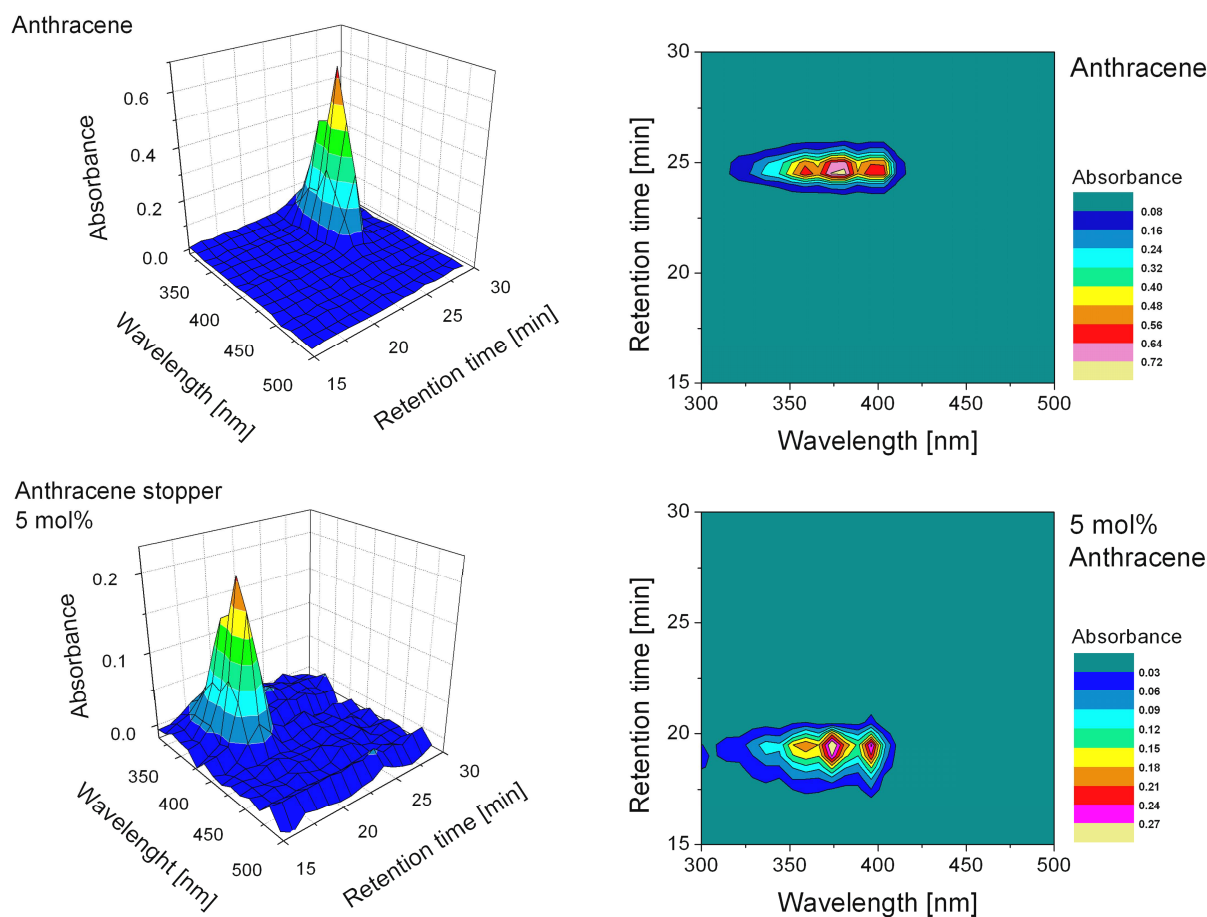


Figure 5.4 SEC measurements of anthracene (top) and poly(4,4-imidazolium hexafluorophosphate) with 5 mol% -(chloromethyl)anthracene stopper (bottom) utilizing a PDA detector.

Table 5.5 Expected and obtained molar masses for the polymerization of poly(4,4-imidazolium bromide) under microwave irradiation (1 h, 120 °C) and in an oil bath (24 h, 80 °C) utilizing benzyl bromide as chain stopper.

Benzyl bromide [mol%]	M_n (calcd.) [g/mol]	M_n (^1H NMR) (microwave) [g/mol]	M_n (^1H NMR) (oil bath) [g/mol]	η (oil bath) [cm ³ /g]	M_{sf} (AUC) (oil bath) [g/mol]
2	40,200	60,600	45,200	11.1	3,100
4	21,000	24,400	22,500	10.2	2,500
6	13,800	24,000	18,700	12.7	2,100
8	10,600	18,700	13,500	9.9	1,800
10	9,500	16,500	11,100	6.5	2,000

Moreover, poly(4,4-imidazolium chloride) was synthesized under microwave irradiation utilizing 1,4-dichlorobutane and benzyl bromide (10 mol%) as chain stopper. In this case a longer reaction time was required, since 1,4-dichlorobutane is less reactive than 1,4-dibromobutane. The GC measurements revealed that nearly all 1,4-dichlorobutane was consumed after 2 h at 120 °C. After an additional hour at 120 °C, no peak could be detected by GC anymore. The number average molar mass found by ^1H NMR spectroscopy (5,700 g/mol) was corresponding well to the calculated molar mass (6,300 g/mol). The same approach was used for the polymerization of 1-(3-chloropropyl)-1*H*-imidazole. In this case, 5 mol% benzyl bromide were used as chain stopper and a polymer with a M_n of 2,300 g/mol (determined by ^1H NMR spectroscopy) was obtained, which is close to the calculated molar mass of 2,900 g/mol.

5.3 Properties

The properties of the synthesized 4,4-imidazolium ionenes, such as thermal behavior, solubility behavior, water uptake and conductivity were investigated in order to investigate possible applications. A thermogravimetric analysis was performed with the 4,4-imidazolium ionenes with an anthracene endgroup. The decomposition temperatures were varying between 316 to 322 °C depending on the different molar masses. These values are similar to the values reported in literature for ammonium ionenes.¹⁸ Figure 5.5 shows that the mass loss already occurs before the decomposition of the polymer starts, which is most likely due to the loss of water indicating its hygroscopic nature.

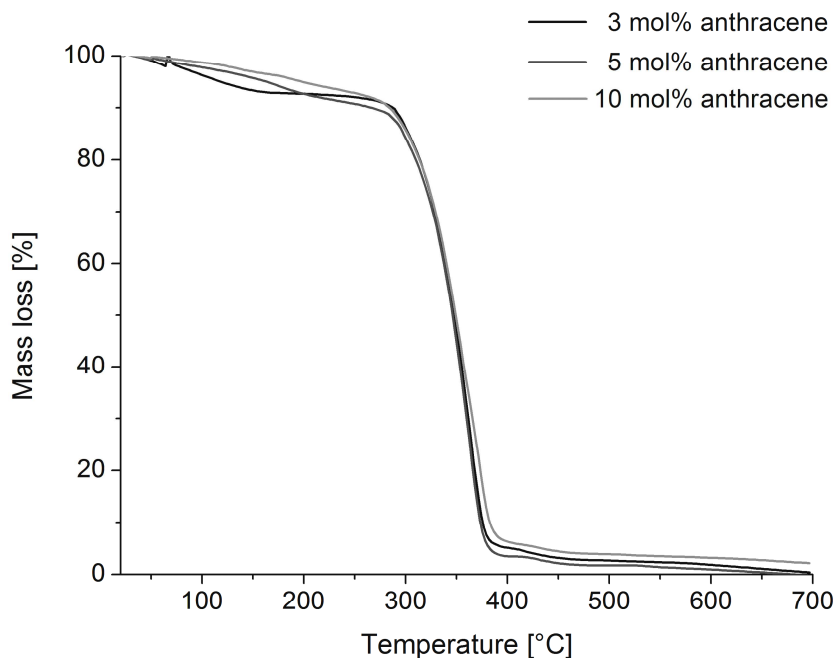


Figure 5.5 Characteristic decomposition behavior (TGA) of 4,4-imidazolium ionenes with an anthracene end group.

The thermal behavior of the synthesized 4,4-imidazolium ionenes was investigated by differential scanning calorimetry (DSC), showing that the 4,4-imidazolium ionenes with a benzyl end group have a glass transition temperature of 58.1 ± 1 °C (no significant differences in

molar mass as found by analytical ultracentrifugation: 1,800 to 3,000 g/mol). In literature, values in the range of 61 to 88 °C were reported for ammonium based ionenes with different molar masses.¹⁸ In case of 4,4-imidazolium ionenes with an anthracene end group, lower glass transition temperatures were found, 45.1 °C for 3 mol% and 35.3 °C for 5 mol% of 9-(chloromethyl)anthracene (Figure 5.6). The decrease in glass transition temperature might be explained by a plasticizing effect of the bulky end groups creating more free volume between the polymer chains. As already described above, the solubility of ionenes can be changed by varying the anions. Therefore, the anions were exchanged from bromide to the more hydrophobic anions such as tetrafluoroborate and hexafluorophosphate (hydrophobicity: $[\text{Br}]^- < [\text{BF}_4]^- < [\text{PF}_6]^-$). The solubility was checked mainly for polar solvents, both protic and aprotic, as well as for the solvents used as eluent for the available SEC systems (Table 5.6). When the anion is exchanged from bromide to tetrafluoroborate the ionenes are now soluble in dimethylsulfoxide, dimethylformamide and dimethylacetamide instead of water and methanol. In case of hexafluorophosphate, the polymers are soluble in dimethylsulfoxide, dimethylformamide and acetone.

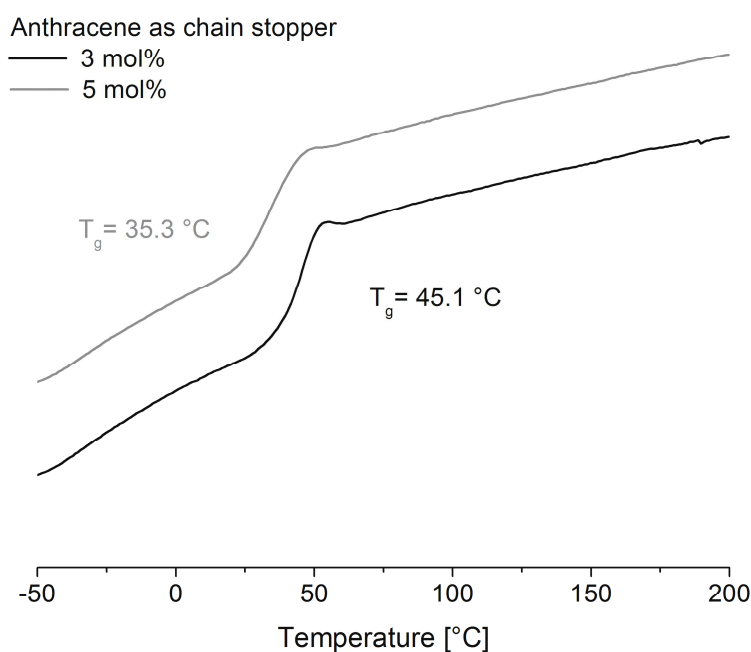
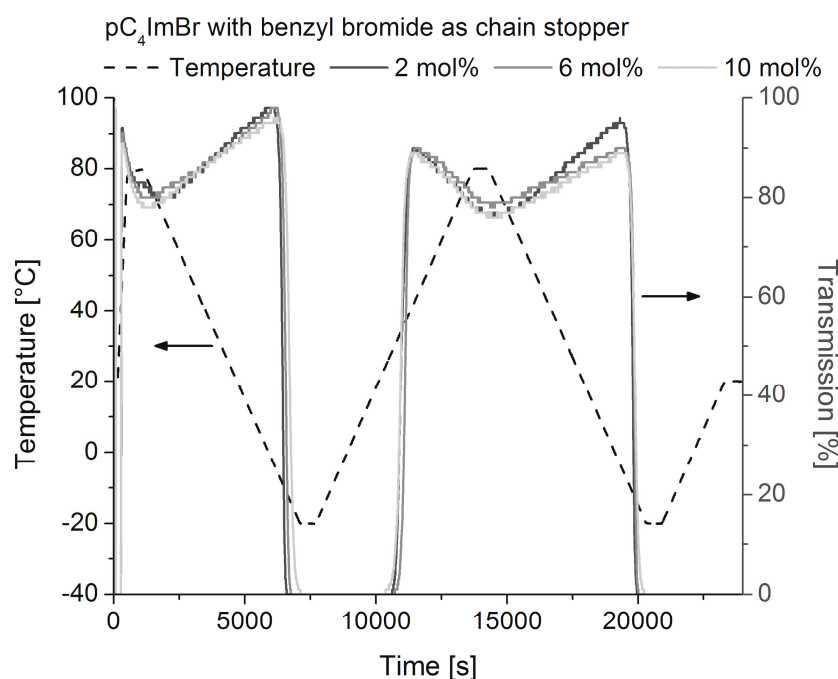


Figure 5.6 Characteristic thermal behavior (DSC) of 4,4-imidazolium ionenes with an anthracene end group.

In case of 4,4-imidazolium ionenes with bromide as counter ion it was found that the polymers are soluble in warm ethanol and that they precipitate at lower temperatures. Thus, the polymers showed an upper critical solution temperature (UCST), which was investigated in more detail by transmission measurements at different temperatures as depicted in Figure 5.7.

