First example of the atom transfer radical polymerisation of an acidic monomer: direct synthesis of methacrylic acid copolymers in aqueous media

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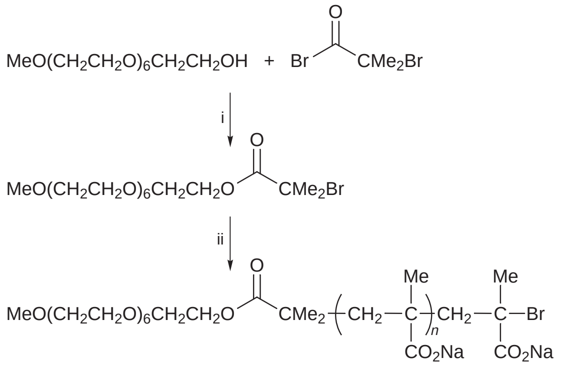
Sodium methacrylate is polymerised directly *via* atom transfer radical polymerisation (ATRP) in aqueous media using a poly(ethylene oxide)-based macro-initiator; the resulting poly(ethylene oxide-*block*-sodium methacrylate) copolymers were obtained in good yield and have narrow molecular weight distributions as evidenced by aqueous GPC.

Recently there has been considerable interest[1–3] in atom transfer radical polymerisation (ATRP), which allows the facile synthesis of styrenic[1,2] and (meth)acrylate[3] homopolymers and copolymers with predetermined degrees of polymerisation and narrow polydispersities. ATRP is usually performed either in bulk or in non-aqueous media and is remarkably tolerant of functional groups. For example, Matyjaszewski and co-workers demonstrated that ATRP can be carried out in the presence of ethylene carbonate, MeOH, MeCN, pyridine or PPh_3 with little or no deleterious effects.[4] More recently, Coca *et al.* have reported successful ATRP of a hydrophilic monomer, 2-hydroxyethyl acrylate, in 50% aqueous solution at 90 °C.[5]

Near-monodisperse acidic copolymers can be readily prepared *via* anionic (group transfer) polymerisation using either *tert*-butyl or benzyl methacrylate as a protected monomer for methacrylic acid.[6,7] In principle ATRP can also be used for such protected monomer syntheses, but in practice Haddleton and co-workers have reported very slow polymerisation for sterically hindered monomers such as *tert*-butyl methacrylate.[8] Moreover, in a recent review article, Patten and Matyjaszewski state that 'acrylic and methacrylic acid cannot be polymerised with currently available ATRP catalysts, because these monomers react rapidly with the metal complexes to form metal carboxylates that are inefficient deactivators and cannot be reduced to active ATRP catalysts'.[9] We report herein the successful ATRP of sodium methacrylate directly in water. Given the problems discussed above, this approach promises to be a useful and versatile route to model acidic copolymers.

Our ATRP formulation (see Scheme 1) is based on that described by Matyjaszewski's group and comprises a monofunctional poly(ethylene oxide) macro-initiator, a Cu^IBr catalyst and 2,2′-bipyridine (bipy). This ligand was selected because it is commercially available, readily forms a water-soluble complex with Cu^I and, unlike the *N*-alkyl-2-pyridylmethanimine ligands reported by Haddleton and co-workers,[8,10] is not prone to hydrolytic instability. The macro-initiator was synthesised by reacting a monomethoxy-capped poly(ethylene oxide) with 2-bromoisobutyryl bromide according to Jankova *et al.*[11] An ^1H NMR spectrum of the purified macro-initiator is shown in Fig. 1(*a*). After several freeze-thaw and de-gassing cycles, the ATRP of sodium methacrylate was carried out at 90 °C under dry nitrogen in doubly-distilled, de-ionised water (*ca.* pH 9). The initial monomer concentration was 33 vol% based on solvent, the initiator concentration was 0.07–0.11 mol dm^{-3} (depending on the molecular weight of the target polymer) and the molar ratio of macro-initiator : Cu^IBr : bipy was 2 : 2 : 5. Polymerisations were terminated by pouring the



Scheme 1 *Reagents and conditions*: i, Et_3N, toluene, 0 °C, 12 h; ii, sodium methacrylate, Cu^IBr, bipy, H_2O, 90 °C, 21 h.

