7.0 Polymer Synthesis in Ionic Liquids

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7.1 Introduction

Ambient-temperature ionic liquids have received much attention in both academia and industry due to their potential as replacements for volatile organic compounds (VOCs).[1-3] These studies have utilised the ionic liquids as direct replacements for conventional solvents and as a method to immobilise transition metal catalysts in biphasic processes.

Many organic chemical transformations have been carried out in ionic liquids, for example, hydrogenation,[4, 5] oxidation,[6] epoxidation[7] and hydroformylation[8] reactions. In addition to these processes numerous synthetic routes involve a carbon-carbon (C-C) bond forming step. As a result many C-C bond forming procedures have been studied in ambient-temperature ionic liquids. Among those reported are the Friedel-Crafts acylation[9] and alkylation[10] reactions, allylation reactions,[11, 12] the Diels-Alder reaction,[13] the Heck reaction,[14] and the Suzuki[15] and Trost-Tsuji coupling[16] reactions.

The C-C bond forming reaction that has received most attention in ionic liquids is the dimerisation of simple olefins (e.g. ethene, propene and butene).[17-20] An existing commercial procedure, the Dimersol process,[21] is widely used for the dimerisation of simple olefins and produces approximately 3 x 10^6 tonnes per annum. The technology in this process has been adapted to function under biphasic conditions using the ternary ionic liquid system [BMIM][Cl-$AlCl_3$-$EtAlCl_2$] (where BMIM is 1-butyl-3-methylimidazolium) as a solvent for the nickel catalysts.[17, 18, 22] Improvements in catalyst activity, better selectivity and simple removal of pure products allowing easy recycling of the ionic liquid and catalyst are the benefits offered over the conventional process.

In these reactions the system is tuned (e.g. by adjusting the reaction temperature and time and modifying the catalyst structure) to maximise the quantity produced of the desired dimers, and to minimise the production of higher molecular weight oligomers and polymers. In other reactions it is the opposite that is true: higher weight products are desired. The most industrially useful C-C bond forming reaction is addition polymerisation. This is used to give polymers that are used for a multitude of applications, for example in coatings, detergents, adhesives, plastics, etc, etc. The use of ambient-temperature ionic liquids as solvents for the preparation of polymers has received little attention especially when compared to studies concerning their use in other synthetic areas. This chapter surveys the polymerisation reactions carried out in ionic liquids thus far.

7.2 Acid catalysed cationic polymerisation and oligomerisation

Strong Brønsted acids that have non-nucleophilic anions (e.g. $HClO_4$ and CF_3CO_2H) are capable of initiating cationic polymerisation with vinyl monomers that contain an electron donating group adjacent to a carbon-carbon double bond, (e.g. vinyl ethers, isobutylene, styrene and dienes). Lewis acids are also used as initiators in cationic polymerisation with the formation of high molecular weight polymers. These include metal halides (e.g. $AlCl_3$, BF_3 and $SbCl_5$), organometallic species (e.g. $EtAlCl_2$) and oxyhalides (e.g. $POCl_3$). Lewis acids are often used in the presence of a proton source (e.g. H_2O, HCl and MeOH) or a carbocation source (e.g. Bu^tCl) which leads to an acceleration in the rate of polymerisation.[23]

The chloroaluminate(III) ionic liquids, for example, [EMIM][Cl-$AlCl_3$] (where EMIM is 1-ethyl-3-methylimidazolium) are liquid over a wide range of $AlCl_3$ concentrations.[24] The quantity of $AlCl_3$ present in the ionic liquid determines the physical and chemical properties of the liquid. When the mole fraction, $X(AlCl_3)$, is below 0.5 the liquids are referred to as basic. When $X(AlCl_3)$ is above 0.5 the liquids are referred to as acidic and at an $X(AlCl_3)$ of exactly 0.5 they are referred to as neutral.

Studies have shown that when protons, using HCl as the source, are dissolved at ordinary temperatures and pressures in the acidic ionic liquid [EMIM][Cl-$AlCl_3$] ($X(AlCl_3) = 0.55$) they are superacidic with a strength similar to a liquid HF-Lewis acid mixture.[25] The precise Brønsted acidity observed depends on proton concentration and on ionic liquid composition. The ambient-temperature chloroaluminate(III) ionic liquids are extremely sensitive to moisture reacting exothermically with moisture to give chlorooxoaluminate(III) species generating HCl. Since moisture is ever-present, even in the most carefully managed systems, chloroaluminate(III) ionic liquids generally possess superacidic protons. In addition, acidic chloroaluminate(III) ionic liquids contain Lewis acid species,[26] for example, $[Al_2Cl_7]^-$ so it is unsurprising that with the combination of these factors acidic chloroaluminate(III) ionic liquids catalyse the cationic oligomerisation and polymerisation of olefins.

Studies on the dimerisation and hydrogenation of olefins with transition metal catalysts in acidic chloroaluminate(III) ionic liquids report the formation of higher molecular weight fractions consistent with cationic initiation.[17, 20, 27, 28] These studies ascribe the occurrence of the undesired side reaction to both the Lewis acid and the proton catalysed routes. Their attempts to avoid these side reactions led to the preparation of alkylchloroaluminate(III) ionic liquids and buffered chloroaluminate(III) ionic liquids.[17, 20, 28]

Attempts to bring the benefits of ionic liquid technology by drawing on the inherent ability of the chloroaluminate(III) ionic liquids to catalyse cationic polymerisation reactions, as opposed to minimising them, were patented by Ambler *et al* of BP Chemicals Ltd in 1993.[29] They used acidic [EMIM][Cl-$AlCl_3$] ($X(AlCl_3) = 0.67$) for the polymerisation of butene to give products that find application as lubricants. The polymerisation can be carried out by bubbling butene through the ionic liquid. The product formed a separate layer that floats upon the ionic liquid and was isolated by a simple process. Alternatively, the polymerisation was carried out by injecting the ionic liquid into a vessel charged with butene. After a suitable settling period the poly(butene) was isolated in a similar fashion. The products from these reactions must be best described as oligomers as opposed to polymers as the product is still in the liquid form. Chain transfer to impurities, ionic liquid, monomer and polymer will terminate the propagation reaction resulting in the low-mass products.

