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Ionic Liquids from (Meth) Acrylic Compounds

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1. Introduction

Ionic Liquids (ILs) are known and used for the past several decades (Davis J.H. et al, 2003; Wasserscheid & Welton, 2008). In general, there are salts made up of an organic cation and inorganic anion. Their ionic structure gives them particular properties: they are usually liquid at room temperature, non volatile even at high temperature, capable of solubilizing organic and inorganic compounds... Because of these properties, enthusiasm for ILs was initially focused on their use as a solvent and at the beginning of 1990, most of the researches consisted in reproducing conventional reactions in this new reaction medium (Earle & Seddon 2000; Rogers & Seddon, 2003; Baudequin C. et al., 2005; Biswas A. et al., 2006). Compared to conventional solvents, ILs present a great advantage: they are tuneable. In modifying the side chain length of the cation or in exchanging the anion for a bigger or a smaller one, you are able to obtain ILs with specific chemical properties and make them miscible in the aqueous or organic phase or allow them to dissolve a particular compound. As a logical course of events, the early 2000's, a new class of ILs was synthesized to meet special needs such as catalyzing a particular reaction or enabling a reaction which is typically not achievable in a conventional organic solvent. Task Specific Ionic Liquids (TSILs) results from the covalent tethering of a functional group to the cation or the anion or both of them of an ordinary IL, giving the latter the capacity to interact with dissolved substrates in specific ways.

The scope of their applications has expanded over the years. They are attracting much interest in many fields of chemistry and industry due to their properties cited above. First seen as an alternative to volatile solvent, they are now used in electrochemistry, catalysis, asymmetric synthesis, extraction, chromatography... (Seddon, 1997; Sheldon, 1993; Cull et al, 2000; Wilkes, 2004; Wasserscheid & Keim, 2000; Welton, 1999; Brennecke & Maginn, 2001; Fredlake et al., 2004; Henderson & Passerini, 2004).

One of the most recent uses of ionic liquids is as an electrolyte in batteries of the new generation. Ionic liquids are introduced in a polymer matrix and leads to better performance and reliability system, thus allowing no electrochemical reactions which could cause damage (electrochemical window), low pressure steam, and a high ionic conductivity even at room temperature.

The cost and availability of ILs, especially those with an atypical function in their side chain are two issues curbing the use of TSILs in protocols on an industrial scale. One of our objectives is to develop an efficient and rapid synthesis of new TSILs with a function in their side chain. To achieve our goal, we chose to use acrylic compounds which are industrial products easily accessible, available in large quantity and relatively inexpensive. Moreover,

our laboratory has a great knowledge of acrylic compounds since we worked in this field for years (Caye et al., 1998; Cerf et al., 1992; Cochez et al., 2000; Curci et al., 1993; Gentilhomme et al., 2005; Jullien et al., 1996a, 1996b; Mancardi et al., 2007; Pees et al., 2001, 2002, 2003, 2004)

The reactivity of acrylic compounds can provide extensive opportunities to access to various original ILs. As shown on Fig. 1, on an acrylic type compound, it is possible to introduce an Ionic Part (IP) on two different sites: via a nucleophilic substitution at the end of the esterifying chain (Way 1) or via a Michael type addition on the activated double bond (Way 2). As a consequence it's possible to obtain cationic or anionic polymerisable monomers using Way 1, depending on the type of ionic part.

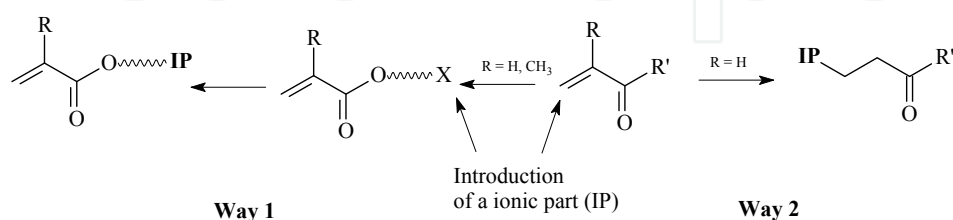


Fig. 1. Reactivity ways of (meth)acrylic compounds

A variety of cations can potentially be used to produce ILs. However later in this chapter, we will only give description of syntheses of ILs with a cation-type N-alkylimidazolium.

1.1 General synthetic method

A mass of methods exist to synthesize ILs. However there is a common denominator among all of them: the first step which lies in the formation of the cation. In the case of an N-alkylimidazole, it consists in quaternization of the molecule's nitrogen atoms. This step is often followed by the metathesis of the resulting counter ions, meaning the exchange of the anion of the molecule by another one, providing different or more interesting properties. The basis of ILs synthetic path is summarized in Figure 2.

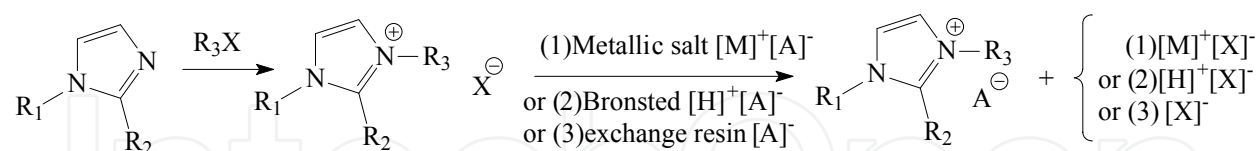


Fig. 2. Typical steps for the ionic liquid (type N-alkylimidazolium)

Depending on haloalkanes and temperature used in the first step, reaction time can vary from one to several hours. Nevertheless, the use of microwaves to perform the nucleophilic substitution can significantly reduce reaction time (Varma & Namboodiri, 2001a; Levêque et al., 2006). Alkyl triflates (Bonhôte et al., 1996) or tosylates (Karodia et al., 1998) may also be used.

It is also possible to easily obtain imidazolium ionic liquids, by performing a one-pot synthesis of 2 steps, using Michael addition. First the counter-ion is introduced via the protonation of N-alkylimidazole by an acid (*p*-toluenesulfonic acid, methanesulfonic acid, tetrafluoroboric acid ...). Then, in a second step, the addition of the N-protonated alkyimidazole on a α, β unsaturated compound (methyl vinyl ketone, methyl acrylate, acrylonitrile ...) leads to the obtention of an imidazolium type IL with a functionalized side (Fig. 3):

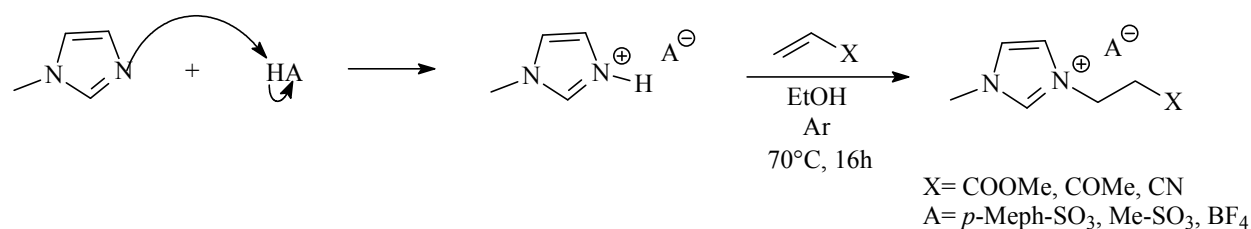


Fig. 3. One pot synthesis of N-methyl-N-alkylimidazolium ionic liquid

In reversing the two steps, i.e. first imidazole addition on a conjugated double bond, then a N-alkylation, the same derivatives may be obtained. The Michael addition of imidazole or its derivatives on an activated double bond can be catalyzed by various reagents: enzyme catalysis (Cai et al., 2004), Montmorillonite catalysis (Martin Aranda et al., 1997, 2002) and activated microwave or ultrasound (Zaderenko et al., 1994), or molecular sieve graft (Blasko-Jimenez et al., 2009), KF (Yang et al., 2005), Cu (Acac)₂ (Lakshmi Kantam et al., 2007), liquid ion ([bMIM] OH) (Xu et al., 2007).

1.2 Acrylic monomers

One of the latest applications of ILs is the synthesis of polymer electrolytes with high ionic conductivity. Polymer electrolytes are an area of active research since the early 1980s and have applications ranging from rechargeable lithium electrochromic flexible displays and to smart windows (Ratner & Shriver, 1988). Most of the time they are made of polymers like polyethylene oxide (PEO) filled with diluted alkali salts leading to conductive solutions. However, their conductivity remains relatively low at room temperature, so the researchers are trying to find ways to improve it. For this they usually carry out doping of the polymer structure using compounds such as ion-NTF₂ (Christie et al., 2005; Reiche et al., 1995) or with salts as plasticizers LiClO₄, and NaCF₃SO₃ LiCF₃SO₃ (MacFarlane et al., 1995; Forsyth et al., 1995). Recently, polymers have also been doped with ionic liquid type imidazolium and pyridinium (Noda & Watanabe, 2000): the conductivity of these compounds is located around 1 mS.cm⁻¹. The team of H. Ohno (Ohno, 2001), has chosen to synthesize polymers bearing ionic function, rather than using the ionic liquid as a dopant. The molecular weights of synthesized polymers were not measured, the authors only report the stickiness and rubbery compounds obtained as proof of proper functioning of the reaction (Yoshizawa & Ohno, 2001; Ohno, 2001). The team of Chen (Chen et al., 2009) studied the effect of random polymer composition of ionic liquid polymerize, while recent publication of Matsumoto (Matsumoto et al., 2010) report the synthesis of Met-IL (1-(2-methacryloxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide), and evaluate molecular weight of homopolymer, after transformation in PMMA. As expected the ionic conductivity of ILs decrease during their polymerization: it's reported that they lose 20% to 33% of their initial conductivity. The authors show that the chain length between the imidazolium cation and the polymeric chain seems to have an influence on the polymer conductivity: if the string is longer, it should have a greater flexibility and as a consequence a higher conductivity. Furthermore the length of the side chain has more influence on the conductivity of a cationic polymer than that of an anionic polymer.

Since the beginning of our researches, one of our main concerns has been to prepare new monomers having an element that can confer flexibility in their esterifying chain: we chose the sulfur atom, known for this property.

2. Synthetic methods modifying the esterifying chain: Way 1

Herein, we wish to report our recent work on the syntheses of new ILs containing (meth) acrylic functions. Looking for interest of potential applications of ILs we focused our attention in two directions:

- Synthesis of new ILs possessing a high conductivity and a polymerisable double bond which can lead, after polymerization, to a novel family of polymer electrolytes,
- Development of new synthetic methods from (meth) acrylic compounds which provide simple and efficient ILs containing a carboxylate function.

