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Atom transfer polymerisation of methyl methacrylate mediated by solid supported copper catalysts

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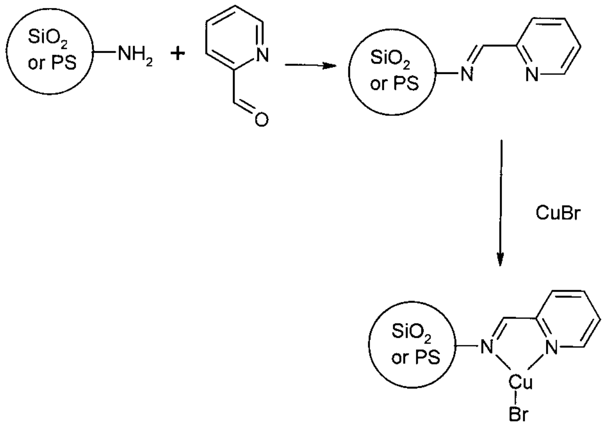
Atom transfer polymerisation of methyl methacrylate can be effected using solid supported copper(I) pyridylmethanimine catalysts which facilitate easy removal and reuse of the catalyst.

Controlled polymerisation of vinyl monomers, such as methacrylates, acrylates and styrene, is of continuing interest for the synthesis of polymers of specific composition and structure.[1] Controlled, or living, free-radical systems are attracting increasing attention as processes which are tolerant to protic species in the medium, *e.g.* from solvents, monomers, impurities, *etc.* Transition metal mediated living radical polymerisation, or atom transfer polymerisation, has been developed by Matyjaszewski[2–4] and Sawamoto,[5,6] utilising Cu(I)X/bipyiridines (X = Cl, Br) and $Ru_2Cl_2(PPh_3)_3$, respectively.[7] In our laboratories we have been developing catalysts based on Cu(I)X and alkylpyridylmethanimine Schiff base ligands.[8–12] The attraction of these catalysts is that the Schiff base ligands are simple to synthesise and allow scope to vary the catalyst properties (*e.g.* redox potential, solubility) by varying the appropriate substituent groups.

Typical [monomer] : [catalyst] ratios are 100 : 1 with stoichiometric amounts of initiator and catalyst, in order for acceptable rates of polymerisation. A potential solution to this problem is the use of supported catalysts. Inorganic supported catalysts, *e.g.* silica, have found widespread use in the polymerisation of olefins.[13] The extension of this approach to the use of functionalised inert poly(styrene) as supports for vanadium ethylene polymerisation catalysts has also been recently described.[14] This recent work prompts us to report our own work where we have been utilising supported catalysts for living radical polymerisation reactions; to the best of our knowledge this is the first example of the use of inert poly(styrene) supports for a non-co-ordination type polymerisation.

We describe herein polymerisation of MMA mediated by Cu(I)Br supported Schiff base complexes (prepared from both primary amine functionalised silica gel and cross-linked poly(styrene) resins) *via* an atom transfer polymerisation process. In order to evaluate the potential of supported catalysts for atom transfer polymerisation, four different solid supports were tried in combination with CuBr. In the first two examples, the ligand was covalently attached to the solid support, either primary amino-functionalised silica gel (SiO_2) or amino-functional cross-linked poly(styrene) beads (PS), Scheme 1. In the second and third examples, free ligand was used in conjunction with primary amine-functionalised and non-functionalised silica gel. The reactions were performed with 33 vol. % MMA in toluene solution with ethyl-2-bromoisobutyrate as the initiator.

Addition of CuBr to ligated silica produces a dark brown–orange free flowing powder, Scheme 1.† Atom transfer polymerisation of methyl methacrylate proceeds effectively at 90 °C, reaching 70.4% conversion with a number average molecular mass, M_n, of 15 500 after 300 min, reaction 1 in Table 1.† The polydispersity index, PDI, remains approximately 1.5 throughout the reaction which is slightly broader than observed in conventional homogeneous atom transfer polymerisation (typically ≈ 1.2[9,12]) but is lower than that obtained for conventional free-radical polymerisation and suggests that the reaction is proceeding by reversible activation of the C–Br ω-terminus of the growing polymer chain, as in conventional atom transfer polymerisation. As conversion increases, M_n also increases but is significantly higher than that predicted and suggests an inefficient initiation process. The reaction mixture remained a deep red–brown colour throughout the polymerisation. Once agitation was ceased the supported catalyst settled to the bottom of the flask leaving a colourless solution which was easily separated from the catalyst.



