Facile synthesis of well-defined water-soluble polymers *via* atom transfer radical polymerization in aqueous media at ambient temperature

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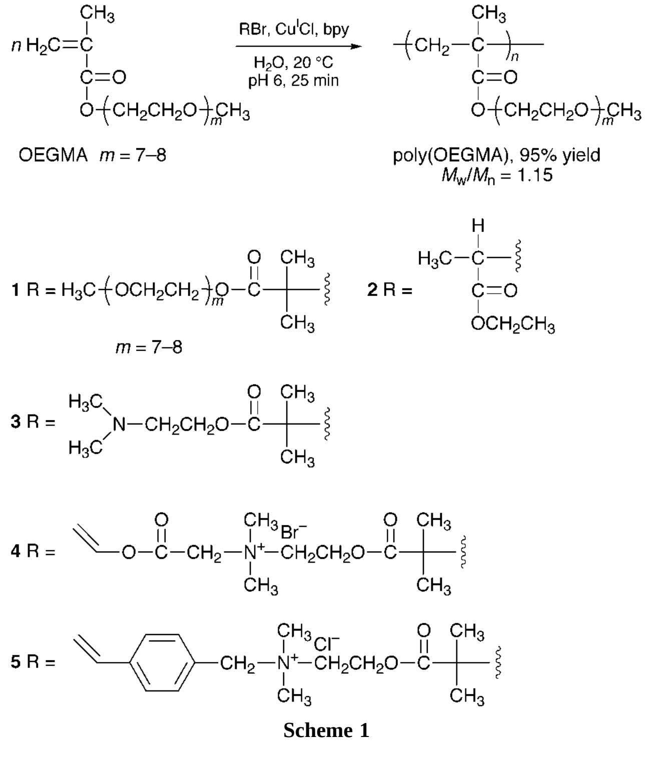
Monomethoxy-capped oligo(ethylene oxide) methacrylate (OEGMA) is readily polymerised in aqueous media by atom transfer radical polymerisation at 20 °C using various initiators; the resulting OEGMA polymers and macromonomers were obtained in high yield (> 95%) within short reaction times and polydispersities were as low as 1.12.

Atom transfer radical polymerisation (ATRP) which is applicable to both styrenic and (meth)acrylate monomers and is remarkably tolerant of functional groups.[1,2] With regard to hydrophilic monomers, recent ATRP publications describe: (i) the polymerisation of 2-hydroxyethyl acrylate in aqueous media at 90 °C;[3] (ii) the (co)polymerisation of 2-(dimethylamino)ethyl methacrylate either in bulk or in non-aqueous media[4] and (iii) the polymerisation of sodium methacrylate at 90 °C.[5] In this latter example polymerisation was slow and incomplete: yields of only 70–80% were obtained after 21 h. Herein we describe the efficient, well-controlled polymerisation of monomethoxy-capped oligo(ethylene oxide) methacrylate (OEGMA) *via* ATRP in aqueous media at 20 °C. Excellent yields (> 95%) are obtained in short reaction times (< 0.5 h) even at 20 °C. Moreover, vinyl functional initiators can be used to prepare well-defined OEGMA macromonomers.

Our ATRP formulation was based on that described by Matyjaszewski's group.[1] The transition metal catalyst was $Cu^{I}Cl$ and the ligand was 2,2′-bipyridine (bpy). Initiator **1** was synthesised according to a literature procedure.[5,6] A typical ATRP synthesis was carried out as follows (Scheme 1). Initiator **1** (232 mg, 0.54 mmol, 1 equiv.) was dissolved in 5 ml of doubly distilled de-ionised water. To this degassed solution was added the bpy ligand (211 mg, 1.08 mmol, 2 equiv.), followed by $Cu^{I}Cl$ (53 mg, 0.54 mmol, 1 equiv.). OEGMA monomer (9.70 g, 23 mmol, 42 equiv.) was added to this reaction mixture using a double-tipped needle and the solution was de-gassed using a nitrogen stream for 10–30 min with continuous stirring at 20 °C. The reaction solution became dark brown and much more viscous, indicating the onset of polymerisation; exotherms of 5–10 °C were typically observed. After 0.5 h, THF (50 ml) was added to the reaction solution, followed by excess $MgSO_4$ (15 g) to absorb the water. After filtration, the THF solution of poly(OEGMA) was passed through an alumina column to remove residual catalyst. THF was then removed under vacuum, yielding off-white polymers.