Synthesis of higher molecular weight polymers via cationic polymerisation requires the formation of charged centres that live for long enough to propagate without chain transfer or termination. For this to occur stabilisation of the propagating species by solvation is generally required. In addition, low temperatures are usually employed in an attempt to reduce side reactions that destroy the propagating centres. Use of a pure *iso*-butene feedstock gives poly(*iso*-butene) with properties that depend upon the reaction temperature. As the temperature is reduced the molecular weight of the product is reported to dramatically increase which is a result of the rates of the side reactions and the rate of polymerisation being reduced, Table 7.1.[29]

Ionic liquid catalysed polymerisation of butene is not limited to the use of pure alkene feedstocks, which can be relatively expensive. More usefully, the technology can be applied to mixtures of butenes, for example, the low value hydrocarbon feedstocks raffinate I and raffinate II have been used. The raffinate feedstocks are principally C4 hydrocarbon mixtures rich in butenes. When these feedstocks are polymerised using acidic chloroaluminate(III) ionic liquids polymeric/oligomeric products are obtained which have higher molecular weights than that obtained by conventional processes, even though higher reaction temperatures are used. With the ionic liquid catalysed process, although *iso*-butene conversion is much higher than the *n*-butenes conversion, the produced polymers have a much higher incorporation of *n*-butenes than would be possible under conventional cationic polymerisation processes, Table 7.2.[29]

The ionic liquid process has a number of advantages over traditional cationic polymerisation processes, for example, the Cosden process which employs a liquid phase aluminium(III) chloride catalyst to polymerise butene feedstocks.[30]

The separation and removal of the product from the ionic liquid phase as the reaction proceeds allows the polymer to be obtained simply and in a highly pure state. Indeed, the polymer contains so little of the ionic liquid that an aqueous wash step can be dispensed with. This separation also means that further reaction (e.g. isomerisation) of the polymer's unsaturated ω-terminus is minimised. In addition to obtaining the desired product easily, the ionic liquid is not destroyed by any aqueous washing procedure so it can be reused in subsequent polymerisation reactions resulting in a reduction of operating costs. The ionic liquid technology does not require a massive capital investment and is reported to be easily retrofitted to existing Cosden process plants.

Further development of this original work which used [EMIM][Cl-$AlCl_3$] ($X(AlCl_3) = 0.67$) as the ionic liquid has found that by replacing the ethyl group attached to the imidazolium ring with alkyl groups of increasing length (e.g. octyl, dodecyl and octadecyl) the catalytic activity of the ionic liquid towards the oligomerisation of the olefins increases. Thus, the longer the alkyl chain the greater the degree of polymerisation achieved.[31] This provides an additional method for altering the product distribution. Increased polymer yield with the raffinate I feedstock was achieved by the use of an [EMIM][Cl-$AlCl_3$] ionic liquid that contains a small portion of the quaternary ammonium salt [NEt_4]Cl. The ternary ionic liquid [NEt_4]Cl-[EMIM][Cl-$AlCl_3$] with the mole ratio 0.08 : 0.25 : 0.67 used under the same reaction conditions as the binary ionic liquid [EMIM][Cl-$AlCl_3$] ($X(AlCl_3) = 0.67$) producing ~70 % of a polymer/oligomer mixture as opposed to ~40 % polymer/oligomer produced with the original binary system. Both systems produce oligomers with $M_n = 1{,}000$ g mol^{-1}.[32] These examples demonstrate the ability to tune the ionic liquid's properties by changing the ancillary substituents. This allows the solvent to be adapted to the needs of the reaction, as opposed to altering the reaction to the needs of the solvent.

This technology has been utilised by BP Chemicals for the production of lubricating oils with well-defined characteristics (e.g. pour point and viscosity index). It is used in conjunction with a mixture of olefins (i.e. different isomers and different chain length olefins) to produce lubricating oils of higher viscosity than that obtainable by conventional catalysis.[33] Unichema Chemie BV have applied these principals to more complex monomers. They use it with unsaturated fatty acids to create a mixture of products.[34]

Apart from one mention in the original patent to the synthesis of a high molecular weight poly(*iso*-butene), Table 7.1,[29] the remaining work, until recently, has been concerned with the preparation of lower weight oligomers. In 2000, Symyx Technologies Inc. protected a method for the production of high molecular weight poly(*iso*-olefin)s without the use of very low temperatures.[35] Symyx used the [EMIM][Cl-$AlCl_3$] ionic liquid to produce poly(*iso*-butene)s with weight average molecular weights (M_w) in excess of 100,000 g mol^{-1} which are of use in the automotive industry due to their low oxygen permeability and mechanical resilience, Table 7.3. The table shows that at temperatures as high as –40°C polymers with molecular weights higher than half a million are obtained. As expected, when the temperature is increased the molecular weight decreases. In all cases the yield is less than 50 %. By running the reaction under biphasic conditions, reducing the concentration of *iso*-butene and by adding ethylaluminium(III) dichloride the reaction yield becomes quantitative, Table 7.4. This shows that in addition to using temperature to control the molecular weight of the product control can also be achieved through the quantity of ethylaluminium(III) dichloride added to the reaction, that is the more alkylaluminum(III) that is added the lower the molecular weight of the product. It might be expected that the ethylaluminium(III) dichloride acts as a proton scavenger which should stop the polymerization thus it seems it acts as either/both a strong Lewis acid or an alkylating agent promoting polymerization.

For the results reported in both Table 7.3 and Table 7.4 the only detail reported concerning the ionic liquid is that it was [EMIM][Cl-$AlCl_3$]. No details are forthcoming about the aluminium(III) chloride content. As with most to the work presented in this chapter data is taken from the patent literature and not from peer review journals. Therefore, many experimental details are not available. This lack of clear reporting complicates issues for the synthetic polymer chemist. Simpler and cheaper chloroaluminate(III) ionic liquids prepared using cations derived from the reaction of a simple amine and hydrochloric acid (e.g. $Me_3N{\cdot}HCl$ and $Bu_2NH{\cdot}HCl$) have been successfully used in the polymerisation of *iso*-butene and styrene.[36] Although these ionic liquids have much higher melting points than their imidazolium analogues they are liquid at temperatures suitable for their use in the preparation of low molecular weight oligomers (i.e. 1,000 to 4,000 g mol^{-1}). This reduces one of the barriers to exploitation of the technology, the relatively high expense of the imidazolium halide salts.