Table 5.6 Solubility of 4,4-imidazolium ionenes with different counter ions

Solvent	[Br] [−]	[BF ₄] [−]	[PF ₆] [−]
H ₂ O	✓	×	×
DMSO	×	✓	✓
DMA	×	✓	×
DMF	×	✓	✓
MeOH	✓	×	×
Acetone	×	×	✓
CHCl ₃	×	×	×
THF	×	×	×

**Figure 5.7** UCST-behavior of 4,4-imidazolium ionenes (5 mg/mL) with bromide as counter ion and benzyl as end group in ethanol.

At the beginning of the measurement, the transmission is at 0% as a consequence of the insolubility of the polymer in ethanol. Subsequently, the mixture is heated and the polymer becomes soluble in ethanol, as a result of the decreased ionic interactions between the polymer chains at elevated temperatures, resulting in a sudden increase in transmission (up to 100%). When the solution is cooling down, the polymer is precipitating and the transmission is decreasing again. From the heating and cooling cycles, the UCST temperatures were determined at 50% transmission. A significant difference in UCST temperature between heating ($\sim 34.8\text{ }^{\circ}\text{C}$) and cooling ($\sim -12.1\text{ }^{\circ}\text{C}$) was found, which might be explained by a slow precipitation of the polymer (precipitation took also place overnight at room temperature). In general, the molar mass did not show any influence on the UCST temperature.

The water uptake represents an important property of polymers and was measured for the 4,4-imidazolium ionenes. As already described in Chapter 3, the “Dynamic Vapor Sorption” (DSV) technique was used in order to determine the water uptake of these polymers. The TGA

measurements gave already a sign that these polymers are hygroscopic. The first trials of 4,4-imidazolium ionenes with bromide as counter ion showed a moderate water uptake (up to 59 wt.-% at 90% relative humidity, Figure 5.8), which is above the values reported for silica particles (26 wt.-%), poly(acrylic acid) (33 wt.-%), poly(vinylimidazole) (40 wt.-%) and poly(2-ethyl-2-oxazoline) at 90% relative humidity, but still below the values for poly(ethylene glycol) (73 wt.-%) and poly(acrylic acid) sodium salt (88 wt.-%).²⁰ A significant difference between absorption and desorption was found at low relative humidities (below 50% relative humidity). In general, lower values were obtained for the water absorption compared to the values for the water desorption, which might be explained by the change in morphology after water absorption or by hydrogen bonding (in this case most probably between the acidic hydrogen of the imidazolium ring and the oxygen of the water molecules)²¹ making it more difficult to release the absorbed water. In general, the molar mass and the end groups did not have any influence on the water uptake.

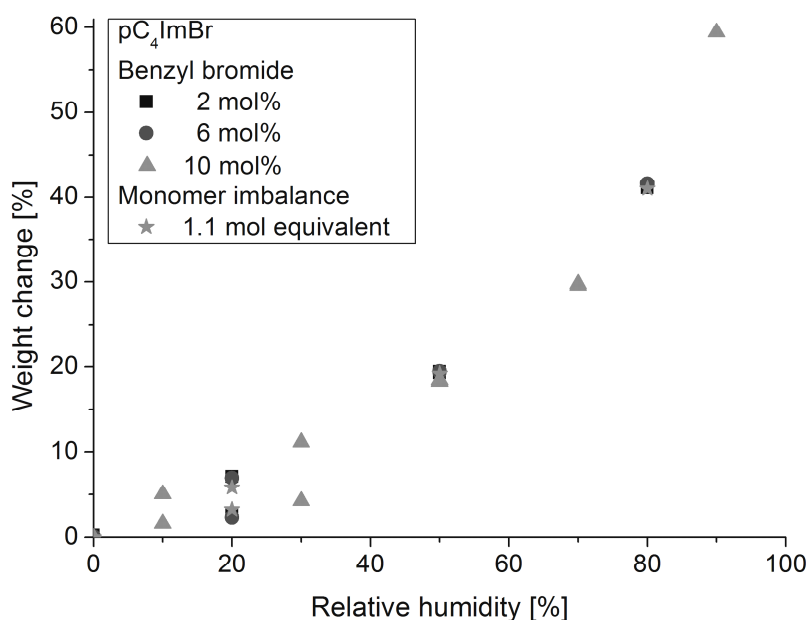


Figure 5.8 Water uptake for 4,4-imidazolium ionenes with bromide as counter ion and different end groups.

In order to improve the water uptake, 4,4-imidazolium ionenes with chloride as counter ion were synthesized as described above. Chlorides are known to be more hydrophilic than bromides as a result of their smaller ionic radius. In general, chloride ions are able to form a hydrogen bond network with water (four hydrogen bonds with almost tetrahedral arrangement), while bromide ions are only able to build hydrogen bond chains (two hydrogen bonds per ion).²² Therefore, higher water uptake values (up to two times) were expected for the ionenes with chloride as anion. The values obtained for the water uptake of ionenes with chloride and bromide anion are depicted in Figure 5.9. Higher water uptake values were observed for the polymers with chloride counter ions (up to 97 wt.-% at 90% relative humidity) compared to their analogues with bromide as counter ion. In particular, large differences were obtained at high relative humidities

(up to 38 wt.-% difference for a relative humidity of 90%). The obtained values were above the values reported for poly(ethylene glycol) (73 wt.-%) and poly(acrylic acid) sodium salt (88 wt.-%).²⁰ In the case of ionenes with chloride as counter ion no difference in water absorption and desorption compared to bromide was found. This might be explained by the hard basic nature of the chloride anion resulting in a stronger hydrogen bond between the cation and chloride compared to bromide, being able to disrupt and break the above mentioned hydrogen bonds between the cation and water.^{21,23}

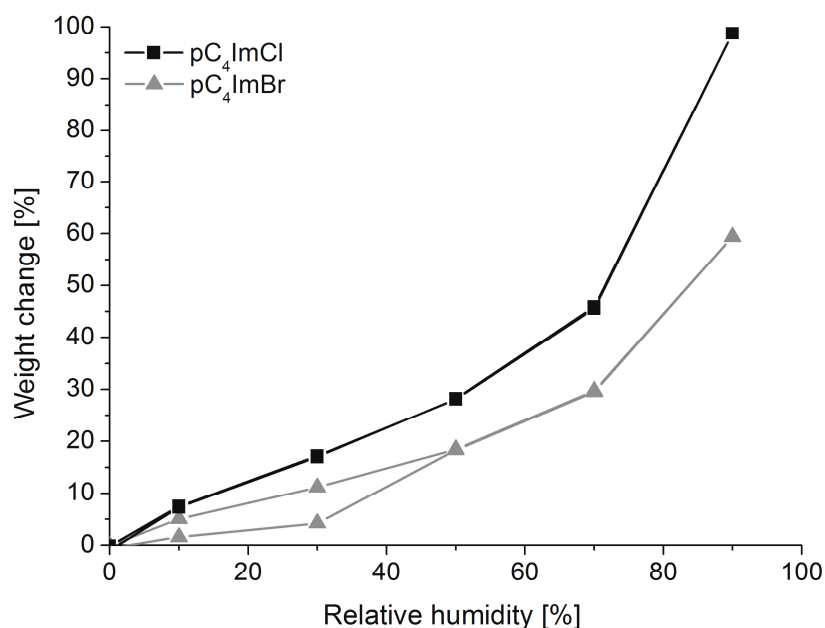


Figure 5.9 Water uptake for 4,4-imidazolium ionenes with bromide and chloride as counter ions.

5.4 Conclusions

New 4,4-imidazolium ionenes were synthesized under microwave irradiation and conventional heating in an oil bath. The polymerization times could be decreased from 24 to 1 h as a result of elevated temperatures above the boiling points of the applied solvents. Different approaches, such as monomer imbalance and monofunctional reagents, were applied in order to control the molar mass of the polymers. Moreover, different molar masses were found for various chain stoppers. In this regard, the best agreement with the expected molar mass was achieved by utilizing benzyl bromide as a chain stopper. In general, higher number average molar masses were found by ¹H NMR spectroscopy for the polymers synthesized under microwave irradiation. Additionally, the ionenes were investigated by analytical ultracentrifugation, showing a significant differences in the determined molar masses compared to ¹H NMR spectroscopy, which is a strong evidence for the formation of macrocycles. The content of linear chains was estimated to be in the range of 7 to 18% depending on the amount of the utilized chain stopper. Furthermore, the properties of the synthesized 4,4-imidazolium ionenes, such as thermal behavior, solubility behavior and water uptake were investigated as well. It was found that the decomposition temperatures were comparable to the values reported in literature for ammonium

ionenes. The obtained glass transition temperatures were lower compared to ammonium ionenes. In addition, the 4,4-imidazolium ionenes showed high water uptake values and can be classified as humidity absorber. The ability to absorb water is mainly depending on the counter ions (chloride showed higher water uptake than bromide).

5.5 Experimental details

Materials

1-Methylimidazole and 1,4-dibromobutane were distilled under reduced pressure prior to use and stored at room temperature. Imidazole, benzyl bromide, sodium hydride and sodium hexafluorophosphate were used as received. THF was dried and deoxygenated using a solvent purification system (PURE SOLV 400-4-MD, Innovative Technology). All other solvents, *e.g.* methanol, dimethylformamide, acetone, diethyl ether and ethylacetate were used as received. All substances used are commercially available.

The synthesis of the polymers was performed in a single-mode microwave reactor (Emrys Liberator, Biotage, Sweden) or in an oil bath. The reactions in the microwave (120 °C) and in the oil bath (60 to 80 °C) were performed in glass vessels (2 to 5 mL) sealed with a septum. The pressure of the system was controlled by a load cell connected to the vessel and the temperature of the reaction mixture was monitored using a calibrated infrared sensor, which is located at the side of the reaction vessel. All experiments were performed using a Teflon[®]-coated magnetic stirring bar. A maximum microwave power of 80 W was used. A maximum pressure of 20 bar was set as a safety threshold.

To remove water of the products either a vacuum oven at 45 °C or a freeze dryer Alpha 1-2 LD from Christ was used. The dried samples were stored under dry conditions in an exsiccator.

¹H NMR spectra were recorded on a Varian Mercury spectrometer using a frequency of 400 MHz at 25 °C. Chemical shifts are given in ppm downfield from tetramethylsilane (TMS). All LDI-TOF-MS experiments were performed on a Voyager-DE PRO Biospectrometry Workstation (Applied Biosystems, Foster City, CA) time-of-flight mass spectrometer in reflector mode. All spectra were obtained in the positive ion mode. Ionization was performed with a 337 nm pulsed nitrogen laser. Samples were dissolved in methanol and spotted on the target without using any matrix. All spectra are averaged over 500 laser shots over the complete sample area. All data were processed using the Data Explorer software package (Applied Biosystems). Elemental analyses were carried out on a EuroVector EuroEA3000 elemental analyzer for CHNS-O.

Melting points (onset of an endothermic peak on heating) were determined on a DSC 204 F1 Phoenix by Netzsch under a nitrogen atmosphere from -100 to 150 °C with a heating rate of 20 K/min (a first heating cycle to 150 °C was not considered for the calculations). Thermogravimetric analyses were performed in a TG 209 F1 Iris by Netzsch under a nitrogen atmosphere in the range from 25 to 600 °C with a heating rate of 20 K/min.

Synthesis of 1,4-di(1*H*-imidazol-1-yl)butane

In a 500 mL round-bottomed flask sodium hydride (3.03 g, 126 mmol) was added to dry THF (220 mL) to give a white suspension. 1*H*-imidazole (7.15 g, 105 mmol) in THF (30 mL) was added slowly at 0 °C. The mixture was stirred for 1 h at room temperature. 1,4-Dibromobutane (6.61 mL, 52.6 mmol) was added dropwise. The reaction mixture was heated to 60 °C for 2 days and subsequently diluted with diethyl ether (100 mL). The reaction mixture was filtered through a paper filter and the residue was washed with diethyl ether (20 mL). All solvents were evaporated to give yellow crystals. Further purification was achieved by dissolving the crude product in warm ethanol and precipitation in water. The white product was filtered and washed three times with water (~ 20 mL). The purified product (4.24 g, 42%) was freeze-dried in order to remove remaining water.

¹H NMR (400 MHz; CD₃OD, 25 °C): δ (ppm) = 1.75 (4 H, m, CH₂), 4.03 (4 H, m, CH₂), 6.95 (1 H, s), 7.09 (1 H, s), 7.63 (1 H, s); IR (neat): 3306 (OH), 2971 (CH alkyl), 2858 (CH alkyl), 2122 (N=C), 1638 (C=C, C=N), 1516 (C-C, C-N), 1446 (CH alkyl deform.), 1383, 1283, 1030 (CH ring deform.) cm⁻¹; LDI-TOF-MS for C₁₀H₁₄N₄ + H⁺(191.12): *m/z* 191 (100%), 192 (25%) g/mol; EA C₁₀H₁₄N₄ (190.12): Calcd. C 63.13, H 7.42, N 29.45, Found C 62.97, H 7.64, N 29.62.

Synthesis of 1-(3-chloropropyl)-1*H*-imidazole

The same approach as described for the synthesis of 1,4-di(1*H*-imidazol-1-yl)butane was used. In this case, an equimolar amount of 1*H*-imidazole and 1-bromo-3-chloropropane was applied. In order to avoid polymerization of the monomer, the solvents were removed by cold distillation.