The (meth) acrylic compounds are of some interest. They are highly reactive due to the presence of the activated double bond. This latter can undergo nucleophilic attack (Michael reaction) or can be subject to radical reaction. The esterifying chain can also be modified by simple (trans) esterification reaction. Moreover they are cheap industrial compounds synthesized on very large scale. Figure 4 describes two aspects of the synthetic methods (process 1 -process 2):

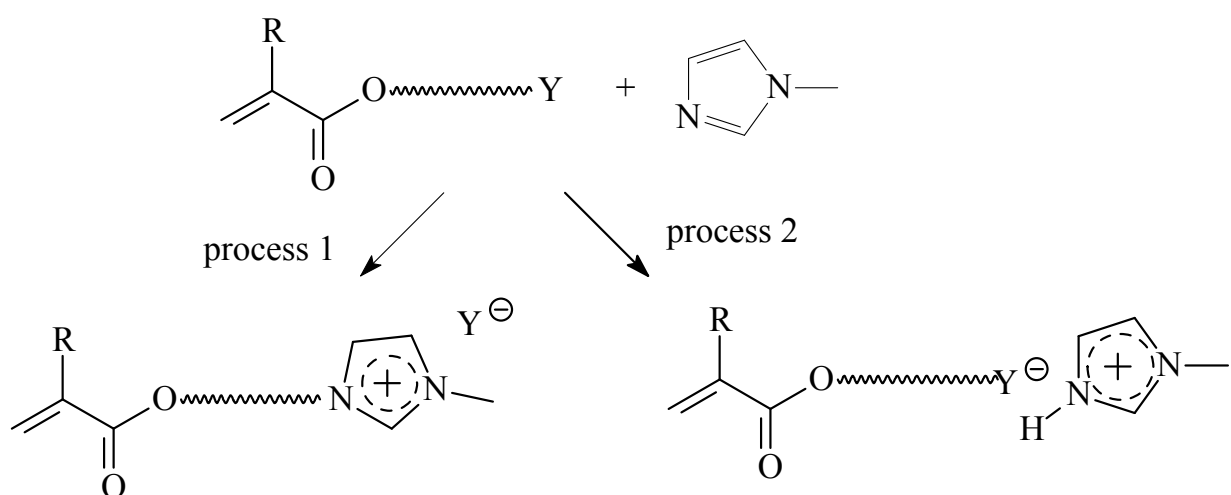


Fig. 4. General scheme of ionic acrylic monomers synthesis

The process consists in modifying the esterifying chain of the (meth) acrylic system thus leading to two types of ILs :

- Cationic ILs, which are (meth)acrylic monomers with a cationic part grafted at the end of their esterifying chain (Fig.5a).
- Anionic ILs, which have this time an anionic part attached to the (meth)acrylate function (Fig.5b).

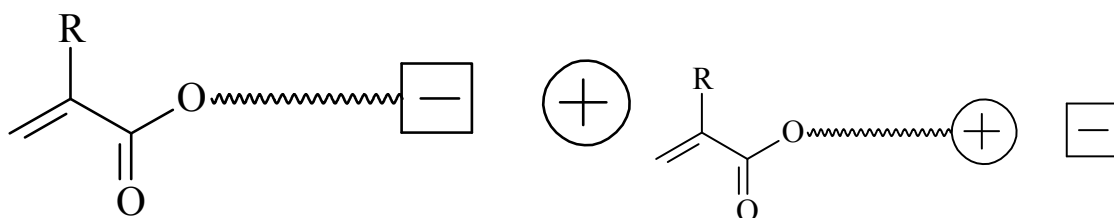


Fig. 5. General structure of cationic (a) and anionic (b) (meth)acrylic IL, (R=H,Me)

2.1 Process 1: Synthesis of cationic monomers

2.1.1 Synthesis

The starting material, halogeno alkyl (meth)acrylate, can easily be prepared through the esterification of a (meth) acrylate type compound with various halogenoalcohols. Two methods are then available: the use of (meth)acrylic acid refluxing in cyclohexane or the one of (meth)acryloyl chloride in the presence of a tertiary amine (pyridine or triethylamine). In order to avoid polymerization during the process, hydroquinone methyl ether (HQME) is added in the reaction medium. Yield depends on the halogenoalkyl chain length and also on the (meth)acrylic system nature. The best results are obtained with $n=6$ and acrylic acid (Fig.6).

Note: halogenoalcohols were purchased from Aldrich chemical or synthesized using the described methods (Ford-Moore & Perry, 1963; Suk-Ku et al., 1985)

At first, we adapted a classical well described method consisting in the reaction of the halogeno(meth)acrylates with N-methylimidazole (Nakajima & Ohno, 2005) (Fig. 6).

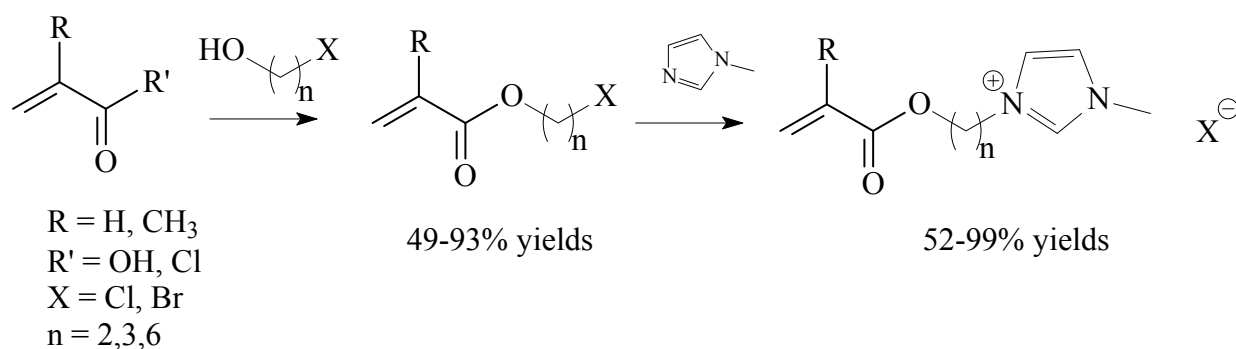


Fig. 6. Synthesis of cationic monomers ($\text{R} = \text{Me}$, $[\text{MAlkylMim}][\text{X}]$ and $\text{R} = \text{H}$, $[\text{AAkylMim}][\text{X}]$)

Unlike Ohno's procedure (i.e. an excess of N-methylimidazole) we used an equivalent amount of N-methylimidazole and halogeno(meth)acrylate which enabled us to avoid a purification step since no N-methylimidazole was left in the final product. Some amount of HQME was added to the other reactants in order to avoid polymerization reaction. The reaction was followed by ^1H NMR and its completeness was unambiguous since the signals of N-methylimidazole moieties at 3.64 (CH_3), 6.86 ($\text{HCN}(\text{Me})$), 7.01 (NCH) and 7.38 (NCHN) ppm have disappeared in favour of those from N-methylimidazolium respectively at 3.74, 7.35, 7.41, 8.5-10 ppm.

We observed that when $n = 6$, the product is well synthesized, both with Br and Cl halides. When $n = 3$, the reaction is really slower. As a consequence, the reaction time must be increased when the less reactive halide ($\text{X} = \text{Cl}$) is present and consequently some polymerization products appears. Nevertheless the final product is easily purified by an ether washing.

All synthesized products are viscous liquids or solids having melting below 130°C which can be considered as ILs. They are also watersoluble. As the reaction is carried out without any solvent, the work up is very easy and yields are generally around 90%. However, as reaction time is somewhat too long, several trials to reduce it were attempted. Sonochemistry (Namboodiri & Varma, 2002; Estager et al., 2007; Levêque et al., 2007) and microwave chemistry (Levêque et al., 2007; Varma & Namboodiri, 2001b) which are well described in the literature and often named as a good way to shorten reaction times, were

used to try to improve our reaction. In the previous synthetic method the quaternarisation of 3-bromopropyl methacrylate with N-methylimidazole leads to 99 % yield in 24 hours. The same reaction was realized using ultrasonic amplitude of 40 % (apparatus: 20 kHz ultrasonic processor, power: 130 W). In a few minutes temperature raised and ^1H NMR follow-up revealed the disappearance of N-methylimidazole protons at the favour of those of imidazolium salt. The final product is obtained with a 99% yield in only 35 minutes (Fig. 7). Still the will to decrease the reaction time of the quaternarisation step, an experiment was realized in a microwave oven (150 W delivered, power is a function of temperature) determinate temperature (75°C) to avoid the polymerization of the methacrylate. After 45 seconds, the quaternarisation is achieved with a 99% yield (Fig. 7). :

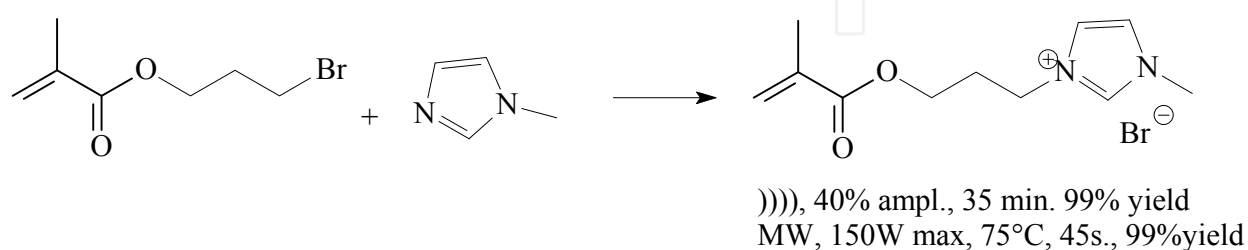


Fig. 7. Synthesis of [MPMIm][Br] using ultrasounds or microwave activation

Remark: the reaction with $n=2$ has not been studied. Indeed The halide in β -position for the ester function is somewhat poor reactive referring to some other works (Dubosclard-Gottardi et al, 1995; Fort et al., 1993; Cerf, 1991) which clearly explain the non-reactivity of the β -C in halogeno(meth)acrylates.

In conclusion, we have demonstrated that synthesis of imidazolium acrylates are possible varying length chain. Moreover, N-(methacryloyloxypropyl)-N'-methylimidazolium bromide [MPMIm][Br] was successfully obtained via quaternarisation using alternative methods: under ultrasounds and under microwave irradiation in a microwave oven. Compared with thermal heating, we observed a rate acceleration and drastically reduced reaction times.

2.1.2 Metathesis of halogenoimidazolium salts

The properties of IL are widely dependent on the nature of the counter-ion: its size or structure can affect the physical properties of the resulting IL, especially its melting point and its viscosity (Handy S.T, 2005). When the anion is small, the structure tends to act as a classical crystal salt like sodium chloride (Fig 8.A). But when the anion becomes more bulky, the structure of the IL is then disorganized and, becomes unsymmetrical: so it acts like a liquid (Fig. 8.B):

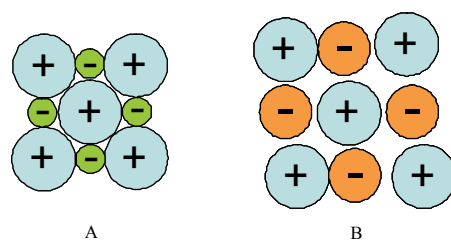


Fig. 8. Ionic structure of crystal salt (A) and liquid (B)

On this basis we explored several ways to realize the counter-ion metathesis (Fig. 9).

- Metathesis of anion with hydricids: at first we applied a well-established method consisting of a reaction between an IL and an hydricids (HY) in an aqueous medium (Gordon et al., 1998). The IL (Br counter-ion) reacts with HY in water: the reaction is very exothermic and HY must be carefully added. The novel IL is obtained by filtration or extraction with an organic solvent, depending on the compound state (solid or liquid). In all cases IL are not (or only lightly) water-soluble. Yields (table 1, entry 1, 3, 5, 7, 9, 11, 13, 15) are depending on the solubility of ILs. When they are partially water-soluble, a small quantity of them is lost and yields decrease.
- Metathesis of anion with ammonium and lithium salts: we try to perform a counter-anion metathesis of the IL with NH_4BF_4 salt in order to try to improve the reaction yield. The solvent used during the reaction is acetone which allows the solubilisation of final product but not the one NH_4Br , by-product of the reaction, which makes the purification easier. Moreover the solvent is simple to remove. The reaction is carried out with one molar equivalence of IL ammonium salt which are soluble in acetone. The by-product is removed by filtration and the filtrate is concentrated under vacuum to get a liquid or a solid. Yields are quite improved compare to the first metathesis (table 1, entry 2, 6, 10, 14).

