Supplementary Material (ESI) for Chemical Communications

Experimental information for the cationic ring opening polymerization of 2–ethyl–2–oxazoline in ionic liquids performed under microwave irradiation.

Polymerization vials were filled under an argon atmosphere with 350 mg of distilled monomer (Etox), 11 mg of destilled initiator (methyl tosylate), and 540 mg of reaction medium (respective ionic liquid (IL) (dried overnight under vacumm at 40 °C) or a 50/50% wt mixture of IL/acetonitrile (dried over molecular sieves (3 Å))), exposed at the desired reaction conditions (temperatures and times) and quenched by cooling the vials with nitrogen gas and by adding 50 μL of purified water into the reaction mixture.

Five different ILs (synthesis grade) 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**). ILs **1**, **3**, and **5** were obtained from Solvent–Innovation GmbH (**5** as a kind gift); ILs **2** and **4** were obtained from Merck KGaA (**2** as a kind gift).

Molecular weights of the synthesized polymers were determined by GPC measurements, which were performed on a Shimadzu system with a RID–6A refractive index detector and a Plgel 5 μm Mixed-D column. A solution of 4% triethylamine and 2% isopropanol in chloroform was used as an eluent at a flow rate of 1 mL/min. Molecular weights were calculated against poly(methyl methacrylate) standards. Conversions were determined by ^{1}H–NMR on a Varian Gemini 300 spectrometer at room temperature using chloroform-*d*.

Supplementary Material (ESI) for Chemical Communications

Determination of the onset of the cationic ring opening polymerization of 2–ethyl–2–oxazoline in 1–butyl–3–methyl–imidazolium hexafluorophosphate performed under conventional and microwave heating.

When performing kinetic measurements of extremely fast reactions, the accurate determination of the onset of the reaction becomes a difficult task. The facts that ionic liquids (ILs) are known to be heated with exceptional efficiency by microwaves[i] and that the living cationic ring opening polymerization (CROP) of 2–ethyl–2–oxazoline **(**Etox) may be accelerated when performed in some ILs and under microwave irradiation make it difficult to determine the onset the polymerizations. Table A shows the results of three CROP of Etox performed in 1–butyl–3–methyl–imidazolium hexafluorophosphate (IL **5**) using 1 s of reaction time (the shortest possible reaction time as programmed in the apparatus) in the microwave platform.

Reaction temperature (°C)	Conversion for 1 s of reaction time (%)	Reaction time above 80 °C (s)
100	16	7
120	35	11
140	67	37

Table A: CROP of Etox in IL **5** experiments for 1 s reaction time (the shortest possible reaction time as programmed in the microwave apparatus) for different temperatures and using the reaction conditions described in the contribution.

The results of Table A reveal that the polymerizations show a considerable conversion at the onset of the experiments even for the shortest possible reaction time in the microwave platform (1 s). This effect is directly related to the time that the microwave apparatus takes to reach the desired reaction temperature (time zero) and to cool the polymerization afterwards. The polymerizations performed during just 1 s, in fact, are exposed to significantly longer reaction times above 80 °C (at lower temperatures the polymerization rate becomes negligible[ii]). The times reported in Table A were estimated from the heat profiles of the 1 s reactions shown in Fig. A.

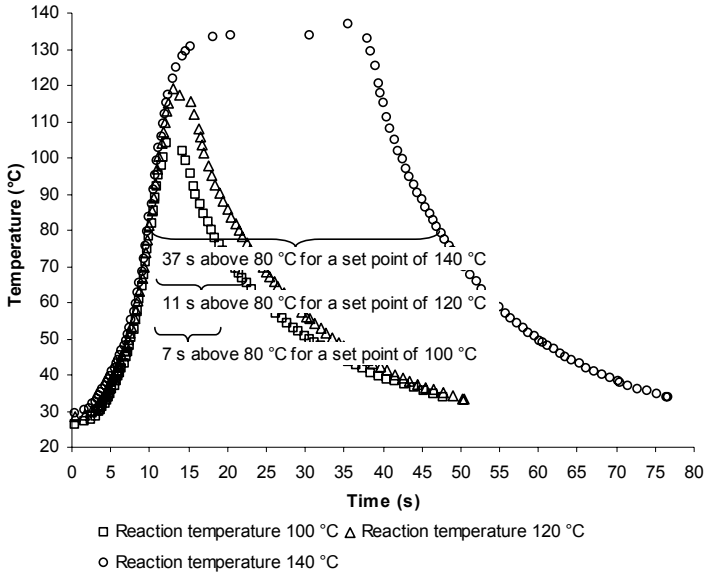

Fig. A: Temperature profiles for the CROP of Etox in IL **5** under microwave irradiation performed during 1 s of reaction time (as programmed in the microwave set–up) for different reaction temperatures.

