

# Poly(ethylene glycol) as solvent for transition metal mediated living radical polymerisation†

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The use of poly(ethylene glycol) (PEG) with low molecular weights as a novel solvent for the transition metal mediated radical polymerisation of methyl methacrylate and styrene is reported. The utilisation of PEG leads to polymerisation kinetics that differ from those observed with more traditional organic solvents. Moreover, the amount of residual copper catalyst in the product is greatly reduced by precipitation of the polymer in ethanol.

Transition metal mediated living radical polymerisation has become one of the most efficient methods to synthesise well-controlled molecular architectures.<sup>1,2</sup> Systems based on Cu(I)X with nitrogen based ligands have shown high versatility for the controlled polymerisation of a wide range of vinyl monomers.<sup>1,2</sup> One of the main drawbacks of these systems is the high level of catalyst required for acceptable rates of polymerisation, which leads to the contamination of the final products, therefore necessitating catalyst removal.

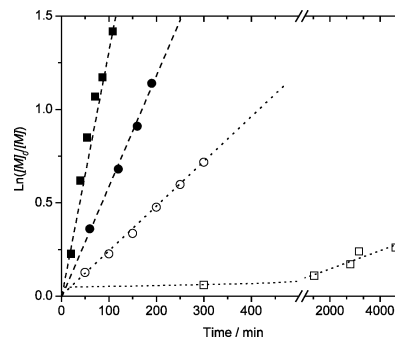
Environmental awareness is currently influencing chemists to choose low VOC content solvents to perform synthetic reactions. In the specific case of transition metal mediated radical polymerisation, techniques leading to the easy removal of the copper catalyst are also desirable. Ionic liquids are so far the best candidates to achieve both goals. Their use as solvent leads to rapid kinetics and good control over the polymerisation of methacrylates and acrylates.<sup>3–8</sup> After reaction, in order to remove the catalyst from the product, the reaction medium is washed with an organic solvent. As ionic liquids are not miscible with most organic solvents, the polymer can be collected in an organic phase while the catalyst stays in the ionic liquid phase.<sup>4</sup> However, such processes are limited by the knowledge of the toxicity of ionic liquids, the high cost and practicability of the process.

Low molecular weight poly(ethylene glycol) (PEG, *e.g.*  $M_n = 400 \text{ g mol}^{-1}$ ) is a polymer of well known toxicity, polar, with a viscosity close to that of ionic liquids. The utilisation of PEG as solvent<sup>9</sup> or co-solvent<sup>10</sup> for organic reactions has previously been reported and the use of PEG derivatives as monomer or initiator in transition metal mediated LRP has been extensively studied.<sup>11</sup> However, to date, the use of PEG as a solvent for polymerisation systems has not been documented. We report in this communication the use of a poly(ethylene glycol) of  $400 \text{ g mol}^{-1}$  as a solvent for the copper mediated living radical polymerisation of methyl methacrylate and styrene. Our initial findings are outlined below and represent the first example of PEG being used as a polymerisation medium.

Poly(ethylene glycol) with a molecular weight of  $400 \text{ g mol}^{-1}$  (PEG 400) was chosen as model solvent for the polymerisation of methyl methacrylate and styrene. Initial tests proved that both PMMA and PS are soluble in PEG 400. In order to facilitate direct comparison with 'conventional' systems, the polymerisation of MMA was undertaken with a complex formed from copper and *N*-(*n*-propyl)pyridylmethanimine at  $90^\circ\text{C}$  (toluene was used as a solvent for the control polymerisation) and that of styrene mediated by a copper/2,2'-bipyridine catalytic complex at  $110^\circ\text{C}$  (xylene was used as a solvent for the control polymerisation).<sup>†</sup> In both

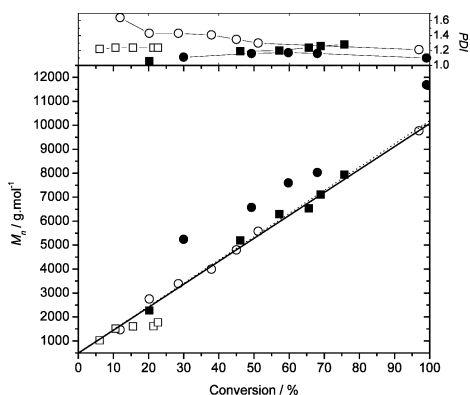
cases, the addition of ligand to a deoxygenated suspension of Cu(I)Br in PEG 400 in a 2:1 molar ratio resulted in the formation of a dark brown homogeneous solution at room temperature. Usually, mixtures of Cu(I)-*N*-(*n*-propyl)pyridylmethanimine in toluene become homogeneous at reaction temperature ( $90^\circ\text{C}$ ) while mixtures of Cu(I)-2,2'-bipyridine in xylene stay heterogeneous during polymerisation (bright green colour).