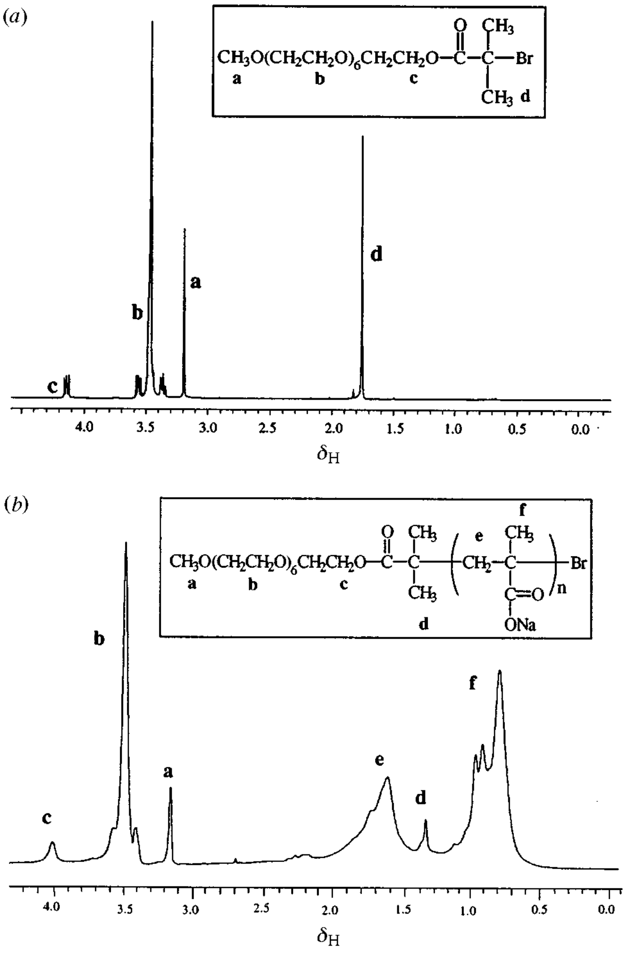


Fig. 1 ^1H NMR spectra for (*a*) the methoxy-capped poly(ethylene oxide) macro-initiator and (*b*) the poly(ethylene oxide-*block*-sodium methacrylate) synthesised using this macro-initiator (entry 3 in Table 1).

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Table 1 A summary of the molecular weights, polydispersities and copolymer compositions of the poly(ethylene oxide-*block*-sodium methacrylate)s synthesised using aqueous ATRP

	Initiator	[Initiator]/ mmol	[Monomer]/ mmol	t/h	M_n			M_w/M_n (GPC)^c	Conversion (%)^d
					Theory^b	NMR	GPC^c		
1	**1**	1.67	46.0	4.3	1645	2000	1500	1.30	47
2	**1**	1.67	46.0	6.2	2660	2500	2100	1.30	76
3	**1**	1.67	46.0	21.0	2800	3100	2900	1.27	80
4	**1**	1.0	92.5	17.0	7560	7400	7300	1.20	72
5^e	—	0.0	46.0	21.0	—	—^{i}	20200	2.18	82
6^f	—	0.0	46.0	21.0	—	—^{i}	4600	2.32	44
7	^{g}	1.67	46.0	21.0	416	—^{i}	3250	2.55	13
8	^{h}	1.67	46.0	21.0	384	—^{i}	2000	2.29	12
9	**2**	1.06	29.6	21.0	1540	1600	1300	1.23	44

[a] All reactions carried out with [CuBr]:[initiator]:[bipyridine] = 2:2:5, under nitrogen at 90 °C in degassed aqueous solution. [b] Calculated using the following formula: M_n (Theory) = 108.07(Δ[Monomer]/[Initiator]p), where p = fractional conversion. [c] Aqueous GPC details: Pharmacia Biotech Superdex® 200 HR 10/30 FPLC® column; eluent: 20% MeCN (HPLC grade) + 80% (0.01 M Na_2HPO_4 + 0.05 M $NaNO_3$); flow rate = 0.5 ml min^{-1}; pH 7–8; poly(sodium styrene-4-sulfonate) standards. [d] Reaction mixture was precipitated into EtOH and dried to constant weight. [e] Control reaction: performed with 5 g monomer and 15 ml water only. [f] Control reaction: catalyst and ligand present, but no initiator. [g] Initiator is sodium bromoisobutyrate. [h] Sodium bromoisobutyrate was used as the initiator, in the presence of monomethoxy-capped poly(ethylene oxide) (1.67 mmol). [i] M_n cannot be calculated from ^{1}H NMR spectra since the end groups are not known.

