

# Atom transfer radical polymerisation (ATRP) of methyl methacrylate in the presence of radical inhibitors

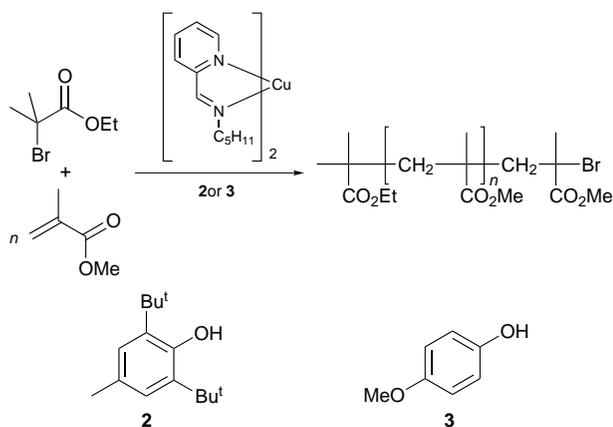
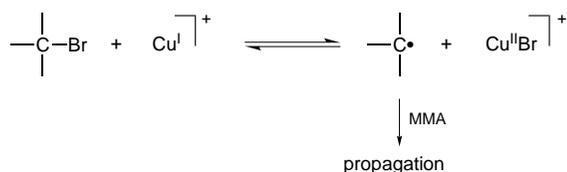
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Atom transfer radical polymerisation of methyl methacrylate mediated by copper(I) bromide, alkyl bromides and *N*-pentyl-2-pyridylmethanimine has been shown to be enhanced by the addition of substituted phenols, traditionally used as radical inhibitors.

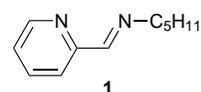
Atom transfer radical polymerisation has emerged as an efficacious method for the living polymerisation of vinyl monomers.<sup>1–8</sup> The ATRP process involves the combination of an alkyl halide and a low valent metal complex, *e.g.* Cu<sup>I</sup>Br–bipyridine,<sup>1–3</sup> Ru<sup>II</sup>Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>,<sup>4</sup> Ni<sup>II</sup>[C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]Br,<sup>7</sup> which is capable of being oxidised to the *n* + 1 state by addition of a halogen atom. The mechanism proposed by both Matyjaszewski *et al.*<sup>1</sup> and ourselves<sup>9</sup> involves abstraction of the halogen atom from the propagating polymer to give a carbon-based radical and a new metal halide with the metal in the *n* + 1 oxidation state, *e.g.* Cu<sup>II</sup>. Propagation is then proposed to be *via* free radical attack of the polymer radical on a monomer as in normal free radical polymerisation. Termination is prevented by the reverse abstraction of halogen atom from the metal halide to give a new polymeric alkyl halide (Scheme 1).

Polymerisation of methyl methacrylate in the presence of copper(I), ruthenium(II) and nickel(II) salts gives polymers with stereochemistry similar to that from normal free radical polymerisation.<sup>2,4,7</sup> All three metal-based catalysts have also been reported to lead to polymerisation which is completely inhibited by free radical inhibitor, *e.g.* galvinoxyl. The reactivity ratios for the copolymerisation of butyl and methyl methacrylate have also been shown to be entirely consistent with free radical propagation.<sup>10</sup> Thus all evidence presented to



date is consistent with free radical propagation where the halogen atom is abstracted from the growing polymer chain. The objective of the present work was to investigate how robust ATRP is towards various functional groups. Surprisingly, we have found that phenolic free radical inhibitors enhance ATRP as opposed to suppressing polymerisation, as would have been expected for a free radical polymerisation or indeed an anionic polymerisation.