In addition to the difficulty of determining the onset of the reaction, it is obvious that during this heating time the polymerization rate is not constant. However, as soon as the desired reaction temperature is reached in the reaction vial, the polymerization rate

becomes constant. The polymerization kinetic at different temperatures can thus be determined if the heating trajectory is reproducible, which is illustrated with the temperature profiles in Fig. B.

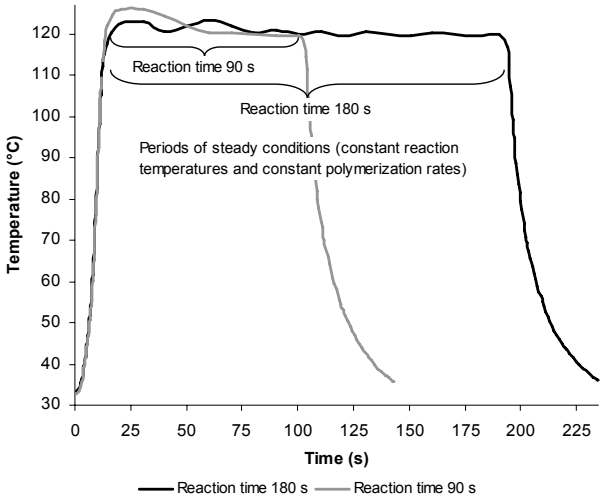

Fig. B: Temperature profiles for the CROP of Etox in IL **5** under microwave irradiation performed at 120 °C for two different reactions times (as programmed in the microwave set–up).

As a consequence of the inaccuracy in determining the onset and the ending of the polymerizations, the kinetic plot (Fig. 1 of the contribution) doest not cross the origin. This inaccuracy remains constant when using the same experimental set–up and does not affect the determination of the values of the slopes as soon as the temperature in the reaction mixture becomes stable.

Some advantages of performing reactions in the described microwave platform are the more efficient heating of ionic media and a better control in the reaction temperature[ii] in comparison to the conventional oil–bath heating. These advantages may be related to the fact that the reaction mixtures absorb directly the heating source (microwaves) and not

like in the case of the conventional oil–bath where the heat is transported from the outside to the inside of the reactor. As a direct consequence of this effect, the control of the reaction temperature is more difficult in the conventional oil–bath set–ups and, therefore, there will be a temperature gradient between the oil and reaction mixture. Fig. C shows the temperature profile of a CROP of Etox performed in a conventional oil–bath (using the same reaction vials of the microwave platform) with temperature sensors in the oil and in the reaction mixture. Firstly, the set point of the oil had to be increased to 129 °C in order to reach an internal temperature of 120 °C in the reaction mixture. Secondly, in the oil–bath set–up (at those conditions) it takes around 60 s to reach the desired temperature in the reaction mixture (Fig. C) whereas in the microwave platform this only takes around 15 s (Fig. B). Thirdly, the temperature overshoot is more pronounced in the oil–bath platform (up to 131 °C for a desired reaction temperature of 120 °C, as it is shown in Fig. C) than in the microwave system (up to 125 °C for a desired reaction temperature of 120 °C, as it is shown in Fig. B) due to the heat generated by the polymerization and the efficiency of the temperature control of the experimental set–ups. Finally, there is also an intrinsic uncertainty in the determination of the onset and ending of the polymerizations in the oil–bath set–up similar to the one described for the microwave platform.

Even though, many factors can influence the determination of the onset and the ending of the polymerizations, when comparing directly the results for polymerizations performed in both oil–bath and microwave set–ups, with similar reaction conditions (120 °C and a reaction time of 240 s, using the criteria mentioned above for each experimental platform), the obtained conversions were quite similar (84% for the oil–bath and 83% for

the microwave). This observation indicates that the findings of this work (modified kinetic of the CROP of Etox) are due to the presence of the IL species and are not related to the so–called non–thermal microwave effects.[ii]