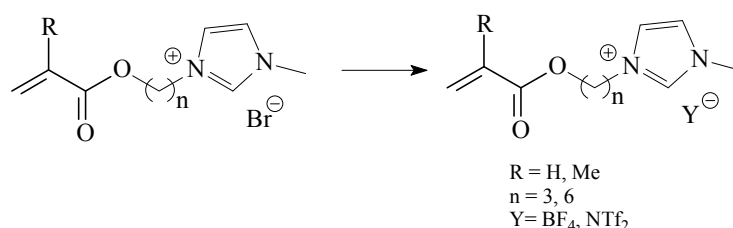


Fig. 9. Metathesis of bromide in [MAlkylMim][Br] or [AAlkylMim][Br]

Entry	Product	n	R	Reagent	Yield	Solubility in water
1	[MPMim][BF ₄]	3	Me	HBF ₄	33%	Partial
2				NH ₄ BF ₄	91%	
3	[MPMim][NTf ₂]	3	Me	HNTf ₂	34%	No
4				LiNTf ₂	91%	
5	[APMim][BF ₄]	3	H	HBF ₄	34%	Partial
6				NH ₄ BF ₄	82%	
7	[APMim][NTf ₂]	3	Me	HNTf ₂	85%	No
8				LiNTf ₂	68%	
9	[MHMim][BF ₄]	6	Me	HBF ₄	56%	Partial
10				NH ₄ BF ₄	87%	
11	[MHMim][NTf ₂]	6	Me	HNTf ₂	78%	No
12				LiNTf ₂	89%	
13	[AHMim][BF ₄]	6	H	HBF ₄	51%	Partial
14				NH ₄ BF ₄	79%	
15	[AHMim][NTf ₂]	6	Me	HNTf ₂	38%	No
16				LiNTf ₂	63%	

Table 1. Results of Metathesis of bromide in [MAlkylMim][Br] or [AAlkylMim][Br]

In a similar way, we tried the same reaction but this time with a lithium salt, LiNTf₂, which is far less expensive than HNTf₂. We chose CHCl₃ as solvent reaction because the reaction by-product, LiBr, isn't soluble in it and so, this latter is easy removable from the reaction mixture. The reaction was performed under the same conditions than those used with the tetrafluoroborate ammonium salt. The IL is obtained by extraction and the solvent is removed under vacuum to get a liquid. We observed that yields are generally improved compare to those from the first method (table 1, entry 4, 8, 12, 16)

In conclusion, the metathesis of anion can be performed in different ways. Laborious reactions with hydric acids can be satisfactorily avoided using the corresponding salts.

2.1.3 Special IL and new development

In cationic ILs, viscosity and conductivity are largely dependant on the flexibility of the esterifying chain of the (meth) acrylic moiety. From this point of view, we tried to insert a sulfur atom in the esterifying chain. The synthesis is realised in three steps and the overall yields are 50% and 58% when R is respectively Me and H (Fig. 10).

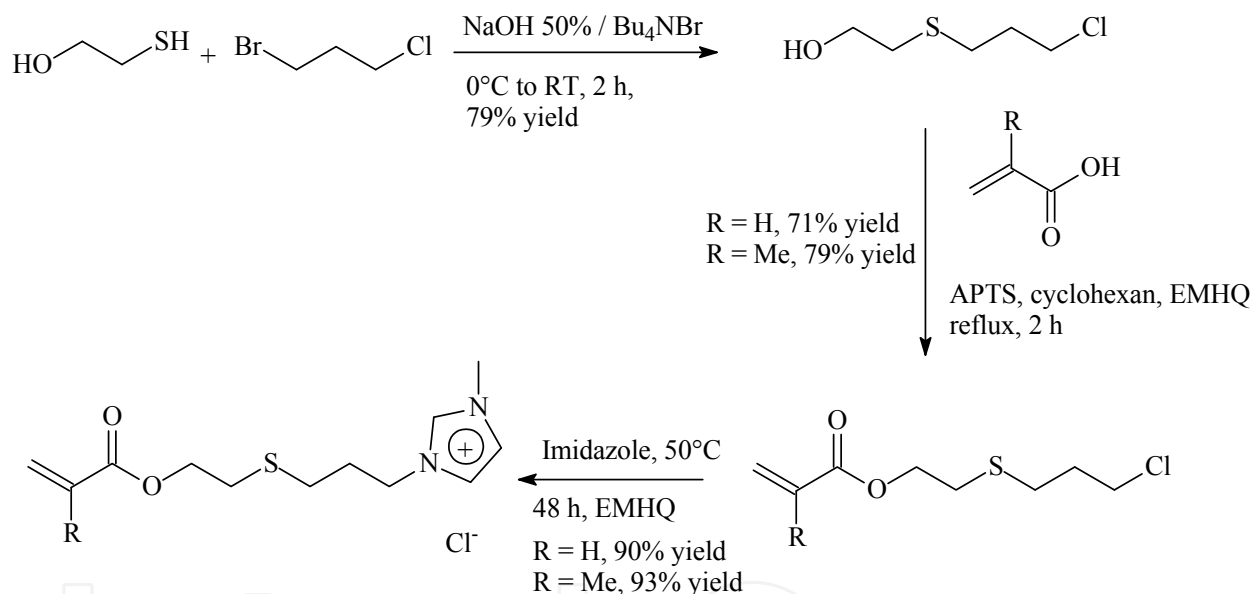


Fig. 10. Synthesis of sulfurated ionic (meth)acrylic monomers

These new compounds are identified without ambiguity with the NMR spectra:

R = H: ¹H NMR, δ ppm (250 MHz; CDCl₃): 8.25 (NCHN, s), 7.86 (2 CHN, d), 6.39 (CH=, dd, J_{gem}=1,5Hz, J_{trans}=16,7Hz), 6.14 (CH=, dd), 5.87 (CH=, dd, J_{gem}=1,5Hz, J_{cis}=10Hz), 4.32 (CH₂O, t), 4.25 (CH₂N, t), 3.74 (CH₃N, s), 2.81 (2 CH₂S, m), 1.98 (CH₂, q). ¹³C NMR, δ ppm (250 MHz; CDCl₃): 165.8 (CO), 136.7 (NCHN), 131.0 (CH₂=), 128.1 (CH=), 122.9 (CHN), 122.4 (CHN), 63.6 (CH₂O), 40.9 (CH₂N), 35.8 (CH₃N), 33.2 (CH₂S), 30.4 (CH₂S), 28.0 (CH₂).

R = Me: ¹H NMR, δ ppm (250 MHz; CDCl₃): 8.25 (NCHN, s), 7.42 (2 CHN, d), 6.12 (CH=, d), 5.55 (CH=, d), 4.36 (CH₂O, t), 4.21 (CH₂N, t), 3.74 (CH₃N, s), 2.80 (2 CH₂S, m), 1.92 (CH₂, q), 1.85 (CH₃, s). ¹³C NMR, δ ppm (250 MHz; CDCl₃): 167.1 (CO), 136.7 (NCHN), 136.0 (C=), 125.8 (CH₂=), 122.9 (CHN), 122.4 (CHN), 63.8 (CH₂O), 41.0 (CH₂N), 35.8 (CH₃N), 33.0 (CH₂S), 30.5 (CH₂S), 28.2 (CH₂).

This work is currently under study.

2.2 Process 2: Synthesis of anionic monomers

As mentioned above, anionic ILs generally have a better conductivity and a lower viscosity than cationic ILs: This is due to the higher lability of the cation in an anionic IL which induces a greater flexibility of the structure. In order to compare physicochemical properties of cationic and anionic IL, we focused our attention on two ionic ILs, we chose to synthesize two anionic ILs which structures are alike with those from cationic ILs described above: one has three carbon atoms in the side chain and the other exhibits a sulfur atom.

2.2.1 Synthesis of 4-(meth)acryloyloxybutanoate N-methylimidazolium salt

1,4 butanediol, in large excess, was reacted with (meth)acryloyloxy chloride to prepare 4-hydroxybutyl(meth)acrylate (Chaudron, 1999). Resulting monomers were reacted with Jones reagent ($\text{CrO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$) in order to prepare corresponding carboxylic acids. Filtration on silica and a liquid-liquid extraction allowed the obtention of pure acids. Finally an acido-basic reaction between carboxylic acids and N-methyl imidazole to led the formation of the corresponding anionic IL (Fig. 11).

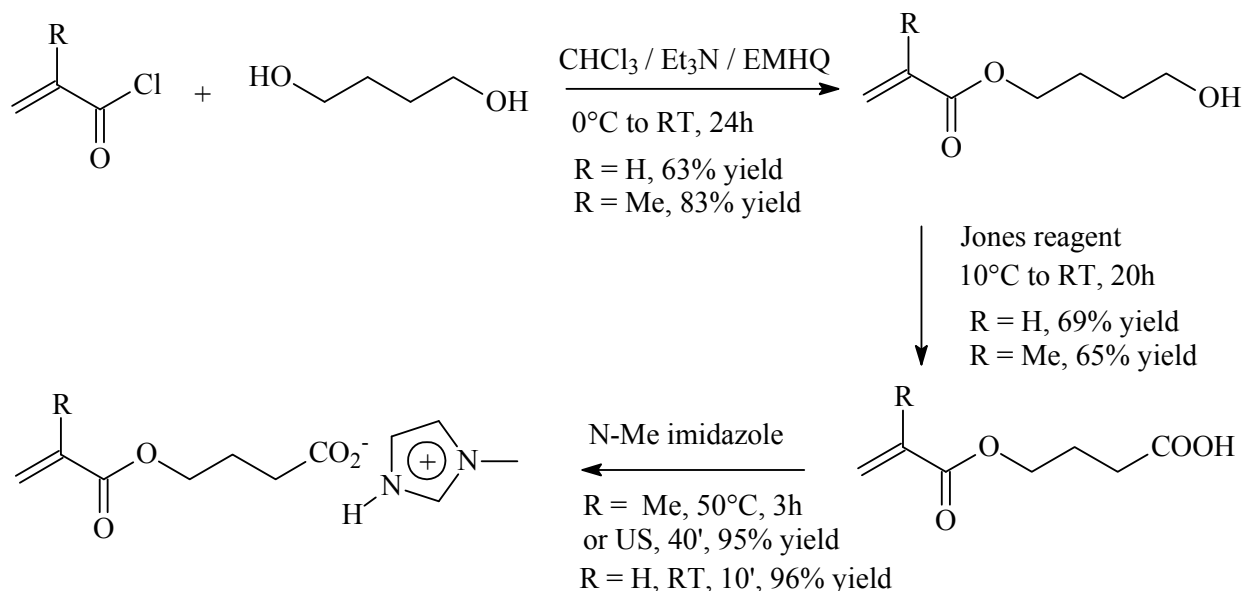


Fig. 11. Synthesis of 4-(meth)acryloyloxybutanoate N-methylimidazolium salt

In a first step, the reaction (R = Me) was performed at 50°C during 48h. Along with the desired IL, we observed the presence of a by-product resulting from the Michael addition of N-methyl imidazole on the activated double bond of the (meth)acrylate compound (Fig. 12).

It seemed that the reaction time was too long. In fact we observed that the reaction was complete after 3h of heating. After this period, if heating continues, IL decomposes to give back initial products which perform a Michael addition. As a consequence it is preferable to stop the reaction as soon as the IL is synthesized. In order to avoid formation of the Michael addition by-product and to decrease reaction time, sonochemistry was tested on this synthesis. In these conditions, it only took 40 minutes to prepare the desired IL. When R = H, the conditions have to be less harsh since the acrylic compounds is more reactive than the methacrylic one and is more inclined to give the Michael by-product. 10 minutes room temperature are enough to obtain the acrylic type IL.

