Facile Synthesis of Acidic Copolymers via Atom Transfer Radical Polymerization in Aqueous Media at Ambient Temperature

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There is growing interest in atom transfer radical polymerization (ATRP) which, unlike living ionic polymerizations, is remarkably tolerant of functional groups.[1,2] With regard to hydrophilic monomers, Matyjaszewski and co-workers have reported the well-controlled (co)polymerization of 2-hydroxyethyl acrylate[3] in aqueous media at 90 °C, 2-(dimethylamino)ethyl methacrylate[4] at 23 °C in bulk or nonaqueous media, and 4-vinylpyridine[5] in alcoholic media at 40 °C. We have recently described the facile polymerization of monomethoxy-capped oligo(ethylene oxide) methacrylate[6] [OEGMA] in aqueous media at 20 °C using a similar protocol. ATRP of acidic monomers have generally proved more problematic. For some time, it was believed that protecting group strategies were necessary since carboxylic acid-based monomers such as methacrylic acid or acrylic acid formed insoluble complexes with the copper catalyst if ATRP was attempted in nonaqueous media.[7] However, we recently demonstrated that methacrylic acid[8] could be polymerized directly in its sodium salt form by ATRP in aqueous solution. Although an important "proof of concept" experiment, the conversion of sodium methacrylate to polymer was both slow and substantially incomplete, with yields of only 70−80% being obtained after 21 h at 90 °C. Herein we describe the efficient, well-controlled (co)polymerization of a second acidic monomer, sodium 4-vinylbenzoate [NaVBA], via ATRP in aqueous media (see Figure 1). In contrast to sodium methacrylate, excellent yields are obtained in very short reaction times even at 20 °C.

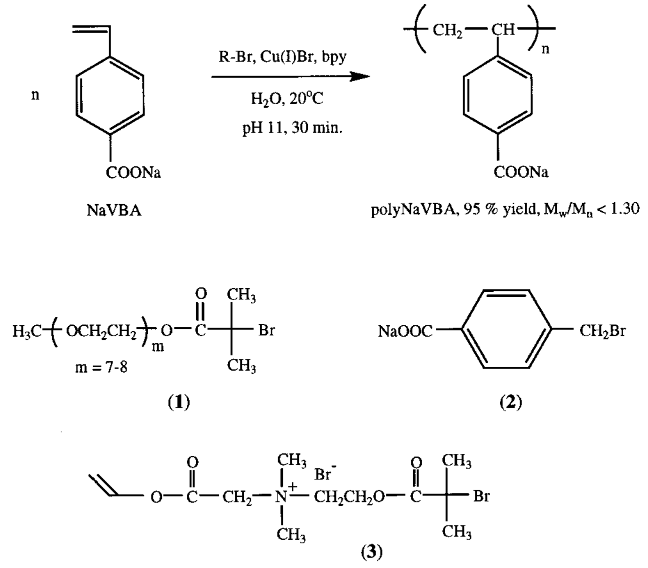

Figure 1. Reaction scheme for the homopolymerization of sodium 4-vinylbenzoate via ATRP at 20 °C in aqueous media using initiators **1**−**3**. Initiator **1** was prepared according to ref 8, **2** was purchased from Aldrich in its free acid form, and **3** was prepared according to ref 6.

Our ATRP formulation was based on that described by Matyjaszewski's group.[1−3] The transition metal catalyst was Cu^IBr and the ligand was 2,2′-bipyridine (bpy). Initiator **1** was synthesized by reacting a near-monodisperse, monomethoxy-capped oligo(ethylene oxide) [M_n = 350 by ^1H NMR spectroscopy and M_w/M_n = 1.10 by GPC] with 2-bromoisobutyryl bromide at 0 °C in the presence of triethylamine according to a literature procedure.[8] Initiator **2** was purchased from Aldrich and was used as received. The synthesis of initiator **3** has been reported recently.[6] A typical ATRP synthesis was carried out as follows. Initiator **2** (0.34 mmol, 1 equiv) was dissolved in 5 mL doubly distilled water with the addition of NaOH (pH 11). To this degassed solution was added the bpy ligand (0.68 mmol, 2 equiv), followed by Cu^IBr (0.34 mmol, 1 equiv). An aqueous degassed solution (20 mL) containing NaVBA (5.0 g, 34 mmol, 100 equiv) at pH 11 was added to this stirred reaction solution at 20 °C using a double-tipped needle. The reaction solution rapidly became dark brown and much more viscous, indicating the onset of polymerization; exotherms of 5−10 °C were typically observed. To terminate the polymerization, the reaction solution was first diluted with water (10 mL) and then added to 3 M HCl (300 mL). The resulting white precipitate was isolated by filtration and dried in a vacuum oven at 20 °C for 16 h.