Our initial attempt in the MMA polymerisation, using a ratio [Initiator]:[Cu(I)] = 1:1, led to faster polymerisations and polymers of higher molecular weight than predicted at early stages in the reaction.<sup>13</sup> We attributed this effect to the fast generation of active species before the redox equilibrium [Cu(I)]:[Cu(II)] settles, which leads to an increase of termination reactions.<sup>2</sup> In order to improve control, a small amount of copper(II) ([Cu(I)]:[Cu(II)] = 0.97:0.03) was initially introduced into the medium. This modification of the system resulted in better control at the start of the reaction up to high conversion, as illustrated on Fig. 1 and 2. Fig. 1 shows good first-order kinetic behaviour indicating a low amount of termination under these conditions. Moreover, the polymerisation undertaken in the presence of PEG 400 is faster when compared to polymerisation in a classic organic solvent (*e.g.* toluene). A conversion of 70% is reached in 1.5 hours in PEG 400, even though a small quantity of Cu(II) is initially present in the system, whilst it takes 3 hours to achieve a similar conversion in toluene. This behaviour was however expected in accordance with previous studies undertaken on the influence on ethylene oxide groups on transition metal mediated living radical polymerisation systems. Indeed, polarity of the solvent and potential competitive metal complexation by PEG and ligand could explain higher rates of polymerisation.<sup>11</sup> Another explanation proposed by a referee is the potential influence of the terminal hydroxy groups of PEG400 on the reaction. Further studies to investigate this effect are being undertaken in our laboratories. Fig. 2 shows the evolution of molecular weight, determined by MMA calibrated SEC, with conversion. The linear evolution of the  $M_n$ , attributed to a low



**Fig. 1** Pseudo first order rate plot for the polymerisation of MMA (respectively styrene) at  $90^\circ\text{C}$  (respectively  $110^\circ\text{C}$ ) initiated by 2-EIBr and mediated by Cu / *N*-(*n*-pentyl)-2-pyridylmethanimine (respectively 2,2'-bipyridine) in PEG 400 (■; [M]:[I]:[Cu(I)]:[Cu(II)]:[L] = 100:1:0.97:0.03:2) (resp □; [M]:[I]:[Cu(I)]:[Cu(II)]:[L] = 100:1:1:0:2) and toluene (●; [M]:[I]:[Cu(I)]:[Cu(II)]:[L] = 100:1:1:0:2) (respectively xylene, ○; [M]:[I]:[Cu(I)]:[Cu(II)]:[L] = 100:1:1:0:2). (Note: The data point for the polymerisation in toluene (respectively xylene) corresponding to 99.10% conversion after 17.2 h (respectively 97% conversion after 70 h) has not been included for the clarity of the graph.)

† Electronic supplementary information (ESI) available: experimental data. See <http://www.rsc.org/suppdata/cc/b3/b313061d/>

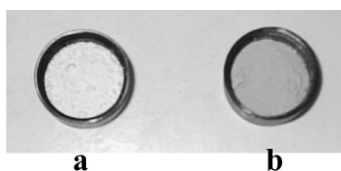


**Fig. 2** Evolution of molecular weight and PDI with monomer conversion for the polymerisation of MMA (respectively styrene) at 90 °C (respectively 110 °C) initiated by 2-EIBr and mediated by Cu / *N*-(*n*-pentyl)-2-pyridylmethanimine (respectively 2,2'-bipyridine) in PEG 400 (■; [M]:[I]:[Cu(i)]:[Cu(n)]:[L] = 100:1:0.97:0.03:2) (respectively □; [M]:[I]:[Cu(i)]:[Cu(n)]:[L] = 100:1:1:0:2) and toluene (●; [M]:[I]:[Cu(i)]:[Cu(n)]:[L] = 100:1:1:0:2) (respectively xylene, ○; [M]:[I]:[Cu(i)]:[Cu(n)]:[L] = 100:1:1:0:2). The theoretical  $M_n$  is indicated by a straight line (respectively dotted line).

molecular weight distribution ( $PDI < 1.3$ ) is a good indication of the living character of the polymerisation. Furthermore, the molecular weights of polymers produced in PEG 400 seem closer to theory than those obtained in toluene. The  $PDI$ , however, is slightly higher.

