Unexpected Viability of Pyridyl Methanimine-Based Ligands for Transition-Metal-Mediated Living Radical Polymerization in Aqueous Media at Ambient Temperature

X. S. Wang, F. L. G. Malet, and S. P. Armes*

School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton BN1 9QJ, UK

D. M. Haddleton* and S. Perrier

Center for Supramolecular and Macromolecular Chemistry, Department of Chemistry, University of Warwick, Coventry, West Midlands CV4 7AL, UK

Received August 8, 2000; Revised Manuscript Received November 14, 2000

ABSTRACT: Pyridyl methanimine-based ligands are used in aqueous media at neutral pH for the efficient living radical polymerization of hydrophilic monomers. High conversions (>90%), good molecular weight control, and low polydispersities (M_w/M_n < 1.20) were obtained for the polymerization of monomethoxy-capped oligo(ethylene glycol) methacrylate at 20 °C; faster rates, reduced control, and higher polydispersities were obtained at elevated temperatures.

Introduction

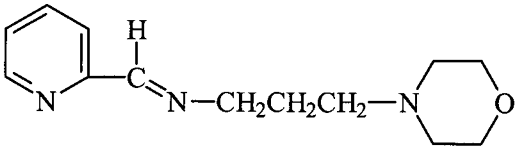
Since its discovery[1] in 1995, transition-metal-mediated living radical polymerization, sometimes known as atom transfer radical polymerization (ATRP), has been shown to be a versatile technique for the controlled polymerization of many monomer classes, including acrylates, methacrylates, and styrenics.[2−4] Generally ATRP syntheses are carried out at high temperatures in the bulk or in nonaqueous media. However, we have recently reported[5] that ATRP is particularly effective for hydrophilic monomers in aqueous media under mild conditions. For example, monomethoxy-capped oligo(ethylene glycol) methacrylate [OEGMA] can be polymerized to over 95% conversion within 0.50 h at 20 °C using 2,2′-bipyridine (bpy) as a ligand for the copper catalyst.[5a] Another common ligand class is the pyridyl methanimines, as developed by Haddleton and coworkers.[6] These ligands are particularly useful for the ATRP of methacrylates, are much cheaper than bpy-based ligands, and are readily synthesized by reacting various primary amines with 2-pyridinecarbaldehyde.

$$R_1CHO + R_2NH_2 \rightarrow R_1CH{=}NR_2 + H_2O$$

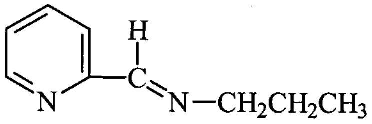
However, at first sight these ligands do not appear to be an attractive option for ATRP in aqueous media, since they might be expected to undergo hydrolysis.[7] Indeed, in our initial experiments with hydrophilic pyridyl methanimine (**1**), only poor conversions of sodium methacrylate were obtained at 90 °C, possibly due to ligand hydrolysis at this temperature. However, this particular monomer is unusually sluggish with respect to aqueous ATRP: many hydrophilic methacrylates are rapidly polymerized by aqueous ATRP under remarkably mild conditions.[8] In this paper we demonstrate that hydrophilic pyridyl methanimine ligands such as (**1**) can be very effective for the ATRP of hydrophilic methacrylates in aqueous media at 20 °C (see Figure 1).

Experimental Section

Ligands **1** and **2** were readily synthesized in ether at 20 °C in high yield from the reaction between 2-pyridinecarbaldehyde and either 4-(3-aminopropyl)morpholine or 3-aminopropane, respectively. ^{1}H NMR spectroscopy was used to confirm their chemical structures and purity.



(1)



(2)

A typical ATRP synthesis was carried out as follows (see Figure 1). A bromo-capped, oligo(ethylene glycol)-based initiator [OEGBr; 489 g mol^{-1}; synthesized as described previously[9]] was dissolved in deionized, doubly distilled water (10 mL, pH 6). OEGMA monomer (10.0 g, M_n = 430, M_w/M_n = 1.10) was added via a double-tipped needle. To this degassed solution was added either ligand **1** or ligand **2**, followed by Cu(I)Cl. Although no exotherm was observed, the reaction solution turned dark brown and became progressively more viscous, indicating the onset of polymerization. Termination was achieved by exposure to air, and the catalyst was removed from the aqueous solution using silica chromatography. Monomer/polymer mixtures were isolated by freeze-drying prior to GPC analysis for the assessment of yield and molecular weight distributions. In the case of ligand **1** the same experimental procedure was repeated at 50 and 80 °C using an oil bath/heater

---

* To whom correspondence should be addressed.