7.3 Free radical polymerisation

Free radical polymerisation is a key method used by the polymer industry to produce a wide range of polymers.[37] It is used for the addition polymerisation of vinyl monomers including styrene, vinyl acetate, tetrafluoroethylene, methacrylates, acrylates, (meth)acrylnitrile and (meth)acrylamides, etc in bulk, solution and aqueous processes. The chemistry is easy to exploit and is tolerant to many functional groups and impurities.

The first use of ionic liquids in free radical addition polymerisation was used as an extension to the doping of polymers with simple electrolytes for the preparation of ion-conducting polymers. Several groups have prepared polymers suitable for doping with ambient-temperature ionic liquids with the aim of producing polymer electrolytes of high ionic conductance. Many of the polymers prepared are related to the ionic liquids employed, for example, poly(1-butyl-4-vinylpyridinium bromide) and poly(1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide.[38-41]

Noda and Watanabe[42] reported a simple synthetic procedure for the free radical polymerisation of vinyl monomers to give conducting polymer electrolyte films. Direct polymerisation in the ionic liquid gives transparent, mechanically strong and highly conductive polymer electrolyte films. This was the first time that ambient-temperature ionic liquids have been used as a medium for free radical polymerisation of vinyl monomers. The ionic liquids [EMIM][BF_4] and [*N*BPY][BF_4] (where *N*BPY is *N*-butylpyridiunium) were used with equimolar amounts of suitable monomers and polymerisation initiated by prolonged heating

(12 hours at 80 °C) using benzoyl peroxide. Suitable monomers for this purpose are monomers that dissolve in the ionic liquid solvent to give transparent homogeneous solutions, Table 7.5, with unsuitable monomers phase separating and therefore not being subjected to polymerisation. Of all the monomers found to give transparent homogeneous solutions only vinyl acetate failed to undergo polymerisation. In all other polymerisations, with the exception of 2-hydoxyethyl methacrylate (HEMA), the polymer is insoluble in the ionic liquid and phase separates. The compatibility of HEMA with the ionic liquids resulted in its use for the preparation of polymer electrolyte films, which were found to be highly conductive. For film formation, the reaction mixtures were simply spread between glass plates and heated; no degassing procedures were carried out. Analysis of the films found that the amount of unreacted monomer was negligible, indicating fast polymerisation. In all of the reactions reported by Noda and Watanabe no characterisation of the polymers or indeed analysis of the polymerisation reactions were carried out.[42]

More recent studies by May and ourselves have looked into the kinetics and the types of polymers formed by the free radical polymerisation reactions of vinyl monomers using ambient-temperature ionic liquids as the solvent. [43] [44] The free radical polymerisation of methyl methacrylate (MMA) in [BMIM][PF_6] initiated by 2,2'-azobisisobutyronitrile (AIBN) at 60°C proceeds rapidly causing a large increase in viscosity that hampers efficient stirring of the reaction mixture. The polymerisation reactions produce poly(methyl methacrylate) (PMMA) with very high molecular weights, Table 7.6. [44] When compared to a free radical polymerisation in a conventional organic solvent, in this case toluene, both conversion and M_n are increased by approximately one order of magnitude. This could be due to one of two reasons. Firstly, the rate of bimolecular termination by either disproportionation or combination is suppressed which might be due in part to the large increase in viscosity of the reaction medium. In this case termination would be dominated by chain transfer to either solvent or monomer. The molecular weights observed are consistent with this explanation. Alternatively, the rate constant of propagation, k_p, may be increased in the ionic liquid due to local environment effects.

The effects of increasing the concentration of initiator (i.e. increased conversion, decreased M_n and broader PDi) and reducing the reaction temperature (i.e. decreased conversion, increased M_n and narrower PDi) for the polymerisations in ambient-temperature ionic liquids are the same as for that observed in conventional solvents. May *et al* reports similar results and in addition uses ^{13}C NMR to investigate the stereochemistry of the PMMA produced in [BMIM][PF_6]. They found that the stereochemistry is almost identical to that for PMMA produced by free radical polymerization in conventional solvents. [43] The homopolymerisation and copolymerisation of several other monomers are also reported. Similar to that found by Noda and Watanabe, in many cases the polymer was not soluble in the ionic liquid and thus phase separates. [43] [44]

7.4 Transition metal catalysed polymerisation

The previous sections show that certain ionic liquids, namely the chloroaluminate(III) ionic liquids, are capable of acting as both catalyst and solvent for the polymerisation of certain olefins, although in a somewhat uncontrolled manner, and other ionic liquids, namely the non-chloroaluminate(III) ionic liquids are capable as acting as solvents for free radical polymerisation processes. In attempts to carry out polymerisation reactions in a more controlled manner several studies have used dissolved transition metal catalysts in ambient-temperature ionic liquids and investigated the compatibility of the catalyst towards a range of polymerisation systems.

7.4.1 Ziegler-Natta polymerisation of ethylene

Ziegler-Natta polymerisation is used extensively for the polymerisation of simple olefins (e.g. ethylene, propene and 1-butene) and is the focus of much academic attention, as even small improvements to a commercial process operated on this scale can be important. Ziegler-Natta catalyst systems, which in general are early transition metal compounds used in conjunction with alkylaluminium compounds, lend themselves to study in the chloroaluminate(III) ionic liquids, especially the ones with an acidic composition.

During studies into the behaviour of titanium(IV) chloride in chloroaluminate(III) ionic liquids Carlin *et al* carried out a brief study to investigate if Ziegler-Natta polymerisation was possible in an ionic liquid.[45] They dissolved $TiCl_4$ and $EtAlCl_2$ in [EMIM][Cl-$AlCl_3$] ($X(AlCl_3) = 0.52$) and bubbled ethylene through for several minutes. After quenching poly(ethylene) with a melting point of 120–130°C was isolated in very low yield, thus demonstrating that Ziegler-Natta polymerisation works in these liquids, albeit not very well.

The same ionic liquid was employed giving higher yields of poly(ethylene) using bis(η-cyclopentadienyl)titanium(IV) dichloride in conjunction with $Me_3Al_2Cl_3$ as catalyst.[46] However, the catalytic activities are still low when compared to other homogeneous systems and may be attributed to, among other things, low solubility of ethylene in the ionic liquids or the presence of alkylimidazole impurities which co-ordinate and block the active titanium sites. In chloroaluminate(III) ionic liquids of a basic composition no catalysis is observed which was ascribed to the formation of the inactive $[Ti(\eta\text{-}C_5H_5)_2Cl_3]^-$ species. In comparison, the zirconium and hafnium analogues, $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ and $[Hf(\eta\text{-}C_5H_5)_2Cl_2]$, showed no catalytic activity towards the polymerisation of ethylene in both acidic and basic ionic liquids. This is presumably due to the presence of stronger M-Cl bonds that preclude the formation of a catalytically active species.