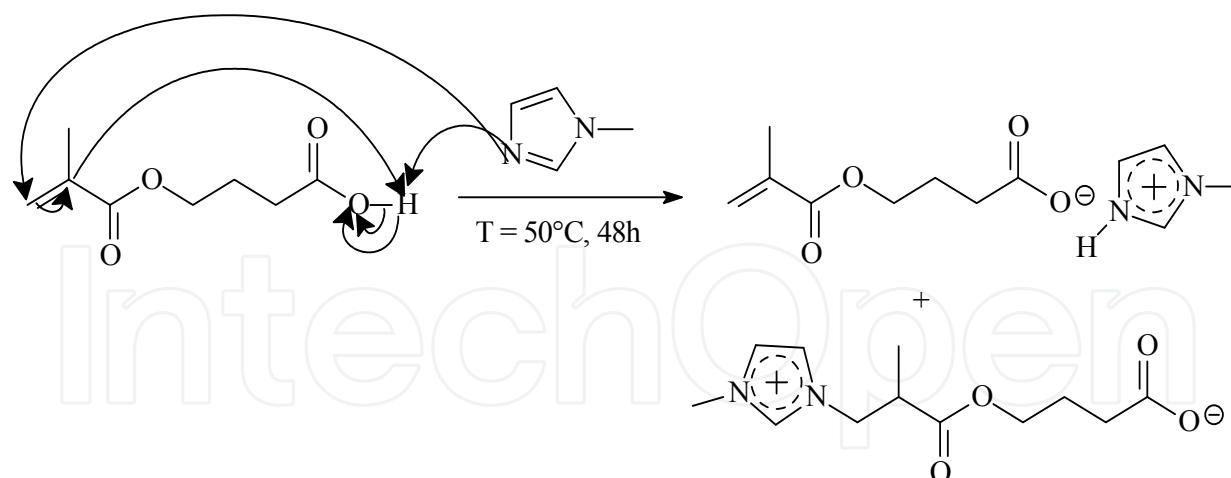


Fig. 12. Scheme for the formation of expected IL an by-product (Michael reaction)

Finally the overall yields are 42% and 54% for the acrylate and methacrylate compounds respectively. These new compounds are identified with the NMR spectra:

R = H :¹H NMR, δ ppm (250 MHz; D₂O): 8.40 (NCHN, s), 7.21 (2 CHN, m), 6,34 (CH=, dd, $J_{gem}=1\text{Hz}, J_{trans}=17.5\text{Hz}$); 6,07 (CH=, dd), 5.82 (CH=, dd, $J_{gem}=1\text{Hz}, J_{cis}=10\text{Hz}$), 4.16 (CH₂O, t), 3.72 (CH₃N, s), 2.44 (CH₂C(O), t), 1.98 (CH₂, m). ¹³C NMR, δ ppm (250 MHz; D₂O): 178 (CO), 166.3 (CO acryl.), 136 (NCN), 130.9 (CH₂=), 128.3 (CH=), 123 (CN), 120 (CN), 65 (CH₂O), 35 (CH₃N), 34 (CH₂CO), 25 (CH₂).

R = Me :¹H NMR, δ ppm (250 MHz; D₂O): 8.41 (NCHN, s), 7.21 (2 CHN, m), 6.06 (CH=, d), 5.5 (CH=, d), 4.17 (CH₂O, t), 3.73 (CH₃N, s), 2.11 (CH₂C(O), t), 1.73 (CH₃ and CH₂, m). ¹³C NMR, δ ppm (250 MHz; D₂O): 182 (CO), 170 (CO acryl), 136 (NCN), 135 (C=), 126.5 (CH₂=), 123 (CN), 120 (CN), 65 (CH₂O), 35 (CH₃N), 34 (CH₂CO), 25 (CH₂), 18 (CH₃)

2.2.2 Synthesis of 6-(meth)acryloyloxy-4-thiahexanoate N-methylimidazolium salt

Tertibutylacrylate was first reacted with mercaptoethanol in the presence of triton B (N-benzyltrimethyl ammonium hydroxyde (Kharasch & Fuchs, 1948; Melwig, 1995) resulting in a Michael reaction with a 99% yield. These conditions tend to be more effective than those used in classical radical reaction which only give 54% yield (Curci, 1992). Resulting alcohol was esterified with (meth)acryloyl chloride under usual conditions. Nevertheless, the choice of the acidic medium during the workup must be taken really carefully. Indeed HCl 10% leads easily to the desired products, while H₂SO₄, hydrolyzes the two ester functions and which recovers HO(CH₂)₂S(CH₂)₂COOH. Tertibutyl group was then removed with formic acid 98%. In a final step, the quaternarization of the acid was realized with N-methyl imidazole using the conditions described above. The reaction time depends on the type of compound: 10 minutes for an acrylate compound and 15 minute for a methacrylate one. Finally the overall yields are 31% and 37% for the acrylate and methacrylate compounds respectively (Fig.13).

We identified these new compounds with the NMR spectra:

8.45 (NCHN, s), 7.21 (2 CHN, m), 6,35 (CH=, dd, $J_{gem}=1.5\text{Hz}, J_{trans}=17\text{Hz}$), 6,08 (CH=, dd), 5.79 (CH=, dd, $J_{gem}=1.5\text{Hz}, J_{cis}=10.2\text{Hz}$), 4.30 (CH₂O, t), 3.72 (CH₃N, s), 2.82 (CH₂C(O), t), 2.71 (CH₂S, t), 2.58 (CH₂S, t)

MHz; CDCl₃): 178 (CO), 168 (CO acryl.), 136 (NCN), 130.6 (CH₂=), 128.3 (CH=), 123 (CN), 120 (CN), 64.6 (CH₂O), 35 (CH₃N), 34 (CH₂CO), 31.5 (CH₂S), 26.9 (CH₂S).
 8.42 (NCHN, s), 7.21 (2 CHN, m), 6.07 (CH=,d), 5.62 (CH=, d), 4.27 (CH₂O, t), 3.71 (CH₃N, s), 2.83 (2 CH₂S, t), 2.82 (CH₂C(O), t), 1.92 (CH₃, s)

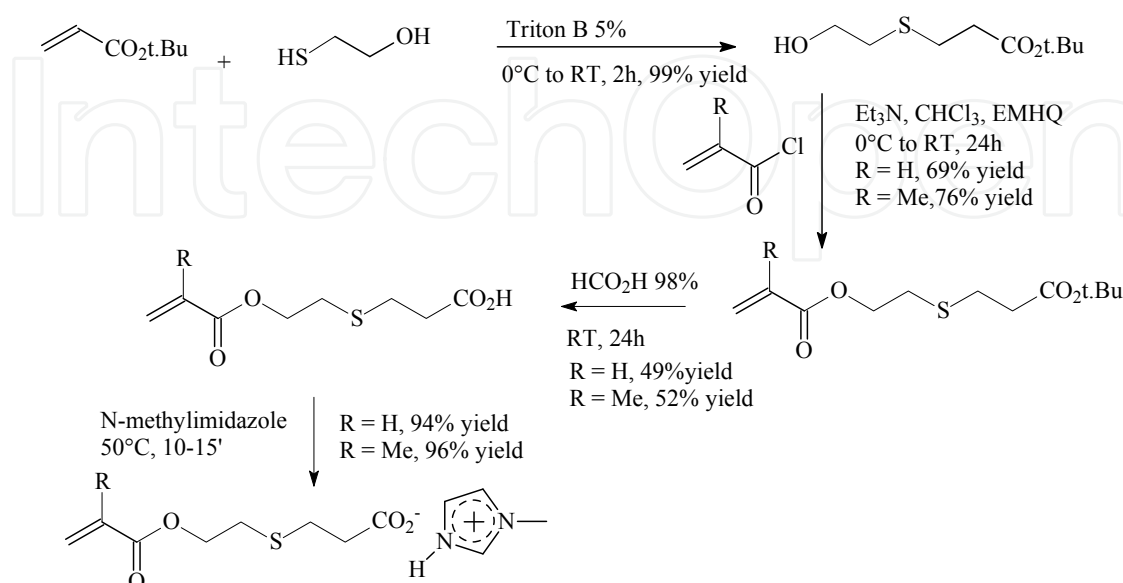


Fig. 13. Synthesis of 6-(meth)acryloyloxy-4-thiahexanoate N-methylimidazolium salts

3. Synthetic methods resulting from aM addition: Way 2

3.1 Synthesis of (N-(2-carboxyethyl)methylimidazolium salts by Michael addition of NMI on acrylic acid

In literature, the high cost of ILs preparation is repeatedly reported. This is mainly due to multi-step syntheses and special counter-ions introduction (NTf₂⁻, OSO₂CF₃⁻...). We developed a “one-pot” reaction, between acrylic acid (AA), N-methylimidazole (NMI) and an fluorinated acid (HBF₄, HPF₆, HNTf₂) (FA), to obtain a fluorine anion. The same reaction was performed several times by switching everytime the introduction order of reactants to see if that parameter has an impact on the result of the reaction. In all cases, two reagents were stirred together and the third one was added after to the mixture. The whole was then stirred (24h) at 50°C (Fig. 14).

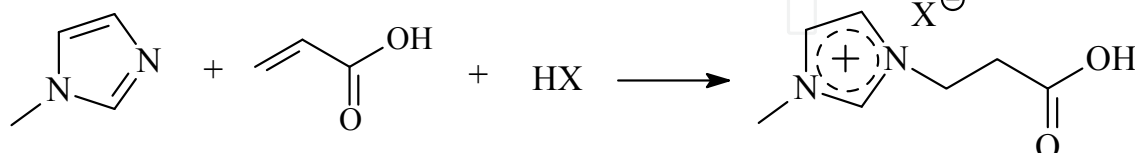


Fig. 14. General scheme of one pot synthesis of carboxylic acid functionalized imidazolium salts by Michael addition

We observed that whatever reactants addition order is, we only obtained the expected product, with a yield of 85% when we use bis(trifluoromethanesulfonyl)imide acid (HNTf₂). With HBF₄ and HPF₆, when NMI and acrylic acid react first, acrylic acid plays the role of an

acid and the imidazolium salt is obtained. According to the work of Wasserscheid (Wasserscheid et al., 2003), it seems important, first, to mix NMI and the fluorinated acid, then to add acrylic acid and heat at 70°C. Following those conditions, we obtained the expected product, respectively with 38 and 33% yield.

The difference of reactivity of these two acids and HNTf_2 can be explained by the fact that HBF_4 and HPF_6 are diluted in water, while HNTf_2 is pure. As water can be a limiting factor, we added a drying step, carried out by microwave heating, before the addition of acrylic acid. Thus, performance can be improved and yields are respectively 83% and 77% for HBF_4 and HPF_6 (Fig. 15):

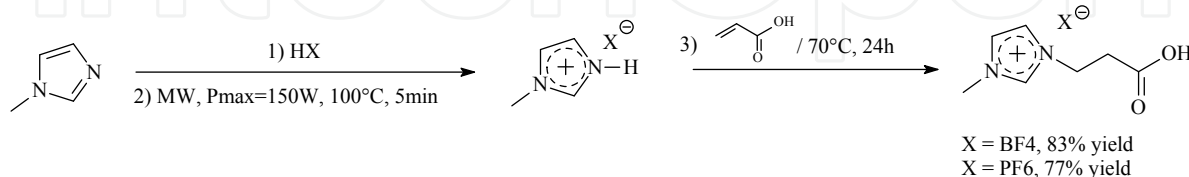


Fig. 15. Preparation of carboxylic acid functionalized imidazolium salts using HBF_4 and HPF_6

However, even if those two acids are highly reactive, they have the disadvantage of being very corrosive. Under certain conditions (high temperature of heating in the presence of water) they decompose in particularly dangerous HF. During a reaction we observed the attack of inner walls of the glass reactor by a small amount of acid formed. To avoid such inconvenience, we developed another path to synthesize these ionic liquids, which does not require the use of HBF_4 and HPF_6 , but the one of corresponding ammonium salt. In the first step of this method we used bromohydric acid in order to realize the quaternization of NMI. The bromide anion is replaced by a fluorinated one in a second step (Fig. 16):

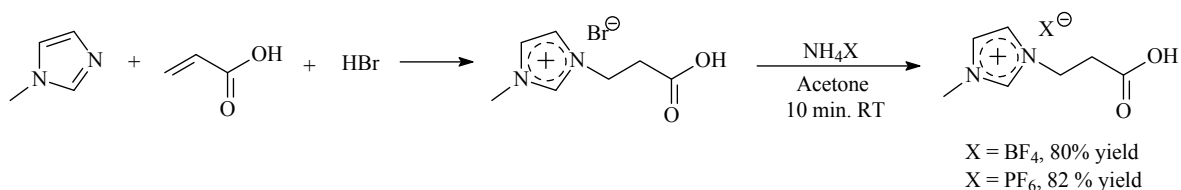


Fig. 16. Preparation of carboxylic acid functionalized imidazolium salts using NH_4BF_4 and NH_4PF_6

The first step can be realized both by reaction of AA with HBr or with NMI (the reaction of NMI with HBr leads to the stable methyl ammonium bromide salt which doesn't react with AA), followed by elimination of water using microwave technical. The exchange of anion using ammonium salt is rapid (10 min in acetone). The ammonium bromide resulting from the counter-anion exchange is insoluble in acetone and, as a consequence, is easily removed from reaction mixture by a simple filtration.