Reaction yields, polymer molecular weights, and polydispersities are summarized in Table 1. The polymerization of NaVBA was monitored by ^1H NMR spectroscopy: Figure 2a illustrates the progressive reduction of monomer vinyl signals at δ 5.3−5.8, accompanied by a concomitant increase in polyNaVBA signals at δ 0.6−2.0, δ 6.1−6.8 and δ 7.1−7.8. Figure 2b shows a typical conversion vs time curve derived from such NMR spectra. Very high conversions of monomer to polymer were achieved with initiator **2** within short reaction times (<0.50 h), and the polymerization followed first-order kinetics at all conversions (see Figure 2b). On the other hand, curved semilogarithmic plots were obtained for initiators **1** and **3**, indicating more complex kinetics. Although high yields were eventually obtained (see Table 1), much slower polymerizations were obtained for these latter initiators compared to initiator **2**. Narrow polydispersities, which are indicative of a living polymerization, were obtained for initiators **1** and **2**. Molecular weight distributions were assessed using either aqueous gel permeation chromatography (1.0 M NaCl eluent containing 50 mM Tris buffer at pH 9, PEO standards, RI detector) or nonaqueous gel permeation chromatography (THF eluent, PMMA standards, RI detector). In the latter case, the NaVBA homopolymer was first converted into its methyl ester using excess methyl iodide in THF at 20 °C in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU);[9] the degree of esterification was at least 98% as judged by ^1H NMR spectroscopy. Finally we note that since styrenic monomers can be polymerized via ATRP selectively in the presence of vinyl acetate groups,[10] using

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Table 1. Summary of the Reaction Yields, Molecular Weights, and Polydispersities of Poly(sodium 4-vinylbenzoates) Synthesized by ATRP in Aqueous Media at 20 °C Using Initiators 1–3[a]

initiator	[initiator], mmol dm^{-3}	reacn time, h	yield, %	$M_{n(theor)}$	$M_{n(exptl)}$	M_w/M_n[c]
1	21.7	16.0	99	9600	9400[b]	1.28
2	13.7	0.50	95	13800	13400[c]	1.32
3	22.8	1.00	80	7000	7400[b]	

[a] Synthesis conditions: [NaVBA] = 1.35 M; initiator:Cu^{I}Br:bpy was 1:1:2. [b] Calculated from ^{1}H NMR spectra. [c] Determined by nonaqueous GPC analysis (THF eluent, PS standards) of the methylated polymers. As a comparison, a polydispersity of 1.27 was obtained by aqueous GPC (see text for details) for the polymer obtained using initiator **1**.

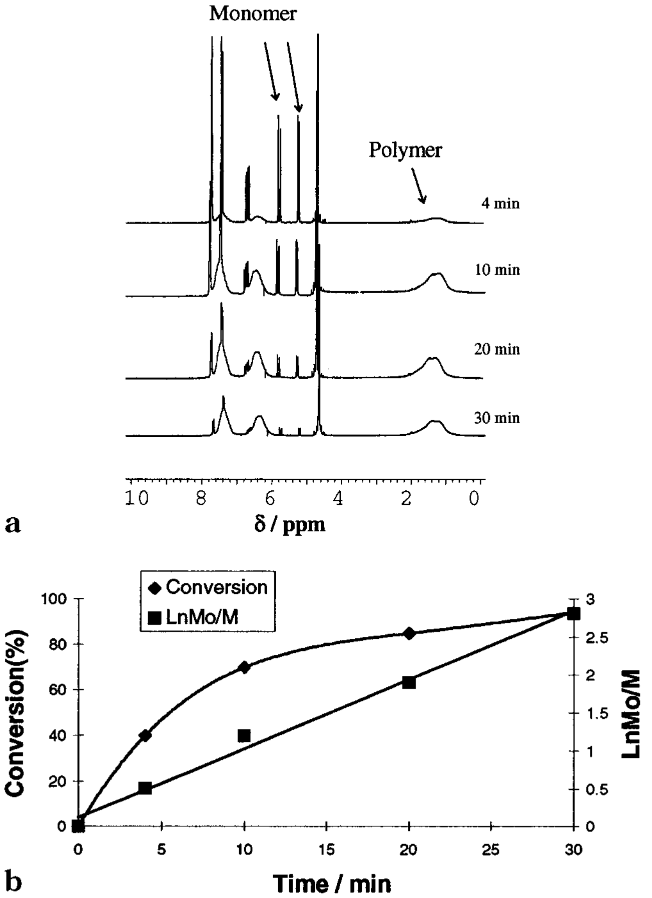

Figure 2. (a) Evolution of ^{1}H NMR spectra (in D_2O) for the ATRP of sodium 4-vinylbenzoate at 20 °C in aqueous media using initiator **2**; (b) typical conversion vs time curve derived from these ^{1}H NMR spectra.

initiator **3** leads to the formation of novel well-defined acidic macromonomers.