7.4.2 Late-transition metal catalysed polymerisation of ethylene

The surge in development of late-transition metal polymerisation catalysts has been due, in part, to the need for systems that can copolymerise ethylene, and related monomers, with polar comonomers under mild conditions. Late-transition metals have a lower oxophilicity relative to early-transition metals and therefore a higher tolerance for a wider ranger of functional groups (e.g. -COOR and -COOH groups).[47] A recent study reports the use of the nickel complex **1** (Figure 7.1) for the homopolymerisation of ethylene in an ambient-temperature ionic liquid.[48] **1** was used under mild biphasic conditions with the ternary ionic liquid $[BMIM][Cl\text{-}AlCl_3\text{-}EtAlCl_2]$ (1.0 : 1.0 : 0.32, $X(Al) = 0.57$) and toluene, producing poly(ethylene) which was easily isolated from the reaction mixture by decanting the upper toluene layer. This permited the ionic liquid and **1** to be recycled for use in further polymerisations. However, before reuse trimethylaluminium(III) was added to overcome the loss of free alkylaluminium species into the separated organic phase.[48] The characteristics of the isolated poly(ethylene) depend upon several reaction conditions. On increasing the reaction temperature from –10 to +10°C the melting point decreases from 123 to 85°C due to a greater amount of chain branching and also results in a decrease in the M_w from 388,000 to 280,000 g mol^{-1}. Reusing the catalyst/ionic liquid solution also has an effect, with subsequent reactions giving a progressive shift from crystalline to amorphous polymer, with a period that gives rise to bimodal product distributions. This change is due to the changing composition of the ionic liquid, as fresh cocatalyst is added after each polymerisation run, which leads to the formation of different active species.

A related study used the air and moisture stable ionic liquids [$C_n$mim][PF_6] (n = 4 - 10) as solvents for the oligomerisation of ethylene to higher α-olefins.[49] The reaction uses the cationic nickel complex **2** (Figure 7.1) under biphasic conditions to give oligomers of up to nine repeat units with better selectivity and reactivity than in conventional solvents. Recycling of the catalyst/ionic liquid solution was possible with little change in selectivity and only a small drop in activity observed.

7.4.3 Metathesis polymerisation

Acyclic diene molecules are capable of undergoing intramolecular and intermolecular reactions in the presence of certain transition metal catalysts, for example, molybdenum alkylidene and ruthenium carbene complexes.[50, 51] The intramolecular reaction, called ring-closing olefin metathesis (RCM), leads to cyclic compounds and the intermolecular reaction, called acyclic diene metathesis (ADMET) polymerisation, leads to oligomers and polymers. Altering the dilution of the reaction mixture can to some extent control the intrinsic competition between RCM and ADMET.

Gürtler and Jautelat of Bayer AG have protected methods that use chloroaluminate(III) ionic liquids as solvents for both cyclisation and polymerisation reactions of acyclic dienes.[52] They employed the neutral ionic liquid [EMIM][Cl-$AlCl_3$] ($X(AlCl_3) = 0.5$) to immobilise a ruthenium carbene complex for biphasic ADMET polymerisation of an acyclic diene ester, Figure 7.2. The reaction is an equilibrium processes, therefore, removal of ethylene drives the equilibrium to products. The reaction proceeds readily at ambient-temperatures producing mostly polymeric materials but also ~10 % dimeric material.

7.4.4 Living radical polymerisation

As discussed in Section 7.3 conventional free radical polymerisation is a widely used technique that is relatively easy to employ. However, it does have its limitations. It is often difficult to obtain predetermined polymer architectures with precise and narrow molecular weight distributions. Transition metal mediated living radical polymerisation is a recently developed method that has been developed to overcome these limitations.[53, 54] It permits the synthesis of polymers with varied architectures (e.g. blocks, stars and combs) and with predetermined end groups (e.g. rotaxanes, biomolecules and dyes).

A potential limitation to commercialisation of this technology is that relatively high levels of catalyst are often required. Indeed, it is common that one mole equivalent is required for each growing polymer chain to achieve acceptable rates of polymerisation, making catalyst removal and reuse problematic. In order to overcome this problem a range of approaches have been reported that include supported catalysts,[55] fluorous biphase reactions[56] and more recently the use of ionic liquids.[57] [44] It was found that copper(I) bromide in conjunction with *N*-propyl-2-pyridylmethanimine as ligand catalyses the living radical polymerisation of MMA in the neutral ionic liquid [BMIM][PF_6]. The reaction progressed in a manner consistent with a living polymerisation, that is, good first-order kinetic behaviour and evolution of number average molecular weight (M_n) with time were observed, and a final product with low M_n and PDi values was obtained.[57] Polymerisation in the ionic liquid proceeded much more rapidly than that in conventional organic solvents, indeed, polymerisation occurred at 30°C in [BMIM][PF_6] at a rate comparable to that found in toluene at 90°C.

The cationic nature of the copper(I) catalyst means that it is immobilised in the ionic liquid. This permits the PMMA product to be obtained, with negligible copper contamination, by a simple extraction procedure using toluene as the solvent (a solvent in which the ionic liquid is not miscible). The ionic liquid/catalyst solution was subsequently reused.

