

Copper(I) mediated living radical polymerisation in an ionic liquid

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1-Butyl-3-methylimidazolium hexafluorophosphate, a room temperature ionic liquid, has been used as solvent for the copper(I) mediated living radical polymerisation of methyl methacrylate; the rate of reaction is enhanced and narrow polydispersity polymers are obtained which are easily isolated from the catalyst.

Transition metal mediated living radical polymerisation is rapidly developing as an efficacious new route for the controlled polymerisation of vinyl monomers.^{1–3} We have been utilising a system based on Cu^IX with alkylpyridylmethanimine ligands.^{4,5} These Schiff base ligands are easily synthesised, and can be readily manipulated in order to vary the properties of the catalyst (e.g. solubility). One of the main constraints of this chemistry is the high level of catalyst required for acceptable rates of polymerisation, often equimolar with respect to initiator. This leads to contamination of products necessitating catalyst removal. Although this is relatively easily achieved in a laboratory, for most polymers, it would be advantageous for this extra process to be eliminated, especially with regards to exploitation of the technology. In order to achieve this we have been examining a number of routes including the use of solid supported catalysts^{6,7} and fluorous biphasic conditions.⁸

Room temperature ionic liquids have been found to be excellent solvents for a number of chemical reactions, e.g. hydrogenation, alkylation, Diels–Alder reactions, etc.^{9,10} However, the only polymerisation reactions reported in ionic liquids, to date, are the Ziegler–Natta polymerisation of ethylene,¹¹ the oligomerisation of butene¹² and the formation of conducting films by the electropolymerisation of arenes.¹³ All of which have been carried out in water sensitive chloroaluminate(III) ionic liquids.

Imidazolium ionic liquids have been developed as air and water-stable reaction media which are tolerant to many functional groups.¹⁴ This permits the use of a wide range of monomers in polymerisation reactions. As such it offers an excellent alternative method to address the problems of transition metal mediated living polymerisation. We have used the room temperature ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆],¹⁵ as a solvent for the Cu^I catalysed living radical polymerisation of methyl methacrylate (MMA). Our initial findings are reported which represent the first example of an ionic liquid being used for living radical polymerisation and indeed the first example of a new generation non-hygroscopic ionic liquid used as a polymerisation medium.

The addition of *N*-propyl-2-pyridylmethanimine to a deoxygenated suspension of Cu^IBr in [bmim][PF₆] in a 1:1 molar ratio results in the formation of a dark brown homogenous solution at room temperature. Mixtures in toluene, the more normal solvent, only become homogeneous at, or near, reaction temperature (typically 90 °C). Polymerisation of MMA, with ethyl-2-bromoisobutyrate, as initiator, in this solution proceeds readily, reaching 87% conversion after 90 min at 70 °C (Table 1).[†] This is a fast reaction when compared to polymerisation in non-polar solvents. The increase in rate is manifested by a broadening of the polydispersity to 1.43, ascribed to free radical–free radical termination reactions. A similar increase in the rate has been observed with other polar/co-ordinating

Table 1 Final molecular mass and conversion data for PMMA synthesised in this work

Reaction ^a	Temperature/°C	Time/min	Conversion (%) ^b	<i>M</i> _n ^c	PDI ^c	<i>k</i> _p [pol*] × 10 ⁴ /s ^{−1} ^d
1 ^e	70	90	87	6440	1.43	5.67
2 ^e	50	90	89	7390	1.41	4.13
3 ^e	30	180	45	6420	1.30	0.56
4 ^f	30	150	69	8390	1.36	1.36
5 ^g	30	300	90	15 500	1.35	1.33

^a All reactions carried were 50% v/v MMA in [bmim][PF₆]. ^b Conversion from integration of ¹H NMR. ^c Determined using SEC against pMMA standards. ^d From slope of first order kinetic plot. [MMA]–[Cu^IBr]–[Ligand]–[Initiator]: ^e = 50:1:1:1; ^f = 50:1:2:1; ^g 100:1:2:1.

solvents, including water¹⁶ and is thought to be due to co-ordination of the solvent to Cu^I. This is highly likely in the present case where only one equivalent of *N*-propyl-2-pyridylmethanimine with respect to copper is used precluding the exclusive presence of tetrahedral L₂Cu species. These observations led us to lower the reaction temperature, in an attempt to avoid excessive premature termination. Polymerisation proceeds efficiently at 50 and 30 °C reaching 45% conversion after 180 min at 30 °C.