10.1021/ma001397u CCC: $20.00

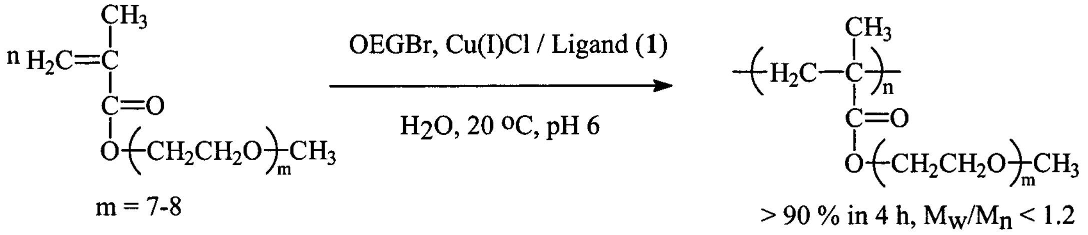


Figure 1. Reaction scheme for the homopolymerization of monomethoxy-capped oligo(ethylene glycol) methacrylate via aqueous ATRP using pyridyl methanimine-based ligands at pH 6 and 20 °C. The relative molar ratios of monomer:initiator:catalyst: ligand is 33:1:1:2; [initiator] = 36 mM.

Table 1. Summary of Synthesis Conditions, Yields, and Final Polydispersities for the Homopolymerization of OEGMA via ATRP in Aqueous Media at pH 6 Using Different Ligands for the Copper Catalyst[a]

entry no.	ligand type	polymerization temp (°C)	OEGMA (wt %)	yield (%); time (h)	final M_w/M_n
1	**1**	20	100[b]	<5; 40	
2	**1**	20	50	93; 4.0	1.18
3	**1**	50	50	90; 1.0	1.25
4	**1**	80	50	90; 0.50	1.35
5	**2**	20	50	75; 5.0	1.45
6	bpy	20	50	>95; 0.50	1.25

[a] The molar ratio of monomer:initiator:catalyst:ligand is 33:1: 1:2 for all entries; [OEGBr] is 72 mM for entry 1 and 36 mM for entries 2–6. [b] Bulk polymerization.

and also in the absence of water (i.e., bulk polymerization) at 20 °C; see Table 1 for a summary of these results. Yields and molecular weight data for each run were obtained from GPC using THF eluent, a refractive index detector, and PMMA calibration standards.[10]

The bulk polymerization of OEGMA using ligand **1** was negligible at 20 °C, with less than 5% conversion observed after 40 h.[11] In contrast, a 50% aqueous solution of OEGMA was polymerized to more than 90% conversion within 4 h at the same temperature. In this case the evolution of M_n with conversion was reasonably linear, and polydispersities remained low throughout the polymerization (see Figure 2a). However, the M_n vs conversion plot for the same polymerization conducted at 50 °C shows a high degree of curvature, with the target molecular weight only being approached at high conversion (see Figure 2b); initial polydispersities are greater than 1.40 but decrease progressively, approaching 1.25 at the end of the polymerization.

For the homopolymerization of OEGMA at ambient temperature, it is clear that the Cu(I)/ligand **1** complex is stable, at least on the time scale of the polymerization. NMR studies of this copper catalyst confirm its unexpected stability toward hydrolysis in aqueous media at 20 °C. It is also noteworthy that the rate of polymerization of OEGMA by aqueous ATRP at 20 °C using ligand **1** is relatively slow compared to that obtained with bpy under identical conditions (compare entries 2 and 6 in Table 1). This reduced rate of polymerization probably results from the lower polymer radical concentration; imine ligands are superior to bpy for the stabilization of transition metals in low oxidation states.[6a] Moreover, the nitrogen atom in the morpholine ring of ligand **1** may also bind to copper; i.e., ligand **1** may act as a tridentate ligand (whereas bpy is a bidentate ligand). This stronger ligand binding might be expected to reduce the rate of ATRP.