The technique of copper(I) bromide mediated living radical polymerisation is compatible with other ambient-temperature ionic liquids. It proceeds smoothly in hexyl- and octyl-3-methylimidazolium hexafluorophosphate and tetrafluorborate ionic liquids. However, using [BMIM][BF_4] for the polymerisation of MMA generates a product with a bimodal product distribution. Figure 7.3 shows this trace together with a trace from a similar reaction carried out in [BMIM][PF_6]. [44] The mass distribution for [BMIM][PF_6] shows a single narrow low molecular weight peak consistent with living radical polymerisation, whereas, the mass distribution for [BMIM][BF_4] shows a similar peak and but also an additional peak that is broad and at high molecular weight. This high molecular weight peak is consistent with the results observed for conventional free radical polymerisation in ionic liquids, as discussed in Section 7.3. This anomalous result can be rationalised in terms of the synthetic method used to prepare the ionic liquids. Of all the ionic liquids used, [BMIM][BF_4] is the only one in the study that was miscible with water, therefore, it was the only one not subjected to an aqueous work-up and is contaminated with halide salts.[58] The halide salts might poison the catalyst with subsequent polymerisation proceeding via two different mechanisms. Alternatively, it might be that under living polymerisation conditions the terminal halide atom on the propagating polymer chain does not fully separate from the polymer during propagation creating a “caged-radical” which undergoes propagation. Under appropriate conditions separation occurs leading to irreversible homolytic fission and the production of free radicals. Conventional free radical polymerisation ensues in competition with the atom transfer mechanism giving high conversion and high mass polymer alongside the low mass polymer from the living mechanism. This implies that the rate of termination in conventional radical propagation is drastically reduced, maybe by co-ordination with the cation or anion from the ionic liquid that also prevents recombination with the halide atom.

In a related study Kubisa has investigated the Atom-Transfer Radical Polymerization (ATRP) of acrylates in [BMIM][PF_6] [59]. The solubility of the monomer in the ionic liquid chosen depends very much upon the substituent on the monomer. Homogeneous polymerization of methyl acrylate gave living polymerization with narrow polydispersity polymers and good molecular weight control. Higher order acrylates gave heterogeneous reactions with the catalyst remaining in the ionic liquid phase. Although deviations away from living polymerization behaviour was observed butyl acrylate showed controlled polymerization. The same group are currently extending this work and also looking at cationic vinyl polymerization and various ring-opening polymerization reactions.

7.5 Preparation of conductive polymers

Electronically conducting polymers have a number of potential applications including as coatings for semiconductors,[60] in electrocatalysis[61] and as charge storage materials.[62] Of these poly(*para*-phenylene) (PPP), which is the simplest of the poly(arene) classes, possesses properties that include excellent thermal stability, high coke number and good optical and electrophysical characteristics.[63] For PPP to be utilised in devices and advanced materials it should have a high relative molecular mass (M_r), a homogenous structure and good submolecular packing.

Poly(*para*-phenylene) can be prepared by a variety of chemical routes, but generally the polymers obtained are of low quality due to low masses and the occurrence of polymerisation via 1,2 linkages leading to a disruption of molecular packing. They are obtained as powders and are often contaminated with oxygen and chlorine products and catalyst residues. The chemical synthesis of PPP can be carried out in ambient-temperature ionic liquids. The oxidative dehydropolycondensation of benzene was carried out in the acidic ionic liquid [*N*BPY]Cl-$AlCl_3$ ($X(AlCl_3) = 0.67$) using $CuCl_2$ as the catalyst.[64, 65] This gave PPP with relative molecular masses considerably higher than in conventional solvents and M_r could be tuned by varying the benzene concentration. The high M_r values observed were attributed to a greater solubility of PPP in the ionic liquid which permits a greater degree of polymerisation before phase separation occurs. The electrochemical synthesis of PPP reduces many of the disadvantages of the chemical route. In the same ionic liquid, the same group carried out the electrochemical polymerisation of benzene preparing PPP as conductive films which were flexible and transparent. The films were prepared with very high relative molecular masses with degrees of polymerisation up to 200 observed.[65, 66] The electrochemical polymerisation of benzene to PPP has not been exclusively carried out in [*N*BPY][Cl-$AlCl_3$] ionic liquids. Other reports use [*N*BPY]Cl-$AlCl_2$(OEt), [*N*CTPY]Cl-$AlCl_3$] (where *N*CTPY is *N*-cetylpyridiunium) and [EMIM][Cl-$AlCl_3$] with the best results observed in the traditional aluminium(III) chloride ionic liquids.[67-69]

The electrochemical oxidation of fluorene in [EMIM][Cl-$AlCl_3$] ionic liquids of an acidic or neutral composition gives poly(fluorene) films that are more stable and have a less complicated electrochemical behaviour than those prepared in acetonitrile, the usual solvent. Basic ionic liquids cannot be used, as chloride ions are more easily oxidised than fluorene.[70] A number of aromatic compounds that contain heteroatoms, e.g, pyrrole, aniline and thiophene can also be oxidised electrochemically in chloroaluminate(III) ionic liquids to give polymer films.[71-74] In ionic liquids of an acidic composition the electrochemical polymerisation of the nitrogen and sulphur containing compounds is either more difficult or not possible at all due to the formation of adducts with $AlCl_3$.[75] Any interactions between benzene and $AlCl_3$ are not significant enough to influence its polymerisation to PPP.[69]

7.6 Conclusions

It is readily apparent that the volume of research concerning polymerisation with any type in ionic liquids is sparse. It is not immediately clear why this is the case and the field has not really started as yet. Ionic liquid technology has brought a number of benefits to the polymer synthesis. For example, the application of chloroaluminate(III) ionic liquids as both solvent and catalyst for the cationic polymerisation of olefins has generated a system that not only produces cleaner polymers than traditional processes but permits the recovery and reuse of the ionic liquid solvent/catalyst. Ionic liquids have allowed the preparation of high molecular weight conducting polymers such as poly(*para*-phenylene), and been useful for the immobilisation of transition metal polymerisation catalysts thus offering a potential solution to a problem that prevents the commercialisation of transition metal mediated living radical polymerisation.

The use of neutral ionic liquids for free radical polymerisation highlights one of their problems: their relatively high viscosity. The viscosity of the reaction mixture has a significant effect on the outcome of polymerisation reactions and these liquids can have viscosities much higher than conventional organic solvents. The free radical polymerisation of MMA in $[BMIM]PF_6$ generates polymers with high molecular weights which, when combined with the reduced fluidity of the ionic liquid, causes the reaction mixture to set after a very short time. This problem can be avoided in polymerisation reactions if phase separation of the product occurs, for example, as with the free radical polymerisation of MMA in $[N\mathrm{BPY}][BF_4]$, or if the reaction is operated under biphasic conditions, for example, the reported ADMET polymerisation of an acyclic diene ester.

