Monohydroxy terminally functionalised poly(methyl methacrylate) from atom transfer radical polymerisation

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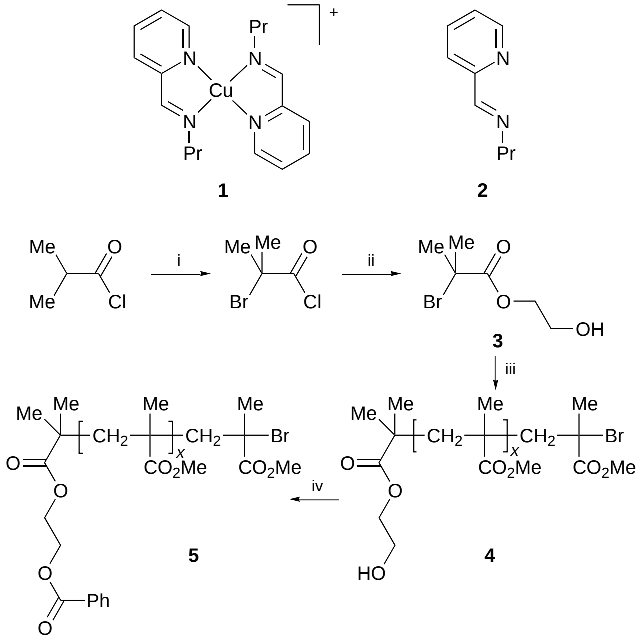
Atom transfer radical polymerisation (ATRP) of methyl methacrylate with a pyridinecarbaldehyde imine copper(I) catalyst and hydroxy functional alkyl bromide initiator leads to α-hydroxy functional PMMA with controlled M_n and PDI $<$ 1.20 without the use of protecting group chemistry.

Atom transfer radical polymerisation (ATRP) is a rapidly emerging method of obtaining pseudo-living polymerisation of vinyl monomers with controlled M_n and narrow molecular weight distribution (MWD).[1–5]

It has been developed from atom transfer chemistry in organic synthesis, *e.g.* intramolecular cyclisation, and is a development of the Kharash reaction.[6] Complexes of a range of metals have been demonstrated to be useful including $Ru(PPh_3)_3Br_2$,[1] CuBr–bipyridine[2,3] and $Ni[C_6H_3(CH_2NMe_2)_2$-2,6]Br.[7] In a previous communication we have demonstrated that pyridine-2-carbaldehyde imine copper(I) complexes such as **1** are very effective for ATRP of methyl methacrylate (MMA) in conjunction with ethyl 2-bromoisobutyrate.[8] The objective of this work was to replace the initiator, ethyl 2-bromoisobutyrate, with a hydroxy containing alkyl bromide so as to produce α-hydroxy terminally functionalised PMMA without the need to employ protecting group chemistry.

2-Hydroxyethyl 2′-methyl-2′-bromopropionate‡ **3** was prepared as shown in Scheme 1. Atom transfer radical polymerisation of MMA using **3** as initiator in conjunction with **2** and CuBr was carried out at 90 °C in xylene, MMA : **3** = 20 : 1, **2** : CuBr : **3** = 3 : 1 : 1, to give PMMA of structure **4**. Polymerisation was stopped at low conversion, 7.65%, after 70 min, so as to reduce the amount of termination by radical–radical reactions (reaction A; Table 1). ^{1}H NMR data (Fig. 1), clearly shows the presence of the hydroxyethyl ester group, originating from **2** and the methoxy α to the bromo group at the propagating end at δ 4.18, 3.82 and 3.74 respectively. The number average molecular mass, M_n, can be calculated directly from NMR which gives a value of 2430 which compares excellently with that obtained from size exclusion chromatography against PMMA standards of 2320, PDI = 1.12 (when precipitated into hexanes M_n = 2960, PDI = 1.12). This excellent agreement indicates that the product has structure **4**. This is confirmed by matrix-assisted laser desorption-ionisation time of flight mass spectrometry, Fig. 2. We see one series of peaks in the MALDI-



Scheme 1 *Reagents and conditions*: i, Br_2–P;‡ ii, ethylene glycol;‡ iii, CuBr, MMA;§ iv, benzoyl chloride§