Scheme 1

To demonstrate the living character of the polymerisation, a regrowth experiment was performed. Firstly, MMA was

Table 1 Molecular weight and conversion data for poly(methyl methacrylate) produced using atom transfer polymerisation with various supported CuBr catalysts

Reaction	Time/min	Conv.(%)	M_n^{theor} [a]	M_n [b]	PDI[b]
1A[c]	60	33.4	3340	12 300	1.59
1B	120	47.3	7730	13 600	1.57
1C	180	56.9	5690	15 200	1.50
1D	240	62.9	6290	15 100	1.53
1E	300	70.4	7040	15 500	1.55
2A[d]	60	36.7	3670	8670	1.54
2B	120	49.4	4940	10 200	1.51
2C	180	60.1	6010	11 100	1.53
2D	240	68.6	6860	11 700	1.51
2E	300	75.2	7520	11 700	1.56
3A[e]	60	55.3	5530	8630	1.40
3B	135	75.0	7500	9770	1.40
3C	180	81.0	8100	10 400	1.39
3D	285	86.6	8660	10 700	1.40
4A[f]	30	34.7	3470	10 100	1.32
4B	80	70.7	7070	13 400	1.32
4C	120	84.1	8410	14 600	1.33
4D	180	95.1	9510	15 700	1.34

[a] Theoretical M_n. [b] Determined using SEC against poly(MMA) standards. [c] Pyridylmethanimine ligand covalently bound to silica gel particles.† [d] Pyridylmethanimine ligand covalently bound to cross-linked poly(styrene) beads.† [e] Physically adsorbed catalyst on silica gel.‡ [f] Physically adsorbed catalyst on amino-functionalised silica gel.‡

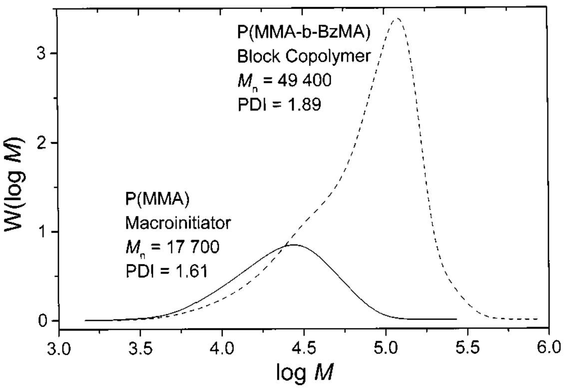


Fig. 1 Molecular weight distributions for the reinitiation of P(MMA) with benzyl methacrylate (BzMA) showing that the majority of chains are still active. Peak areas scaled for conversion.

polymerised under similar conditions to reaction 1, yielding a polymer of M_n = 17 700 and PDI = 1.61. This polymer was then isolated by precipitation into hexanes and used as a macroinitiator in homogenous atom transfer polymerisation to polymerise benzyl methacrylate (BzMA), yielding a block copolymer of M_n = 49 400 and PDI = 1.89. Fig. 1 shows the molecular weight distributions of both the macroinitiator and the final block copolymer. The increase in molecular weight suggests formation of block copolymer. Broadening on the low molecular weight side indicates that some termination has occurred removing active end-groups thus reducing re-initiation efficiency.

The solid supported catalyst was used in several subsequent reactions, Fig. 2. The initial polymerisation was performed under similar conditions to reaction 1, except three times as much silica supported ligand was used in order to achieve a higher rate of reaction. Reuse of the catalyst was achieved by the addition of MMA, toluene and initiator (no additional CuBr or ligand) to the washed supported catalyst. The second use of catalyst leads to polymer in high conversion on leaving overnight. This was repeated three additional times giving a total of five uses of the same solid supported catalyst over a five day period, Fig. 2. Care was taken to keep the catalyst under nitrogen at all stages to avoid degradation from exposure to oxygen. It is apparent that the catalyst is effective for each reuse; however, activity is reduced as observed by the decrease in the rate of polymerisation. The reduction in catalytic activity may be due to several reasons: (i) some loss of the supported catalyst when removing the polymer solution and subsequent washing, (ii) oxidation of the Cu(I) to Cu(II) during the reaction, and (iii) degradation due to side reactions compounded over several uses. The polydispersity indices for this series of polymers are higher than observed in reaction 1 (≈ 2 *vs.* ≈ 1.5) and seem to be due to the higher concentration of solid supported ligand leading to an increased reaction rate which in turn leads to a higher concentration of free radicals in solution and thus a higher amount of termination due to radical–radical reactions.