Increasing the ratio of *N*-propyl-2-pyridylmethanimine to Cu^I to 2:1 (entries 4 and 5, Table 1) results in the rate of polymerisation approximately doubling indicating the reaction is approximately first order in ligand over this range. All reactions at 30 °C show very good first-order kinetic behaviour (Fig. 1) indicating a low amount of termination under these conditions. This taken together with the relatively low PDI values and low *M*_n of the products indicates that the polymerisation shows living characteristics as observed in more conventional organic solvents. When the [M]/[I] was doubled from 50 to 100 (reactions 4 and 5) an approximate doubling of the *M*_n is observed, as would be expected for a living polymerisation. Fig. 2 shows the evolution of the *M*_n as a function of conversion for reaction 4, which increases linearly again as would be expected for living polymerisation. Polymer produced at early stages in the reaction is of higher mass than

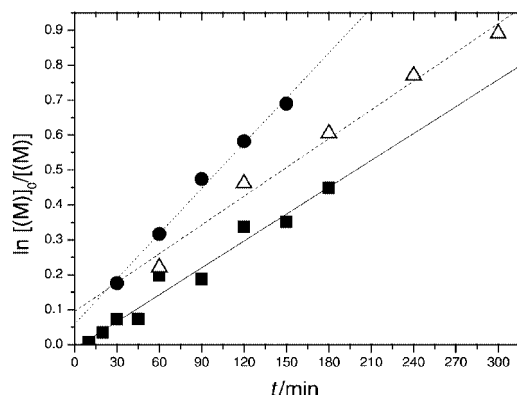


Fig. 1 First order rate plots for the polymerisation of MMA in [bmim][PF₆] at 30 °C. (■) reaction 3, (●) reaction 4 and (▲) reaction 5.

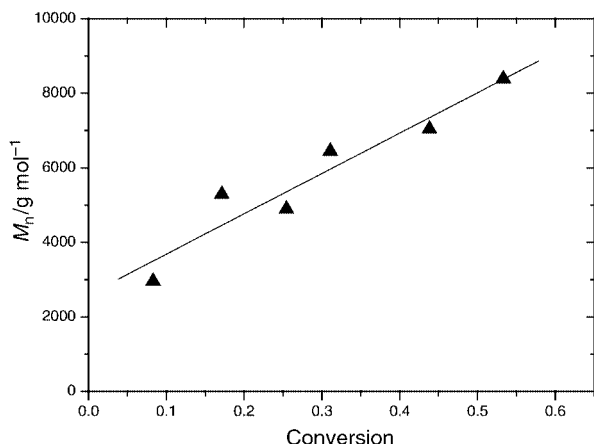


Fig. 2 Evolution of molar mass with conversion for reaction 4, line drawn is the linear regression fit through the data.

would be predicted which is ascribed to radical–radical coupling which occurs efficiently with low mass species as is often observed with living radical polymerisation.⁵

The Cu^I catalyst is very soluble in [bmim][PF₆], which in turn is immiscible with organic solvents, such as toluene. This allows the reaction solution to be washed with toluene so as to extract the poly(methyl methacrylate) (PMMA) product. The catalyst remains in the ionic liquid layer allowing isolation of the polymer product whilst leaving the catalyst solution for potential re-use. Analysis of the PMMA (reaction 4) for residual copper by ICP, shows a copper content of $3.4 \times 10^{-3}\%$ (2% expected if no copper is removed).

In summary, the room temperature ionic liquid [bmim][PF₆] has been demonstrated to be an excellent solvent for Cu^I–*N*-propyl-2-pyridylmethanimine mediated living radical polymerisation of MMA. Reactions are relatively fast as has been observed for other polar/co-ordinating solvents. The polymer is recovered essentially copper free by a simple solvent wash. Optimisation of this process and the potential to recycle the recovered ionic liquid–catalyst mixture are currently in progress.

Notes and references

† In a typical polymerisation reaction [bmim][PF₆] (10 cm³) and Cu^IBr (0.142 g, 0.990 mmol) were placed in a Schlenk tube and degassed by pumping *in vacuo* for 30 min. MMA (5.34 cm³, 49.9 mmol) was added and the mixture freeze–pump–thawed three times. *N*-Propyl-2-pyridylmethanimine ligand (0.309 cm³, 1.98 mmol) was added to give a brown solution and a final freeze–pump–thaw cycle carried out. The Schlenk tube was immersed in a thermostated oil bath at 30 °C. When the contents stabilised at the reaction temperature, ethyl-2-bromoisobutyrate (0.146 cm³, 0.995 mmol) was added *via* a degassed syringe. The polymerisation was sampled at suitable time periods throughout the reaction. Polymer for SEC analysis was obtained by an extraction of the reaction mixture with toluene followed by removal of the toluene *in vacuo*. Copper content of extracted polymer was obtained by ICP analysis at Warwick.

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