Polymerization proceeded more rapidly at higher temperatures, as expected: only 1.0 and 0.50 h were required for 90% conversion of the OEGMA at 50 and 80 °C, respectively (see Figure 3a). However, judging by the GPC data poorer control was achieved: at 50 °C the final M_w/M_n was 1.25, whereas at 80 °C the final M_w/M_n was 1.35 (see Figure 3b). In addition, there were large discrepancies between the target molecular weight and the actual molecular weight at lower conversions (<50%).

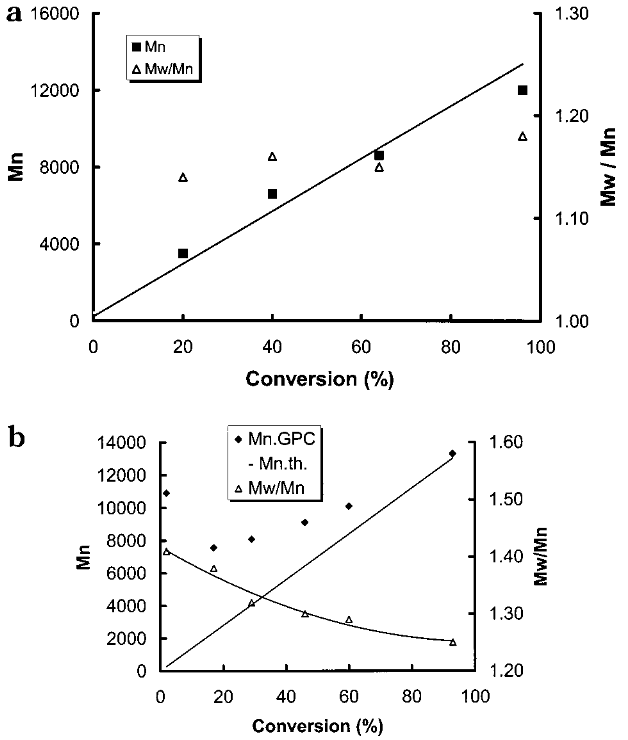


Figure 2. Evolution of molecular weight and polydispersity with conversion for the homopolymerization of monomethoxy-capped oligo(ethylene glycol) methacrylate via aqueous ATRP using ligand **1**: (a) at 20 and (b) at 50 °C. Conditions: the relative molar ratios of monomer:initiator:catalyst:ligand is 33: 1:1:2; [initiator] = 36 mM.

Variable temperature ^{1}H NMR spectroscopy studies (not shown) of the copper catalyst complexed with ligand **1** in D_2O indicated that there was no detectable ligand hydrolysis on the time scale of the polymerization (1–4 h) at either 20 or 50 °C. However, there is some spectroscopic evidence for decomposition of the copper complex after heating at 80 °C for 0.5 h. No decomposition was detected for the ligand **2**/copper complex in D_2O at ambient temperature for the time scale of the polymerization (5–10 h). However, although both ligands are stable toward hydrolysis at 20 °C, comparison of entries 2 and 5 in Table 1 indicates that the performance of ligand **2** is markedly inferior to that of ligand **1** under these particular conditions (see Supporting Information). Using ligand **2** leads to rather lower

