

Room Temperature Waterborne ATRP of *n*-Butyl Methacrylate in Homogeneous Alcoholic Media

Steve McDonald and Steve P. Rannard*

Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, CH63 3JW, England

Received August 23, 2001

Of all of the advances in “living” polymerization over the past two decades, atom transfer radical polymerization (ATRP)¹ arguably has the highest potential for direct application in the industrial production of polymers with controlled architecture. Other techniques such as group transfer polymerization,² aluminum porphyrin mediated “immortal” polymerization,³ reversible addition fragmentation chain transfer (RAFT),⁴ and nitroxide-mediated polymerization⁵ either have been studied for many years and found to be difficult to scale up, are too limited in the range of applicable monomers, involve undesirable reactants, or have not been studied enough to fully assess their potential. ATRP also has several drawbacks, most importantly the purification of the final polymer, but many groups continue to develop new methodologies to aid catalyst removal.⁶

The applicability of ATRP has recently been extended to include large volumes of water.⁷ More recently, Armes and co-workers have impressively used water as the sole polymerization solvent and successfully synthesized a range of water-soluble polymers with excellent control of molecular weight, dispersity, and architecture at ambient temperature.⁸ This has huge environmental implications for the large-scale commercial synthesis of controlled polymers.

Several reports of “waterborne” ATRP have been published describing emulsion and dispersion polymerizations at elevated temperature⁹ although no reports have currently been published using water to enhance the homogeneous solution polymerization of hydrophobic monomers. Sawamoto and co-workers have reported the polymerization of methyl methacrylate (MMA) in various alcohols as a comparison with toluene/water mixtures using Ru(II) catalysts at 80 °C.¹⁰ Armes and co-workers, however, have reported an alcohol/water polymerization of 2-hydroxyethyl methacrylate (HEMA) at room temperature,¹¹ and we believe that this is the first report of a homogeneous room temperature synthesis of a water-insoluble polymer from the “living” polymerization of a hydrophilic/water-soluble monomer.

Herein we report the first homogeneous room temperature “waterborne” ATRP of a hydrophobic monomer under “living” conditions to form a hydrophobic polymer.

Poly(*n*-butyl methacrylate) (pBuMA) is a hydrophobic polymer formed from the polymerization of the hydrophobic monomer, *n*-butyl methacrylate (BuMA). Our interest in pBuMA is derived from its unusual solubility in 2-propanol (IPA). To evaluate the viability of an H₂O/IPA polymerization, the tolerance of a solution of pBuMA in HPLC grade IPA ($M_n = 8100$, 2 g in 10 mL) to water was tested by slow addition of small amounts

* Corresponding author. Current e-mail address: steven.rannard@unilever.com.

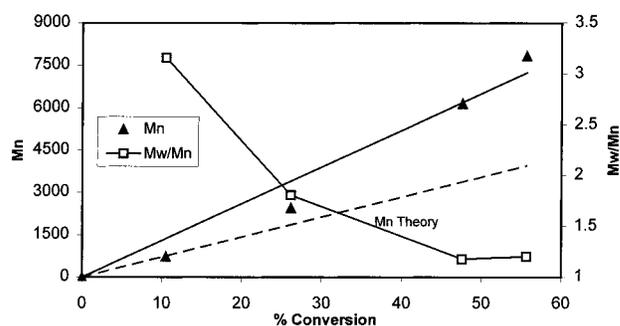


Figure 1. Correlation of M_n and M_w/M_n vs conversion in the 2-propanol solution polymerization of *n*-butyl methacrylate at room temperature.

of water to the solution and allowing time to reach equilibrium before further addition. At >10% (v/v) water content, the solution phase separated into two layers, indicating a maximum amount of water that may be present in a homogeneous ATRP.

Throughout this study a target molecular weight $M_n = 7550$ (degree of polymerization (DP) = 50) was chosen. Each polymerization was degassed using N₂ and involved 35.2 mmol (5 g) of BuMA, 0.7 mmol of initiator, 0.35 mmol of Cu(I)Br, and 0.7 mmol of 2,2'-bipyridine (bpy) ligand, all used as supplied and without purification. All kinetic studies were conducted by gravimetry, and gel permeation chromatography (GPC) analysis was undertaken in THF using a range of MMA standards. The reactions were conducted in 25 mL of solvent or solvent mixture and utilized the tertiary bromide terminated oligoethylene oxide initiator, OEG-Br (MW = 450), reported by Wang and Armes.¹²

Initially, the ATRP of BuMA was studied in 100% IPA solution without added water and evaluated for “living” polymerization behavior. The polymerization proceeded slowly at ambient temperature, only attaining 55% conversion after 4 h, and exhibited poor M_n control (at 55%, $M_n(\text{found}) = 8200$, $M_n(\text{theory}) = 3900$), unusual development of dispersity over the course of the polymerization, and nonlinear correlation of $\ln[M]_0/[M]$ (Figure 1).

