Macromolecules **2005,** *38,* 8131−8134

Atom Transfer Radical Polymerization in Microemulsion

Ke Min and Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received July 28, 2005
Revised Manuscript Received August 20, 2005

Extending atom transfer radical polymerization (ATRP) to various aqueous dispersed media not only remains a continuing challenge but also is economically and environmentally important for commercial products.[1−3] The first step at expanding the scope of ATRP in this direction was taken when ATRP was conducted in an emulsion system.[4−6] However, continued research in the field of aqueous biphasic ATRP and other controlled/living radical polymerizations has resulted in the emergence of miniemulsion as the preferred modus operandi because the problem of mass transport of monomers through the aqueous phase can be circumvented in a miniemulsion process, thereby providing significantly improved control over polymerization.[7−9] Homopolymers,[10] block copolymers,[11,12] and gradient copolymers[13] have been successfully prepared in miniemulsion by ATRP. Suspension polymerization is another aqueous heterogeneous system that does not require mass transfer and has also been reported to be successful for ATRP.[14−17]

It is therefore surprising that microemulsion ATRP has not yet been investigated, particularly since microemulsion polymerization processes have been the subject of considerable research interest because of their small latex size and complex structural behavior, resulting in preparation of materials for a broad range of hi-tech applications.[18] These include cleaning formulations, pharmaceutical formulations for improved drug solubilization/delivery, coating formulations, and many others.[19] Because of the small particle size attained in microemulsion systems, the products possess a significantly large interfacial area which leads to an attractive alternative to emulsion-based polymerization procedures for the preparation of ion-containing membranes.[20] Moreover, microemulsion has found application for synthesis of templates for the design of mesoporous structures[21] and opened up possibilities for the preparation of inorganic nanomaterials.[22]

Unlike a regular emulsion polymerization, a microemulsion polymerization system is a thermodynamically stable, optically transparent or translucent, isotropic dispersion of oil in water, containing domains of nanometer dimensions, all stabilized by suitable surfactants.[23−25] The initial microemulsion polymerization systems employed an aliphatic alcohol as a cosurfactant.[26,27] However, subsequently attention has been focused on the kinetics and mechanisms of three-component microemulsion polymerizations containing only water, oil (monomer), and surfactant.[28] Most studies have dealt with the polymerization of hydrophobic monomers, where the initial oil-in-water microemulsion can be polymerized, typically forming a stable latex composed of polymer particles with particle size ranging from 10 to 100 nm. Though small polymeric particles were produced, the polymers usually displayed high molecular weight and broad molecular weight distribution.

A micellar nucleation mechanism is generally accepted for polymerization of hydrophobic monomers in a microemulsion process, which means the polymerizations are postulated to occur in monomer-swollen micelles.[29] Therefore, in microemulsion polymerization, similar to miniemulsion, there are no large monomer droplets (with the size of several micrometers) suspended in the dispersed media prior to polymerization. Since the monomer-solubilizing micelles behave as nanoreactors during microemulsion polymerization and the mass transfer can be essentially ignored, microemulsion polymerization provides a feasible reaction environment for a controlled/living radical polymerization. Additionally, microemulsion was considered a feasible medium for ATRP because there is no need for catalyst transportation during the polymerization.

In this communication, we report the first results of conducting an ATRP in a microemulsion. Both normal and reverse ATRP[30] were examined as initiating procedures for microemulsion ATRP. In addition, the newly developed AGET technique[12,31] was used to provide the most convenient method to initiate an ATRP in a microemulsion system.

To date, an ionic surfactant is usually selected for conventional microemulsion polymerizations to provide better colloidal stability. However, for ATRP in aqueous dispersed media, nonionic surfactants proved to be the best choice.[1] Therefore, Brij 98 was used as the surfactant in this study. As previously discussed, selection of a hydrophobic ligand for formation of the catalyst complex is crucial for a well-controlled ATRP in aqueous dispersed media.[1] Bis(2-pyridylmethyl)octadecylamine (BPMODA) was selected as the ligand for this study since it is sufficiently hydrophobic and therefore can ensure that the catalyst remains inside the organic phase, i.e., the prepolymeric particles.[1] Methyl methacrylate (MMA) was selected as monomer.

Table 1 lists the polymerizations that will be discussed below and provides the stoichiometry for each of the examples in addition to the molecular weight and molecular weight distribution of each polymer prepared.