Scheme 1

Molecular weight distributions were assessed using GPC (THF eluent; PMMA standards; RI detector). Polymer molecular weights, polydispersities and yields are summarised in Table 1. Conversion of OEGMA to polymer was monitored by ^{1}H NMR spectroscopy: Fig. 1(*a*) illustrates the progressive reduction of monomer vinyl signals at δ 5.4–5.8, accompanied by a concomitant increase in poly(OEGMA) signals (*e.g.* at δ 3.8–4.0). Fig. 1(*b*) shows a typical conversion *vs.* time curve derived from the NMR spectra. High conversions of monomer to polymer were obtained in short reaction times and the consumption of monomer followed first order kinetics, as expected. Narrow polydispersities (M_w/M_n < 1.12–1.30), indicative of a living polymerisation, were obtained for initiators **1**, **2** and **4**. At present we have no explanation for the somewhat higher polydispersities obtained with initiator **3**.

Overlapping peaks prevented discrimination between the NMR signals due to the oligo(ethylene oxide) initiator **1** and the OEGMA residues. However, inspection of the ^{1}H NMR spectra ($CDCl_3$ or D_2O) of the cleaned-up polymers prepared using initiators **2** and **4** confirmed the presence of the initiator, as expected. The peak integral of the NMR signal assigned to the α-proton of **2** at δ 2.1–2.2 (or to the azamethylene protons of **4** at δ 4.6) was compared to that due to the ethylene oxide protons of the OEGMA residues at δ 3.8–4.0 in order to determine the degree of polymerisation of the OEGMA chains by end-group analysis. Such calculations yielded number-average molecular weights (M_n) which were in excellent agreement with those expected from the corresponding monomer/initiator ratios (see Table 1). Moreover, in the case of initiator **4**, well-defined vinyl acetate-capped macromonomers were obtained, which are expected to be useful reactive stabilisers for poly(vinyl acetate) latex syntheses. Facile synthetic routes to such well-defined hydrophilic macromonomers are very rare in the literature, although similar selectivity has been reported by Matyjaszewski's group for the preparation of hydrophobic polystyrene-based macromonomers by ATRP utilizing a vinyl chloroacetate initiator.[7] Our attempts to prepare the analogous styrene-capped macromonomers using initiator **5** under the same conditions were not successful. High molecular weights and broad polydispersities were obtained (see Table 1), which suggests insufficient selectivity: the styrenic end-groups probably copolymerise with the OEGMA even at 20 °C.

Table 1 A summary of the molecular weights and polydispersities of various OEGMA-based polymers synthesised using ATRP in aqueous media at 20 °C. Synthesis conditions: [initiator] = 0.54–2.14 mmol; initiator:Cu^{I}Cl:bpy was 1:1:2 in all experiments

			M_n			
Initiator	t/h	Conversion (%)	Target	^{1}H NMR	GPC	M_w/M_n
1	0.5	> 99[a]	8500	—	6500[b]	1.12
1	0.5	> 99[a]	16300	—	9700[b]	1.17
2	2.0	> 99[a]	11200	10600	6000[b]	1.17
3	8.0	> 99[a]	2400	2500	3500[c]	1.38
3	0.5	> 99[a]	5100	5300	4700[c]	1.42
4	1.0	> 99[a]	14600	14500	9700[c]	1.21
4	0.5	98	5000	4900	5500[c]	1.30
5	2.0	> 99[a]	18700		31500[c]	1.86
5	0.5	98	6000		15000[c]	1.89

[a] No residual monomer signal detected in ^{1}H NMR spectrum. [b] THF eluent; PMMA standards. [c] Aqueous eluent; PEO standards.

