

Fast and “green” living cationic ring opening polymerization of 2-ethyl-2-oxazoline in ionic liquids under microwave irradiation†

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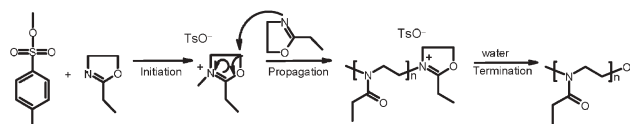
The living cationic ring opening polymerization of 2-ethyl-2-oxazoline performed in an ionic liquid under microwave irradiation showed an enhanced polymerization rate in comparison to the reaction in common organic solvents; the ionic liquid was efficiently recovered and reused in new reaction cycles, completely avoiding the use of organic volatile compounds.

Due to the increase in environmental awareness, it is a matter of great concern for scientists to design more efficient and cleaner technologies in chemical manufacturing and to decrease the consumption of volatile organic solvents (VOS). Four main strategies are available to achieve this task: (i) solvent-free processes, (ii) use of water, (iii) use of supercritical carbon dioxide (CO₂), and (iv) use of ionic liquids as reaction media. The polymer industry uses the first two alternatives with a satisfactory performance.¹ However, solution polymerization processes in VOCs are still common due to the intrinsic drawbacks of the first two processes (*i.e.* high viscosities in bulk polymerizations² and the fact that water is not allowed in moisture-sensitive processes such as ionic polymerizations³). During the last decade, the use of supercritical CO₂ arose as an alternative replacement for VOCs in polymer synthesis and processing. CO₂ is a readily available, inexpensive, nontoxic, and nonflammable natural product; therefore an environmentally benign reaction medium. Heterogeneous polymerizations in liquid and supercritical CO₂ have been studied intensively.⁴ However, a main drawback of the use of CO₂ is the utilization of high pressures to reach critical conditions (73.8 bar at 31.1 °C). Finally, the use of ionic liquids (ILs) as reaction media to synthesize diverse polymers has been explored in recent years.⁵ ILs have shown some advantages for this purpose. Some free radical polymerizations conducted in ILs have shown an increased polymerization rate and yield polymers with higher molar masses in comparison to the ones in VOS.⁶ The feasibility of synthesizing block copolymers in ILs by a free radical mechanism has been described.⁷ Furthermore, copolymerizations carried out in ILs can show significantly different reactivity ratios from those performed in bulk or in VOS, which allowed the preparation of “new” statistical copolymers.⁸ ILs have also been

investigated recently as solvents to perform controlled free radical and living cationic polymerizations.⁹ Despite this progress, clear understanding of how to efficiently use ILs and avoid completely the utilization of VOS in specific polymer systems is still lacking, since many factors must be optimized including polymer isolation, IL recycling, toxicity, cost, *etc.* Polymer isolation and IL recycling using an environmentally friendly approach have been discussed recently.¹⁰ This approach takes advantage of the poor solubility of many polymers in most water-soluble ILs to perform heterogeneous polymerizations, which facilitates the polymer isolation and the IL recycling avoiding VOS. In reaction systems where water must be avoided, such as the living cationic ring opening polymerization (CROP) of 2-ethyl-2-oxazoline (Etox),³ ILs can be good candidates to replace the respective VOS (acetonitrile and ethyl ether for this specific case).

The feasibility of performing “living” cationic^{9c} and cationic ring opening^{9d} polymerizations in ILs has already been reported but the influence of ILs on the cationic polymerization mechanism is still not understood. This communication reports for the first time the use of ILs to perform the CROP of Etox under microwave irradiation (Scheme 1). The investigated CROP system in ILs shows faster polymerization rates in comparison to the polymerization in VOS.³ Moreover, the CROP of Etox in one of the investigated ILs keeps its living character, opening the possibility of constructing well-defined block copolymers with an environmentally-friendly approach. Furthermore, it is shown that the polymer is efficiently extracted with water at the end of the polymerization and the IL is fully recyclable to conduct additional reaction cycles.