3.2 Synthesis of IL by Michael addition on esters

In order to broaden the series of product available, Michael addition can be realized on acrylic esters, using imidazole (Fig. 17). Quaternization of intermediate products by nucleophilic substitution of the halogen leads to the corresponding ILs. The use of ultrasound is very effective in the 2 steps of this synthetic path since it reduces impressively reaction times.

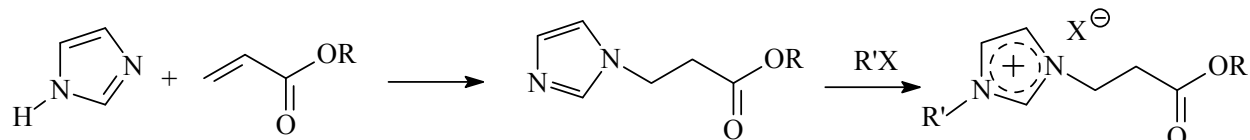


Fig. 17. Synthesis of ester functionalized imidazolium salts

Depending of R substituent (methyl, ethyl, $\text{CH}_2\text{CH}_2\text{Cl}$, Butyl, *t*-butyl, octyl), this reaction can take between 30 min. and 3 h. under ultrasonic activation instead of 24h. by heating at 50°C . The N-alkylation is easy with bromide derivatives but far less with chlorides ones. So far, we realized nucleophilic substitution with 3-bromopropanol, and other radicals are under study.

4. Thermodynamics data

Interactions between IL cations and anions are the consequence of energetic and geometric factors leading to a variety of strongly organized and oriented structures. These features confer to ILs numerous applications in organic synthesis, separation processes, and electrochemistry (Seddon, 1997; Sheldon, 1993; Cull et al, 2000; Wilkes, 2004; Wasserscheid & Keim, 2000; Welton, 1999; Brennecke & Maginn, 2001; Fredlake et al., 2004; Henderson & Passerini, 2004). The aim of this work is to determine the influence of the (meth)acrylic moiety on the thermodynamic properties of the ionic liquid. For this purpose, the study of (*N*-methacryloyloxyhexyl-*N*-methylimidazolium bromide [MHMim][Br] and *N*-acryloyloxypropyl-*N*-methylimidazolium bromide [APMim][Br] permitted to determine its selectivity toward a hexane/benzene mixture and its interactions toward other compounds using the Linear solvation Energy Relationship (LSER) descriptor.

All of these measurements were performed using the inverse gas chromatography technique. Column packing of 1 m length containing from 7 to 26% of stationary phases (RTIL) on Chromosorb W-AW (60-80 mesh) were prepared using the rotary evaporator technique. After evaporation of the dichloromethane under vacuum, the support was equilibrated at 323 K over 6 h.

LSER characterization: Ionic liquids can easily adsorb onto solid surfaces and may form a strongly structured interface at the support surface. This interface may induce the adsorption of polar solutes. For this reason, it was decided to use the above-described experimental procedure that allows the separation of the adsorption contribution. To quantify intermolecular solute-IL interactions, we used the LSER equation developed by Abraham et al. (Abraham et al., 1987, 1990, 1991, Abraham, 1993). This method allows one to correlate thermodynamic properties of phase transfer processes. The most recent representation of the LSER model is given by (Mutelet, 2008):

$$\log SP = c + eE + sS + aA + bB + lL \quad (1)$$

Both ionic liquids studied in this work were analyzed using the above-described (eq 1) LSER approach. Coefficients *c*, *e*, *s*, *a*, *b*, and *l* of the ILs were obtained by multiple linear regression of the gas-liquid partition coefficients logarithm $\log K_L$ of 30 solutes (Mutelet et al., 2008). The system constants for the two ionic liquids studied in this work at 313.15 K and other ionic liquid stationary phases are summarized in Table 2.

Ionic liquid	System constant					
	e	s	a	b	l	c
<i>n</i> -acryloylpropyl-N-methylimidazolium bromide	0	2.88	5.5	0	0.48	-1.03
<i>n</i> -methacryloylhexyl-N-methylimidazolium bromide	0	2.46	5.36	0	0.57	-0.87
1-propenyl-3-methylimidazolium bromide	0	2.16	5.19	0	0.53	-1.86
1-propenyl-3-octylimidazolium bromide	0	1.72	4.96	0	0.57	-1.60
1-propenyl-3-decylimidazolium bromide	0	1.73	4.89	0	0.66	-1.58
1-propenyl-3-dodecylimidazolium bromide	0	1.44	4.87	0	0.7	-1.51
1-butyl-3-methylimidazolium octyl sulfate	0	1.47	4.05	0	0.68	-0.237
1-ethyl-3-methylimidazolium tosylate	0.54	2.40	4.81	0.17	0.48	-0.84
<i>n</i> -butylammonium thiocyanate	0.14	1.65	2.76	1.32	0.45	-0.75
di- <i>n</i> -propylammonium thiocyanate	0.3	1.73	2.66	0.68	0.47	-0.6
Ethylammonium nitrate	0.27	2.21	3.38	1.03	0.21	-0.87
<i>n</i> -propylammonium nitrate	0.25	2.02	3.50	0.9	0.36	-0.97

Table 2. LSER descriptors of ionic liquids imidazolium type, determined at 313.5K

LSER coefficients of both ILs studied in this work are slightly different from those obtained with other ionic liquids of the imidazolium bromide type.

- The $(c + l)$ term gives information on the effect of the cohesion of the ionic liquids on solute transfer from the gas phase. In general, the ionic liquids are cohesive solvents (Poole, 2004).
- The ionic liquid interacts weakly via nonbonding and π -electrons (e system constant is zero) and is not much different from other polar nonionic liquids.
- Dipolarity/ polarizability of ionic liquids is slightly higher than most of dipolar/polarizable nonionic stationary phases ones. The polarizability decreases slightly when the alkyl chain length is increased on the imidazolium ring. But introducing a (meth)acryloyloxyalkyl chain in imidazolium bromide-based ionic liquids considerably increases its dipolarity/polarizability (s system constants).

The hydrogen-bond basicity of the ionic liquid (a system constants) is considerably larger than values obtained for nonionic phases (0 to 2.1) (Poole, 2004), whereas its hydrogen-bond acidity is inexistent ($b=0$). Ionic liquids have structural features that would facilitate hydrogen-bond acceptor basicity interactions (electron-rich oxygen, nitrogen, and fluorine atoms). Imidazolium bromide based ionic liquids containing a (meth)acryloyloxyalkyl chain have the highest hydrogen-bond basicity, with an a constant of 5.36 and 5.50. This is great support for the idea that the interactions between the -OH group and ionic liquids I and II are very strong.

Selectivity determination: Ionic liquids are solvents that may have great potential in chemical analysis. Specifically, the applications of RTILs are found in chromatography or

extraction chemistry. These compounds, thermally stable, non-toxic with low vapor pressure, can act as stationary phases in inverse gas chromatography (Pacholec, 1982, 1983). Numbers of organic molten salts were evaluated as stationary phases for gas chromatography. Nevertheless only ionic liquids containing imidazolium cation lead to high selectivity toward polar and non-polar solutes.

The selectivity, S_{12}^{∞} , which indicates the suitability of a solvent for separating mixtures of components 1 and 2 by extractive distillation is given by Tiegs (Tiegs et al., 1986)

$$S_{12}^{\infty} = \frac{Y_{1/LI}^{\infty}}{Y_{2/LI}^{\infty}}$$

$Y_{1/LI}^{\infty}$ is the activity coefficient at infinite dilution of compound 1 (hexane) relative to the IL $Y_{2/LI}^{\infty}$ is the activity coefficient at infinite dilution of compound 2 (benzene) relative to the IL The selectivity values, S_{12}^{∞} , relative either to the IL studied in this work and other liquid solvents used in industry for the separation of benzene and n-hexane, are reported in Table 3.

Entry	Solvent	S_{12}^{∞}	Reference
1	[MAHMIm][Br]	50,4	Mutelet et al., 2008
2	[APMIm][Br]	27,6	Mutelet et al., 2008
3	Dichloroacetic acid	6,1	Tiegs et al., 1986
4	sulfolane	30,5	Tiegs et al., 1986
5	1-propenyl-3-methylimidazolium bromide	6,96	Mutelet et al., 2006
6	1-propylboronic acid-3-octylimidazolium bromide	9,91	Mutelet et al., 2006
7	1-ethyl-3-methylimidazolium tetrafluoroborate	61,6	Foco et al., 2006

Table 3. Selectivity value for the solute Hexane (1) and benzene (2) in solvents

The selectivity of both ionic liquids studied in this work at 313.15 K is very large as compared to the value for classical solvents (entry 1,2). These values are largely higher than those of usual industrial compounds (entry 3,4). Compared to similar IL containing bromide ion we can suspected that (meth)acrylic alkyl chain is of some importance because usually the selectivity increases with decreasing length of the alkyl chain (entry 1,2,4,6). In the same way the proximity of (meth)acrylic function decreases the selectivity (enter 1,2). Only 1-ethyl-3-methylimidazolium tetrafluoroborate has a higher selectivity (entry 7) but it is obvious that the chemical nature of the cation and the anion play an important role in separation of mixtures of aromatic and aliphatic compounds

Through this work, we demonstrated that interfacial adsorption could play a significant role in the retention mechanism of organic compounds. Results indicate that the introduction of (meth)acryloyl substituents on the IL imidazolium cation affects strongly the behavior of organic compounds in mixtures with this IL. For instance, the IL used in the separation of aliphatic hydrocarbons from aromatic hydrocarbons, shows a higher selectivity than the one found by previous workers using classical organic solvents

5. Catalytic properties of IL adsorbed on nanoparticles

One of the recent developments of IL is their use in catalysis (Olivier-Bourbigou et al., 2010). Their catalytic properties are well known, and a broad range of reactions have already been studied (oxidation, polymerization, enantioselective reactions...). Moreover, the capability to support these catalytic species is an attractive alternative to classic use of ionic liquids, because these latter can be recycled. These SILCAs (Supported Ionic Liquids CAtalystS) are formed of different IL immobilized on several supports: active carbon cloth (Mikkola et al. 2007; Virtanen et al. 2007; Maki-Arvela et al. 2006) or silica gel (Riisager et al. 2003; Mehnert et al. 2002). They may also contain metal species like rhodium (Riisager et al. 2003; Mehnert et al. 2002) or palladium (Mikkola et al. 2007; Virtanen et al. 2007; Maki-Arvela et al. 2006). In our case, we realized the adsorption of our monomers on aluminum oxide nanopowder. The use of nanoparticules is really interesting since they are more likely to provide a wide and homogeneous dispersion of the catalyst in the reaction medium. The preparation of these SILCAs is usually based on alumina saturation. After dilution of IL in an organic solvent (Komulski et al. 2005; Zilkova et al. 2006; Li et al. 2007), it is then adsorbed on alumina nanoparticles surface. This procedure is easy to carry out and does not involve the use of metal species in opposition to other methods found in literature (Mikkola et al. 2007; Virtanen et al. 2007; Maki-Arvela et al. 2006; Riisager et al. 2003; Mehnert et al. 2002).