¹H NMR (400 MHz; d₆-DMSO, 25 °C): δ (ppm) = 2.16 (2 H, m, CH₂), 3.55 (2 H, t, *J* = 6.4 Hz, CH₂), 4.09 (2 H, t, *J* = 6.9 Hz, CH₂), 6.90 (1 H, s), 7.18 (1 H, s), 7.63 (1 H, s); IR (neat): 3343 (OH), 3173 (CH ring), 3135 (CH alkyl), 2984 (CH alkyl), 2864 (CH alkyl), 2096 (N=C), 1647 (C=C, C=N), 1566 (C-C, C-N), 1453 (CH alkyl deform.), 1383, 1327, 1163 (CH ring deform.), 1113, 1037 cm⁻¹; EA C₆H₉ClN₂ (144.60): Calcd. C 49.84, H 6.27, Cl 24.52, N 19.37, Found C 49.36, H 6.65, N 19.38.

Representative synthesis of poly(4,4-imidazolium bromide) – monomer balance

1,4-di(1*H*-imidazol-1-yl)butane (200 mg, 1.051 mmol) was dissolved in either a mixture of MeOH (0.526 mL) and DMF (0.526 mL) or pure MeOH (1.05 mL). The reaction mixture was filled in a 0.5–2 mL Biotage pressure vial. 1,4-Dibromobutane (0.127 mL, 1.051 mmol) was added under stirring and the vessel was closed. The reaction mixture was stirred with a magnetic stirring bar for 15 h at 60 °C. The conversion of 1,4-dibromobutane was checked by GC and was found to be 99.7%.

¹H NMR (400 MHz; CD₃OD, 25 °C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH₂), 4.40 (4 H, m, CH₂), 7.78 (2 H, s), 9.31 (1 H, s); imidazole end group δ (ppm) = 7.14 (1 H, s), 7.34 (1 H, s), 8.04 (1 H, s).

End group functionalization

Functionalization of the imidazole end groups

To a solution of poly(4,4-imidazolium bromide) (367 mg) in MeOH (0.526 mL) and DMF (0.526 mL) in a 0.5–2 mL Biotage pressure vial benzyl bromide (0.75 mL, 6.31 mmol) was added under stirring. The reaction mixture was stirred with a magnetic stirring bar for 15 h at 60 °C and subsequently poured into a large excess of diethyl ether. The ether phase was decanted and the polymer was dissolved in methanol and re-precipitated in diethyl ether. The procedure was repeated once more to separate the polymer from the remaining benzyl bromide. The benzylated polymer was found to yield 320 mg (87%).

^1H NMR (400 MHz; CD_3OD , 25 °C): polymer backbone δ (ppm) = 2.05 (4 H, m, CH_2), 4.39 (4 H, m, CH_2), 7.78 (2 H, s), 9.30 (1 H, s); benzyl end group δ (ppm) = 5.50 (2 H, s), 7.41–7.53 (5 H, m, $\text{H}_{\text{arom.}}$).

Functionalization of the bromo end groups

Poly(4,4-imidazolium bromide) (320 mg) was dissolved in MeOH (1.5 mL) and the reaction mixture was filled in a 0.5–2 mL Biotage pressure vial. 1-Methylimidazole (0.5 mL, 6.27 mmol) was added under stirring and the vessel was closed. The reaction mixture was stirred with a magnetic stirring bar for 20 h at 60 °C and subsequently precipitated in diethyl ether. The crude product was dissolved in water and washed three times with ethyl acetate. The water was evaporated to yield 272 mg (90%) of the functionalized polymer.

^1H NMR (400 MHz; CD_3OD , 25 °C): polymer backbone δ (ppm) = 2.05 (4 H, m, CH_2), 4.38 (4 H, m, CH_2), 7.77 (2 H, s), 9.29 (1 H, s); benzyl end group 5.50 (2 H, s), 7.43–7.55 (5 H, m, $\text{H}_{\text{arom.}}$); methyl end group δ (ppm) = 3.98 (3 H, s, CH_3).

Representative synthesis of poly(4,4-imidazolium bromide) – monomer imbalance

1,4-Di(1*H*-imidazol-1-yl)butane (105 mg, 0.55 mmol) was dissolved in either a mixture of MeOH (0.25 mL) and DMF (0.25 mL) or pure MeOH (0.5 mL). The reaction mixture was filled in a 0.5–2 mL Biotage pressure vial. 1,4-Dibromobutane (0.06 mL, 0.5 mmol) was added under stirring and the vessel was closed. The reaction mixture was stirred with a magnetic stirring bar for 1 h at 120 °C and subsequently poured into diethyl ether to precipitate the polymer (83% yield).

^1H NMR (400 MHz; CD_3OD , 25 °C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH_2), 4.40 (4 H, m, CH_2), 7.78 (2 H, s), 9.31 (1 H, s); IR (neat): 3395 (OH), 3148 (CH ring), 3097 (CH alkyl), 2946 (CH alkyl), 2871 (CH alkyl), 2058 (N=C), 1629 (C=C, C=N), 1564 (C-C, C-N), 1453 (CH alkyl deform.), 1333, 1159 (CH ring deform.), 1107, 1031, 835, 753 cm^{-1} ; EA ($\text{C}_{14}\text{H}_{22}\text{Br}_2\text{N}_4$)_n (406.16): Calcd. C 41.40, H 5.46, Br 39.35, N 13.79, Found C 41.57, H 5.71, N 13.97.

Representative synthesis of poly(4,4-imidazolium bromide) – chain stopper

1,4-Di(1*H*-imidazol-1-yl)butane (400 mg, 2.1 mmol) was dissolved in either a mixture of MeOH (1.05 mL) and DMF (1.05 mL) or pure MeOH (2.1 mL). The reaction mixture was filled in a 0.5 to 2 mL Biotage pressure vial. A mixture of 1,4-dibromobutane (0.06 mL, 0.5 mmol) and benzyl bromide (0.025 mL, 0.21 mmol) was added under stirring and the vessel was closed. The reaction mixture was heated for 1 h at 120 °C under microwave irradiation or for 24 h at 80 °C. The polymer solutions were subsequently precipitated in either diethyl ether, ethylacetate or a mixture with acetone.

¹H NMR (400 MHz; CD₃OD, 25° C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH₂), 4.40 (4 H, m, CH₂), 7.78 (2 H, s), 9.31 (1 H, s); benzyl end group δ (ppm) = 5.50 (2 H, s, *N*-CH₂), 7.41–7.53 (5 H, m, H_{arom.}); IR (neat): 3391 (OH), 3148 (CH ring), 3103 (CH alkyl), 2952 (CH alkyl), 2864 (CH alkyl), 2068 (N=C), 1623 (C=C, C=N), 1564 (C-C, C-N), 1446 (CH alkyl deform.), 1339, 1159 (CH ring deform.), 1106, 1025 cm⁻¹; EA (C₁₄H₂₂Br₂N₄)_n (406.16): Calcd. C 41.40, H 5.46, Br 39.35, N 13.79, Found C 41.10, H 5.62, N 13.49.

1-Methylimidazole as stopper

¹H NMR (400 MHz; CD₃OD, 25° C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH₂), 4.40 (4 H, m, CH₂), 7.78 (2 H, s), 9.31 (1 H, s); methyl end group δ (ppm) = 3.98 (3 H, s, CH₃); IR (neat): 3377 (OH), 3145 (CH ring), 3103 (CH alkyl), 2947 (CH alkyl), 2868 (CH alkyl), 2065 (N=C), 1634 (C=C, C=N), 1564 (C-C, C-N), 1454 (CH alkyl deform.), 1339, 1161 (CH ring deform.), 1018, 833, 748 cm⁻¹; EA (C₁₄H₂₂Br₂N₄)_n (406.16): Calcd. C 41.40, H 5.46, Br 39.35, N 13.79, Found C 41.80, H 5.76, N 14.05.

9-(Chloromethyl)anthracene as stopper

¹H NMR (400 MHz; CD₃OD, 25° C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH₂), 4.40 (4 H, m, CH₂), 7.78 (2 H, s), 9.31 (1 H, s); anthracene end group δ (ppm) = 6.56 (2 H, s, *N*-CH₂), the signals of the anthracene rings overlap with the signals of the imidazolium ring; IR (neat): 3393 (OH), 3148 (CH ring), 3135 (CH alkyl), 3104 (CH alkyl), 2946 (CH alkyl), 2877 (CH alkyl), 2058 (N=C), 1629 (C=C, C=N), 1564 (C-C, C-N), 1446 (CH alkyl deform.), 1333, 1161 (CH ring deform.), 1107, 1018 cm⁻¹; EA (C₁₄H₂₂Br₂N₄)_n (406.16): Calcd. C 41.40, H 5.46, Br 39.35, N 13.79, Found C 41.04, H 5.82, N 14.23.

Representative synthesis of poly(3-imidazolium chloride) – chain stopper

1-(3-Chloropropyl)-1*H*-imidazole (144.6 mg, 1 mmol) was dissolved EtOH (1 mL). The reaction mixture was filled in a 0.5–2 mL Biotage pressure vial. Benzyl bromide (6 μ L, 0.05 mmol) was added under stirring and the vessel was closed. The reaction mixture was heated for 3 h at 120 °C under microwave irradiation. The polymer solution was precipitated into cold ethanol or diethyl ether.

¹H NMR (400 MHz; CD₃OD, 25° C): polymer backbone δ (ppm) = 2.06 (4 H, m, CH₂), 4.40 (4 H, m, CH₂), 7.78 (2 H, s), 9.31 (1 H, s); benzyl end group δ (ppm) = 5.50 (2 H, s, *N*-CH₂), 7.41–7.53 (5 H, m, H_{arom.}); IR (neat): 3369 (OH), 3167 (CH ring), 3129 (CH alkyl), 2971 (CH

alkyl), 2102 (N=C), 1636 (C=C, C=N), 1566 (C-C, C-N), 1459 (CH alkyl deform.), 1333, 1163 (CH ring deform.), 1113, 1012 cm^{-1} ; EA ($\text{C}_6\text{H}_9\text{ClN}_2$)_n (144.60): Calcd. C 49.84, H 6.27, Cl 24.52, N 19.37, Found C 49.78, H 6.43, N 19.13.

Anion exchange

Poly(4,4-imidazolium bromide) (50 mg) was dissolved in water (1 mL) and sodium hexafluorophosphate (300 mg, 1.79 mmol) or sodium tetrafluoroborate (196 mg, 1.79 mmol) were added to the solution. The reaction mixture was stirred for 15 min with a magnetic stirring bar at room temperature. Subsequently, the polymer was precipitated, filtered off and washed three times with water. In order to remove remaining water, the polymer was dried either in a vacuum oven or in a freeze dryer overnight.

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Chapter 6

New routes for ‘old’ polymers

Abstract

The combination of the thermal auto-initiated free radical polymerization of styrene and the precipitation polymerization were investigated in order to develop a fast and environmentally friendly approach to produce polystyrene. To achieve high reaction temperatures in short time, microwave irradiation was utilized as heating source. Styrene was used without any purification, *e.g.* without distillation or column filtration. Due to the auto-initiation of styrene at high temperatures no radical initiator was required. Different solvent (water and ethanol) to styrene ratios were heated far beyond their boiling points resulting in relatively high pressures for the auto-initiated polymerization of styrene. The obtained molar masses could be controlled by the ethanol-to-styrene ratio in the case of ethanol as the solvent although the monomer conversions were rather low under the applied conditions. Moreover, the effect of a commercially available stable free nitroxide on the polymerization process was investigated. It has been observed that a control of the molar mass of the polymer could be achieved by changing the ratio of styrene to free nitroxide (varied from 10:1 to 400:1) and that moderate polydispersity indices ($PDI = 1.3$ to 1.9) could be obtained. Finally, the developed polymerization processes only require a simple purification step due to the precipitation of the polystyrene in the reaction solvent. In addition, preliminary experiments were conducted to pre-polymerize polyamide 12 under microwave irradiation utilizing the hydrolytic ring-opening polymerization. The obtained pre-polymer was characterized by SEC, TGA, DSC and end group titration.

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6.1 Trials to simplify the free-radical polymerization of styrene

Polystyrene is a commercially important amorphous thermoplastic and used in a variety of applications, *e.g.* packaging of food, household goods, construction, energy and communications technology as well as thermal insulation for refrigerator liners. The popularity of polystyrene derives from the fact that it possesses many interesting properties, such as good processability, rigidity, transparency, low water absorption, and that it can be produced at low costs. Another key property is the excellent electrical insulation characteristic.¹⁻⁵

The main production of polystyrene is conducted by bulk and suspension free-radical polymerization processes.^{6,7} A polymerization at low temperatures (<100 °C) requires the presence of chemical initiators, but at higher temperatures (>100 °C) styrene auto-polymerizes and no initiator is required.^{8,9} The thermally initiated polymerization can be controlled by temperature (0.1%/h at 60 °C, 2%/h at 100 °C and 16%/h at 130 °C, respectively).⁸ However, some of the disadvantages of the thermally initiated polymerization are the formation of low-molar-mass oligomers and the difficulty to control the polymerization temperature.¹⁰ It is possible to remove the undesired oligomers by dissolution and precipitation of the polymerization solution.