CROP of Etox were conducted in different ILs using similar reaction conditions (same microwave set-up as for reactions in acetonitrile) to those reported elsewhere.^{3,†} Five different ILs were investigated as a reaction medium: 1-ethyl-3-methyl-imidazolium tosylate (**1**), trihexyl(tetradecyl)-phosphonium chloride (**2**), 1-butyl-3-methyl-imidazolium tetrafluoroborate (**3**), 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate (**4**), and 1-butyl-3-methyl-imidazolium hexafluorophosphate (**5**).[‡] Etox is soluble in all the investigated ILs. However, results showed that only in ILs **3–5** was polymer obtained under the investigated reaction conditions. The polymerizations performed in ILs **3** and **4** revealed



Scheme 1 Reaction mechanism of the cationic ring opening polymerization of 2-ethyl-2-oxazoline.

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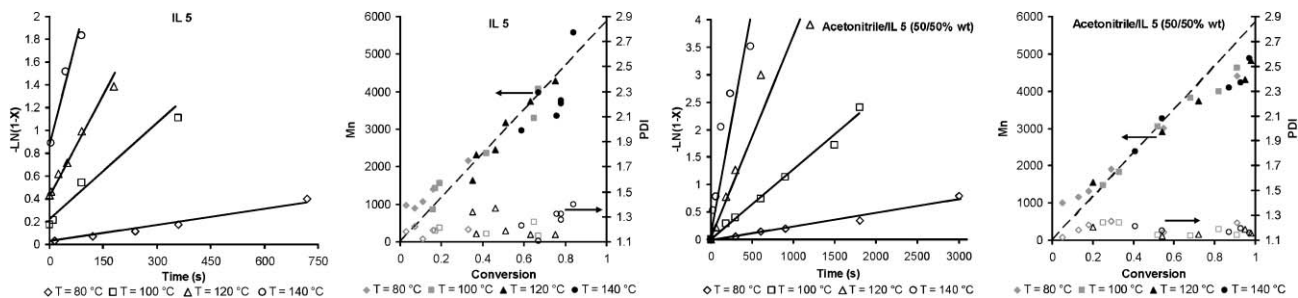


Fig. 1 Plots of monomer conversion (X) (as represented by $-\ln(1 - X)$) against time and number-average molecular weights (M_n) against monomer conversion at different temperatures for CROP of Etox performed in IL **5** (left) and in an acetonitrile/IL **5** mixture (50/50% wt) (right).

similar characteristics to those carried out in IL **5**. However, this work focuses on the use of IL **5**, which facilitates the polymer isolation and IL recycling due to the fact that poly(2-ethyl-2-oxazoline) is more soluble in water than in IL **5** and IL **5** is a hydrophobic IL; therefore a simple extraction with water is suitable to isolate the polymer and to recover the IL.

Fig. 1 shows the results of the polymerizations performed in IL **5** and in a mixture of IL **5**/acetonitrile (50/50% wt). The results show a pseudo-first order kinetic reaction for different temperatures and reveal the living nature of the polymerization by the linear dependences of monomer conversion (X) and represented by $-\ln(1 - X)$ on time and the number-average molecular weights (M_n) on monomer conversion.^{3,†} All the polymers exhibited low polydispersity indices as is also shown in Fig. 1. The final proof for the livingness of the polymerization under the investigated reaction conditions was provided by chain extension experiments performed at 120 °C. The GPC traces[‡] of Fig. 2, before and after the second monomer addition, demonstrate the existence of living chain ends, which allowed for the preparation of chain extended polymers (4.1 kDa (PDI = 1.27) from a 1.8 kDa precursor (PDI = 1.33) in IL **5**, and 5.9 kDa (PDI = 1.26) from a 2.7 kDa precursor (PDI = 1.31) in an acetonitrile/IL **5** mixture (50/50% wt)). The results of Fig. 2 show that the synthesis of block copolymers may be feasible. In order to obtain a more efficient chain extension process, the second monomer addition must be mixed properly into the reaction system to incorporate new monomeric units into all the living chain ends homogeneously. This is due to the relatively high viscosity produced in the system (intrinsic viscosities of the polymer and IL), which may be minimized using hydrophobic ILs (or co-solvents) of low viscosity since the heat and mass transfers may improve.