As well as viscosity, other factors to be aware of include the purity of the ionic liquids. The presence of residual halide ions in neutral ionic liquids can poison transition metal catalysts and different levels of proton impurities in chloroaluminate(III) ionic liquids can alter the product distribution of the reaction. The reduced temperatures required for many polymerisation reactions in ionic liquids together with the reduced solubility of oxygen in ionic liquids compared to conventional solvents means that two of the most common quenching methods are reduced in effectiveness. When detailed studies are being carried out, in particular kinetic studies, it is necessary to completely stop further reaction so accurate data is obtained.

The controlled synthesis of polymers, as opposed to their undesired formation, is an area that has not received much academic interest. Most of the interest to date has been commercial, and focused on a narrow area, that is, in the use of chloroaluminate(III) ionic liquids for cationic polymerisation reactions. The lack of publications in the area, together with the lack of detailed and useful synthetic information in the patent literature, places hurdles in front of those with limited knowledge of ionic liquid technology who wish to employ it for polymerisation studies. The expanding interest in ionic liquids as solvents for synthesis, most notably for the synthesis of discrete organic molecules, should stimulate interest in their use for polymer science.

Even within the small numbers of studies conducted to date we are already seeing potentially dramatic effects. Free radical polymerisation proceeds at a much faster rate and there is already evidence that both the rate of propagation and rate of termination are effected. Whole polymerisation types have yet to be attempted in ionic liquids. Such as ring opening polymerisation to esters and amides, condensation polymerisation of any type, for example polyamides, polyesters. This field is in its infancy and we look forward to the coming years with great anticipation.

7.7 References

[1] J. D. Holbrey, K. R. Seddon, *Clean Products and Processes* **1999**, *1*, 223-236.

[2] T. Welton, *Chem. Rev.* **1999**, *99*, 2071-2083.

[3] P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3772-3789.

[4] C. J. Adams, M. J. Earle, K. R. Seddon, *J. Chem. Soc., Chem. Commun.* **1999**, 1043-1044.

[5] Y. Chauvin, L. Mussmann, H. Olivier, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2698-2700.

[6] J. Howarth, *Tetrahedron Lett.* **2000**, *41*, 6627-6629.

[7] G. S. Owens, M. M. Abu-Omar, *J. Chem. Soc., Chem. Commun.* **2000**, 1165-1166.

[8] C. C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, *Organometallics* **2000**, *19*, 3818-3823.

[9] C. J. Adams, M. J. Earle, G. Roberts, K. R. Seddon, *J. Chem. Soc., Chem. Commun.* **1998**, 2097-2098.

[10] C. E. Song, W. H. Shim, E. J. Roh, J. H. Choi, *J. Chem. Soc., Chem. Commun.* **2000**, 1695-1696.

[11] W. Chen, L. Xu, C. Chatterton, J. Xiao, *J. Chem. Soc., Chem. Commun.* **1999**, 1247-1248.

[12] C. M. Gordon, A. McCluskey, *J. Chem. Soc., Chem. Commun.* **1999**, 1431-1432.

[13] M. J. Earle, P. B. McCormac, K. R. Seddon, *Green Chemistry* **1999**, *1*, 23-25.

[14] A. J. Carmichael, M. J. Earle, J. D. Holbrey, P. B. McCormac, K. R. Seddon, *Org. Lett.* **1999**, *1*, 997-1000.

[15] C. J. Mathews, P. J. Smith, T. Welton, *J. Chem. Soc., Chem. Commun.* **2000**, 1249-1250.

[16] C. de Bellefon, E. Pollet, P. Grenouillet, *J. Mol. Catal. A-Chemical* **1999**, *145*, 121-126.

[17] Y. Chauvin, B. Gilbert, I. Guibard, *J. Chem. Soc., Chem. Commun.* **1990**, 1715-1716.

[18] Y. Chauvin, S. Einloft, H. Oliver, *Ind. Eng. Chem. Res.* **1995**, *34*, 1149-1155.

[19] S. Einloft, F. K. Dietrich, R. F. de Souza, J. Dupont, *Polyhedron* **1996**, *15*, 3257-3259.

[20] B. Ellis, W. Keim, P. Wasserscheid, *J. Chem. Soc., Chem. Commun.* **1999**, 337-338.

[21] D. Commereuc, Y. Chauvin, G. Leger, J. Gaillard, *Revue de L'Institut Francais du Petrole* **1982**, *37*, 639-649.

[22] D. Commereuc, Y. Chauvin, F. Hugues, L. Saussine, A. Hirschauer, *French Patent* **1988**, FR 2,611,700.

[23] G. Odian, *Principles of Polymerization*, Wiley, New York, **1991**.

[24] A. A. Fannin, D. A. Floreani, L. A. King, J. S. Landers, B. J. Piersma, D. J. Stech, R. L. Vaughn, J. S. Wilkes, J. L. Williams, *J. Phys. Chem.* **1984**, *88*, 2614-2621.

[25] G. P. Smith, A. S. Dworkin, R. M. Pagni, S. P. Zingg, *J. Am. Chem. Soc.* **1989**, *111*, 5075-5077.

[26] J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem* **1986**, *51*, 480-483.

[27] P. A. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Polyhedron* **1996**, *15*, 1217-1219.

[28] P. Wasserscheid, W. Keim, *World Patent* **1998**, WO 98/47616.

[29] P. W. Ambler, P. K. G. Hodgson, N. J. Stewart, *European Patent* **1993**, EP 0558187.

[30] K. Weissermel, H. -J. Arpe, *Industrial Organic Chemistry*, VCH, Weinheim, **1997**.

[31] A. A. K. Abdul-Sada, P. W. Ambler, P. K. G. Hodgson, K. R. Seddon, N. J. Stewart, *World Patent* **1995**, WO 95/21871.

[32] A. A. K. Abdul-Sada, K. R. Seddon, N. J. Stewart, *World Patent* **1995**, WO 95/21872.

[33] P. M. Atkins, M. R. Smith, B. Ellis, *European Patent* **1997**, EP 0791643.

[34] G. Roberts, C. M. Lok, C. J. Adams, K. R. Seddon, M. J. Earle, J. Hamill, *World Patent* **1998**, WO 98/07679.

[35] V. Murphy, *World Patent* **2000**, WO 00/32658.

[36] F. G. Sherif, L. J. Shyu, C. P. M. Lacroix, A. G. Talma, *US Patent* **1998**, US 5731101.

[37] G. Moad, D. H. Solomon, *The Chemistry of Free Radical Polymerization*, Pergamon, Oxford, **1995**.