In order to evaluate the catalytic properties of our SILCAs, we chose to test them on a classic and simple reaction. As our laboratory has a great interest in heteroatomic compounds especially sulfurs (Robert et al. 1996; Pees et al. 2001; Thomas et al. 2006), we chose a thioether synthesis, and benzyl phenyl thioether in particular (Harmand, 2009). Conversion rates of reaction between thiols and halides depend on reaction conditions which are in most cases not really environment friendly (extraction difficulties, catalysts loss and so on). To prepare SILCAs, three steps are necessary; first the solubilization of IL in chloroform, then the addition of the alumina nanoparticules in the solution and finally the solvent removal evaporation. This method allows the obtention of a supporting material coated with a thin and uniform IL layer. We first compare the reaction between phenyl bromide and thiophenol in a basic aqueous solution in methylene chloride, with (table 4, entry 2–21) or without (table 4, entry 1) prepared SILCAs (Fig. 18).

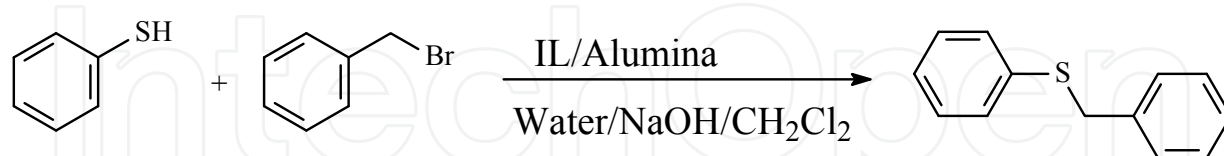


Fig. 18. Synthesis of benzylphenyl thioether, using SILCA as catalysts.

The principal advantage of this method is the simplified working up: after 4h reflux, the solution is filtered to recover the supported catalyst, and then the filtrate is decanted to allow organic layer recovery. Without catalyst the conversion rate is very low as predicted in a heterogeneous system (table 4, entry 1). Rates are improved in the presence of SILCA and results of this preliminary study are satisfactory. Nevertheless depending on the molecular structure, results are different. Generally, conversion rates are best when n is equal to 6 whenever R is H or Me. For similar chain length, rates are higher when R is a methyl. We are currently studying this phenomenon, which could be due to polymerization of monomers on the alumina area during SILCAs preparation. Finally, we can note that the

highest conversion rates are reached with $n = 6$ and are quantitative when $R = \text{Me}$ (table 4, entry 12-16).

Entry	IL	Conversion (%)
1	none	25
2	[MPMim][Cl]	96
3	[MPMim][Br]	96
4	[MPMim][PF ₆]	100
5	[MPMim][BF ₄]	73
6	[MPMim][NTf ₂]	75
7	[APMim][Cl]	90
8	[APMim][Br]	68
9	[APMim][PF ₆]	65
10	[APMim][BF ₄]	73
11	[APMim][NTf ₂]	53
12	[MHMim][Cl]	100
13	[MHMim][Br]	100
14	[MHMim][PF ₆]	100
15	[MHMim][BF ₄]	100
16	[MHMim][NTf ₂]	100
17	[AHMim][Cl]	90
18	[AHMim][Br]	99
19	[AHMim][PF ₆]	92
20	[AHMim][BF ₄]	100
21	[AHMim][NTf ₂]	84

Table 4. Results of the synthesis of benzylphenylsulfide using SILCA

In conclusion, after adsorption on alumina nanoparticles surface, these new polymerisable compounds, presented in this work, are used as a new kind of catalysts in the synthesis of benzyl phenyl thioether. These SILCAs give better results than a traditional phase transfer agent. Moreover, they are totally recoverable at the end of the reaction. As a consequence they can be considered as environmentally friendly catalysts.

6. Conclusion and perspectives

We described here the synthesis of several new molecules deriving from acrylates, common industrial compounds which are really reactive and available in large quantities. These molecules exhibit characteristics of ILs like their melting points which are below 100°C and others, such as viscosity and conductivity are being investigated. Moreover they have demonstrated some physical chemical applications such as in catalysis or in separation process.

In the future our laboratory will develop the work described herein, in three directions.

First, our attention will be focused on new heteroatomics IL synthesis. We already synthesized some sulfurated IL and we wish to develop this class of compounds and incorporate some novel heteroatom (P, Si...).

Many IL synthesized have a polymerizable double bond, so as a second way of action, we planned to polymerize these molecules, in order to obtain electrolytes polymers type. These

highly ion-conducting electrolytes could have potential applications in a wide range of areas such as in lithium battery and dye-sensitized solar cell (Choi N.S. et al., 2004; Shibata Y. et al., 2003). ILs have good chemical and thermal stability, low vapor-pressure and high conductivity. These properties could be used to product new polymer with particularly good properties as some described by Ohno (Washiro S. et al., 2004).

In a third way we would like to use our work to develop some potential applications in green chemistry. We already began to synthesize some compounds using glycerol as starting material (Fig. 19). Glycerol is a cheap industrial product which is, for example, currently used in acrylic acid synthesis. From glycerol we intend to build dendritic structures presenting terminal groups functionalized with the type of function described in this work, in order to obtain new green ion-conducting electrolytes.

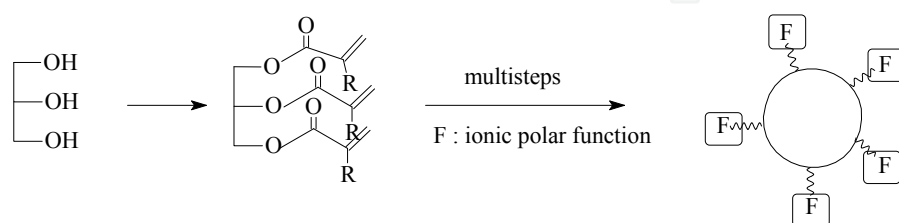


Fig. 19. Dendritic structure starting from glycerol and (meth)acrylic compounds.

7. References

- Abraham M.H., Grellier P.L. & McGill R.A., (1987). Determination of olive oil-gas and hexadecane-gas partition coefficients, and calculation of the corresponding olive oil-water and hexadecane-water partition coefficients, *J. Chem. Soc. Perkin Trans II*, n°6, pp.797-803 (June 1987), ISSN 0300-9580
- Abraham M.H., Whiting G.S., Doherty R.M. & Shuely W.J. (1990). Hydrogen bonding. Part 13. A new method for the characterisation of GLC stationary phases—the laffort data set, *J. Chem. Soc. Perkin Trans II*, n°8, pp.1451-1460 (August 1990), ISSN 0300-9580
- Abraham M.H., Whiting G.S., Doherty R.M. & Shuely W.J. (1991). Hydrogen bonding: XVI. A new solute solvation parameter, π_2H , from gas chromatographic data, *J. Chromatogr. A*, vol.587, n°2, pp.213-228, (December 1991), ISSN 0021-9673
- Abraham M.H. (1993). Scale of solutes hydrogen bonding: their construction and application to physicochemical and biochemical processes, *Chem. Soc. Rev.*, vol.22, n°2, pp.73-83 (March 1993), ISSN 0306-0012
- Baudequin C., Brégeon D., Levillain J., Guillen F., Plaquevent J.C. & Gaumont A.C. (2005). Chiral ionic liquids, a renewal for the chemistry of chiral solvents? Design, synthesis and applications for chiral recognition and asymmetric synthesis. *Tetrahedron: Asymmetry*, vol.16, pp.3921-3945 ISSN 0957-4166
- Biswas A., Shogren R.L., Stevenson D.G., Willett J.L. & Bhowmik P.K. (2006), Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein, *Carbohydrate Polymers*, vol.66, n°4, pp.546-550, (November 2006), ISSN 0144-8617
- Blasco-Jimenez D., Lopez-Peinado A.J., Martin-Aranda A.M., Ziolek M. & Sobczak I. (2009). Sonocatalysis in solvent-free conditions: an efficient eco-friendly methodology to prepare N-alkyl imidazoles using amino-grafted NbMCM-41, *Catalysis today*, 6th

- International Symposium on Group Five Elements, Poznań, Poland*, vol.142, n°3-4 pp.283-287, (April 2009), ISSN 0920-5861
- Bonhôte P., Dias A.-P., Papageorgiou N., Kalyanasundaram K. & Grätzel M. (1996). Hydrophobic, Highly Conductive Ambient-Temperature Molten Salts, *Inorg.Chem.*, vol.35, n°5, pp.1168-1178, (February 1996), ISSN 0020-1669
- Brennecke J.F. & Maginn E. (2001). Ionic liquids: Innovative fluids for chemical processing, *J. AIChE*, vol.47, n°11, pp.2384-2389, (November 2001), Online ISSN: 1547-5905
- Cai, Y., Yao S.-P., Wu Q. & Lin X.F. (2004). Michael addition of imidazole with acrylates catalysed by alkaline protease from *Bacillus subtilis* in organic media, *Biotechnology letters*, vol.26, n°6, pp.525-528, (March 2004), ISSN 0141-5492
- Caye F., Sindt M., Mieloszynski J.L. & Paquer D. (1998). A convenient high yield synthesis of functional methacrylates via dethioacetalization. Synthesis of methacrylate S,S-acetals derivatives as intermediate, *Phosphorus, Sulfur, and Silicon*, vol.143, n°1, pp. 197-220 (December 1998) ISSN 1042-6507
- Cerf M. (1991). Etude de monomères acryliques et thioacryliques soufrés et phosphorés, University Paul Verlaine Metz, Thesis
- Cerf M., J.L. Mieloszynski & D. Paquer (1992). Préparation de monomères (méth)acryliques soufrés à l'aide d'une catalyse par transfert de phase, *Sulfur letters*, vol 15, pp. 61 ISSN 0278-6117
- Chaudron P. (1999). Synthèse de monomères méthacryliques phosphorés. Application à l'ignifugation. University Paul Verlaine, Metz, Thesis
- Chen H., Choi J.H., Salas-de -la Cruz D., Winey K.I. & Elab Y.A. (2009). Polymerized Ionic Liquids: the effect of random copolymer composition on ion conduction, *Macromolecules*, vol.42, n°13, pp.4809-4816, (May 2009), ISSN 0024-9297
- Choi N.S., Lee Y.M., Lee B.H., Lee J.A. & Park J.K. (2004). Nanocomposite single ion conductor based on organic-inorganic hybrid, *Solid State Ionics*, vol.167, n°3-4, pp. 293-299 (February 2004), ISSN 0167-2738
- Christie A.M., Lilley S.J., Staunton E., Andreev Y.G. & Bruce P.G. (2005). Increasing the conductivity of crystalline polymer electrolytes, *Nature*, vol.433, n°7021, pp. 50-53 (January 2005), ISSN 0028-0836
- Cochez M., Ferriol M., Weber J. V., Chaudron P., Oget N. & Mieloszynski J.L. (2000). Thermal degradation of methyl methacrylate polymers functionalized by phosphorus-containing molecules I. TGA/FT-IR experiments on polymers with the monomeric formula $\text{CH}_2\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ (R=H, $(\text{CH}_2)_4\text{CH}_3$, $\text{C}_6\text{H}_5\text{Br}$, C_{10}H_7), *Polym. Degrad. Stab.*, vol.70, n° 3, pp. 455-462 (November 2000) ISSN 0141-3910
- Cruickshank A.J.B., Windsor M.L., & Young C.L. (1966). The Use of Gas-Liquid Chromatography to Determine Activity Coefficients and Second Virial Coefficients of Mixtures. I. Theory and Verification of Method of Data Analysis, *Proc. R. Soc. London, A*, vol.295, n°1442, pp.259-270. ISSN 1471-2954
- Cull S.G., Holbery J.D., Vargas-Mora V., Seddon K.R. & Lye G. J. (2000). Room-temperature ionic liquids as replacements for organic solvents in multiphase bioprocess operations, *Biotechnol. Bioeng.*, vol.69, n°2, pp.227-233 (July 2000), Online ISSN: 1097-0290
- Curci M. (1992). Synthèse de monomères (méth)acryliques soufrés et/ou phosphorés comportant des fonctions pouvant générer des sels, Université Paul Verlaine, Metz, Thesis