reaction solution into excess EtOH in order to isolate the precipitated copolymer [the Cu^I catalyst, bipy ligand and sodium methacrylate monomer are all soluble in EtOH]. Copolymer molecular weights, polydispersities and yields are summarised in Table 1. Moderate to good yields, good control over molecular weight and narrow polydispersities ($M_w/M_n < 1.30$) were achieved under ATRP conditions (see entries 1–4).

A proton NMR spectrum (D_2O) of a poly(ethylene oxide-*block*-sodium methacrylate) [entry 3, Table 1] clearly shows signals arising from the macro-initiator at δ 3.15 and 3.35–3.65. In order to demonstrate genuine block copolymer formation, the isolated polymers were subjected to Soxhlet extraction with refluxing THF for 3 h (the macro-initiator is THF-soluble). The NMR spectra obtained before and after THF extraction were identical, confirming that the macro-initiator is covalently attached to the poly(sodium methacrylate) chains. The peak integrals assigned to the ethylene oxide residues can also be used to determine the block copolymer M_n by end-group analysis. These values are included in Table 1 and are in reasonably good agreement with the aqueous GPC data.

Virtually all vinyl monomers are susceptible to radical initiation if heated for prolonged periods, even in the absence of initiator. Thus it was no surprise that non-living thermally-initiated polymerisation occurred on heating an aqueous solution of sodium methacrylate to 90 °C for 21 h in the absence of any macro-initiator or catalyst; the resulting polymer had a broad molecular weight distribution and a relatively high molecular weight (see entry 5, Table 1). Similarly, heating an aqueous solution of sodium methacrylate in the presence of the Cu^IBr and bipy ligand, but in the absence of initiator (entry 6), yielded polymer of high polydispersity (M_w/M_n = 2.32) but much lower molecular weight. Here the Cu^I [or traces of Cu^{II} formed by oxidation] probably acts as a polymerisation retarder.[12] Both control experiments support the hypothesis that the macro-initiator initiates ATRP of sodium methacrylate.

Subsequent experiments confirmed that the choice of pH is critical for successful ATRP. Below pH 6, sodium methacrylate does not undergo ATRP; the bipy ligand becomes protonated and no longer solubilises the Cu^IBr catalyst. Above pH 6, controlled polymerisation is evident and the optimum pH lies between 8 and 9. It is well known that the rate of radical polymerisation of methacrylic acid in water is very sensitive to pH.[13] However, this reaction usually favours low pH, because at high pH the rate of propagation is reduced due to the build-up of anionic charge density on the polymer backbone. In the present case it appears that there is a balance between reduced propagation at high pH and competing protonation of the ligand at low pH. Furthermore, synthesis of high molecular weight poly(sodium methacrylate) by aqueous ATRP has so far proved problematic: relatively broad molecular weight distributions are obtained if target molecular weights are greater than 10000.

Choice of initiator is also important. Polymerisation of sodium methacrylate using sodium 2-bromoisobutyrate as initiator (entry 7) gave only low conversion and polydisperse polymer, with an M_n much higher than expected. To determine whether the ethylene oxide residues of the macro-initiator might be contributing to the polymerisation, we performed the same reaction in the presence of the monomethoxy-capped poly(ethylene oxide) starting material, with no improvement (entry 8). In contrast, the monomeric analogue of the macro-initiator, 2-hydroxyethyl 2-methyl-2-bromopropionate **2**, successfully initiated the polymerisation of sodium methacrylate (entry 9) to produce near-monodisperse homopolymer, but with somewhat lower monomer conversion (44%).

In summary, we have demonstrated that ATRP of sodium methacrylate works well in aqueous media. Well-defined low molecular weight poly(sodium methacrylate)-based blocks can be prepared directly, without requiring protection chemistry for the carboxylic acid residues.

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