Atom transfer radical polymerisation of methyl methacrylate (MMA) was carried out with ethyl 2-methyl-2-bromopropionate as initiator in conjunction with *N*-pentyl-2-pyridylmethanimine **1** and copper(I) bromide in xylene solution at

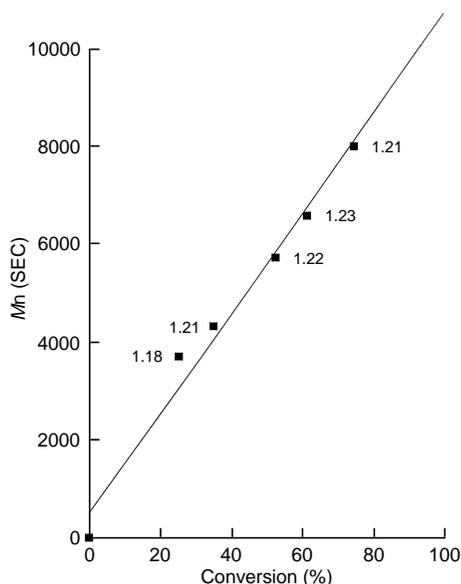


90 °C (Scheme 2) in the presence of 2,6-di-*tert*-butyl-4-methylphenol **2** or 4-methoxyphenol **3**, or in the absence of phenol, as a control reaction. Both **2** and **3** are commonly added to commercial monomers to prevent polymerisation on transport and storage. Although phenolic inhibitors are more effective in the presence of oxygen they still inhibit radical reactions *via* transfer of a phenolic hydrogen atom in the absence of oxygen.<sup>11</sup> Polymerisation of methyl methacrylate in the presence of an equimolar amount of **2** with respect to initiator leads to poly(methyl methacrylate) with a polydispersity index (PDI) of 1.21 after 240 min (Table 1). Increasing the amount of **2** ([**2**]:[initiator] = 10:1) again leads to polymer with narrow PDI with *M<sub>n</sub>* increasing linearly with conversion (Fig. 1), as would be expected for a living polymerisation. Indeed this increase in the amount of **2** results in an acceleration in the rate of polymerisation so that 74.6% conversion is achieved in 240 min as opposed to 56.8% with stoichiometric equivalents of initiator and **2**. The same is observed when **2** is replaced with **3**. Fig. 2 shows the increase in

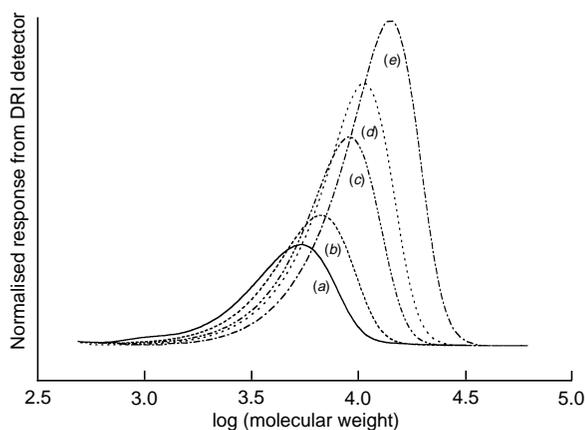
Table 1 Polymerisation of methyl methacrylate *via* ATRP

Phenol <sup>a</sup>	[Phenol]: [initiator]	<i>t</i> /min	Conversion (%) <sup>b</sup>	<i>M<sub>n</sub></i> (SEC)	PDI (SEC)
<b>2</b>	1	240	56.8	7460	1.21
<b>2</b>	10	30	25.1	3700	1.18
<b>2</b>	10	60	34.8	4320	1.21
<b>2</b>	10	120	52.4	5710	1.22
<b>2</b>	10	180	61.2	6560	1.23
<b>2</b>	10	240	74.6	7970	1.21
<b>3</b>	1	240	54.4	7010	1.23
<b>3</b>	10	30	31.0	4120	1.18
<b>3</b>	10	60	35.7	4690	1.25
<b>3</b>	10	120	51.5	6460	1.22
<b>3</b>	10	180	61.3	7240	1.25
<b>3</b>	10	240	74.0	8970	1.25
None	—	240	54.0	6790	1.21

<sup>a</sup> All reactions carried out with [MMA]:[initiator]:[**1**]:[CuBr] = 100:1:3:1, under nitrogen at 90 °C at 37 mass% in degassed xylene solution. <sup>b</sup> From gravimetry.