An alternative approach to produce polystyrene in a simple way is by precipitation polymerization.¹¹⁻¹³ The advantage of this method is the absence of expensive and difficult to remove stabilizers in comparison to other heterogeneous polymerization techniques, such as emulsion and suspension polymerizations. The precipitation polymerization starts as a homogenous solution and the desired polymer is precipitating during the polymerization, while unreacted monomer and possible oligomers stay in solution. In the recent years, research was intensified using supercritical carbon dioxide as an environmentally friendly solvent.¹¹

6.1.1 Temperature-initiated polymerization of styrene under near-critical water conditions

At temperatures in the range from 250 to 350 °C and high pressures, the polarity and hydrogen-bonding ability of water are changing, as depicted in Figure 6.1, which leads to different solvent properties, *e.g.* near critical water (NCW) has a density and a dielectric constant similar to that of acetone and a higher ionization constant in comparison to water at ambient conditions. These special properties allow the dissolution of organic and ionic species and the swelling of polymers, which are insoluble in water at ambient conditions, as well as performing chemical transformations. Furthermore, the increased ionization constant provides hydronium and hydroxide ions which are able to react as acidic or basic catalysts in chemical reactions.¹⁴ In addition, the purification of the reaction product becomes very easy since the product is precipitating at lower temperatures.^{15,14}

This approach was already successfully applied in organic chemistry¹⁶ and we investigated its suitability for the free-radical polymerization of styrene. Polystyrene has a high decomposition temperature (~ 310 °C) and therefore styrene can be polymerized at temperatures up to 300 °C. Furthermore, styrene itself auto-initiates the polymerization at high temperatures and no additional initiator is required.⁹ The mechanism of the autopolymerization of styrene was first

proposed by Mayo.¹⁷ The polymerization starts with an initial [2+4] Diels-Alder reaction between two styrene molecules, resulting in the nonaromatic Mayo adduct, which reacts further with another styrene molecule to form radicals.^{9,18,17}

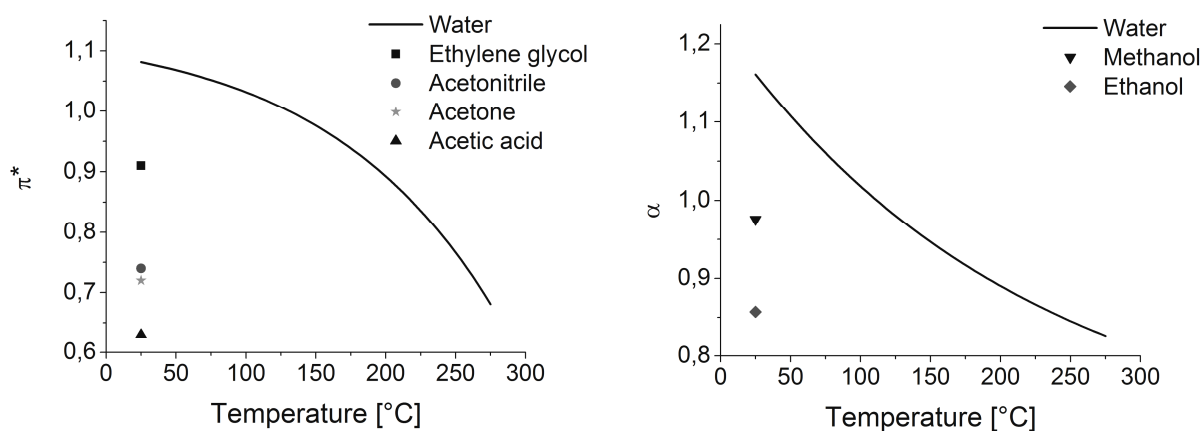


Figure 6.1 Dependency of the Kamlet–Taft solvent parameters π^* (polarizability, left side) and α (hydrogen bond donating ability, right side) of water¹⁵ on temperature in comparison to selected organic solvents.¹⁹

Although water and styrene are not miscible at ambient temperature, at higher temperatures the solubility parameters of water are changing, which might lead to dissolution of styrene in the water phase. In order to achieve temperatures up to 280 °C, the Synthos 3000 microwave reactor from Anton Paar, equipped with quartz reaction vessels, was used. This system allows reactions up to 300 °C and 80 bar. A typical heating curve for the polymerization of styrene in water is shown in Figure 6.2.

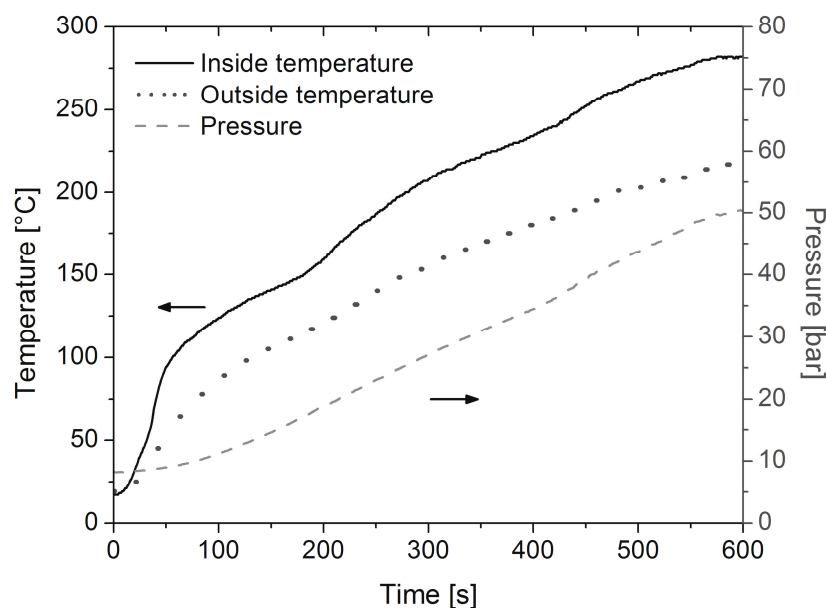


Figure 6.2 Temperature and pressure profiles of the temperature-initiated polymerization of styrene in water.

The temperature and pressure inside a reference vessel were measured with a temperature/pressure sensor equipped with a gas thermometer, whereas the temperature of the vessel outside was measured by an IR sensor. The fast heating of the reaction mixture (within 10 minutes to the preset value of 280 °C) was achieved by the good microwave absorption of water (dielectric constant: 80.4)²⁰ due to its polar structure. In contrast, styrene is apolar (dielectric constant: 2.4)²⁰ and a poor microwave absorbing molecule and therefore heated indirectly *via* the water in this system. While heating above the boiling point of water a pressure of 50 bar was reached during the reaction. For the initial experiments a ratio of water to styrene of 10 to 1 was used and polystyrene with a M_n of 25,800 g/mol and a PDI value of 2.40 was obtained in moderate yield (31%). Before the polymerization, styrene was phase separated as a layer on top of the water phase, while the resulting polystyrene was on the bottom of the reaction vessel after the polymerization. In order to investigate the influence of the temperature on the thermally initiated polymerization of styrene, polymerization temperatures of 240, 200, 150, 120 and 90 °C were investigated as well. At lower temperatures, *e.g.* 120 and 90 °C, no polymer was obtained after 10 min and size exclusion chromatography (SEC) indicated that only very little auto-initiation occurred. The obtained SEC traces for temperatures above 120 °C (Figure 6.3) were shifting to lower molar masses at higher temperatures. Presumably, the radical concentration is relatively high at higher reaction temperatures, which increases the rate of termination reactions more than the rate of propagation. The relative intensity of the shoulders, which appear at higher elution volumes, is increasing with the polymerization temperature, leading to broader molar mass distributions. This indicates that the life time of the thermally initiated propagating chain is much lower at higher temperature because of a higher concentration of the radicals resulting in more termination reactions compared to propagation reactions. Therefore, lower number average molar masses were calculated with higher polydispersity indices, as listed in Table 6.1.

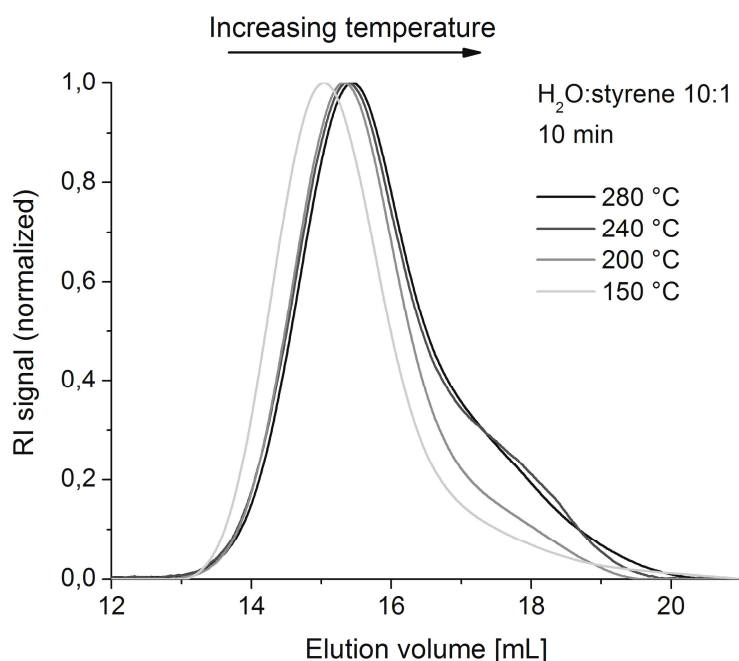


Figure 6.3 SEC curves of the temperature-initiated precipitation polymerization of styrene at different temperatures (10 min, water:styrene ratio = 10:1).

Table 6.1 Data of the thermally initiated polymerization of styrene after 10 min under microwave irradiation at different reaction temperatures (10 to 1 ratio of water to styrene).

Temperature [°C]	Conversion [%]	M _n [g/mol]	PDI
280	31	25,800	2.40
240	31	28,900	2.27
200	32	36,700	1.93
150	31	46,000	1.82

The number average molar masses as a function of the polymerization temperatures show a linear dependency, as visible in Figure 6.4, indicating that the M_n can be 'controlled' by temperature. Surprisingly, the styrene conversion was not affected by the reaction temperature. From these initial experiments it can not be concluded whether the styrene and water were homogeneously mixed at elevated temperatures. To clarify this point, different solvent to monomer concentrations were applied under similar polymerization conditions. If the styrene dissolves in water at high temperatures, lower molar masses are expected for lower monomer concentrations as a result of a reduced radical formation for more diluted reaction mixtures. In contrast, when styrene and water do not mix, all monomer concentrations should provide similar results since the polymerization would always take place in bulk styrene. Water to styrene ratios of 10 to 1, 10 to 2, 10 to 3 and 10 to 4, respectively, were used and the reaction temperature was set to 200 °C. All experiments revealed similar molar masses and molar mass distributions (Table 6.2), although the monomer concentration was increasing. Therefore it can be concluded that styrene is not soluble in water at high temperatures and that the polymerization behaves like a bulk polymerization.

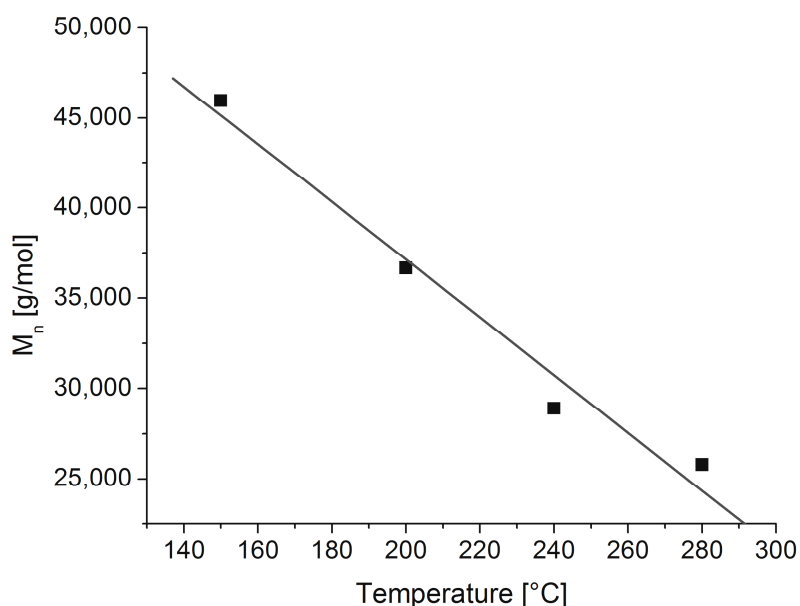
**Figure 6.4** Dependency of the polymerization temperature on the number average molar masses of the temperature-initiated polymerization of styrene (10 min, 10 to 1 ratio of water to styrene). The data was fitted using a linear curve fitting.

Table 6.2 Data of the thermally initiated polymerization of styrene after 10 min for different water to styrene ratios (200 °C, 10 min).

H ₂ O:styrene	Conversion [%]	M _n [g/mol]	PDI
10:1	32	37,800	1.87
10:2	50	36,300	1.96
10:3	51	37,100	1.96
10:4	49	38,900	2.03

Nevertheless, polystyrene with moderate molar masses was synthesized in short reaction times under microwave irradiation. The polydispersity indices (PDI's) for a homogeneous conventional free-radical polymerization can approach at best 1.5 to 2.0 depending on the termination (coupling or disproportionation, respectively).^{21,22} In case of emulsion polymerization the molar mass distribution is broadening as a result of bimolecular termination between radicals reaching PDI's of 2 and 4 for coupling and disproportionation, respectively.²² The values obtained in this thesis were in the range of 2 or slightly better. The conversions are increasing with the amount of styrene due to a higher radical formation at higher monomer concentrations.