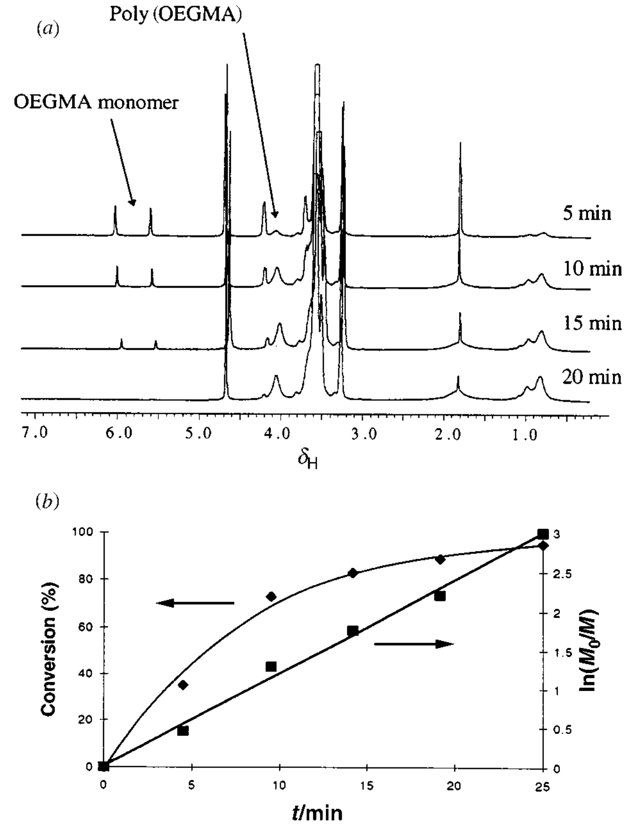


Fig. 1 (*a*) Evolution of ^{1}H NMR spectra (D_2O) for the homopolymerisation of OEGMA by ATRP at 20 °C in aqueous media using initiator **1**, (*b*) Typical conversion *vs*. time curve derived from the ^{1}H NMR spectra: (◆) conversion and (■) In (M_o/M).

As far as we are aware, there have been no previous reports of rapid ATRP in aqueous media at ambient temperature. However, ATRP of hydrophobic monomers at ambient temperature is well-documented. Haddleton *et al.* described[8] the relatively slow bulk polymerisation of methyl methacrylate at 25 °C, with 92% conversion requiring a reaction time of 20 h. In contrast, Matyjaszewski and co-workers reported[9] the rapid bulk polymerisation of methyl acrylate at 22 °C. In this latter case it was shown that the choice of ligand for the Cu^I catalyst was critical for efficient polymerisation: much slower rates were obtained with a dialkyl-substituted bipyridine ligand than for a multifunctional ligand, hexamethylated tris[2-(dimethylamino)ethyl]amine. The same research group has also shown[10] that solvent polarity can be an important parameter in ATRP. Thus the rate of polymerisation of *n*-butyl acrylate in polar solvents such as ethylene carbonate was unexpectedly faster than that observed for bulk polymerisation, even though the monomer and initiator concentrations were significantly higher in the latter case. This observation was attributed to the mononuclear nature of the Cu^I catalyst. Since water is a very polar solvent, it is perhaps understandable that the ATRP of hydrophilic monomers such as OEGMA is particularly fast in aqueous media, even at room temperature. We also note that the Cu^I[bpy]$_2$ catalyst is more likely to be mononuclear in aqueous media, with more complex binuclear halo-bridged structures being formed in non-aqueous media.[11] One referee believes that the rapid ATRP of OEGMA described herein is due to complexation of the ethylene oxide residues to the Cu catalyst. We believe that this hypothesis is unlikely because we observe similar rates of polymerization for the ATRP of unrelated monomers such as sodium 4-vinylbenzoate.[12] The second referee pointed out that, since OEGMA is a sterically hindered monomer, its rate coefficient for termination may be anomalously low; similar observations have been recently reported for *n*-dodecyl methacrylate.[13] This would be consistent with the apparent lack of termination observed even at high conversions (see Fig. 1). This referee also suggested that the Cu–Cl bond may be more easily cleaved in water than in non-aqueous media. Thus the rate of deactivation would be reduced and faster polymerisations would ensue.

In summary, ATRP of OEGMA is facile and well-controlled under environmentally-friendly conditions; this discovery has considerable potential for commercial exploitation.

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