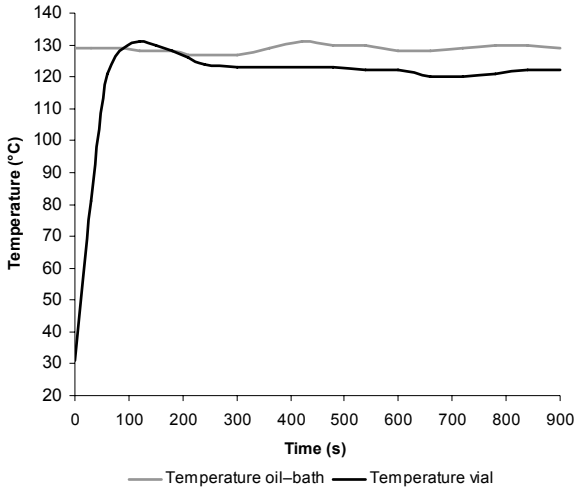

Fig. C: Temperature profiles for the CROP of Etox in IL **5** performed in a conventional heating source (oil–bath) (reaction temperature of 120 °C, temperature profiles for the oil and for the reaction mixture).

Qualitatively recycling of 1–butyl–3–methyl–imidazolium hexafluorophosphate during the cationic ring opening polymerization process of 2–ethyl–2–oxazoline .

Due to the relatively small reaction volumes used for the kinetic studies of this work, the recycling procedure of 1–butyl–3–methyl–imidazolium hexafluorophosphate (IL **5**) during the living cationic ring opening polymerization (CROP) of 2–ethyl–2–oxazoline **(**Etox) is shown in a qualitatively way in order to make it more illustrative as depicted in Fig. D (Fig. 4 of the manuscript). Therefore, the recycling procedure was performed as described in the following part.

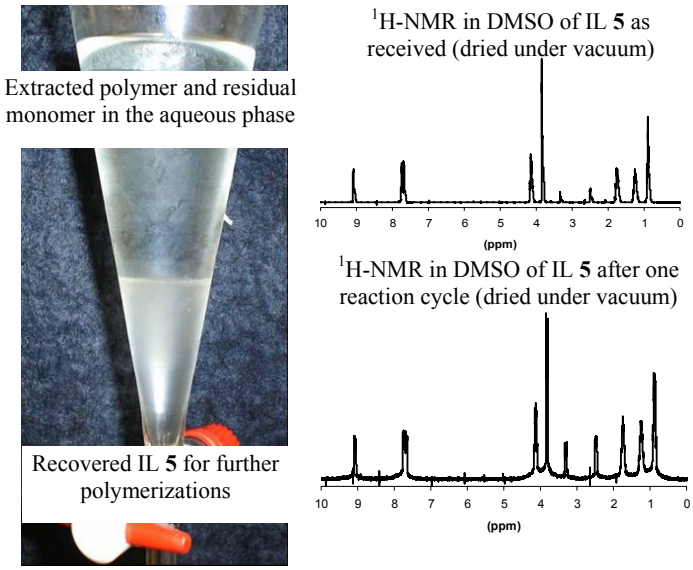

Fig. D: Efficient IL 5 recovering and polymer isolation by a post–reaction extractive process with water (left). ^{1}H–NMRs of IL 5 as received from the supplier and after one reaction cycle (right).

For the CROP experiments performed in pure IL **5** in different polymerization vials (different reaction temperatures and times), all remaining reaction mixtures (after molecular weight and conversion determinations) were combined and mixed with a 3–fold excess of purified water in order to extract the polymer and un–reacted monomer (which is preferable soluble in water than in IL **5**) into the aqueous phase. This mixture (15 reaction vials) was magnetically stirred for 0.5 h at room temperature. The resulting heterogeneous mixture was placed into a extraction funnel until a clear phase separation occurred (Fig. D). Finally, IL **5** was recovered from the funnel, dried under vacuum at 40 °C, and analyzed by ^{1}H–NMR (which confirmed the absence of polymer and monomer in the IL **5)**. The recovered IL **5** was utilized in a second series of polymerization experiments yielding similar results to the ones obtained in the first cycle. In addition, the

polymer can be isolated by evaporation of the water. The yield of the polymerization (isolated polymer) will depend, mainly, on the reached conversion during the reaction, which is ruled by the reaction conditions, reaction temperature and time. This is due to the fact that the ^{1}H–NMR results of the recycling procedure showed a complete extraction of the polymer and residual monomer from IL **5** into the aqueous phase, allowing also for a high efficiency polymer isolation procedure.

REFERENCES:

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[ii] F. Wiesbrock, R. Hoogenboom, C. H. Abeln and U. S. Schubert, *Macromol. Rapid Commun.*, 2004, **25**, 1895.