The control reaction was a conventional radical polymerization of MMA in a microemulsion system with a water-soluble initiator 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50). The nucleation process started 5 min after the injection of the initiator solution, as indicated by the appearance of a bluish color and reduced transparency of the system. This is because of an increase in the size of the disperse phase due to micelle agglomeration as initiation progressed and the higher refractive index of the polymer generated.[32] The final microlatex appeared as a translucent liquid with size of the final particle ~42 nm according to the dynamic light scattering (DLS) measurement (Table 1). The molecular weight distribution of the final polymer was broad, as expected for a conventional radical polymerization.

---

* Corresponding author. E-mail: km3b@andrew.cmu.edu.

10.1021/ma051675v CCC: $30.25

Table 1

no.	process	monomer	$[M]_0$:$[I]_0$:$[cat.]_0$:$[V\text{-}50]_0$:$[ascorbic acid]_0$[b]	[surf.]/[M][c]	DLS[d] D_h (nm)	CV	TEM D (nm)	M_n (g/mol)	PDI
1	conventional	MMA	200:0:0:0.5:0	2.5	42	0.16		61 500	6.10
2	normal ATRP	MMA	200:1:1:0:0	2.5	34	0.17	25 ± 4	bimodal	
3	normal ATRP	MMA	200:1:1:0:0	2	45	0.15		bimodal	
4	reverse ATRP	MMA	200:0:1:0.5:0	2.5	70	0.20	36 ± 15	41 000	1.61
5	AGET ATRP	MMA	200:1:1:0:0.5	2.5	43	0.16	31 ± 3	30 000	1.28
6	AGET ATRP	MMA	200:1:1:0:0.5	1.5	80	0.15		31 000	1.25
7	AGET ATRP	styrene	200:1:1:0:0.5	2.5	38	0.16		17 800	1.33

[a] The reaction temperature was 65 °C for MMA and 80 °C for styrene. Polymer content (100% conversion) was set as 3%. [b] The ATRP initiator was ethyl 2-bromoisobutyrate (EBiB). The catalyst was $CuBr_2$/BPMODA, except for no. 2 and no. 3 (CuBr/BPMODA). [c] Weight ratio of surfactant to monomer. [d] DLS measurement provides average hydrodynamic diameter, D_h, and size distribution index, CV (coefficient of variation), which is obtained as follows: $\bar{D} = \sum_{i=1}^{n} D_i/n$; $S = [\sum_{i=1}^{n}(D_i - \bar{D})^2/(n - 1)]^{1/2}$; $CV = S/\bar{D}$, where $\bar{D}$ is the average diameter, D_i is the diameter of the particle i, n is the total number counted, and S is the particle size standard deviation.

Initially a normal ATRP was attempted in microemulsion prepared by emulsification of catalysts and monomer and surfactant in aqueous suspending media through magnetic stirring. The hydrodynamic diameter (D_h) of initial micelles was around 10 nm according to DLS measurements. After deoxygenating the formed microemulsion, the alkyl halide initiator was added to initiate the polymerization. After the injection of the ATRP initiator, the system turned slightly translucent from a transparent state, indicating a fast nucleation. The nucleation period was short, since the particle size approached the final value after 30 min.

Given the initial micelle size (d = 10 nm), and assuming the micelle volume was occupied by monomer MMA (density = 0.936 g/cm^3), on average there were 5 × 10^{-21} mol × N_A = ~3000 MMA molecules per micelle before polymerization. According to the initial stoichiometry, in each micelle there should be ~15 Cu complexes. For quantitative initiation, ~15 ATRP initiators should diffuse into each micelle generating polymer chains with designed molecular weight $M_n \sim 20\,000$ g/mol. However, since the initial catalyst inside the micelles was exclusively in the Cu(I) state, the polymerization could be initiated by atom transfer from any entering ATRP initiator, leading to a single propagating radical and a single Cu(II) complex in a micelle. If the Cu(II) species stays in the micelle, it could deactivate the growing radical and mediate controlled radical polymerization. Subsequently, if more ATRP initiators enter the micelle and join the polymerization, some termination could occur, as in any ATRP, generating excess Cu(II) species. However, since the Cu(II) complex has much higher solubility in water than Cu(I) complex, it could also diffuse out of the micelle.[33] As discussed, at the initial state only one single Cu(II) species was generated; its escape from the micelle should lead to a rapid conventional radical polymerization and consumption of all MMA in this micelle (ca. 3000 monomer molecules), resulting in a polymer with $M_n \sim 300\,000$ g/mol. Indeed, the polymers produced from normal ATRP in microemulsion displayed two peaks in GPC traces: one peak of $M_n \sim 25\,000$ g/mol with polydispersity of 1.3 and the other peak of $M_n \sim 300\,000$ g/mol with polydispersity of 1.7 (Figure 1).