Table 1

Reaction^a	3/ 10^4 mol	MMA/ mol	t/min	Conversion (%)^d	M_n SEC	PDI SEC
A^b	9.61	0.187	70	—	2530	1.10
B^c	9.72	0.047	120	—	4540^e	1.22^e
C^c	9.72	0.047	120	—	3130	1.22
D^b	9.61	0.187	60	0.21	—	—
E^b	9.61	0.187	120	2.27	—	—
F^b	9.61	0.187	180	15.74	4980	1.21
G^b	9.61	0.187	240	48.20	12 330	1.26
H^b	9.61	0.187	300	59.75	15 580	1.29
I^b	9.61	0.187	360	66.18	17 920	1.27
J^b	9.61	0.187	420	72.11	19 500	1.27
K^b	9.61	0.187	480	75.05	20 100	1.28
L^b	9.61	0.187	480	—	19 427^e	1.31^e

[a] All reactions carried out with **2** : CuBr : **3** = 3 : 1 : 1. [b] 20 ml MMA in 40 ml xylene, [c] 5 ml MMA in 6 ml xylene. [d] From gravimetry. [e] After precipitation, otherwise as taken from reaction flask.

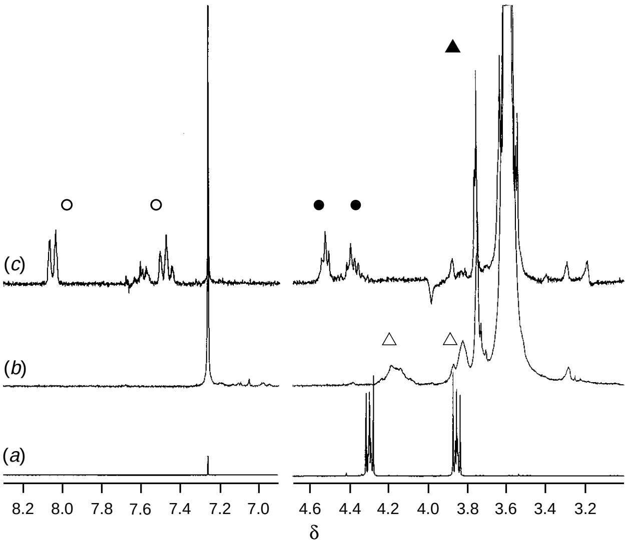


Fig. 1 Selected region from the ^{1}H NMR spectra of (*a*) **3**, (*b*) **4** (△ = CH_2O groups and ▲ = OMe α to Br), (*c*) **5** (● = CH_2O groups, ▲ = OMe α to Br and ○ = aromatic protons from benzoyl group)

TOF MS indicating only one predominant structure, *i.e.* **4**. For example, the peaks at *m/z* 1319.0 and 1419.2 correspond to lithium adducts of **4** where x = 10 and 11 respectively, calculated *m/z* 1318.3 and 1418.4. Control over M_n and PDI is obviously not affected detrimentally by the presence of the primary alcohol group present in the initiator, which might have been expected to complicate the reaction by coordination to the copper catalyst. Indeed the PDI is narrower and the rate of polymerisation faster with **3** than that obtained using a non-functional initiator. Thus ATRP with **1** as catalyst can be utilised to give PMMA of structure **4** as the only detectable product under these conditions. The hydroxy group can be further reacted with benzoyl chloride to give **5** quantitatively.

The terminal benzoyl group of **5** is observed by ^{1}H NMR, Fig. 1(*c*), and is detected by SEC with UV detection at 200 nm, **4** shows no absorption at this wavelength. MALDI-TOF MS shows a new series of peaks corresponding to **5**, *e.g.* peaks are now observed at *m/z* 1423.0 and 1522.8 for x = 10 and 11, calculated *m/z* 1422.3 and 1522.4; this reaction is quantitative and no peaks from residual **4** are observed. When the reaction is carried out at a higher MMA : **3** ratio for 120 min a higher molecular weight polymer is produced, *M*n = 4540, PDI = 1.22, as expected (reactions B and C). Again analysis shows terminal hydroxy functionality.

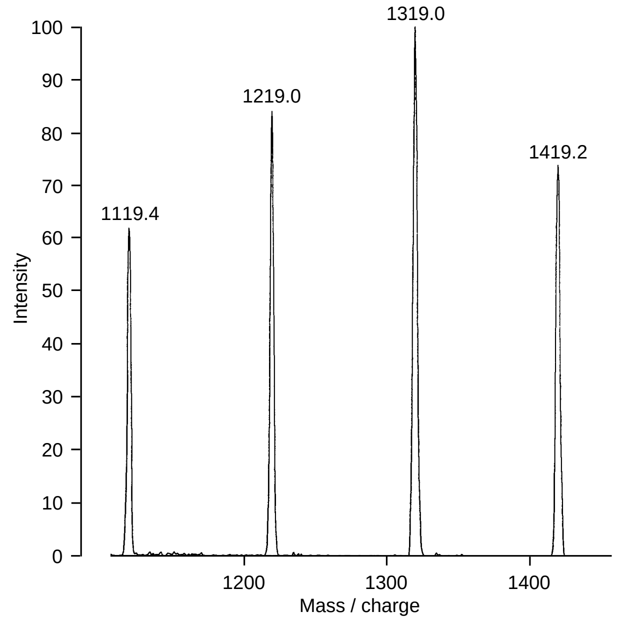


Fig. 2 Partial MALDI-TOF MS of **3** between x = 8 and 11, peaks correspond to lithium adducts of molecular ions with no observable fragmentation