The GPC chromatogram of the sample after 1 h showed significant oligomer formation and a separate peak at higher molecular weight. The low molecular weight peaks persisted throughout the later samples, although they become less significant as pBuMA continued to increase in molecular weight and abundance. This result suggests that the reaction underwent significant termination in the initial stages of the polymerization, which explains the lack of molecular weight control.

The addition of water to the IPA solution was expected to have a marked effect on polymer formation, and as phase separation had occurred upon addition of 10% (v/v) water, 7.5% (v/v) water was chosen to avoid the potential complication of precipitation during polymerization. BuMA was fully soluble in this IPA/water mixture, as were the initiator and Cu(I)Br/bpy complex.

Analysis of the polymerization kinetics in the presence of 7.5% (v/v) water showed that the formation of pBuMA is rapid at room temperature, attaining 90% conversion after 6 h (Figure 2), and is much faster than the reported polymerizations of BuMA at elevated

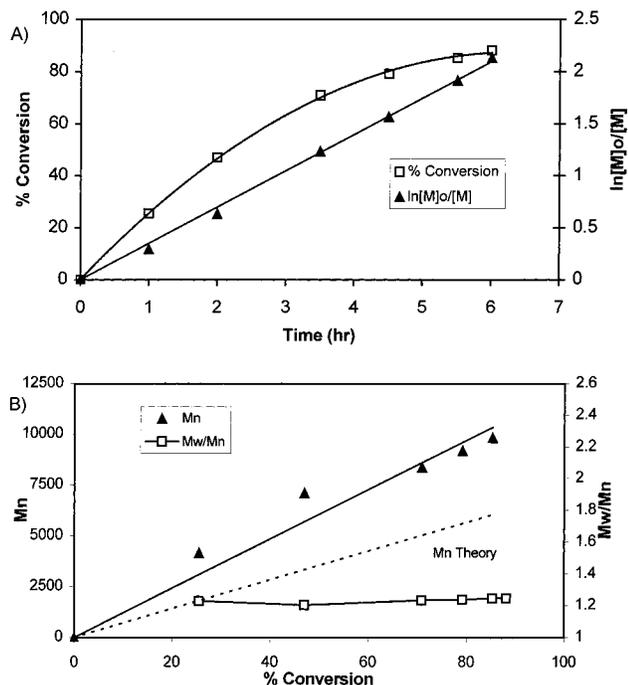


Figure 2. Plots of (A) conversion and $\ln[M]_0/[M]$ vs time and (B) M_n and M_w/M_n vs conversion for the polymerization of *n*-butyl methacrylate in 2-propanol/ H_2O (92.5/7.5 v/v) at room temperature (5 g of monomer in 25 mL of solvent).

temperature¹³ under heterogeneous conditions and the aqueous ATRP of many water-soluble monomers such as oligoethylene oxide methacrylate (OEGMA).¹² The correlation of $\ln[M]_0/[M]$ is extremely good with an $r^2 = 0.9979$ (Figure 2, plot A), showing the absence of termination reactions and a steady concentration of propagating radicals throughout the polymerization.

Comparison of the M_n and M_w/M_n vs conversion (Figure 2, plot B) shows a linear development of molecular weight during the consumption of monomer ($r^2 = 0.949$) and the formation of a controlled dispersity in the early stages which is maintained throughout the polymerization ($M_w/M_n = 1.23$ at 25% conversion, $M_w/M_n = 1.24$ at 90% conversion).

A brief study of the reaction under increased concentration (12.5 mL, IPA/ H_2O (92.5/7.5 v/v)) showed a faster polymerization (90% conversion in 5 h). This is possibly due to a more efficient initial radical production, leading to not only a higher concentration of active species but also an apparent reduction in the control of the polymerization (Figure 3).

A series of polymers of increasing DP (20–80 units) have been synthesized (Table 1). Polydispersity and molecular weight control improved as higher mass material was targeted, with DP = 80, showing good achievement of the target M_n and $M_w/M_n = 1.12$. This may be due to the termination events that occur in the initial stages of the formation of the Cu(I)/Cu(II) equilibrium, leading to oligomers which contribute heavily to the dispersity at low molecular weight but become less significant at higher molecular weights. Further studies of the system will include block copolymer formation.