6.1.2 Temperature-initiated polymerization of styrene in ethanol

As described above, it was found that styrene is insoluble in near-critical water. Therefore, the solvent was changed to ethanol, which is known to be a “green solvent” as well.²³ Styrene dissolves easily in ethanol resulting in a homogeneous solution. However, the resulting polystyrene is not soluble in ethanol and precipitates from the polymerization solution, while styrene stays in solution, allowing separation by simple filtration. From literature it is known that the thermal precipitation polymerization of styrene in ethanol at 150 °C for 5 h results in polystyrene with a M_n of 47,000 g/mol and a polydispersity value of 1.9.²⁴ Only low conversions (9%) were obtained, which might be explained by induced transfer reactions of the ethanol inhibiting the polymerization. Nevertheless, we performed comparable experiments for 1 hour in the Biotage microwave synthesizer at 150 °C. Different ratios of ethanol to styrene were used (from 10:0.1 to 10:4) to investigate the influence of the monomer concentration on the molar mass. The results of the SEC measurements are depicted in Figure 6.5. In general, the molar masses are shifting to higher molar masses with higher styrene concentrations. In particular, a clear change in molar mass was detected for the ethanol:styrene ratios from 10:0.1 to 10:3. The increase in molar mass might be explained by the lower polarity of the styrene-ethanol mixture with higher styrene concentrations. The solubility of polystyrene is enhanced due to the lower polarity of the solvent mixture and higher molar mass polystyrene is precipitating. The obtained molar masses, molar mass distributions and conversions are summarized in Table 6.3. The molar masses of polystyrene varied between 6,000 and 46,000 g/mol using different styrene concentrations. The polydispersity indices were found to be in the range from 1.4 to 1.8 for a reaction time of 1 h, which is relatively low for a free radical polymerization. Unfortunately, the

conversions remained very low as described previously in literature.²⁴ Also longer reaction times did not increase the conversion resulting in comparable molar masses.

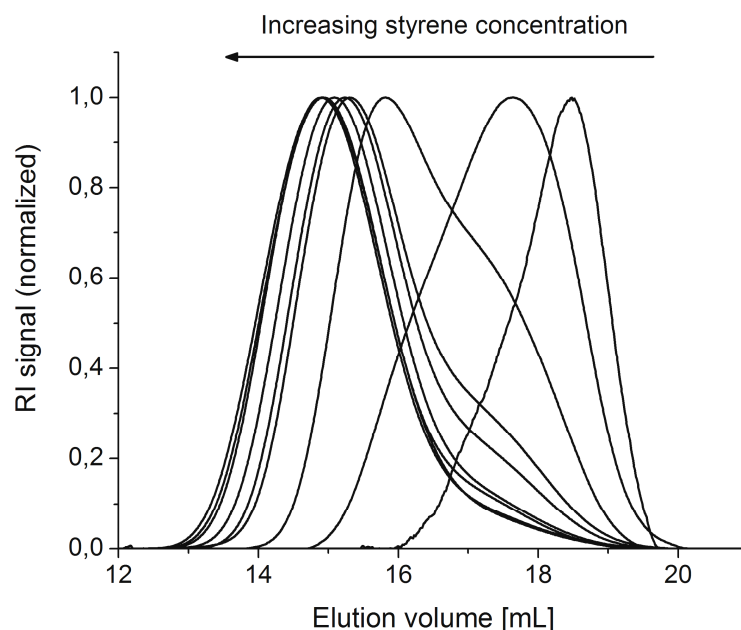


Figure 6.5 SEC curves of the temperature-initiated precipitation polymerization of styrene for different ethanol to styrene ratios (150 °C, 1 h).

Table 6.3 Data of the thermally initiated polymerization of styrene for different ethanol to styrene ratios at 150 °C.

Ratio EtOH:styrene	Time [h]	Conversion [%]	M _n [g/mol]	PDI
10:0.1	1	8	6,000	1.40
10:0.5	1	13	9,500	1.59
10:1	1	7	16,900	1.78
10:1	3	3	19,600	1.86
10:1	5	8	16,800	1.93
10:1.5	1	5	26,900	1.79
10:2	1	9	29,800	1.79
10:2.5	1	1	37,800	1.67
10:3	1	1	44,400	1.66
10:3.5	1	3	42,600	1.72
10:4	1	9	46,100	1.67

In addition, the precipitated polymer showed no clear phase separation, which might be correlated to the low conversions obtained. The number average molar masses as a function of the ethanol to styrene ratios are shown in Figure 6.6. The experimental data were fitted with an exponential decay function (1st order) showing a clear dependency of the molar mass on the styrene to ethanol concentration. In principle, the required ethanol to styrene ratio for a desired molar mass for the polymerization of styrene (1 h at 150 °C) can be estimated from the obtained plot.

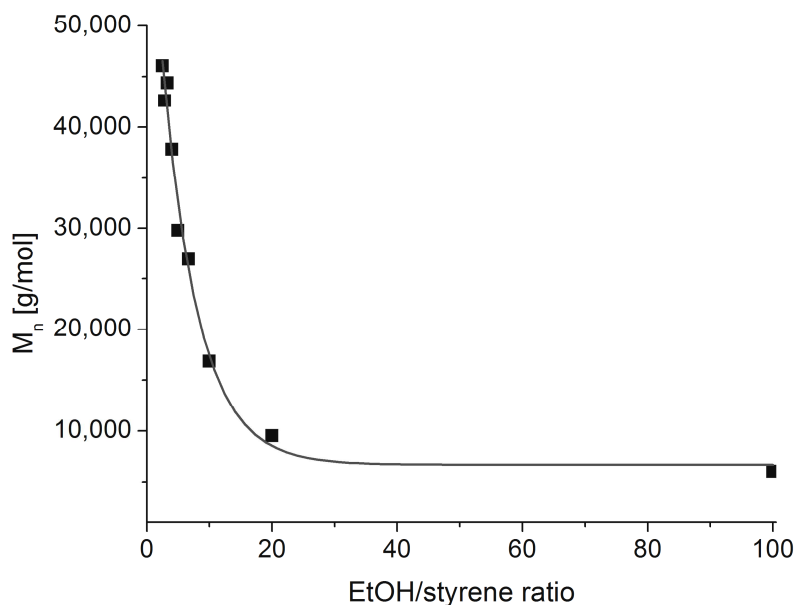
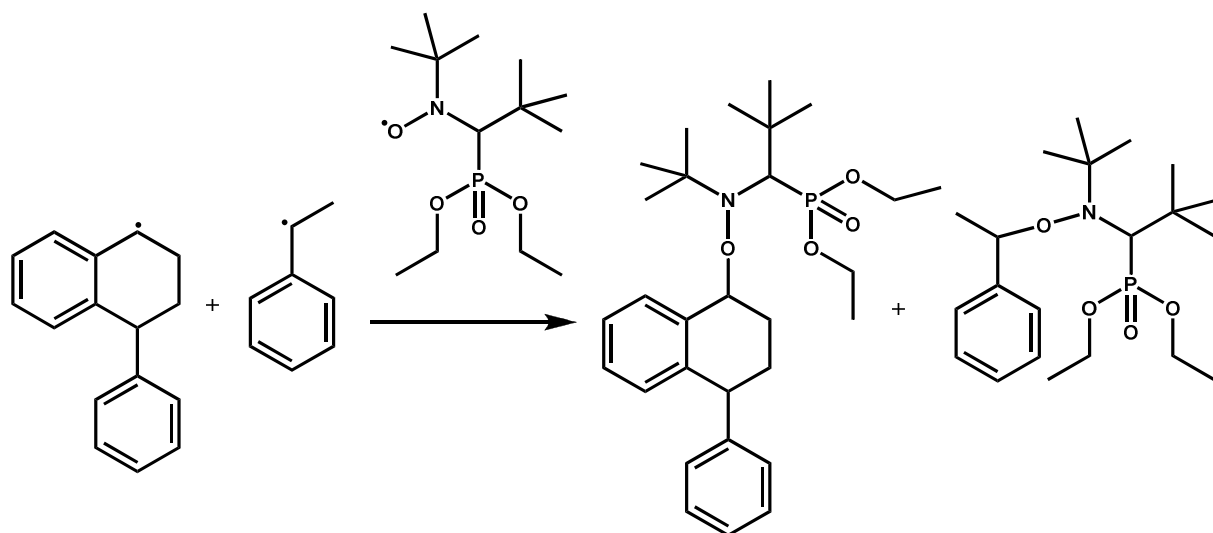


Figure 6.6 Dependency of the number average molar masses on the ethanol to styrene ratio of the temperature-initiated polymerization of styrene for 1 h at 150 °C. The data was fitted using an exponential curve fitting.

In order to improve the temperature-initiated polymerization of styrene in ethanol the stable free nitroxide *N,N*-*tert*-butyl-*N*-[10-diethylphosphono-2,20-dimethylpropyl] nitroxide (SG-1) was added to the polymerization system. From the literature it is known that the addition of free nitroxide, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), can improve the thermal polymerization at low temperatures (125 °C) resulting in narrow polydispersity indices (PDI ~ 1.20 to 1.30).^{18,25} At higher temperatures, *e.g.* 145 °C, broader molar mass distributions were obtained (PDI ~1.65). As a result of the TEMPO addition the molar mass could be controlled during the thermal polymerization in bulk. However, an incubation period was observed depending on the amount of TEMPO. During the inhibition time, which can be several hours, no polymer is formed until the excess of TEMPO is consumed. It was also reported that a high excess of TEMPO is leading to the formation of a *bis*-TEMPO adduct, which is a bad initiating system for the thermal polymerization of styrene, resulting in broad molar mass distributions.¹⁸ In this thesis, we have used SG-1 as a free nitroxide, since it has been reported to control the nitroxide mediated polymerization of styrene in organic solvents rather well.²⁶⁻³⁰ The addition of the free nitroxide leads to the formation of a new mediating system consisting of the radicals formed during the thermal initiation and SG-1 as depicted in Scheme 6.1. Presumably, the excess of SG-1 reacts with the auto-initiated radical centers and, thus, proceeds like a nitroxide mediated polymerization. The radical concentration is relatively low in controlled radical polymerization techniques.^{31,32} Therefore, the termination reactions are minimized leading to controlled molar masses with low polydispersity indices. The introduction of SG-1 as an end group also improved the precipitation behavior of the polymer and lead to a clear phase separation.



Scheme 6.1 Schematic representation of the general initiation step of the thermally initiated polymerization of styrene in the presence of SG-1.

Different concentrations of SG-1 were investigated, varying from 400 to 10 (styrene to SG-1). For all polymerizations with SG-1, an ethanol to styrene ratio of 10 to 3 was used, which is equal to a monomer concentration of 2 M. The SEC traces for the polymerizations of styrene are shown in Figure 6.7. In general, the molar masses are shifting more gradually with different SG-1 concentrations than with different styrene concentrations in ethanol in the absence of SG-1. In particular for high SG-1 concentrations the changes in molar mass are more pronounced. The molar masses, molar mass distributions and conversions are summarized in Table 6.4.

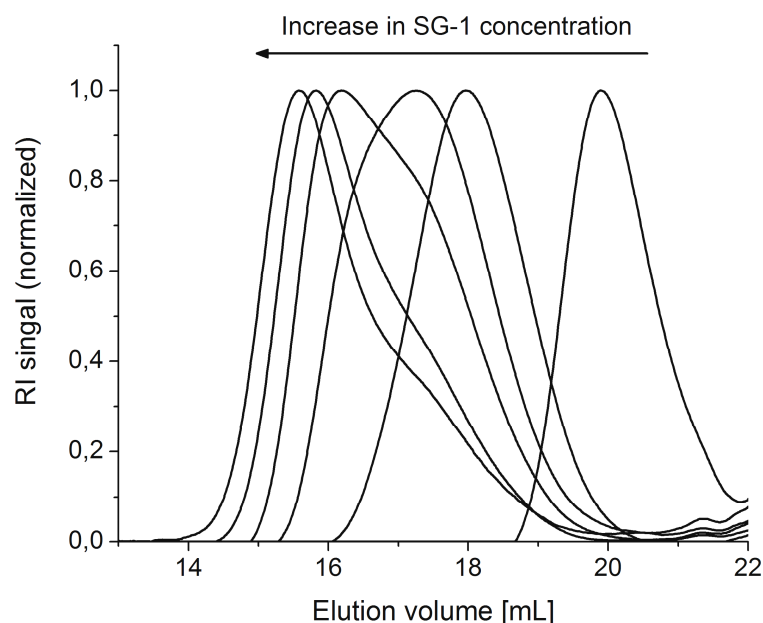


Figure 6.7 SEC curves of the thermally initiated precipitation polymerization of styrene for different SG-1 concentrations (2 M, 150 °C, 1 h).

Table 6.4 Data of the thermally initiated polymerization of styrene with different styrene to SG-1 ratios and polymerization times at 150 °C.