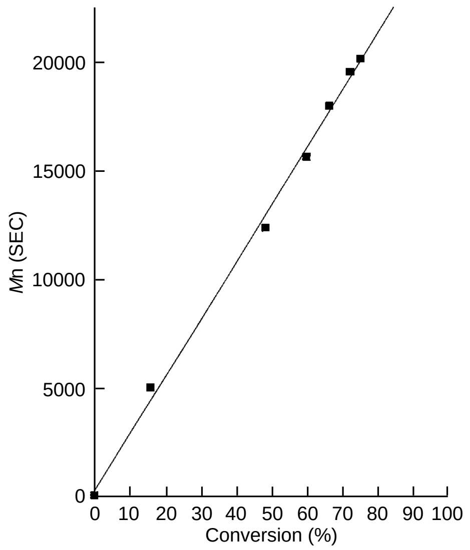


Fig. 3 Plot showing how M_n from SEC increases with conversion for experiments D–K

Living or pseudo-living polymerisations have a low rate of termination relative to rate of propagation. This is demonstrated by following a reaction with time (reactions D–K; L is the final product from this reaction). Fig. 3 shows that M_n increases linearly with conversion, up to approx. 80%, whilst PDI remains narrow for reaction with MMA : **3** = 200. In this case the expected M_n(theory) at 100% conversion = [100/1 × 100.14 (mass of MMA)] + 220 (mass of end groups) = 20 248. The PDI is broader than would be expected for a true living polymerisation with fast initiation (theoretically 1 + 1/DP). However, PDI does not increase with increasing conversion as would be expected for a reaction with significant termination and this is most probably due to slow initiation relative to propagation.[9]

In summary, atom transfer radical polymerisation with **1** as catalyst and **3** as initiator leads to α-hydroxy functional PMMA. The presence of the hydroxy group during the polymerisation does not reduce the control over the polymerisation, and a narrow PDI polymer with controlled M_n is obtained.

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Footnotes

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‡ 0.25 g of red phosphorus (8.06×10^{-3} mol) were added to 35.4 ml (0.338 mol) of isobutyryl chloride. The mixture was placed under gentle reflux and 20 ml of bromine (0.388 mol) were added slowly over 8 h. The mixture was refluxed for a further 4 h and the crude reaction mixture added slowly to 350 ml of anhydrous ethylene glycol (6.27 mol). The reaction mixture was refluxed for 4 h, filtered into 500 ml of distilled water and the product extracted into chloroform. After washing with water and sodium hydrogen carbonate and drying over magnesium sulfate the product was isolated as a colourless liquid after the removal of solvent and vacuum distillation at 64.5 °C and 0.1 Torr. ^{1}H NMR ($CDCl_3$, 373 K, 250.13 MHz) δ 4.30 (t, *J* 9.6 Hz, 2 H), 3.85 (t, *J* 9.6 Hz, 2 H), 1.94 (s, 6 H): $^{13}C\{^1H\}$ NMR ($CDCl_3$, 373 K, 100.6 MHz) δ 171.83, 67.30, 60.70, 55.72, 30.59. IR (NaCl, film) 3436 (br), 2977, 1736 (s), 1464, 1391, 1372, 1278, 1168, 1112, 1080, 1023, 950, 644. EI MS: 213, 211 (mass peaks), 169. 167, 151, 149, 123, 121.

§ *Typical polymerisation procedure.* 0.1376 of copper(I) bromide (98%, 9.6×10^{-4} mol) were added to 40 ml of xylene and 20 ml of methyl methacrylate (0.187 mol). 0.4272 g of **2** (2.89×10^{-3} mol) were added and the mixture deoxygenated by one freeze-pump-thaw cycle prior to the addition of 0.2029 g of **3** (9.61×10^{-4} mol) at room temperature. The deep red solution was heated at 90 °C for 70 min. The final product was isolated by precipitation into hexanes.

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