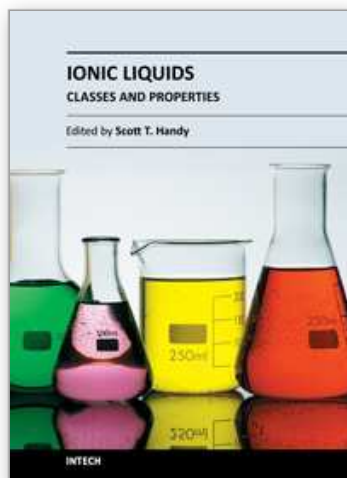
- Curci M. (1993). Synthesis of functionalized acrylates, *Organic Preparations and Procedures international*, vol.25, n°6, pp.649-657 (December 1993), ISSN 0030-4948
- Davis J.H. Jr, Gordon C.M., Hilgers C. & Wasserscheid P. (2003). *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, pp. 7-21, ISBN 978-3-527-30515-7, Weinheim, Germany
- Dubosclard-Gottardi C., Caubère P. & Fort Y. (1995). New selective syntheses of (meth)acrylic monomers: Isocyanates, isocyanurates, carbamates and ureas derivatives, *Tetrahedron*, vol.51, n°9, pp.2561-2572, (February 1995), ISSN 0040-4020
- Earle M.J & Seddon K.R. (2000). Ionic liquid. Green solvents for the future, *Pure Appl. Chem.*, vol.72, n°7, pp1391-1398, (July 2000), ISSN 0033-4545
- Estager J., Levêque J-M., Cravotto G., Boffa L., Benrath W. & Draye M. (2007). One-Pot and Solventless Synthesis of Ionic Liquids under Ultrasonic Irradiation. *Synlett* vol.13, pp. 2065-2068, (2007), ISSN 0936-5214
- Foco G.M., Bottini S. B., Quezada N., De La Fuente J.C. & Peters C. J. (2006). Activity Coefficients at Infinite Dilution in 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids, *J. Chem. Eng. Data*, vol.51, n°3, pp.1088-1091, (March 2006), ISSN 0021-9568
- Ford-Moore A.H. & Perry B.J. (1963), Triethylphosphite, *Organic Syntheses IV*, Coll. Vol 4, pp.955
- Forsyth M., MacFarlane D.R., Meakin P., Smith M.E & Bastow T.J. (1995) An nmr investigation of ionic structure and mobility in plasticized solid polymer electrolytes, *Electrochimica Acta, International symposium on polymer electrolytes*, vol.40, n°13-14, pp. 2343-2347, (October 1995), ISSN 0013-4686
- Fort Y., Gottardi C. & Caubère P. (1993). New selective syntheses of (meth)acrylic monomers: Isocyanates, carbamates, ureas and isocyanurates derivatives, *Tetrahedron. Letters*, vol.34, n°24, pp.3857-3860, (June 1993), ISSN 0040-4039
- Fredlake C.P., Crosthwaite J.M., Hert D.G., Aki S.N.V.K. & Brennecke J.F.J. (2004). Thermophysical Properties of Imidazolium-Based Ionic Liquids, *Chem. Eng. Data*, vol.49, n°4, pp.954-964, (June 2004), ISSN 0021-9568
- Gentilhomme A., Cochez M., Ferriol M., Oget N. & Mieloszynski J.L. (2005). Thermal degradation of methyl methacrylate polymers functionalized by phosphorus-containing molecules. III: Cone calorimeter experiments and investigation of residues, *Polym. Degrad. Stab.*, vol.88, n°1, pp. 92-97 (April 2005), ISSN 0141-3910
- Gordon C.M., Holbrey J.D., Kennedy A.R. & Seddon K.R. (1998). Ionic liquid crystals : hexafluorophosphate salts, *J. Mater. Chem.*, vol.8, n°12, pp.2627-2636, (December 1998), ISSN 0959-9428
- Grant D.W. (1971). *Gas-Liquid Chromatography*, van Nostrand Reinhold company, London.
- Handy S.T. (2005). Room temperature ionic liquids: Different classes and physical properties, *Current Organic Chemistry* (2005), vol.9, n°10, pp.959-988, (July 2005), ISSN 1385-2728
- Harmand J., Rogalski M., Sindt M. & Mieloszynski J.L. (2009). Preparation of molten salt-type (meth)acrylic monomers and their application as catalysts in the synthesis of benzyl phenyl sulfide: an alternative to the usual toxic sulfides synthesis. *Environ. Chem. Letters*, vol.7, n°3, pp.255-260, (September 2009), ISSN 1610-3653
- Henderson W.A. & Passerini S. (2004). Phase Behavior of Ionic Liquid-LiX Mixtures: Pyrrolidinium Cations and TFSI- Anions, *Chem. Mater.*, vol.16, n°15, pp.2881-2885. ISSN 0897-4756

- Jullien Y., Melwig J.Y., Wilhelm J.C., Curci M., Mieloszynski J.L & Paquer D. (1996a). Réaction particulières de cyanoalkyle sulfures. Application à l'obtention de dérivés acryliques, *Phosphorus, Sulfur, and Silicon*, vol. 118, n°1, pp. 95-104 (November 1996), ISSN 1042-6507
- Jullien Y., Melwig J.Y., Curci M., Mieloszynski J.L & Paquer D. (1996b). Nouvelle voie de synthèse de dérivés acryliques via des réactions de protection/déprotection, *Phosphorus, Sulfur, and Silicon*, vol.118, pp.105-111 (November 1996). ISSN 1042-6507
- Karodia N., Guise S., Newlands C. & Andersen J.-A. (1998). Clean catalysis with ionic solvents - phosphonium tosylates for hydroformylation, *Chem.Comm.*, n°21, pp.2341-2342, (November 1998), ISSN 1359-7345
- Kharasch M.S. & Fuchs C.F. (1948). The peroxide effect in the addition of reagents to unsaturated compounds. XXXVIII. The addition of mercaptans to methyl acrylate, *J. Org. Chem.*, vol. 13, n°1, pp.97-100, (January 1948), ISSN 0022-3263
- Kosmulski M., Szafran M., Saneluta C. & Marczevska-Boczkowska M. (2005). Low-temperature ionic liquids immobilized in porous alumina. *J. Colloid. Interface Sci.* vol.291, n°1, pp.214-217, (November 2005), ISSN 0021-9797
- Lakshmi Kantam M., Neelima B., Venkat Reddy C. & Chakravarti R. (2007). Aza-Michael addition of imidazoles to α,β -unsaturated compounds and synthesis of β -amino alcohols via nucleophilic ring opening of epoxides using copper(II) acetylacetonate ($\text{Cu}(\text{acac})_2$) immobilized in ionic liquids. *Ind. Eng. Chem. Res.*, vol.46, n°25, pp.8614-8619, (June 2007), ISSN 0888-5885
- Levêque J.-M., Desset S., Suptil J., Fachinger C., Draye M., Benrath W. & Cravotto G. (2006). A general ultrasound-assisted access to room-temperature ionic liquids, *Ultrason. Sonochem.*, vol.13, n°2, pp.189-193, (February 2006), ISSN 1350-4177 (ref aussi dans partie 2)
- Levêque J.-M., Estager J., Draye M., Cravotto G., Boffa L. & Benrath W. (2007) Synthesis of Ionic Liquids Using Non-Conventional Activation Methods: An Overview, *Monatsh. Chem.*, vol.138, n°11, pp.1103-1113 (August 2007), ISSN 0026-9247
- Li DY, Lin YS, Li YC, Shieh DL, Lin JL (2007) Synthesis of mesoporous pseudoboehmite and alumina templated with 1-hexadecyl-2,3-dimethyl-imidazolium chloride. *Microporous Mesoporous Mater.*, vol.108, n°1-3, pp.276-282, (February 2008), ISSN 1387-1811
- MacFarlane D.R., Sun J., Meakin P., Fasoulopoulos P., Hey J. & Forsyth M. (1995). Structure-property relationships in plasticized solid polymer electrolytes, *Electrochimica Acta, International symposium on polymer electrolytes*, vol.40, n°13-14, pp. 2131-2136, (October 1995), ISSN 0013-4686
- Maki-Arvela P., Mikkola J.P., Virtanen P., Karhu H., Salmi T. & Murzin D.Y. (2006) Supported ionic liquids catalyst (SILCA) in the hydrogenation of citral. *Stud. Surf. Sci. Catal.*, vol.162, pp.87-94, (september 2006), ISSN 0-444-52827-X
- Mancardi D., Sindt M., Paul J.M. & Mieloszynski J.L. (2007). Convenient synthesis of tributylsilyl methacrylate, *Synth. com.*, vol.37, n°21, pp. 3873-3878 (January 2007) ISSN: 0039-7911
- Martin-Aranda R.M., Vicente-Rodriguez M.A., Lopez-Pestana J.M., Lopez-Peinado A.J., Jerez A., Lopez-Gonzalez J.deD. & Banares-Munoz M.A. (1997). Application of basic clays in microwave activated Michael addition : Preparation of N-substituted imidazoles, *J. Mol. Catal. A : Chem.*, vol. 124, n° 2-3, pp.115-121, (October 1997), ISSN 1381-1169
- Martin-Aranda R.M., Ortege-Cantero E., Rojas-Cervantes M.L, Vicente-Rodriguez M.A. & Banares-Munoz M.A. (2002). Sonocatalysis and basic clays. Michael addition