Nevertheless, after nucleation all the polymerization should occur only inside micelles/polymeric particles, which resulted in a narrow distribution of particle size from normal ATRP in microemulsion. According to DLS analysis, the size of the final latex was ~34 nm. As measured from TEM images (Figure 2), the particle size was slightly smaller (Table 1) because the vacuum applied in TEM analysis results in particle shrinkage due to removal of any attached water molecules.

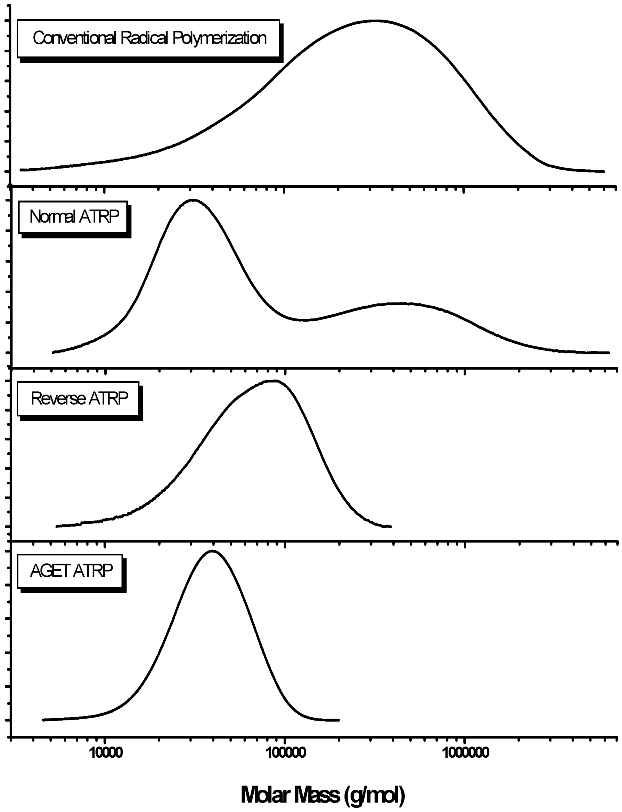

Figure 1. Typical GPC traces of the polymers from conventional radical polymerization, normal ATRP, reverse ATRP, AGET ATRP of MMA in microemulsion.

Normal ATRP was not considered the preferred choice for the initiation process for microemulsion. The relatively long emulsification process (around 30 min) at higher temperature (60 °C) leads to a partial loss of catalysts. The easily oxidized catalyst requires an extremely stringent deoxygenating process. Furthermore, the initial high ratio of [Cu(I)]/[Cu(II)] results in inefficient deactivation and loss of control over polymerization. In contrast, a reverse ATRP is much easier to perform in microemulsion. The Cu(II) complexes, added as activator precursors, are not air-sensitive which leads to a simpler emulsification process. After addition and decomposition of the radical initiator V-50, newly born Cu(I) activator complexes are formed by the reaction of the initiating/propagating radicals and excess Cu(II) species. Cu(I) complexes are more hydrophobic than the Cu(II) complexes, and therefore they

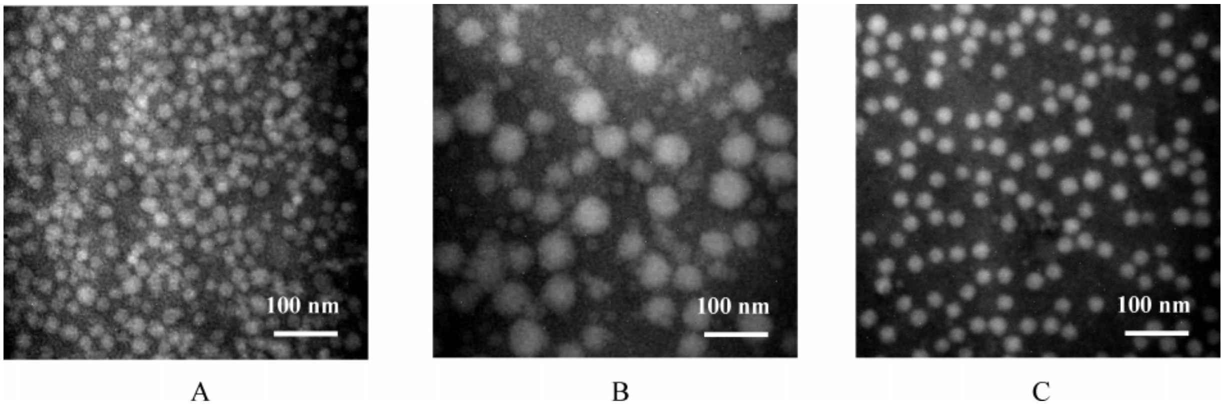

Figure 2. Transmission electronic microscopic (TEM) images of the microlatex from normal ATRP (A), reverse ATRP (B), and AGET ATRP (C).

preferentially stay inside the microlatex. Because the initial catalyst was in the Cu(II) state, the polymerization cannot be initiated until the ratio of [Cu(I)]/[Cu(II)] increased to a sufficient value. This process ensures the presence of deactivators and therefore a better control.