Styrene/SG-1	Time [min]	Conversion [%]	M _n [g/mol]	PDI
10	60	19	1,300	1.32
25	60	53	6,100	1.37
25	80	67	5,600	1.39
25	100	69	5,300	1.40
25	120	67	4,900	1.35
50	60	56	9,700	1.54
100	60	50	12,800	1.64
200	60	41	17,300	1.66
200	120	52	17,400	1.71
200	180	53	16,500	1.74
200	240	53	15,400	1.83
400	60	33	18,600	1.83

The molar masses of polystyrene (from 1,000 to 19,000 g/mol) increase with decreasing styrene/SG-1 ratios. The PDI values varied between 1.32 and 1.83. In particular for high SG-1 concentrations the PDI values are similar to the ones obtained by the alkoxyamine initiated nitroxide mediated polymerization (PDI < 1.5). For a styrene to SG-1 ratio of 25 and 200, different reaction times were tested and in all cases polymers with more or less comparable molar masses (slight decrease with increasing reaction time) were obtained, demonstrating that this is not a controlled radical polymerization, since the molar mass is not increasing with time. The relatively narrow molar mass distributions obtained could be caused by the precipitation during the polymerization. Only a slight improvement in conversion was obtained for longer reaction times. In general, the conversions were much higher in comparison to the approach where only ethanol was used. Currently we have no explanation for the improved conversions when SG-1 is added to the polymerization mixture. The values of the number average molar masses were plotted against the styrene to SG-1 ratios as shown in Figure 6.8. The experimental data was fitted to an exponential decay function (1st order). The plot illustrates the clear dependency of the molar mass on the SG-1 concentration. In principle, the required SG-1 concentration to obtain polystyrene with a certain molar mass can be calculated from this equation.

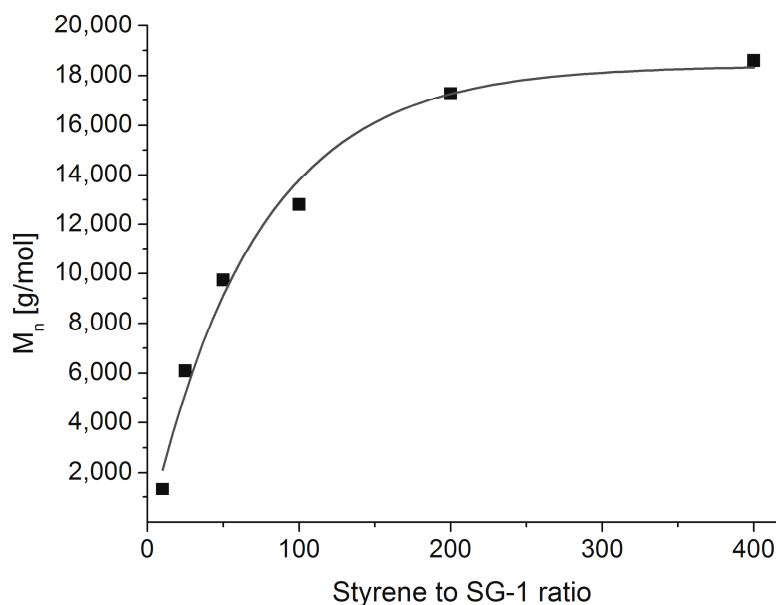
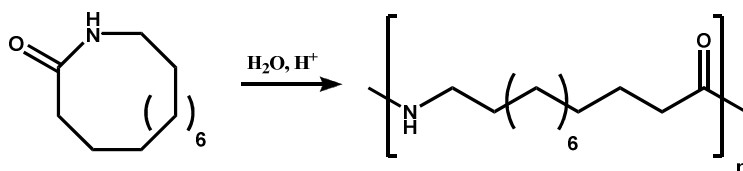


Figure 6.8 Dependency of the number average molar masses on the styrene to SG-1 ratio of the temperature-initiated polymerization of styrene for 1 h at 150 °C. The data was fitted using an exponential curve fitting.

6.2 Microwave-assisted hydrolytic ring-opening polymerization of laurolactam

Besides polystyrene, also polyamide is an important polymer with a worldwide production of around 3 million ton/year.³³ Polyamide is mainly used for the manufacturing of synthetic fibers for clothing and carpets; it is also used as a thermoplastic for injection molding in mechanical engineering and electronics. In industry mostly Nylon 6 and Nylon 6,6 are produced for these kind of applications. Other polyamides are important for more specialized applications.³³ For instance, polyamide 12 is the most widely used polyamide for fuel lines.³⁴ In addition, polyamides are also employed in other fields, *e.g.*, in the automotive and sport industry, in medical applications, in high-performance cables, and in food processing.³⁵ In industry, polyamides are produced by polycondensation of diamines with dicarboxylic acids, or with aminocarboxylic acids. Other possibilities for their formation are the utilization of nylon salts and the ring-opening polymerization of lactams. In general, two different approaches, namely the anionic ring-opening polymerization and the hydrolytic ring-opening polymerization, are utilized for the polymerization of lactams.³⁶ During the hydrolytic polymerization of lactams typically 5–10% water (water has a strong accelerating effect on the ring cleavage) and an initiator (nylon salt or amino caproic acid) are used. In case of polyamide 12, a higher amount of water (~ 38%) and phosphinic acid are utilized as an initiator during the hydrolytic polymerization of laurolactam (Scheme 6.2). On the other hand, a larger amount of water gives rise to high steam pressures at the temperatures required for the reaction (*i.e.* 280 °C). Thus, special equipment such as a pressure reactor is needed in order to perform the polymerization.³⁷ First the pre-polymer is formed, then the pressure is released and the polymer finally polymerizes under a nitrogen flow (removal of water from the polymerization system).



Scheme 6.2 Schematic representation of the hydrolytic ring-opening polymerization of laurolactam.

Literature examples show that the utilization of microwaves as heating source can lead to cleaner products with less side products due to the more even temperature profile inside the reactor, as well as faster heating and cooling compared to conventional heating.³⁸ In addition, the technical microwave systems are equipped with online temperature and pressure measurement systems, and therefore making their handling easy and safe. First trials to produce the polyamide pre-polymer under microwave irradiation were performed. Since high temperatures and pressures are required for the polymerization, the Synthos 3000 (Anton Paar) microwave reactor was used, which can attain high pressures (up to 80 bar) and temperatures (up to 300 °C).³⁹ The polymerizations were carried out at 280 °C at different reaction times (3, 5 and 7 hours, respectively). After 5 hours reaction time no monomer could be detected by GC measurements indicating full conversion. In addition, the TGA in Figure 6.9 only showed the decomposition of the pre-polymer at 452 °C, while the monomer has a decomposition temperature of 240 °C.

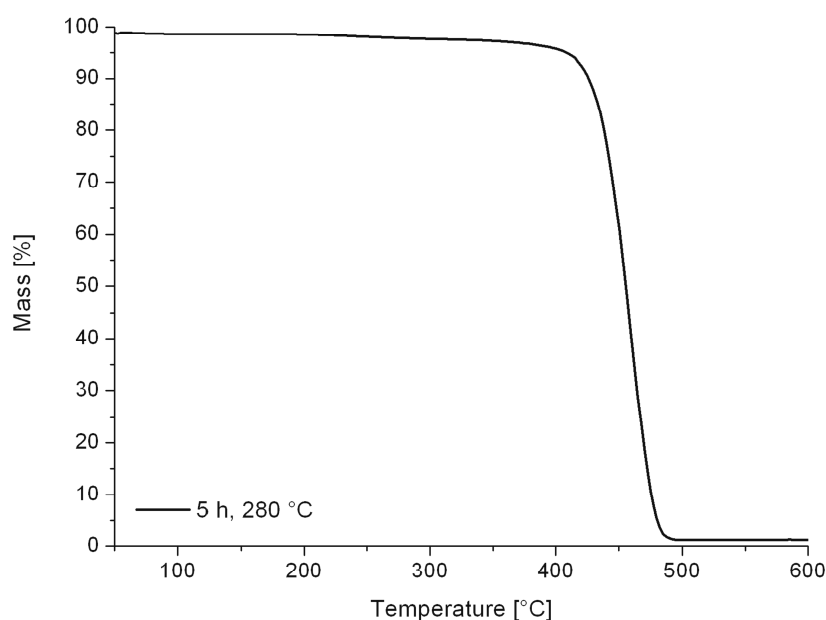


Figure 6.9 TGA measurement of the PA 12 pre-polymer after hydrolytic ring-opening polymerization for 5 h at 280 °C under microwave irradiation.

The synthesized pre-polymers were characterized by size exclusion chromatography (SEC, eluent: HFIP/CF₃COO⁻K⁺) and the M_n values found were in the range of 1,900 g/mol (PMMA standard).⁴⁰ The SEC curves obtained before and after precipitation in dimethylformamide are depicted in Figure 6.10 and the values obtained for the molar masses and molar mass

distributions are summarized in Table 6.5. The SEC curves clearly show that the monomer is still left after 3 h reaction time and that the polymer can be purified by dissolving the crude product in warm dimethylformamide. In addition, the SEC curves seem to indicate that less side products (cyclodimer) are formed during the microwave-assisted polymerization, when compared to the commercial thermal process. These findings still need further investigation and quantification of the side products in order to study if the utilization of microwave irradiation can provide advantages over thermal heating.

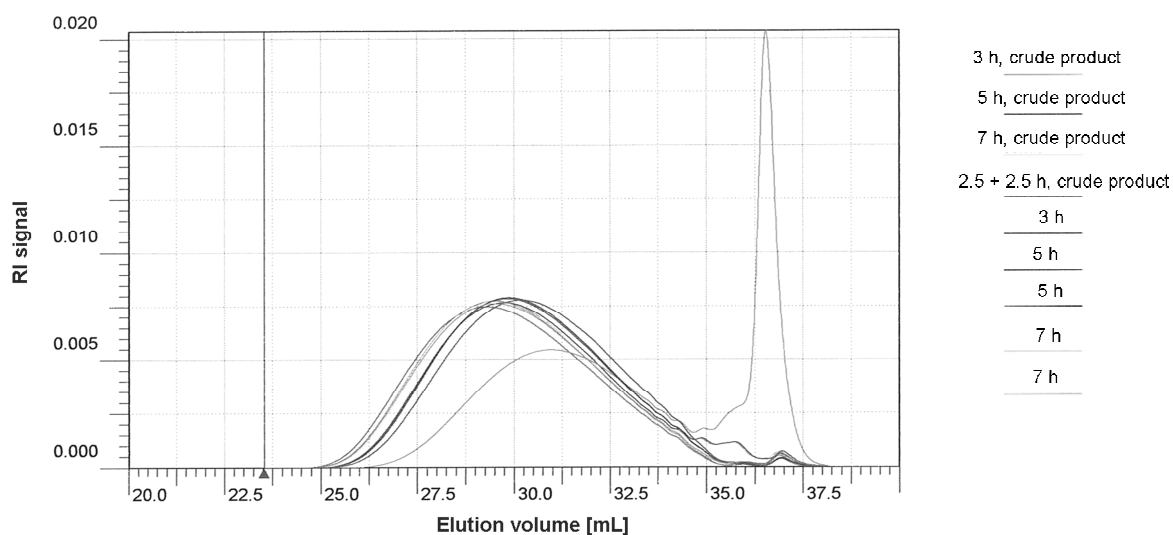


Figure 6.10 SEC curves (eluent: $\text{HFIP}/\text{CF}_3\text{COO}^-\text{K}^+$, standard: PMMA) of the PA 12 pre-polymer after hydrolytic ring-opening polymerization for 3, 5 and 7 h at 280 °C under microwave irradiation (before and after precipitation in dimethylformamide).⁴⁰

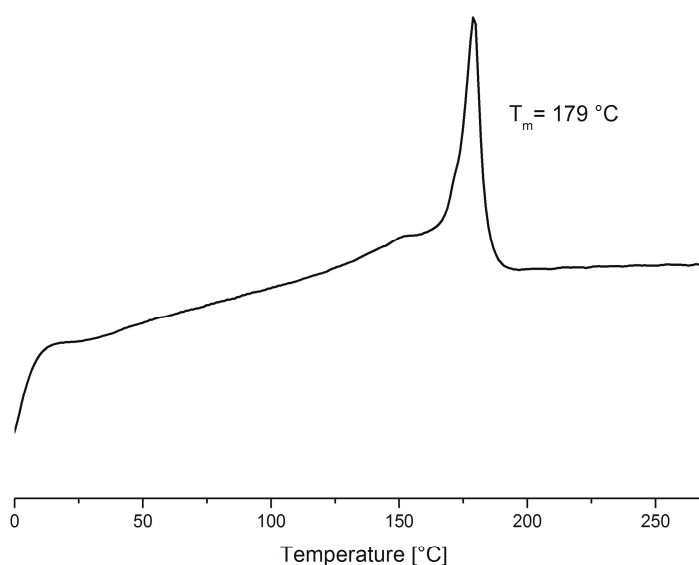
Table 6.5 Data of the hydrolytic ring-opening polymerization of laurolactam with different polymerization times at 280 °C (before and after precipitation).

Time [h]	Product	M_n [g/mol]	M_w [g/mol]	PDI
3	crude	300	3,800	14.05
	precipitated	2,000	7,700	3.90
5	crude	1,800	8,600	4.64
	precipitated	2,600	8,600	3.35
7	crude	1,900	9,300	4.91
	precipitated	2,300	9,700	4.17

Furthermore, the concentration of the amine and the carboxyl end groups was determined by titration (Table 6.6) and revealed that the two end groups are present in nearly equimolar amounts.⁴⁰ Unfortunately, the dimethylformamide seems to interact with the amine end group, since the concentration is significantly decreased after precipitation. In addition, a melting point of 179 °C was found for the pre-polymer by DSC measurement, which is typical for polyamide 12 (Figure 6.11).⁴¹

Table 6.6 End group titration of the polyamide 12 pre-polymers before and after precipitation.