Inspection of the ^{1}H NMR spectra (D_2O) of the purified NaVBA homopolymer prepared using initiator **1** confirmed the presence of the initiator fragment, as expected. The peak integral of the ethylene oxide protons at δ 3.4 was compared to that due to the aromatic protons of the NaVBA residues at δ 6–8 in order to determine the number-average degree of polymerization of the NaVBA chains by end group analysis (such NMR calculations proved impossible for polymers prepared using initiator **2** since its aromatic protons were indistinguishable from those of the NaVBA residues). This approach yielded final M_n values which were in excellent agreement with those calculated from the corresponding monomer/initiator ratios. Furthermore, the evolution of M_n with conversion was linear, as expected for a living polymerization (see Figure 3).

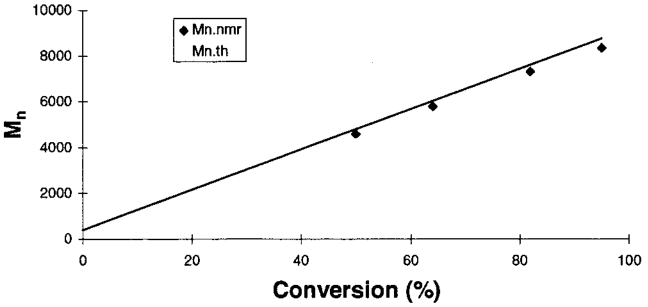

Figure 3. Evolution of number-average molecular weight with conversion for the ATRP of sodium 4-vinyl benzoate in aqueous media at 20 °C using initiator **1**. The solid line represents the theoretical molecular weight expected for a given conversion, and the data points were calculated from ^{1}H NMR spectra.

To further demonstrate the living character of this polymerization, NaVBA was also block copolymerized with OEGMA at 20 °C. In this synthesis the OEGMA monomer (3.0 g; 7.1 mmol) was polymerized first using initiator **1**, and the NaVBA (1.0 g; 6.8 mmol) was added to the reaction solution after approximately 90% conversion of the OEGMA.[11] Thus, the final OEGMA:NaVBA diblock copolymer, which contained 57 mol % OEGMA, had a polydispersity of 1.27 (recorded for the methylated copolymer using THF GPC), and was obtained in approximately 90% yield, contained a short tapered sequence located between the two pure blocks. However, this small structural imperfection did not prevent the diblock copolymer undergoing reversible self-assembly in aqueous media on adjusting the solution pH from pH 8 to pH 3. On protonation, ^{1}H NMR studies confirm that the styrenic block becomes hydrophobic and forms the dehydrated micelle core, with the OEGMA block forming the solvated micelle corona. The intensity-average micelle diameter was approximately 20 nm, as judged by dynamic light scattering. We have recently reported similar results for related water-soluble diblock copolymers prepared by TEMPO-mediated polymerization.[12]

ATRP of hydrophobic monomers at ambient temperature is well-documented. Haddleton et al. described[13] the relatively slow bulk polymerization of methyl methacrylate at 25 °C, with 92% conversion requiring a reaction time of 20 h. In contrast, Matyjaszewski and co-workers reported[14] the rapid bulk polymerization of methyl acrylate (76% conversion within 45 min) at 22 °C. In this case it was shown that the choice of ligand for the Cu(I) catalyst was critical for efficient polymerization: much slower rates were obtained with a dialkyl-substituted bipyridine ligand than for a multifunctional ligand (hexamethylated tris[2-(dimethylamino)ethyl]-amine; Me_6TREN). The same research group has also shown[15] that solvent polarity can be an important parameter in ATRP. Thus, the rate of polymerization of *n*-butyl acrylate in polar solvents such as ethylene carbonate was unexpectedly faster than that observed for *bulk* polymerization, even though the monomer and initiator concentrations were significantly higher in the latter case. This observation was attributed to the monomeric 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 NaVBA is particularly fast in aqueous solution, even at room temperature. We also note that the Cu(I) catalyst is more likely to be monomeric in this medium, with more complex binuclear halo-bridged structures being formed in nonaqueous solvents.[16] As far as we are aware, with the exception of our recent communication[6] on the homopolymerization of OEGMA, there have been no previous reports of rapid ATRP in aqueous solution at ambient temperature.

In summary, sodium 4-vinylbenzoate undergoes well-controlled ATRP at ambient temperature in aqueous media. *Moreover, on the basis of the results reported herein and other, as yet unpublished work,[17] we believe that the ATRP of many hydrophilic monomers is best conducted in aqueous media.* Water is cheap, nontoxic, promotes rapid polymerization, and may also facilitate removal of catalyst residues (e.g., by using silica column chromatography). These environmentally friendly conditions are expected to be particularly attractive for the eventual commercial exploitation of ATRP.

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References and Notes

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