In reverse ATRP the nucleation period was longer than in a normal ATRP because of the slow decomposition of the conventional radical initiator V-50. At 65 °C, the half-lifetime of V-50 is around 2 h. This slow decomposition not only resulted in a larger particle size (D_h = 72 nm) and a broader particle size distribution (as seen in Figure 2) but also led to slow initiation. Consequentially, the molecular weight of the polymers produced from reverse ATRP in microemulsion was higher than theoretical values. Initiation efficiency for V-50 was only around 55%. No bimodality in GPC traces was observed in polymers prepared by reverse ATRP in microemulsion, but the molecular weight distribution was broader than in bulk ATRP.

The newly developed AGET ATRP was expected to be the best choice for microemulsion because it can solve problems arising from both normal ATRP and reverse ATRP. In this new initiation technique, a reducing agent is added to the ATRP system that contains deactivators, Cu(II) complexes. Because no activators are used before polymerization is initiated, the emulsification process is easily performed. Ascorbic acid was selected as the reducing agent because it is water-soluble. Therefore, it can be completely dissolved in aqueous phase and react with Cu(II) complexes either at the surface of the monomer swollen micelles or in aqueous phase.[12] On one hand, the activation process is efficient since in AGET ATRP all initiators are already present in the organic phase, and fast redox reaction between the reducing agent and Cu(II) is applied instead of the slow decomposition of conventional radical initiators in a reverse ATRP. On the other hand, the deactivation is also efficient because the initial catalyst is present in the deactivating Cu(II) state. This provides efficient deactivation and consequently fine control over polymerization.

The final particle size in AGET ATRP was comparable to that obtained in the control reaction or the normal ATRP process, and the size distribution was very narrow (Figure 2).

The final particle size was affected by the ratio of the surfactant to the monomer. By decreasing surfactant concentration (Table 1, no. 2 and no. 3, no. 5 and no. 6), a stable microlatex was still obtained but with a larger particle size.

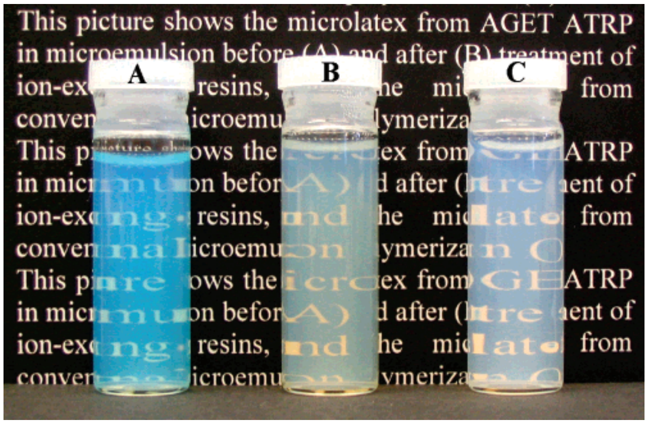

Figure 3. Appearance of microlatex from ATRP in microemulsion before (A) and after (B) treatment of ion-exchange resins and the microlatex from conventional microemulsion polymerization (C).

Styrene is another monomer which has been successfully polymerized by ATRP in microemulsion (Table 1, no. 7). The polymerization rate was slower as compared with MMA using the same catalyst system. Nevertheless, a controlled polymerization was attained with the final molecular weight M_n = 17 800 g/mol and PDI = 1.33. The final product was a stable translucent microlatex with the D_h = ~38 nm.

Despite the difference among the initiation techniques, ATRP in microemulsion resulted in the formation of translucent stable microlatexes with particle size around 40 nm. The small particle size indicates a relatively large surface area, which suggests that after the polymerization has been terminated by exposure to air the resulting Cu(II) complexes can be easily removed by surface exchange treatments. Dowex MSC-1 ion-exchange resin was used for an exemplary treatment, and the resin was stirred together with the microlatex after ATRP for 2 h. It was observed that the blue color from the microemulsion, resulting from the presence of Cu(II), almost completely disappeared. The microlatex showed a similar stability and appearance to that from a conventional microemulsion polymerization (Figure 3).