[38] M. Watanabe, S. Yamada, N. Ogata, *Electrochimica Acta* **1995**, *40*, 2285-2288.

[39] J. Fuller, A. C. Breda, R. T. Carlin, *J. Electrochem*. *Soc* **1997**, *144*, L67-L70.

[40] M. Hirao, K. Ito-Akita, H. Ohno, *Polym. Adv. Technol.* **2000**, *11*, 534-538.

[41] H. Ohno, *Electrochimica Acta* **2001**, *46*, 1407-1411.

[42] A. Noda, M. Watanabe, *Electrochimica Acta* **2000**, *45*, 1265-1270.

[43] H. Zhang, L. Bu, M. Li, K. Hong, J. W. Mays, R. D. Rogers, *ACS Symposium series chapter, in press* **2001**, .

[44] A. J. Carmichael, D. A. Leigh, D. M. Haddleton, *ACS Symposium series chapter, in press* **2002**, .

[45] R. T. Carlin, R. A. Osteryoung, J. S. Wilkes, J. Rovang, *Inorg. Chem* **1990**, *29*, 3003-3009.

[46] R. T. Carlin, J. S. Wilkes, *J. Mol. Cat.* **1990**, *63*, 125-129.

[47] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1203.

[48] M. F. Pinheiro, R. S. Mauler, R. F. de Souza, *Macromol. Rapid Commun.* **2001**, *22*, 425-428.

[49] P. Wasserscheid, C. M. Gordon, C. Hilgers, M. J. Muldoon, I. R. Dunkin, *J. Chem. Soc., Chem. Commun.* **2001**, 1186-1187.

[50] A. Fürstner, *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3012-3043.

[51] M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565-1604.

[52] C. Gürtler, M. Jautelat, *European Patent* **2000**, EP 1035093.

[53] K. Matyjaszewski, *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *10*, 1785-1801.

[54] K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921-2990.

[55] D. M. Haddleton, D. Kukulj, A. P. Radigue, *J. Chem. Soc., Chem. Commun.* **1999**, 99-100.

[56] D. M. Haddleton, S. G. Jackson, S. A. F. Bon, *J. Am. Chem. Soc.* **2000**, *122*, 1542-1543.

[57] A. J. Carmichael, D. M. Haddleton, S. A. F. Bon, K. R. Seddon, *J. Chem. Soc., Chem. Commun.* **2000**, 1237-1238.

[58] K. R. Seddon, A. Stark, M. J. Torres, *Pure Appl. Chem.* **2000**, *12*, 2275-2287.

[59] T Biedron, P Kubisa, *Macromol. Rapid Commun.* **2001**, *22*, 1237-1242.

[60] A. J. Frank, K. Honda, *J. Phys. Chem.* **1982**, *86*, 1933-1935.

[61] R. A. Bull, F. R. Fran, A. J. Bard, *J. Electrochem. Soc.* **1983**, *130*, 1636-1638.

[62] B. J. Feldman, P. Burgmayer, R. W. Murray, *J. Am. Chem. Soc.* **1985**, *107*, 872-878.

[63] P. Kovacic, M. B. Jones, *Chem. Rev.* **1987**, *87*, 357-379.

[64] V. M. Kobryanskii, S. A. Arnautov, *J. Chem. Soc., Chem. Commun.* **1992**, 727-728.

[65] V. M. Kobryanskii, S. A. Arnautov, *Synth. Met.* **1993**, *55*, 1371-1376.

[66] S. A. Arnautov, V. M. Kobryanskii, *Macromol. Chem. Phys.* **2000**, *201*, 809-814.

[67] S. A. Arnautov, *Synth. Met.* **1997**, *84*, 295-296.

[68] D. C. Trivedi, *J. Chem. Soc., Chem. Commun.* **1989**, 544-545.

[69] L. M. Goldenberg, R. A. Osteryoung, *Synth. Met.* **1994**, *64*, 63-68.

[70] L.. Janiszewska, R. A. Osteryoung, *J. Electrochem. Soc.* **1988**, *135*, 116-122.

[71] P. G. Pickup, R. A. Osteryoung, *J. Am. Chem. Soc.* **1984**, *106*, 2294-2299.

[72] J. Tang, R. A. Osteryoung, *Synth. Met.* **1991**, *45*, 1-13.

[73] L.. Janiszewska, R. A. Osteryoung, *J. Electrochem. Soc.* **1987**, *134*, 2787-2794.

[74] R. T. Carlin, R. A. Osteryoung, *J. Electrochem. Soc.* **1994**, *141*, 1709-1713.

[75] T. A. Zawodzinski, L. Janiszewska, R. A. Osteryoung, *J. Electroanal. Chem.* **1988**, *255*, 111-117.

Table and figure captions

Table 7.1 Polymerisation of *iso*-butene using the acidic ionic liquid [EMIM]Cl-$AlCl_3$ ($X(AlCl_3) = 0.67$).[29]

Table 7.2 Polymerisation of Raffinate I using the acidic ionic liquid [EMIM]Cl-$AlCl_3$ ($X(AlCl_3) = 0.67$): conversion of the individual components.[29]

Table 7.3 Polymerisation of *iso*-butene to high molecular weight poly(*iso*-butene)s using the ionic liquid [EMIM]Cl-$AlCl_3$.[35]

Table 7.4 Polymerisation of *iso*-butene to high molecular weight poly(*iso*-butene)s using the ionic liquid [EMIM]Cl-$AlCl_3$ under biphasic conditions.[35]

Table 7.5 Compatibility of the ionic liquids [EMIM]BF_4 and [*N*BPY]BF_4 with monomers and their polymers.[42]

Table 7.6 Free radical polymerisation of MMA in the ionic liquid [BMIM]PF_6. [44]

Figure 7.1 Nickel catalysts used for the polymerisation and oligomerisation of ethylene in ambient-temperature ionic liquids.[48, 49]

Figure 7.2 Acyclic diene metathesis polymerisation (ADMET) reaction carried out in neutral ionic liquid [EMIM]Cl-$AlCl_3$ ($X(AlCl_3) = 0.5$).[52]

Figure 7.3 SEC traces for the Cu(I)Br mediated living radical polymerization of MMA in the ionic liquids [BMIM][X] (X = PF_6 or BF_4). [44]

Table 7.1

Reaction temperature (°C)	Yield (% w/w)	Molecular weight of product (g mol^{-1})
-23	26	100,000[a]
0	75	3000 & 400[b]

[a] Polystyrene equivalents. [b] Bimodal.