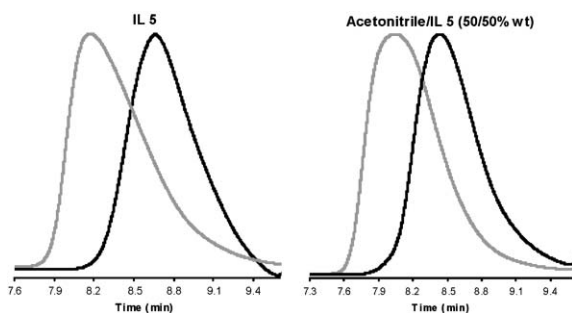


Fig. 2 GPC traces for chain extension experiments of the CROP of Etox performed in IL **5** (left) and in an acetonitrile/IL **5** mixture (50/50% wt) (right). Precursor (black) and chain extended (grey) polymers.

Fig. 1 reveals that the reactions performed in IL **5** show faster polymerization rates than the ones carried out in the mixture of acetonitrile/IL **5** and for their part, these latter reactions show faster polymerization rates than those performed in acetonitrile.³ From the data of Fig. 1, the apparent reaction rate constant (k_{app}) for the investigated temperatures was calculated from the slopes in the $-\ln(1 - X)$ vs. time plots (assuming that the standard pseudo-first order reaction kinetic analysis for living polymerizations¹¹ is still valid under microwave irradiation) to obtain the respective Arrhenius plots shown in Fig. 3.

Table 1 compares the activation energies values obtained from the plots of Fig. 3 to the one reported for the same polymerization carried out in acetonitrile.³ According to Table 1 the polymerization performed in IL **5** showed the lowest activation energy value of the three reaction systems, confirming the observed enhancement of the polymerization rates. These results suggest that, at least for the investigated reaction conditions, the presence of other ionic species (ILs) during the CROP of Etox may modify the association between the living polymer chain ends and their respective counter-ion, resulting in a modified kinetic process that can reduce the reaction times. Similar effects were reported for the anionic polymerization process in the presence of polar additives.¹¹

In Fig. 1 it is also observed that for the polymerizations carried out in IL **5** at temperatures above 100 °C the origin is not intercepted in the plot of monomer conversion against time. This

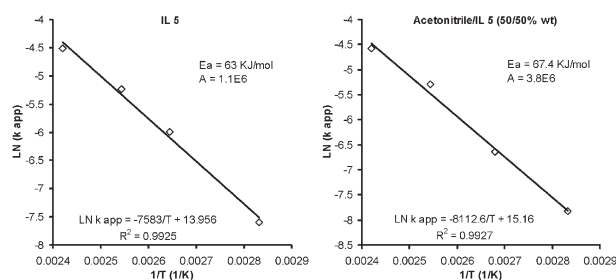


Fig. 3 Arrhenius plots derived from the kinetic data of Fig. 1.

Table 1 Activation energies for the CROP of Etox performed in different solvents

Solvent	Activation energy (kJ/mol)
Acetonitrile	73.4 ^a
Acetonitrile/IL 5 (50/50% wt)	67.4
IL 5	63.0

^a Data from reference 3.