In conclusion, we have demonstrated that ATRP can be successfully carried out in a microemulsion system resulting in the preparation of stable translucent microlatexes. The polymerization of methyl methacrylate and styrene was well controlled, resulting in small particles with narrow particle size distribution. The recently developed initiation technique, AGET ATRP, was better than either normal ATRP or reverse ATRP in microemulsion, not only because it is easily performed but also because a better control was obtained over both the polymerization and the particle size. This success expands the scope of ATRP and other controlled radical polymerization processes.

Acknowledgment. The financial support from NSF grant (CHE-04-05627) and the CRP Consortium at Carnegie Mellon University is greatly appreciated. Ke Min acknowledges support from Bayer Fellowship.

Supporting Information Available: Experimental part including description of all materials and their purification, polymerization methods, and measurements techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Qiu, J.; Charleux, B.; Matyjaszewski, K. *Prog. Polym. Sci.* **2001**, *26*, 2083−2134.
(2) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(3) Matyjaszewski, K. *Chem.—Eur. J.* **1999**, *5*, 3095−3102.
(4) Makino, T.; Tokunaga, E.; Hogen-Esch, T. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 288−289.
(5) Gaynor, S. G.; Qiu, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5951−5954.
(6) Chambard, G.; De Man, P.; Klumperman, B. *Macromol. Symp.* **2000**, *150*, 45−51.
(7) Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4724−4734.
(8) Cunningham, M. F. *C. R. Chim.* **2003**, *6*, 1351−1374.
(9) de Brouwer, H.; Tsavalas, J. G.; Schork, F. J.; Monteiro, M. J. *Macromolecules* **2000**, *33*, 9239−9246.
(10) Li, M.; Min, K.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 2106−2112.
(11) Li, M.; Jahed, N. M.; Min, K.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 2434−2441.
(12) Min, K.; Gao, H.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2005**, *127*, 3825−3830.
(13) Min, K.; Li, M.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3616−3622.
(14) Lecomte, P.; Drapier, I.; Dubois, P.; Teyssie, P.; Jerome, R. *Macromolecules* **1997**, *30*, 7631−7633.
(15) Sarbu, T.; Pintauer, T.; McKenzie, B.; Matyjaszewski, K. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3153−3160.
(16) Bicak, N.; Gazi, M.; Tunca, U.; Kucukkaya, I. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1362−1366.
(17) Limer, A.; Heming, A.; Shirley, I.; Haddleton, D. *Eur. Polym. J.* **2005**, *41*, 805−816.
(18) Chow, P.; Gan, L. M. *Adv. Polym. Sci.* **2005**, *175*, 257−298.
(19) Lindman, B.; Friberg, S. E. In *Handbook of Microemulsion Science and Technology*; Kumar, P., Mittal, K. L., Eds.; Marcel Dekker: New York, 1999.
(20) Chow, P. Y.; Chew, C. H.; Ong, C. L.; Wang, J.; Xu, G.; Gan, L. M. *Langmuir* **1999**, *15*, 3202−3205.
(21) El-Safty, S. A.; Hanaoka, T.; Mizukami, F. *Chem. Mater.* **2005**, *17*, 3137−3145.
(22) Cao, M.; Wu, X.; He, X.; Hu, C. *Langmuir* **2005**, *21*, 6093−6096.
(23) Gilbert, R. G. *Emulsion Polymerization*; Academic Press: London, 1995.
(24) Antonietti, M.; Basten, R.; Lohmann, S. *Macromol. Chem. Phys.* **1995**, *196*, 441−466.
(25) Candau, F. *Polym. Organ. Media* **1992**, 215−282.
(26) Stoffer, J. O.; Bone, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2641−2648.
(27) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4279−4280.
(28) Ferrick, M. R.; Murtagh, J.; Thomas, J. K. *Macromolecules* **1989**, *22*, 1515−1517.
(29) Kuo, P. L.; Turro, N. J.; Tseng, C. M.; El-Aasser, M. S.; Vanderhoff, J. W. *Macromolecules* **1987**, *20*, 1216−1221.
(30) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7572−7573.
(31) Jakubowski, W.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 4139−4146.
(32) Guo, J. S.; El-Aaser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 691−710.
(33) Matyjaszewski, K.; Qiu, J.; Tsarevsky, N. V.; Charleux, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4724−4734.

MA051675V