Time [h]	Product	$\eta_{\text{rel}}(\text{m-cresol})$	$c(\text{NH}_2)$ [mmol/kg]	$c(\text{COOH})$ [mmol/kg]
3	crude	1.1	340 / 339	360 / 362
	precipitated	1.16	139 / 140	288 / 285
5	crude	1.19	336 / 339	360 / 362
	precipitated	1.18	166 / 166	286 / 285
7	crude	1.19	319 / 319	365 / 362
	precipitated	1.19	165 / 166	306 / 315

**Figure 6.11** DSC measurement of the PA 12 pre-polymer after hydrolytic ring-opening polymerization for 5 h at 280 °C under microwave irradiation.

6.3 Conclusions

In order to develop a fast and environmental friendly approach to polymerize styrene, we combined two polymerization techniques: the thermally initiated free radical polymerization and the precipitation polymerization. The advantages of both polymerization techniques are the absence of a chemical initiator and the easy purification conditions (polymerization and precipitation in one step). Furthermore, microwave irradiation was used for fast heating and styrene was utilized without further purification to simplify the polymerization conditions.

First experiments were carried out using near-critical water (water in the temperature range of 250 to 350 °C) as solvent, because the polarity and hydrogen-bonding of water are highly depending on the temperature; therefore near-critical water was applied as the polymerization solvent at high temperatures. The polymerization of styrene in near-critical water always led to polymers with comparable molar masses although different styrene concentrations were applied. Thus, we can conclude that styrene and polystyrene are not dissolved in high temperature water.

However, moderate M_n values ($\sim 38,000$ g/mol) were obtained within a short time (only 10 min) with moderate yields ($\sim 31\%$).

Due to the insolubility of styrene in water, the solvent was changed to ethanol. In this case styrene was dissolved in the solvent and the polymer was precipitating during the polymerization. The molar mass could be varied by changing the styrene to ethanol concentration. Unfortunately, monomer conversions were very low even after longer reaction times, because ethanol is inhibiting the polymerization.

The addition of SG-1 led to a polymerization system with moderate yields in only one hour of reaction time. The molar mass could be varied by the amount of SG-1 and for high concentrations rather narrow polydispersity indices for a free-radical polymerization could be observed. An additional precipitation step was not required.

For the styrene polymerizations in ethanol with and without SG-1 structure-property relationships were elucidated that allow a first prediction of the molar mass when varying the styrene concentration or SG-1 amount.

Polyamide 12 pre-polymer was synthesized under microwave irradiation at high temperatures and pressures, indicating the presence of less side products compared to thermal heating. Further investigations are required in order to study if the utilization of microwave irradiation can provide advantages over thermal heating, *e.g.* in less side products.

6.4 Experimental details

Materials

Styrene (Aldrich), ethanol (Biosolve, Ltd.) and *N,N*-*tert*-butyl-*N*-[10-diethylphosphono-2,20-dimethylpropyl] nitroxide (SG-1 from Arkema) were used without further purification. Deionized water was utilized as solvent for the near-critical water experiments.

For the near-critical water experiments and polyamide synthesis the microwave system Synthos 3000 (Anton Paar) was used. In this multi-mode microwave system, the microwave power could be set in steps of 1 up to 1400 W. The temperature inside a reference vessel was measured by a gas thermometer and the outside temperature of all the vessels was obtained by an IR-sensor at the bottom of the microwave cavity. A safety-limit of 300 °C was set for the inside and 280 °C for the outside temperature. The maximum allowed pressure is 120 bar and the system was operated up to 80 bar.

For all other experiments utilizing ethanol as solvent, the microwave system Emrys Liberator (Biotage) was used. In this single-mode microwave system, a power of either 150 or 300 W can be chosen. The temperature was measured with an IR-sensor, located at the side of the microwave cavity. The maximum temperature and pressure were 250 °C and 20 bar, respectively.

Gas chromatography (GC) measurements were performed on an Interscience Trace GC instrument with a Trace Column RTX-5 connected to a CTC PAL autosampler. For the injection of polymerization mixtures, a special Interscience liner with additional glass wool was used. Size exclusion chromatography (SEC) was measured on a Shimadzu SEC, equipped with a

system controller SCL-10Avp, a LC-10AD pump, a RID-10A refractive index detector, a UV/VIS detector DPD-10A, a PSS ETA-2010 differential viscometer, degasser DGU-14A and a CTO-10A column oven and two PSS GRAM 10 μm , 8×300 mm, 1000/30 Å columns utilizing DMA/LiCl (2.1 g/L) as eluent (flow rate 1 mL/min, column temperature 60 °C). PS calibration was used as standard. For the polyamide 12 pre-polymers a SEC from Evonik utilizing two PFG 7 μm columns (50 mm, and 3×300 mm, 1000/300/30 Å) and HFIP/ $\text{CF}_3\text{COO}^-\text{K}^+$ as eluent was used. In this case PMMA was utilized as standard. Melting points were determined on a DSC 204 F1 Phoenix by Netzsch under a nitrogen atmosphere from –100 to 150 °C with a heating rate of 20 K/min (a first heating cycle to 150 °C was not considered for the calculations). Thermogravimetric analyses were performed in a TG 209 F1 Iris by Netzsch under a nitrogen atmosphere in the range from 25 to 600 °C with a heating rate of 20 K/min.

Polymerization of styrene

In water

For the polymerization of styrene in pure water, 2 to 8 mL styrene were added to 20 mL distilled water in a 60 mL quartz vessel (Synthos 3000). The system was closed and polymerized for 10 min at 150 to 280 °C under microwave irradiation. The obtained polymer was filtered and dried overnight in the vacuum oven at 45 °C. The conversions were determined gravimetrically and the molar mass and molar mass distributions were measured by SEC.

In ethanol

For the polymerization of styrene in pure ethanol, 0.02 to 0.8 mL styrene were added to 2 mL ethanol in a microwave vessel (2 to 5 mL, Emrys Liberator). The system was closed and purged with argon for 10 min. The reaction mixture was heated for 1 h at 150 °C under microwave irradiation. Ethanol was removed from the reaction mixture and the obtained polymer was dried overnight in the vacuum oven at 45 °C. The conversions were determined by GC measurements and the molar mass and molar mass distributions were measured by SEC.

In ethanol with SG-1

For the polymerization of styrene in ethanol with SG-1 a stock solution of 7.33 mL of styrene in 24.67 mL ethanol was prepared. A volume of 3 mL was transferred to a microwave vessel (2 to 5 mL, Emrys Liberator). To the stock solutions 5.14 to 178.47 mg SG-1 were added. The system was closed and purged with argon for 10 min. The reaction mixture was heated for 1 h at 150 °C under microwave irradiation. Ethanol was removed from the reaction mixture by simply decanting and the obtained polymer was dried overnight in the vacuum oven at 45 °C. The conversions were determined by GC measurements and the molar mass and molar mass distributions were measured by SEC.

Polymerization of lauro lactam

For the preparation of the pre-polymer, 6.3 mL of distilled water and 2 μ L were added to 10 g of lauro lactam. The mixture was purged with argon for 15 min before closing the 60 mL quartz vessel (Synthos 3000). The polymerization was performed for 5 h at 280 °C under microwave irradiation. The obtained polymer was dried overnight in the vacuum oven at 45 °C. The conversions were determined by GC and the polymer was characterized by SEC.

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Summary

The concept of sustainable chemistry represents an area of innovation, which not only preserves resources, but also stands for a progress in the chemical industry. The principle of sustainable chemistry comprises important elements in areas like environment, economy and society, dealing with the whole life of intrinsic safe chemicals and products, including their production, processing, use and disposal. One of the largest amounts of auxiliary wastes in industry is produced by the usage of solvents. Therefore, alternative reaction media are investigated in order to reduce or replace organic solvents. The most widely used green solvents in, *e.g.*, polymer research are ionic liquids, supercritical CO₂ and water. In addition, also alternative energy sources, such as photochemistry, microwave energy, electron beam and ultrasound, are investigated in order to replace conventional heat sources for, *e.g.*, polymer processing. The main goal of utilizing alternative energy sources is to improve the efficiency of the process by reducing the polymerization time.

Ionic liquids are considered to be ‘green’ solvents on account of their non-volatility and non-flammability – which are results of their negligible vapor pressure – as well as their reusability. On the basis of ecological concerns, ionic liquids seem to be an attractive alternative to conventional volatile organic solvents. Ionic liquids with a linear alkyl side chain can be synthesized in a fast and efficient way at elevated temperatures (170 °C) by using microwave irradiation. In case of the ionic liquids with branched alkyl side chains, the synthesis could be accelerated as well, but the equilibrium was shifting towards undesired side products compared to the synthesis at conventional conditions (80 °C). In this regard, several new branched ionic liquids, *e.g.* 1-(1-ethylpropyl)-3-methylimidazolium iodide and 1-(1-methylbenzyl)-3-methylimidazolium chloride and their tetrafluoroborate containing analogues, were synthesized applying two different synthetic approaches. The direct scaling for the ionic liquids with linear alkyl side chain was investigated from small scale (0.01 mol) to large scale (1.15 mol). In this case, comparable results were obtained for the direct up-scaling utilizing different microwave reactors under otherwise similar reaction conditions. The results of the continuous flow experiments indicated that 1-butyl-3-methylimidazolium chloride can be synthesized with short reaction times by using continuous flow microwave systems. However, direct scaling from the batch experiments was not possible. Even when employing a residence time of 16 min, a complete conversion could not be obtained. Nonetheless, for the first time, the synthesis of ionic liquids in continuous flow reactors was achieved. In case of [C₂MIM][Et₂PO₄], higher conversions were achieved, since the reaction proceeds in a homogeneous phase, but unfortunately only strongly colored ionic liquids could be obtained with the applied conditions, while not showing any decomposition products in the ¹H NMR spectrum. In order to elucidate first structure–property relationships, the synthesized ionic liquids, both linear and branched, were investigated by thermogravimetric analysis, differential scanning calorimetry, and water uptake measurements of selected ionic liquids. The results obtained for the decomposition temperature support a S_N2 (alkyl) and S_N1 (aryl)

decomposition pathway for branched ionic liquids with alkyl and aryl side chain, respectively, containing chloride as counter ion. In case of tetrafluoroborate containing ionic liquids a decomposition mechanism initiated by the anion seems to take place. Moreover, tetrafluoroborate containing ionic liquids and ionic liquids with linear alkyl side chains revealed lower glass transition temperatures compared to the ionic liquids with chloride anion or branched alkyl side chains, respectively. In general, the ionic liquids with an aromatic group showed the highest T_g values of all the investigated ionic liquids. In addition, the water uptake of the ionic liquids was measured and revealed a systematic dependency on the length of the alkyl side chain and on the branching. It was found that the water absorption decreased with the length of the alkyl chain and that branched alkyl chains increased the water uptake as a result of their decreased ability to self-assembly. The described results provide a better insight into the structure-property relationship of ionic liquids, allowing the fine-tuning of the chemical and physical properties.

Cellulose is the most abundant natural polymer in nature and its derivative products have many important applications. However, cellulose is insoluble in water and most common organic solvents, because of its fibril structure and the pronounced presence of inter- and intermolecular hydrogen bonding. In recent years, ionic liquids were found to dissolve cellulose, but the candidates known are still limited. In order to extend the range of suitable ionic liquids, we screened known but also new tailor-made ionic liquids. In particular, the influence of different alkyl chain lengths, branched alkyl side chains and the anion on the dissolution of cellulose was investigated. A strong odd-even effect of the alkyl chain length on the solubility of cellulose in the ionic liquid was observed for imidazolium based ionic liquids with linear and branched alkyl side chains bearing chloride as counter ion. Alkyl side chains with an odd number of CH_2 repeating units showed in general good dissolving properties, whereas an even number of CH_2 repeating units was not able to dissolve cellulose. The difference in solubility might be explained by a different range of conformations for odd and even alkyl chains. In general, only the ionic liquids with chloride, acetate and phosphate counter anions showed good dissolving properties for cellulose. Moreover, the microwave-assisted dissolution of cellulose was investigated and optimized. Selected ionic liquids were used as solvent in the tritylation reaction. It was found, that pyridine is required to capture hydrogen chloride and that the reaction time could be reduced from 48 h (reaction in DMA/LiCl) to 3 h ($[\text{C}_4\text{MIM}][\text{Cl}]$) in order to reach the desired DS of nearly 1.0. Unfortunately, recycling of the ionic liquid could not be achieved when pyridine was used as a base. However, this was possible when triethylamine was used as a base.

New 4,4-imidazolium ionenes were synthesized under microwave irradiation. The polymerization times could be decreased from 24 to 1 h as a result of elevated temperatures above the boiling points of the applied solvents. Different approaches, such as monomer imbalance and monofunctional reagents, were applied in order to control the molar mass of the polymers. Analytical ultracentrifugation measurements indicate the formation of macrocyclic rings to a large extend (82 to 93%). Furthermore, the properties of the synthesized 4,4-imidazolium

ionenes, such as thermal behavior, solubility behavior and water uptake were investigated as well. It was found that the decomposition temperatures were comparable to the values reported in literature for ammonium ionenes, while the glass transition temperatures obtained were lower compared to values reported in literature. In addition, the 4,4-imidazolium ionenes showed a high water uptake. The ability to absorb water is mainly depending on the counter ions (chloride showed a higher water uptake than bromide).