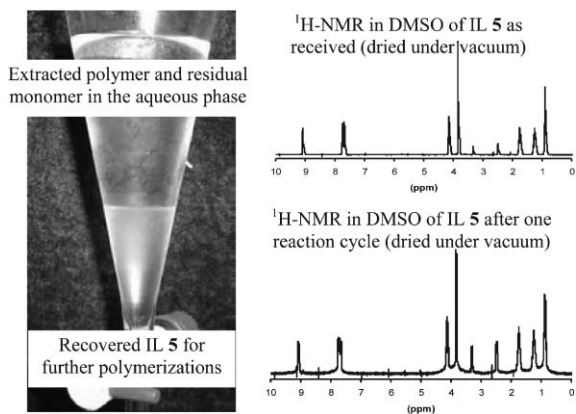


Fig. 4 Efficient IL **5** recovery and polymer isolation by a post-reaction extractive process with water (left). $^1\text{H-NMR}$ spectra of IL **5** as received from the supplier and after one reaction cycle (right).

can be explained by the fact that ILs are known to be heated with exceptional efficiency by microwaves¹² and, the finding of this work, that the CROP of Etox shows faster polymerization rates when performed in IL **5** and under microwave irradiation. When combining these effects the accurate determination of the onset of the polymerization becomes difficult. For instance, experiments performed during just 1 s (as programmed in the microwave set-up) revealed already monomer conversions of 16%, 35%, and 67% for the reaction temperatures of 100 °C, 120 °C, and 140 °C, respectively. This effect is related to the time that the microwave set-up takes to reach the desired reaction temperature (time zero) and to quench the polymerization. The polymerizations performed during just 1 s, in fact, are exposed to longer reaction times above 80 °C (at lower temperatures the polymerization rate becomes negligible³). These times (as obtained from the data of the experimental set-up) are 7 s, 11 s and 37 s for the reaction temperatures of 100 °C, 120 °C, and 140 °C, respectively. However, as soon as the desired reaction temperature is stable, the polymerization rate becomes steady and can be measured (an explanation of this effect and a comparison between polymerizations performed under conventional and microwave heating sources can be found in the ESI).

Further investigations were aimed at the efficient recovery of the IL and polymer isolation. As mentioned, the selection of IL **5** facilitates this task by a simple extraction with water, avoiding completely the use of VOCs during the purification step. This is illustrated qualitatively in Fig. 4 for the IL **5** recycling of the combined vials from the kinetic study (see the ESI for details). The $^1\text{H-NMR}$ spectra of Fig. 4 reveal that IL **5** remains practically unmodified after one reaction cycle. Moreover, the recovered IL **5** was used in a second polymerization cycle yielding similar results to those presented in Fig. 1.

It is worth mentioning that the polymerizations performed in IL **5** above the boiling point of the monomer (Etox, 128.4 °C) and at long reaction times showed a limited conversion (around 90% for a reaction temperature of 140 °C), which was much less pronounced when the mixture of acetonitrile/IL **5** or lower reaction temperatures were used. This effect can be attributed to the absence of VOS in the system since ILs have negligible vapor

pressure¹³. Consequently, in the polymerizations carried out at a temperature higher than the boiling point of the monomer, the vapor phase in the reactor will be mainly saturated with monomer that does not polymerize. When the mixture of acetonitrile/IL **5** was used, higher conversions were obtained since acetonitrile saturates the vapor phase faster than the monomer. This effect may be minimized by applying an over-pressure in the reactor with a different inert substance (nitrogen).

It is known that ILs containing $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ anions may hydrolyse under acidic conditions and release hydrogen fluoride.¹³ However, in this work pH measurements of the system during different stages of the process revealed the absence of strong acidic conditions. Although the main IL (IL **5**) investigated in this work is composed of $[\text{PF}_6]^-$ anions, this does not mean that the approach presented here is restricted to the use of this particular IL; *i.e.* to avoid completely the formation of strong acids in the entire process or in the environment, more stable hydrophobic ILs may be tested for the same purpose (*i.e.* 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate). Nowadays there are many commercially available ILs that may offer additional advantages to the ones discussed here when performing different polymerizations.

Thus, the use of ILs may offer some kinetic advantages (higher reaction rates) when performing the living CROP of Etox. It was also demonstrated that the synthesis of block copolymers in ILs by the living CROP mechanism is feasible. Finally, it was shown that ILs can be utilized efficiently for these kinds of processes, opening opportunities for the development of “green” technologies.

Notes and references

‡ See ESI for experimental details.

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