**Fig. 1** Plot showing how  $M_n$  from SEC increases with conversion for ATRP of MMA in the presence of **2** in a ten-fold excess with respect to initiator. SEC carried out in THF at  $1 \text{ ml min}^{-1}$  with calibration against poly(methyl methacrylate) narrow molecular weight standards. Polydispersity index (PDI) is given for each point.

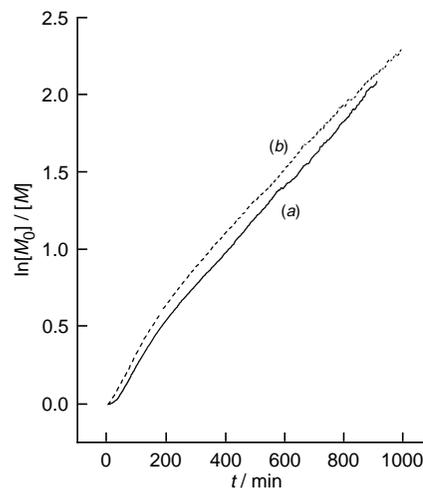


**Fig. 2** SEC traces for ATRP of MMA in the presence of **3** in a ten-fold excess with respect to initiator. The area beneath each trace has been normalised for conversion where conversion at 240 min is 74%: (a) 30 min, PDI = 1.18; (b) 60 min, PDI = 1.25; (c) 120 min, PDI = 1.22; (d) 180 min, PDI = 1.25; (e) 240 min, PDI = 1.25.

molecular weight with conversion (time) with a ten-fold excess of **3** with respect to initiator, as observed by size exclusion chromatography (SEC).

Fig. 3 shows the results of following the polymerisation by automated dilatometry, collecting one data point every 20 s over 8 h, in the presence and absence of a stoichiometric equivalent of **3** with respect to initiator. The final rate of polymerisation is similar in both the presence and absence of **3**. Both are fairly constant between 60 and 180 min prior to showing a decrease in  $k_p[\text{Pol}^*]$ , the gradient of the graph (where  $\text{Pol}^*$  is the active polymerisation centre). However, in the absence of **3** an induction period is present of *ca.* 60 min as observed by an increase in  $k_p[\text{Pol}^*]$ ; an induction period has previously been observed in ATRP of MMA using  $\text{Ni}^{\text{II}}$  catalyst.<sup>7</sup> The induction period is removed by **3**, accounting for the increase in yield in the presence of substituted phenols.

Atom transfer radical polymerisation of MMA with bis(*N*-pentyl-2-pyridylmethanimine)copper(I) is enhanced by



**Fig. 3** First order plots from automated dilatometry for the ATRP of MMA (a) in the absence of added phenol, and (b) with an equimolar amount of **3** with respect to initiator

substituted phenolic radical inhibitors. This indicates that propagation does not take place *via* a carbon-centred free radical. It is more likely that the copper(I) coordinates to the bromide, weakening the carbon–bromine bond and allowing single electron nucleophilic attack on monomer resulting in the transfer of a bromine atom in a concerted fashion. The active copper(I) species is not a simple four coordinate *pseudo*-tetrahedral compound as might have been expected. It appears that the active catalyst is formed during the initial stages of the reaction. Formation of the active species is accelerated by phenolic compounds. The role of the phenol is currently under investigation in our laboratory. In summary, ATRP does not take place *via* a normal free radical mechanism and the living polymerisation is enhanced by the addition of certain substituted phenols in excess relative to the amount of initiator.

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#### Footnote

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