The combination of the thermal auto-initiated free radical polymerization of styrene and the precipitation polymerization were investigated in order to develop a fast and environmentally friendly approach to produce polystyrene. To achieve high reaction temperatures in a short time, microwave irradiation was utilized as heating source. Styrene was used without any purification, *e.g.* without distillation or column filtration. First experiments were carried out using near-critical water (water in the temperature range of 250 to 350 °C) as solvent, because the polarity and hydrogen-bonding of water are highly temperature depending. Due to the auto-initiation of styrene at high temperatures no radical initiator was required. The polymerization of styrene in near-critical water always led to polymers with comparable molar masses although different styrene concentrations were applied. In case of ethanol as solvent, the obtained molar masses could be controlled by the ethanol-to-styrene ratio although the monomer conversions were rather low under the applied conditions (1 to 13%). In order to achieve a better control over the molar mass SG-1, a commercially available stable free nitroxide, was applied to mediate the polymerization. It was found that the molar masses can be controlled by different styrene:SG-1 ratios (from 10:1 to 400:1). In this case moderate polydispersity indices ($PDI = 1.3$ to 1.9) could be obtained. Finally, the developed polymerization processes only require a simple purification step due to the precipitation of the polystyrene in the reaction solvent. Another example of using near-critical water is the hydrolytic ring-opening polymerization of polyamide. In this thesis a polyamide 12 pre-polymer was synthesized under microwave irradiation at high temperatures and pressures, indicating that less side products are formed compared to the thermal polymerization. Since these are preliminary results, further experiments are required in order to investigate if the utilization of microwave irradiation can provide advantages over thermal heating.

In general, it was shown that microwave irradiation and ionic liquids are interesting alternatives to conventional energy sources and solvents. In particular, a better understanding of the structure-property relationships of branched ionic liquids was achieved resulting in a superior knowledge about the influence of the alkyl side chains of ionic liquids on the cellulose dissolution process. New concepts (combination of thermal and precipitation polymerization, near-critical water) and polymers (imidazolium ionenes) were investigated utilizing microwave irradiation as heating source to achieve short reaction times.

Samenvatting

Het concept duurzame chemie vertegenwoordigt een gebied van innovatie, dat niet alleen middelen bewaart, maar is ook een ontwikkelingsproces in de chemische industrie. Het principe van duurzame chemie bestaat uit belangrijke elementen op gebieden zoals milieu en economie en maatschappij, die het gehele leven van intrinsiek veilige chemicaliën en producten, met inbegrip van hun productie, verwerking, gebruik en verwijdering behandelt. Één van de grootste hoeveelheden hulpafval in industrie wordt veroorzaakt door het gebruik van oplosmiddelen. Daarom worden alternatieve reactiemedië onderzocht om de hoeveelheid organische oplosmiddelen te verminderen of zelfs te vervangen. De meest gebruikte groene oplosmiddelen in bijv. het polymeer onderzoek zijn ionische vloeistoffen, superkritisch CO₂ en water. Bovendien worden alternatieve energie bronnen onderzocht, zoals fotochemie, microgolf energie, elektrotraal en ultrasoon geluid, om de conventionele hittebronnen te vervangen. Het belangrijkste doel om alternatieve energie bronnen te gebruiken is het verbeteren van de effectiviteit van het proces door bijv. het reduceren van de polymerisatietijd.

Ionische vloeistoffen worden beschouwd als ‘groene’ oplosmiddelen doordat ze niet vluchtig en niet ontvlambaar zijn – welke beide het gevolg zijn van de lage dampspanning – evenals de mogelijkheid om gerecycled te worden. Door ecologische overwegingen, blijken de ionische vloeistoffen een aantrekkelijk alternatief ten opzichte van de meer conventionele, vluchtige organische oplosmiddelen. De ionische vloeistof met een lineaire alkyl zijketen kunnen op een snelle en efficiënte manier worden gesynthetiseerd door het gebruik van microgolfstraling. De ionische vloeistoffen met een vertakte alkyl zijketen zouden bij verhoogde temperatuur eveneens kunnen worden versneld, echter verschoof het evenwicht naar het ongewenste bijproduct. In dit verband, verschillende nieuwe ionische vloeistoffen met een vertakte zijketen, bijv. [3-C₅MIM][I] en [MBnMIM][Cl], werden gesynthetiseerd waarbij twee verschillende synthetische methoden zijn toegepast. Voor de ionische vloeistoffen met een lineaire alkyl zijketen was de synthese uitgevoerd van kleine (0.01 mol) naar grote schaal (1.15 mol). Over het algemeen werden vergelijkbare resultaten gevonden voor vergelijkbare reactie condities voor zowel kleine als grote schaal ook al werden er verschillende microgolf apparaten gebruikt. De resultaten voor de continue stroom experimenten laten zien dat [C₄MIM][Cl] kon worden gesynthetiseerd met korte reactietijden. Het bleek echter dat direct schalen van de batch experimenten niet mogelijk was. Zelfs wanneer een langere verblijftijd werd gebruikt kon er geen volledige omzetting worden verkregen. Toch was dit de eerste keer dan de synthese van ionische vloeistoffen is gedaan in een continue stroom reactor. In het geval van [C₂MIM] [Et₂PO₄], werden hogere conversies bereikt omdat de reactie plaats vindt in een homogene fase, maar jammer genoeg werd de ionische vloeistof donkerder van kleur tijdens de gebruikte condities.

Om de eerste structuur-eigenschap relaties te onderzoeken, werden geselecteerde ionische vloeistoffen, zowel lineair als vertakt, onderzocht met thermogravimetrische analyse, differentiële scanning calorimetrie en water opname metingen. De verkregen resultaten van de

decompositie temperatuur steunen een S_N2 en S_N1 decompositie route voor vertakte ionische vloeistoffen met een alkyl en aryl zijketen, respectievelijk, beide chloride als tegen ion bevattend. In het geval van ionische vloeistoffen die tetrafluoroborate bevatten wordt het decompositie mechanisme geïnitieerd met het anion. Verder, voor ionische vloeistoffen die tetrafluoroborate bevatten of een lineaire alkyl zijketen hebben blijken een lagere glas overgangstemperatuur te hebben in vergelijking met de ionische vloeistoffen met een chloride anion of een vertakte zijketen. Over het algemeen toonden de ionische vloeistoffen met een aromatische groep de hoogste T_g waarden van alle onderzochte ionische vloeistoffen. Bovendien werd de water opname van de ionische vloeistoffen gemeten en liet een schematische afhankelijkheid zien van de lengte van de alkyl zijketen en van de vertakking. Er werd gevonden, dat de water absorptie verminderd bij het variëren van de alkyl zijketen en dat de vertakte alkyl zijketens de water opname verhoogden, mede door hun verminderde capaciteit tot zelfpakking. De beschreven resultaten geven een beter inzicht in de structuur-eigenschap relaties van ionische vloeistoffen zodat chemische en fysische eigenschappen kunnen worden verfijnd.

Cellulose is een natuurlijk polymeer dat het meest aanwezig is in de natuur en de afgeleide producten van cellulose hebben vele belangrijke toepassingen. Cellulose is echter onoplosbaar in water en de meest gebruikelijke organische oplosmiddelen vanwege zijn fibrilstructuur en aanwezigheid van inter- en intramoleculaire waterstof bruggen. In de laatste jaren werden ionische vloeistoffen gevonden die cellulose kunnen oplossen, maar de kandidaten hiervoor zijn nog steeds gelimiteerd. Om de range van beschikbare ionische vloeistoffen uit te breiden hebben we bekende, maar ook de nieuw gesynthetiseerde ionische vloeistoffen onderzocht. In het bijzonder, de invloed van verschillende lengten alkyl zijketens, vertakte alkyl zijketens en de invloed van de anion is onderzocht op het vermogen cellulose op te lossen. Een sterk even - oneven effect is waargenomen van de lengte van de alkyl zijketen (lineair en vertakt) van imidazolium gebaseerde ionische vloeistoffen met chloride als tegen ion op de oplosbaarheid van cellulose. Alkyl zijketens met een oneven nummer of CH_2 groepen laten over het algemeen goede eigenschappen zien voor het oplossen van cellulose, daarentegen de ionische vloeistoffen met een even nummer CH_2 groepen blijken niet in staat cellulose op te lossen. Het verschil in oplosbaarheid kan misschien worden verklaard door een verschillende conformatie voor oneven en even alkyl ketens. Over het algemeen, alleen de ionische vloeistoffen met chloride, acetaat en fosfaat tegen anionen laten goede eigenschappen zien voor het oplossen van cellulose. Verder werd het oplossen van cellulose onderzocht in een microgolf reactor en geoptimaliseerd. Geselecteerde ionische vloeistoffen werden gebruikt als oplosmiddel in de tritylation reactie. Er werd gevonden dat pyridine benodigd is en dat de reactie tijd kon worden verminderd van 48 uur (DMA/LiCl) naar 3 uur ([C4MIM][Cl]) om de gewenste omzettingsgraad van bijna 1.0 te halen. Door het gebruik van pyridine als base was het helaas niet mogelijk de ionische vloeistof te recyclen. Wanneer triethylamine werd gebruikt als base was recycling van de ionische vloeistof wel mogelijk.

Nieuwe 4,4-imidazolium ionenes werden gesynthetiseerd onder microgolfstraling. De polymerisatietijden konden worden gereduceerd van 24 naar 1 uur als gevolg van gebruikte

temperaturen boven het kookpunt van de toegepaste oplosmiddelen. Verschillende benaderingen zijn toegepast, zoals monomeer imbalans en monofunctionele reagentia, om de molecuulmassa van de polymeren te controleren. Uit de resultaten van de analytische ultracentrifugatie blijkt dat hoofdzakelijk macro cyclisch ringen zijn gevormd (82 tot 93%). Verder werden de eigenschappen van de gesynthetiseerde 4,4-imidazolium ionenes, zoals thermisch gedrag, oplosbaarheid en water opname onderzocht. Er werd gevonden dat de decompositie temperaturen voor ammonium ionenes vergelijkbaar waren met de gerapporteerde waarden in literatuur, terwijl de gemeten glastransitie temperaturen lager waren in vergelijking met waardes gemeten in literatuur. Bovendien toonden de 4,4-imidazolium ionenes een hoge water opname. De capaciteit om water te absorberen is voornamelijk afhankelijk van de tegen ionen.

De combinatie van de thermische auto-geïnitieerde vrije radicaal polymerisatie van styreen en de precipitatie polymerisatie waren onderzocht om een snelle en milieuvriendelijke manier te ontwikkelen voor het produceren van polystyreen. Om hoge reactietemperaturen te bereiken in een korte tijd, werd microgolffstraling gebruikt als warmtebron. Styreen werd gebruikt zonder enige zuivering. De eerste experimenten werden uitgevoerd met bijna kritisch water als oplosmiddel, omdat de polariteit en de waterstof bruggen van bijna kritisch water sterk afhankelijk zijn van de temperatuur. Door de auto-initiatie van styreen bij hoge temperaturen was er geen radicaal initiator nodig. De polymerisatie van styreen in bijna kritisch water leidde altijd tot polymeren met vergelijkbaar molecuulgewicht ook al werden er verschillende styreen concentraties gebruikt. Wanneer ethanol als oplosmiddel werd gebruikt konden de molecuulgewichten worden gecontroleerd met de ethanol-styreen ratio hoewel de monomeer conversies wel laag waren bij de toegepaste condities. Verder werd het effect van commercieel beschikbare stabiele vrije nitroxide onderzocht op het polymerisatie proces. Het blijkt dat het mogelijk is om het molecuulgewicht van het polymeer te controleren door de ratio styreen-vrije nitroxide te veranderen en gematigde polydispersiteit indexen konden worden verkregen. Uiteindelijk was er voor het ontwikkelde polymerisatie proces nog een simpele zuiveringsstap nodig om het polymeer in handen te krijgen, namelijk het precipiteren van de polystyreen in het reactieoplosmiddel. Polyamide 12 pre-polymeer was gesynthetiseerd onder microgolffbestraling bij hoge temperatuur en druk. Verdere onderzoeken zijn nodig om de mogelijkheid te bestuderen of het gebruik van microgolffbestraling verdere voordelen heeft ten opzichte van het thermisch verwarmen, bijv. minder bijproducten.

Concluderend kan gesteld worden dat microgolffirradiatie en ionische vloeistoffen interessante alternatieven zijn voor conventionele energiebronnen en oplosmiddelen. Een beter begrip van de relatie tussen chemische structuur en specifieke eigenschappen van ionische vloeistoffen met vertakte alkyl zijketen werd bereikt. Dit resulteerde in een superieure kennis over de invloed van het oplossen van cellulose. Nieuwe concepten (combinatie van thermische en precipitatie polymerisatie, bijna kritisch water) en polymeren (imidazolium ionenes) werden onderzocht onder microgolffirradiatie om korte reactietijden te bereiken.

Curriculum vitae



Tina Erdmenger was born on 3rd of July 1981 in Erfurt (Germany) and finished her secondary education in 2000. Afterwards she started her study at the Friedrich-Schiller-University Jena (Germany). In 2003 she obtained her bachelor degree in chemistry and in 2005 she received her master degree in environmental chemistry under the supervision of Prof. Dr. Bernd Ondruschka at the technical chemistry department of the Friedrich-Schiller-University Jena. Her graduation project was dealing with the investigation of device parameters of technical microwave systems and first trials of validating microwave-assisted reactions. In September 2005 she started her PhD under supervision of Prof. Dr. Ulrich S. Schubert at the Eindhoven University of Technology (The Netherlands) in the field of polymer science utilizing alternative solvents and energy sources. The results of her research are presented in this thesis.

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