- between imidazole and ethyl acrylate. *Catalysis Letters*, vol.84, n°3-4, pp.201-204, (December 2002), ISSN 1011-372X
- Matsumoto K, Talukdar B. & Endo T. (2010). Methacrylate-based ionic liquid: radical polymerization/copolymerization with methyl methacrylate and evaluation of molecular weight of the obtained homopolymers, *Polym. Bull*, vol.66, n°2, pp.199-210, (January 2011), ISSN 0170-0839
- Mehnert C.P., Cook R.A., Dispenziere N.C. & Afeworki M. (2002). Supported ionic liquid catalysis—a new concept for homogeneous hydroformylation catalysis. *J. Am. Chem. Soc.*, vol.124, pp.12932–12933, (October 2002), ISSN 0002-7863
- Melwig J.Y. (1995). Etude de la synthèse de composés acryliques via une réaction de protection-déprotection de la fonction polymérisable. Université Paul Verlaine, Metz, Thesis
- Mikkola J.P.T., Virtanen P.P., Korda`s K., Karhu H. & Salmi T.O. (2007). SILCA—supported ionic liquid catalysts for fine chemicals. *Appl. Catal. A* vol.328, n°1, pp.68–76, (August 2007), ISSN 0926-860X
- Mutelet F., Jaubert J.N., Rogalski M., Harmand J., Sindt M. & Mieloszynski J.L. (2008). Activity Coefficients at Infinite Dilution of Organic Compounds in 1-(Meth)acryloyloxyalkyl-3-methylimidazolium Bromide Using Inverse Gas Chromatography, *J. Phys. Chem. B*, vol.112, n°12, pp.3773-3785, (March 2008), ISSN 1520-6106
- Mutelet F., Jaubert J.N., Rogalski M., Boukherissa M. & Dicko A. (2006). Thermodynamic Properties of Mixtures Containing Ionic Liquids: Activity Coefficients at Infinite Dilution of Organic Compounds in 1-Propyl Boronic Acid-3-Alkylimidazolium Bromide and 1-Propenyl-3-alkylimidazolium Bromide Using Inverse Gas Chromatography, *J. Chem. Eng. Data*, vol.51, n°4, pp.1274-1279, (April 2006), ISSN 0021-9568
- Nakajima H., Ohno H. (2005). Preparation of thermally stable polymer electrolytes from imidazolium-type ionic liquid derivatives, *Polymer*, vol. 46, n°25 pp.11499-11504, (December 2005), ISSN 0032-3861
- Namboodiri V.V.& Varma R.S. (2002). Solvent-Free Sonochemical Preparation of Ionic Liquids, *Org. Lett.*, vol.4, n°18, pp.3161-3163, (August 2002), ISSN 1523-7060
- Noda A. & Watanabe M. (2000). Highly conductive polymer electrolytes prepared by in situ polymerization of vinyl monomers in room temperature molten salts, *Electrochimica Acta*, vol.45, n°8-9, pp.1265-1270, (January 2000), ISSN 0013-4686
- Ohno H. (2001). Molten salt type polymer electrolytes, *Electrochimica Acta*, vol.46, n°10-11, pp.1407-1411, (March 2001), ISSN 0013-4686
- Olivier-Bourbigou H., Magna L. & Morvan D. (2010). Ionic liquids and catalysis : Recent progress from knowledge to applications, *Appl. Catal. A* vol.373, n°1-2, pp.1–56, (January 2010), ISSN 0926-860X
- Pacholec F., Butler H. T. & Poole C. F. (1982). Molten organic salt phase for gas-liquid chromatography, *Anal. Chem.*, vol.54, n°12, pp.1938-1941, (October 1982), ISSN 0003-2700
- Pacholec F. & Poole C. F., (1983). Stationary phase properties of the organic molten salt ethylpyridinium bromide in gas chromatography, *Chromatographia*, vol.17, n°7, p.370-374 (July 1983), ISSN 0009-5893
- Pees B., Cahuzac A., Sindt M., Ameduri B., Paul J.M., Boutevin B., & Mieloszynski J.L. (2001). Synthesis of fluorinated acrylic monomers bearing a functionalized lateral

- chain. Part 1 : Preparation of sulfurated monomers, *J.Fluor. Chem.*, vol.108, n°2, pp. 133-142 (May 2001) ISSN 0022-1139
- Pees B., Sindt M., Paul J.M. & Mieloszynski J.L. (2002). Synthèse et caractérisation physico-chimiques de polyacrylates d' ω -perfluorooctyl-alkyle : effet pair- impair. *Eur. Polym. Jour.*, vol.38, n°5, pp. 921-931 (May 2002), ISSN 0014-3057
- Pees B., Paul J.M., Oget N., Sindt M., & Mieloszynski J.L. (2003). Synthesis of fluoro-substituted monomers bearing a functionalised lateral chain. Part 2: Preparation of sulfoxides and sulfones containing monomers, *J. Fluor.Chem.*, vol.124, n°2, pp.139-146 (December 2003) ISSN 0022-1139
- Pees B., Paul J.M., Corpart J.M., Sindt M., & Mieloszynski J.L. (2004). Surface properties of ω -perfluorooctyl-alkyl polyacrylates : odd-even effect, *Eur. Polym. Jour.*, vol.40, n°12, pp. 2727-2730 (December 2004) ISSN 0014-3057
- Poole C.F. (2004). Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids, *J. Chromatogr., A*, vol.1037, n°1-2, pp.49-82 (May 2004), ISSN 0021-9673
- Ratner M.A., Shriver D.F. (1988). Ion transport in solvent-free polymers, *Chem.Rev.*, vol.88, pp. 109-124, (January 1984), ISSN 0009-2665
- Reiche A., Steurich T., Sandner B., Lobitz P. & Fleischer G. (1995). Ion transport in gel electrolytes, *Electrochimica Acta, International symposium on polymer electrolytes*, vol.40, n°13-14, pp. 2153-2157, (October 1995), ISSN 0013-4686
- Riisager A., Wasserscheid P., Van Hal R. & Fehrmann R. (2003). Continuous fixed-bed gas-phase hydroformylation using supported ionic liquid phase (SILP) Rh catalysts. *J. Catal.*, vol.219, n°2, pp.452-455, (October 2003), ISSN 00219517
- Robert D., Schneider M., Born M., Mieloszynski J.L. & Paquer D. (1996). Influence of heteroatomic systems on anti-wear and extreme pressure properties of organo-sulfur compounds. *C. R. Acad. Sci., série IIb*, vol.323, pp.127-132, (1996), ISSN 0320-8437
- Rogers R.D. & Seddon K.R. (2003). Ionic Liquids--Solvents of the Future?, *Science*, Vol. 302, n°5646, pp. 792-793 (October 2003), ISSN 0036-8075
- Seddon K.R. (1997). Ionic Liquids for Clean Technology, *J. Chem. Technol. Biotechnol.*, vol. 68, n°4, pp.351-356, (April 1997), ISSN 0268-2575
- Sheldon R.A. (1993). The role of catalysis in waste minimization. *Precision Process Technology, Perspectives for Pollution PreVention*; Weijnen, M. P. C.; Drinkenburg, A. A. H. Editors; Kluwer: Dordrecht.
- Shibata Y., Kato T., Kado T., Shiratuchi R., Takashima W. & Kaneto K. (2003). Quasi-solid dye sensitized solar cells filled with ionic liquid-increase in efficiencies by specific interaction between conductive polymers and gelators, *Chem. Commun.*, n°21, pp. 2730-2731 (November 2003), ISSN 1359-7345
- Suk-Ku K., Won-Sup K. & Byoung-Ho M. (1985). An Effective Method for the Preparation of ω -Bromoalkanols from α,ω -Diols, *Synthesis*, n°12, pp.1161-1162, (December 1985), ISSN 0039-7881
- Thomas H., Oget N. & Mieloszynski J.L. (2006). A fast and efficient route to 5-chloromethyl-1,4,7,10-tetrathiacyclotridecane and its behavior in a chloroform solution. *J. Incl. Phenom. Macrocycl. Chem.* vol.54, n°3-4, pp.139-145, (April 2006), ISSN 0923-0750
- Tiegs D., Gmehling J., Medina A., Soares M., Bastos J., Alessi P. & Kikic I. (1986). Activity Coefficients at Infinite Dilution, *Chemistry Data Series, vol.IX, Part 1*, DECHEMA. ISBN 3-921567-79-3, Main, Frankfurt

- Varma R.S. & Namboodiri V.V. (2001a). An expeditious solvent-free route to ionic liquids using microwaves, *Chem. Comm.*, n°7, pp.643-644, (April 2001), ISSN 1359-7345
- Varma R.S. & Namboodiri V.V. (2001b). Solvent-free preparation of ionic liquids using a household microwave oven, *Pure Appl. Chem.*, Vol. 73, No. 8, pp. 1309-1313, ISSN 0033-4545
- Virtanen P., Karhu H., Kordas K. & Mikkola J.P. (2007). The effect of ionic liquid in supported ionic liquid catalysts (silca) in the hydrogenation of α,β -unsaturated aldehydes. *Chem. Eng. Sci.*, vol.62, n°14, pp.3660-3671, (July 2007), ISSN 0009-2509
- Washiro S., Yoshizawa M., Nakajima H. and Ohno H. (2004). Highly ion conductive flexible films composed of network polymers based on polymerizable ionic liquids, *Polymer* vol.45, n°5, pp. 1577-1582 (March 2004), ISSN 0032-3861
- Wasserscheid P. & Keim W.A. (2000). Ionic Liquids—New “Solutions” for Transition Metal Catalysis, *Ang. Chem. Int. Ed.*, vol.39, pp.3772-3789, (November 2000), Online ISSN: 1521-3773
- Wasserscheid P., Driëßen-Hölscher B., Van Hal R., Steffens H.C. & Zimmermann J. (2003). New functionalised ionic liquids from Michael-type reactions—a chance for combinatorial ionic liquid development, *Chem. Comm.*, vol. 39, n°16, pp.2038-2039, (August 2003), ISSN 1359-7345
- Wasserscheid P. & Welton T. (2008). *Ionic liquid in synthesis*, 2nd ed., Wiley-CH, ISBN 978-3-527-31239-9, Weinheim.
- Welton T. (1999). Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis, *Chem. Rev.*, vol.99, n°8, pp.2071-2083 (July 1999), ISSN 0009-2665
- Wilkes J.S. (2004). Properties of ionic liquid solvent for catalysis, *J. Mol. Catal. A: Chem.*, vol.214, n°1, pp.11-17, (May 2004), ISSN 1381-1169
- Xu J.M., Qian C., Liu B.K., Wu Q. & Lin X.F. (2007). A fast and highly efficient protocol for Michael addition of N-heterocycles to α,β -unsaturated compound using a basic ionic liquid [bmIm]OH as catalyst and green solvent. *Tetrahedron*, vol.63, n°4, pp.986-990, (January 2007), ISSN 0040-4020
- Yang L., Xu L.W. & Xia C.G. (2005). Highly efficient KF/Al₂O₃-catalyzed versatile hetero-Michael addition of nitrogen, oxygen, and sulfur nucleophiles to α,β -ethylenic compounds. *Tetrahedron Letters*, vol.46, n°19, pp.3279-3282, (May 2005), ISSN 0040-4039
- Yang L., Xu L.W., Zhou W., Li L. & Xia C.G. (2006). Highly efficient aza-Michael reactions of aromatic amines and N-heterocycles catalysed by basic ionic liquid under solvent-free conditions. *Tetrahedron Letters*, vol.47, n°44, pp.7723-7726, (October 2006), ISSN 0040-4039
- Yoshizawa M. & Ohno H. (2001). Synthesis of molten salt-type polymer brush and effect of brush structure on the ionic conductivity, *Electrochimica Acta*, vol.46, n°10-11, pp.1723-1728, (March 2001), ISSN 0013-4686
- Yu B., Zhou F., Wang C. & W. Liu (2007). A novel gel polymer electrolyte based on poly ionic liquid 1-ethyl 3-(2-methacryloyloxy ethyl) imidazolium iodide, *Eur. Polym. J.*, vol.43, n°6, pp.2699-2707 (June 2007), ISSN 0014-3057
- Zaderenko P., Soledad Gil M. & Ballesteros P. (1994). Synthesis and regioselective hydrolysis of 2-imidazol-1-ylsuccinic ester, *J. Org. Chem*, vol.59, n°21, pp.6268-6273, (October 1994), ISSN 0022-3263
- Zilkova N., Zukal A. & Cejka J. (2006). Synthesis of organized mesoporous alumina templated with ionic liquids. *Microporous Mesoporous Mater.*, vol.95, n°1-3, pp.176-179, (October 2006), ISSN 1387-1811



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Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanamide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

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