In the case of styrene polymerisation, more ambiguous results were obtained. In opposition to observations for MMA polymerisation, the molecular weights of the polymers produced in PEG 400 were lower than expected (Fig. 2) and the polymerisation was slower than that performed in an organic solvent (xylene, Fig. 1). Indeed, 23% of PS is obtained after 77 hours in PEG 400, while a conversion of 97% is reached in 70 hours in xylene (Fig. 1). Chambard *et al.* have discussed the influence of polar solvents on copper mediated living radical polymerisation and have also observed slower kinetics in styrene polymerisations.<sup>14</sup> Potential explanations include the variation of the catalyst structure by competitive coordination of the solvent and ligand on the metal centre and the difference in solubility of the catalyst complex. We are currently investigating this effect further. In order to control the living character of the poly(styrene) chains produced, a chain extension reaction was performed. A poly(styrene) sample ( $M_n = 2,400 \text{ g mol}^{-1}$ ,  $PDI = 1.24$ ) was isolated and further used as macroinitiator to yield a polymer of  $M_n = 5,500 \text{ g mol}^{-1}$ ,  $PDI = 1.21$ .

Transition metal mediated polymerisation often requires a complex workout to eliminate the catalyst from the polymer product. In our study, the reaction solution was directly poured into ethanol, without the filtration through basic alumina which is generally performed for these systems. The copper metal is dragged into the solution by complexation to the alcohol-soluble PEG, while the polymer precipitates. In the case of PMMA, which is usually more difficult to purify than PS, ICP analyses revealed a copper content of  $5.1 \times 10^{-3}\%$  (1.5% expected if all the catalyst remained in the polymer, Fig. 3). This value compared well with previous



**Fig. 3** Precipitated PMMA from reaction in PEG 400 (a,  $M_n = 7,900 \text{ g mol}^{-1}$ ,  $PDI = 1.28$ ) and toluene (b,  $M_n = 8,000 \text{ g mol}^{-1}$ ,  $PDI = 1.16$ ), without filtration through basic alumina.

published data of residual copper catalyst in MMA polymerisation aiming to reduce the amount of residual copper in the final product (for instance,  $3.4 \times 10^{-3}\%$  when using ionic liquids as solvent).<sup>4</sup> See reference 15 for other data.

As far as we are aware, we are the first to report the use of poly(ethylene glycol) as a solvent for polymerisation synthesis. PEG is cheap, non-toxic and easily degradable. In the specific case of transition metal mediated living radical polymerisation, it also facilitates the easy removal of catalyst from the final product. MMA polymerisation possesses all the characteristics of living polymerisation with a higher polymerisation rate than when performed in organic solvents. Styrene polymerisation, on the other hand, is slower than when mediated in xylene, but initial results seem to confirm its living character. We are currently investigating this system further by testing other types of polymerisations, varying the reaction conditions and extending its use to other monomers.

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## Notes and references

‡ All polymerizations were carried out using standard Schlenk techniques under an inert atmosphere of nitrogen. All reagents were dried previous to use. In the specific case of PEG 400, the polymer was dissolved in dichloromethane and dried over magnesium sulfate. Dichloromethane was removed *in-vacuo* and PEG 400 was kept in an oven at 40 °C. Cu(i)Br (1 equiv, 0.125 g,  $8.7 \times 10^{-4} \text{ mol}$ ) and ligand (2 equiv,  $1.7 \times 10^{-3} \text{ mol}$ ) were placed in a oven-dried Schlenk tube. The tube was fitted with a rubber septum and then evacuated and flushed with dry nitrogen three times in order to remove oxygen. Ethyl-2-bromoisobutyrate (1 equiv, 0.170 g,  $8.7 \times 10^{-4} \text{ mol}$ ), monomer (100 equiv,  $8.7 \times 10^{-3} \text{ mol}$ ) and solvent (50% v/v with monomer) were transferred to the tube *via* a degassed syringe. The resulting solution was degassed by three freeze-pump-thaw cycles. The mixture was stirred rapidly under nitrogen and brought to reaction temperature in a stirred, thermostatically controlled oil bath. Samples for kinetic data were taken periodically using degassed syringes for conversion and molecular weight analysis. Conversions were measured either by NMR or gravimetry; molecular weights were determined by size exclusion chromatography using THF as eluent and PMMA or PS as standards.

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