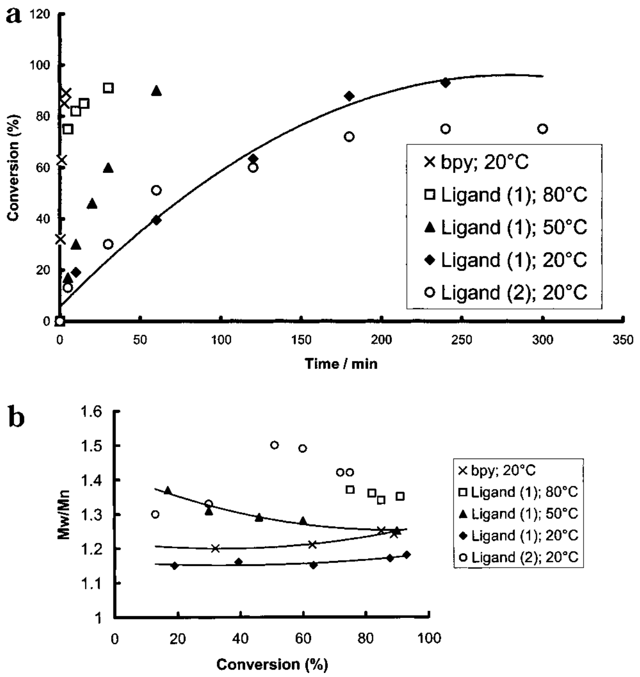


Figure 3. Homopolymerization of OEGMA in aqueous media with bpy, ligand **1**, and ligand **2**: (a) comparison of conversion vs time curves and (b) evolution of polydispersities with conversion.

conversion (only 75% after 5 h at 20 °C) and higher polydispersity; the final M_w/M_n after 5 h is 1.45.

In summary, it is shown that, perhaps contrary to intuition, pyridyl methanimine-based ligands such as **1** have sufficient hydrolytic stability to allow the efficient polymerization of hydrophilic methacrylates via aqueous ATRP at neutral pH. Polymerization at 20 °C is slower but better controlled compared to that at 50 or 80 °C. This unexpected success can be attributed to the remarkably rapid rate of aqueous ATRP under mild conditions. In this context the recent work by German's group is of interest, since it suggests that the propagation rate constant (k_p) of methacrylic monomers may be significantly higher in water than in nonaqueous media.[12]

Acknowledgment. EPSRC is acknowledged for a ROPA postdoctoral grant (X.S.W.), and Atofina and Uniqema are thanked for funding PhD studentships for F.L.G.M. and S.P., respectively.

Supporting Information Available: An additional figure illustrating the evolution of molecular weight and polydispersity with monomer conversion for the ATRP of OEGMA using ligand **2** in water at 20 °C at an initiator concentration of 36 mM and relative molar ratios of OEGMA:initiator:CuCl:bpy of 33:1:1:2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kato, M.; Kamagaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(2) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371.

(3) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.

(4) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, T. *Science* **1996**, *272*, 866.

(5) (a) Wang, X.-S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817. (b) Wang, X.-S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, *33*, 255. In addition, aqueous ATRP of an acrylamide at 20 °C has been reported to be rapid but uncontrolled. See: Rademacher, J. T.; Baum, R.; Pallack, M. E.; Brittain, W. J.; Simonsick, W. J. *Macromolecules* **2000**, *33*, 284.

(6) (a) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190. (b) Haddleton, D. M.; Crossman, M. C.; Dana, B. H.; Duncalf, D. J.; Heming, A. J.; Kukulj, D.; Shooter, A. J. *Macromolecules* **1999**, *32*, 2110. (c) Haddleton, D. M.; Kukulj, D.; Duncalf, D. J.; Heming, A. J.; Shooter, A. J. *Macromolecules* **1998**, *31*, 5201.

(7) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; Wiley-Interscience: Chichester, UK, 1992.

(8) Armes, S. P.; Wang, X.-S. *ACS Polym. Prepr.* **2000**, *41* (1), 413.

(9) Ashford, E. J.; Naldi, V.; O'Dell, R.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1999**, 1285.

(10) Linear PMMA would not normally be expected to be an appropriate calibration standard for the branched OEGMA homopolymers. However, we have observed surprisingly good agreement between PMMA standards and OEGMA homopolymers of similar molecular weight prepared by group transfer polymerization [Bütün, V.; Vamvakaki, M.; Billingham, N. C.; Armes, S. P. *Polymer*, **2000**, *41*, 3173].

(11) In contrast, over 90% conversion within 15 h at 20 °C was obtained for the bulk polymerization of OEGMA using the bpy ligand [Wang, X.-S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640].

(12) Kuchta, F. D.; van Herk, A. M.; German, A. L. *Macromolecules* **2000**, *33*, 3641.

MA001397U