In conclusion, we report a highly robust polymerization technique for the controlled synthesis of poly(*n*-butyl methacrylate) with no need to purify reagents. We believe this synthesis is the first report of a room temperature “living” polymerization of a hydrophobic

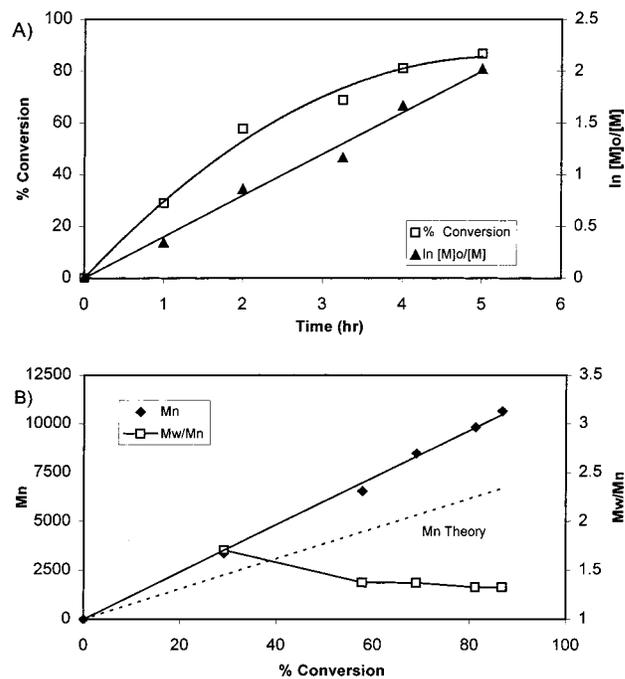


Figure 3. Plots of (A) conversion and $\ln[M]_0/[M]$ vs time and (B) M_n and M_w/M_n vs conversion for the room temperature polymerization of *n*-butyl methacrylate in 2-propanol/ H_2O (92.5/7.5 v/v) at higher monomer concentration (5 g of monomer in 12.5 mL of solvent).

Table 1. Characterization of Poly(*n*-butyl methacrylate) Synthesized in 2-Propanol/ H_2O (92.5/7.2 v/v) at Room Temperature at Low Concentration (5 g of Monomer in 25 mL of Solvent Mixture)

sample ^{a,b}	$[M]_0/[I]_0$	M_n theory	M_n (GPC) ^c	M_w/M_n
1	20/1	3290	6030	1.39
2	50/1	7560	9180	1.25
3	80/1	11800	10650	1.12

^a All reactions left to stir at ambient temperature for 7 h. ^b All reactions gave a purified yield > 90%. ^c Calibrated using MMA standards.

monomer under homogeneous waterborne conditions. Evidence for the “living” nature of the reaction was achieved by analysis of the kinetics of the polymerization, the formation of polymers with low polydispersity, and control of M_n .

References and Notes

- (a) Wang, J. S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (b) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371.
- Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; Rajanbabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
- Inoue, S.; Aida, T.; Kuroki, M.; Hosokawa, Y. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 255.
- Chieffari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
- Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987.
- (a) Haddleton, D. M.; Jackson, S. G.; Bon, S. F. *J. Am. Chem. Soc.* **2000**, *122*, 1542. (b) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4802. (c) Carmichael, A. K.; Haddleton, D. M.; Bon, S. A. F.; Seddon, K. R. *Chem. Commun.* **2000**, 1237.
- Coca, S.; Jasieczek, C. B.; Beers, K. L.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1417.
- (a) Wang, X.-S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817. (b) Malet, F. L. G.; Billingham, N. C.; Armes, S. P. *Polym. Prepr.* **2000**, *41* (2), 1811.

- (c) Ashford, E. J.; Naldi, V.; O'Dell, R.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1999**, 1285. (d) Furlong, S. A.; Armes, S. P. *Polym. Prepr.* **2000**, 41 (1), 450. (e) Wang, X.-S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, 33, 255.
- (9) (a) Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, 38, 4724. (b) Qiu, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **1999**, 32, 2872.
- (10) Nishikawa, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, 32, 2204.
- (11) Robinson, K. L.; Khan, M. A.; de Banez, M. V.; Wang, X. S.; Armes, S. P. *Macromolecules* **2001**, 34, 3155.
- (12) Wang, X.-S.; Armes, S. P. *Macromolecules* **2000**, 33, 6640.
- (13) Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Macromolecules* **1998**, 31, 5951.

MA0115186