Table 7.2

Raffinate I feedstock		
Olefin fraction	Concentration (% w/w)	Reacted (% w/w)
iso-butene	46	91
1-butene	25	47
trans-2-butene	8	34
cis-2-butene	3	37

Table 7.3

Quantity of ionic liquid (μl)	Quantity of *iso*-butene (μl)	Temperature (°C)	Yield (%)	M_w (g mol^{-1})
10	483	-40	38	526,000
10	483	-30	33	302,000
10	483	-20	45	128,000

Table 7.4

Quantity of ionic liquid (μl)	Quantity of hexane (μl)	Quantity of *iso*-butene (μl)	Quantity of $EtAlCl_2$ (μl)	Yield (%)	M_w (g mol^{-1})
50	321	25	11	100	276,000
50	310	25	23	100	235,000
50	298	25	34	100	186,000

Conditions: temperature = -30°C; [$EtAlCl_2$] = 1 M solution in hexane.

Table 7.5

	$[EMIM]BF_4$		$[\mathit{N}BPY]BF_4$	
	Monomer	Polymer	Monomer	Polymer
Methyl methacrylate	X	-	O	X
Acrylonitrile	O	X	O	X
Vinyl acetate	O	No reaction	O	No reaction
Styrene	X	-	X	-
2-Hydoxyethyl methacrylate	O	ρ	O	ρ

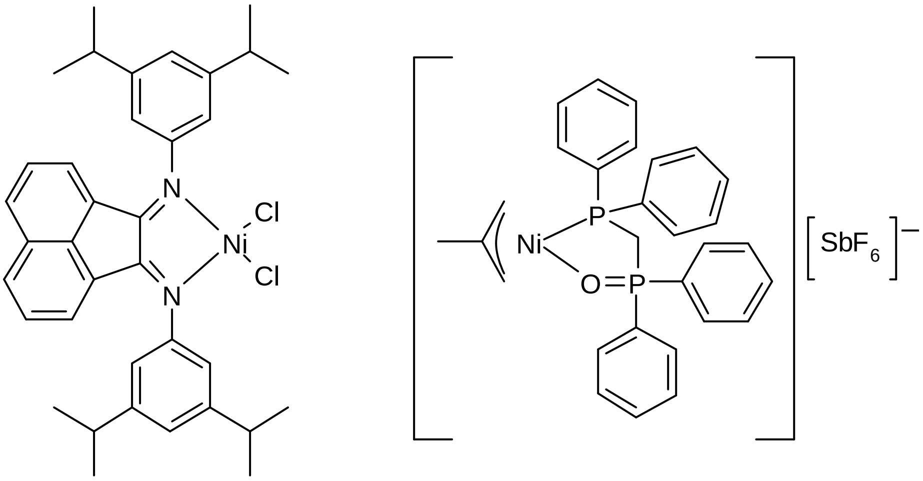
Legend: O, transparent homogenous solution; X, phase separated; ρ, translucent gel.

Table 7.6

Reaction media	[AIBN] (w/v%)	Conversion (%)	M_n (g mol^{-1})	*PDi*
[BMIM][PF$_6$]	1	25	669,000	1.75
[BMIM][PF$_6$]	2	27	600,000	1.88
[BMIM][PF$_6$]	4	36	416,000	2.22
[BMIM][PF$_6$]	8	56	240,000	2.59
toluene	1	3	58,300	1.98

Conditions: temperature = 60°C; time = 20 min; 20% v/v monomer in ionic liquid.

Figure 7.1



1 **2**

Figure 7.2

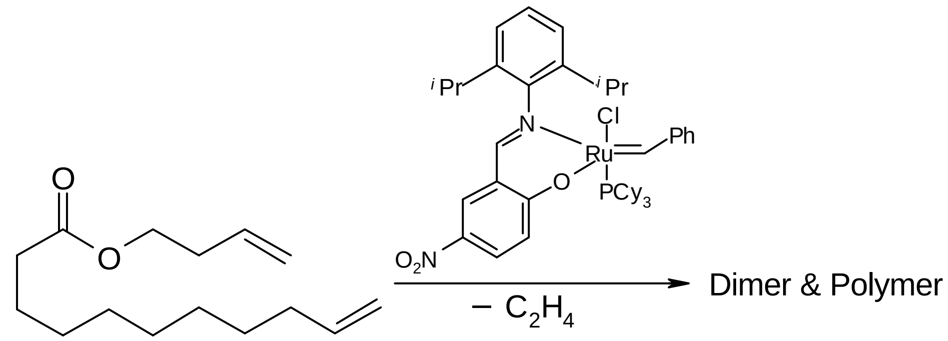
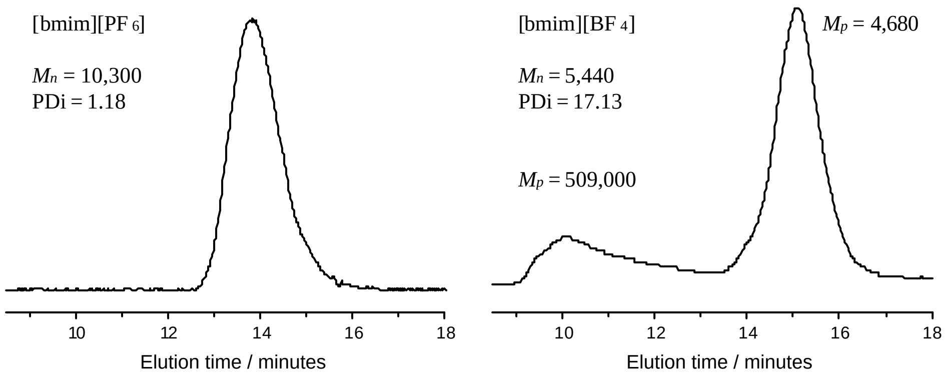


Figure 7.3


[bmim][PF 6]
Mn = 10,300
PDi = 1.18
10
12
14
16
18
Elution time / minutes
[bmim][BF 4]
Mn = 5,440
PDi = 17.13
Mp = 509,000
Mp = 4,680
10
12
14
16
18
Elution time / minutes