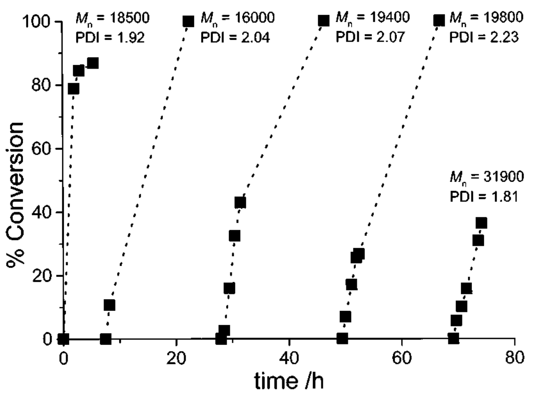


Fig. 2 Conversion *vs.* time for the four monomer additions in reaction 1.

Catalyst derived from pyridylmethanimine ligand covalently bound to cross-linked poly(styrene) beads, reaction 2, Table 1,† performs similarly to that on silica. Atom transfer polymerisation of MMA with this catalysts gives 75.2% conversion with a number average molecular mass, M_n, of 11 700 after 300 min. Again, M_n increases only slightly with conversion (but is higher than predicted), the polydispersity indices are similar, ≈ 1.5, and the catalyst settles to the bottom of the flask when stirring is ceased leaving a colourless solution. The rates of polymerisation for reactions 1 and 2 are very similar.

In addition to using catalysts covalently bound to the support, silica gel and amino functionalised silica gel (reactions 3 and 4, respectively‡) were added to a conventional atom transfer polymerisation to physically adsorb the catalyst, Table 1. Both of these reactions give lower polydispersity indices, ≈ 1.4 for silica and ≈ 1.3 for amino-functional silica, than the covalently bound catalysts of reactions 1 and 2. Indeed, the polydispersities are comparable to those of homogenous atom transfer polymerisation. After allowing the support to settle, a slight yellow colour remained in the solution due to some free catalyst/ligand.

In summary, solid supported atom transfer polymerisation catalysts promote effective polymerisation of methyl methacrylate. This allows the facile removal of the catalyst and also reuse of the catalyst in subsequent reactions. It is also possible to use the polymers produced to reinitiate polymerisation and produce block copolymers.

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Notes and references

† The supported catalyst was prepared by adding pyridine-2-carbaldehyde (0.714 g) to amine functionalised silica gel (3.00 g, 1.05 × 10^{-3} mol NH_2 g^{-1}) (or amino functional cross-linked poly(styrene) beads, 2.8 × 10^{-3} mol NH_2 g^{-1}) in 50 mL of dry toluene and refluxed for 5 h. The suspension was allowed to settle and the solvent was decanted off. Take up of the aldehyde on the support was monitored by NMR and UV of the residual pyridine-2-carbaldehyde in the solution against internal standards. To the support (0.967 g) was added MMA (10.0 mL), toluene (20.0 mL) and ethyl-2-bromoisobutyrate (0.137 mL) and the mixture degassed by three freeze–pump–thaw cycles followed by the addition of CuBr (0.134 g). Supported copper concentration was monitored by ICP analysis. The mixture was then placed in an oil bath at 90 °C. At the end of the reaction the reaction flask was removed from the oil bath and the insolubles allowed to settle (approximately 30 min due to the viscosity of the solution). The clear solution was removed *via* cannula.

‡ A solution of toluene (20 mL), MMA (10 mL), ethyl-2-bromoisobutyrate (0.137 mL) and *N*-(*n*-pentyl)-2-pyridylmethanimine (0.342 g) and silica gel (1.02 g) (or amine functionalised silica gel) and CuBr (0.134 g) was added and the flask placed in an oil bath at 90 °C.

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