ACS Macro Letters

Mini Monomer Encapsulated Emulsion Polymerization of PMMA Using Aqueous ARGET ATRP

Roselynn Cordero,^{†,‡}[®] Ali Jawaid,[§] Ming-Siao Hsiao,[§] Zoë Lequeux,[†] Richard A. Vaia,[§][®] and Christopher K. Ober^{*,†}[®]

[†]Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States [‡]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States [§]Air Force Research Laboratory, Wright-Patterson Air Force Base, Dayton, Ohio 45433, United States

S Supporting Information

ABSTRACT: A new emulsion polymerization based on Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) has been developed to produce poly(methyl methacrylate) (PMMA). The critical components of single-pot synthesis via a mini Monomer Encapsulated ARGET ATRP emulsion polymerization will be discussed. In this method, monomer is isolated in a micelle by pre-emulsification in a nonionic surfactant through high power stirring while acetone is introduced to the polymerization to aid in reactant transport and tetrabutylammonium salts are used as phase transfer agents. Polymerizations using tetrabutylammonium bromide (TBAB) were more controlled and demonstrated low $D (M_w/M_n < 1.17)$, where those using tetrabutylammonium chloride (TBAC) exhibited higher $D (M_w/M_n > 1.50)$. First-order linear kinetics for MMA polymerizations at 100 mM TBAB was demonstrated, while the reactions deviated from linearity at higher concentrations of TBAB and all concentrations of TBAC.

D ispersed phase-controlled radical polymerization has recently advanced in such water-borne systems as microemulsion, miniemulsion, and emulsion polymerization due to the development of living polymerization options.¹⁻⁶ These aqueous dispersed reactions use mild conditions, are eco-friendly, and provide a high safety margin for industrial scale-up due to effective heat dissipation.⁷ Miniemulsion polymerization, for example, has recently been the preferred method for copolymerizing highly water-insoluble monomers that are difficult to polymerize in emulsion due to limited transport through the aqueous phase.¹ By coupling atom transfer radical polymerization, we gain the ability to create narrow disperset polymers.⁸⁻¹⁰

ARGET ATRP has been previously implemented in miniemulsion and emulsion polymerization offering controlled polymerizations in environmentally benign systems.^{11–13} ARGET ATRP typically uses parts per million levels of catalyst suppressing any side reactions between the chain end and the catalyst, thereby allowing the formation of high molecular weight polymers with low dispersity.^{14,15} ARGET ATRP also employs a reducing agent (e.g., ascorbic acid or tin(II) 2-ethylhexanoate) to reduce the oxidatively stable Cu^{II} –Br₂/ligand species to Cu^{I} –Br/ligand activator to create a reducing/reactivating cycle that eliminates radical traps (e.g., oxygen). Although ARGET ATRP in emulsion systems has many advantages, commercially available ATRP ligands (e.g., TPMA and Me₆TREN) that perform well in low-catalyst concent



trations are not useful in aqueous dispersed media because of their higher affinity toward water than the oil-phase, leading to uncontrolled polymerizations.¹³

Recently, Wang et al.¹¹ successfully conducted a miniemulsion polymerization using TPMA ligand and the anionic surfactant, sodium dodecyl sulfate (SDS); however, emulsion polymerizations with TPMA and a nonionic surfactant still remain a challenge. Another challenge of water-based ATRP is controlling localization of the reaction, something that takes place naturally in conventional emulsion polymerization, but is often complex in other dispersed polymerization reactions.

In this report, our intention is to use some of the recent ideas of ARGET ATRP in emulsion and miniemulsion polymerization, combined with ideas of reaction localization first developed by Ugelstad,^{16–18} to create an emulsion polymerization method for methyl methacrylate that addresses the limitations of traditional dispersed polymerizations. We introduce here mini monomer encapsulated (mini Me) ARGET ATRP emulsion polymerization that circumvents many of the issues of monomer transport through an aqueous phase by shifting the limiting step of the polymerization.¹⁹ The incorporation of acetone to aid solubility of several components in the aqueous phase, the use of a phase transfer agent such as

Received: January 13, 2018 Accepted: March 16, 2018



"The polymerization begins with (A) a monomer encapsulated micelle and ATRP catalyst, ligand, TBAB, and initiator dissolved in the aqueous phase. Slow addition of ascorbic acid into the reaction reduces the $Cu^{II}-Br_2/TPMA$ deactivator to the $Cu^{I}-Br/TPMA$ activator species with initiation occurring in the aqueous phase. (B) These ATRP components are transported in and out of the micelle by TBAB. Polymerization occurs within the micelle until (C) polymeric nanoparticles are formed. The aqueous phase is composed of 20% acetone and 80% water.

tetrabutylammonium bromide (TBAB) or tetrabutylammonium chloride (TBAC) to shuttle into the micelle halogen ion, a water-soluble initiator, and a transition metal catalyst are key aspects to this polymerization system.

This combination allows the use of commercially available ligand (TPMA) affording controlled polymerizations with low D (<1.17) and molecular weights over 70,000 g/mol. The halide associated with the phase transfer agent has been found to be crucial in this study as it will dictate the rate of polymerization as well as the dispersity. A faster rate and lower dispersities are observed when TBAB is used as the phase transfer agent due to faster exchange of the halide at the chain end.

Scheme 1 outlines a proposed mechanism to our emulsion system. There are two major differences between prior work in this area and mini Me ARGET ATRP emulsion polymerizations. The first is the introduction of acetone to the aqueous continuous phase and the second is the use of a tetrabutylammonium halide salt whose purpose is 2-fold. First, it serves as the source of extra halide in ARGET ATRP to form the stable deactivator and increase control of the polymerization.¹⁵ Second, it is used as a phase transfer agent to aid in the transport of transition metal catalyst into the micelle. Ascorbic acid is slowly fed into the reaction vessel, reducing Cu^{II}-Br₂/TPMA (deactivator) to Cu^I-Br/TPMA (activator), allowing for the polymerization to commence once it enters the monomer swollen micelle. The ratio of monomer to initiator was chosen according to a similar ratio used by Simakova et al.¹⁵ in aqueous ARGET ATRP. Pluronic F127 was the nonionic surfactant of choice with an HLB of 22 illustrating superiorresults over other nonionic surfactants. Five halide salts were tested in this system: TBAB, TBAC, tetramethylammonium bromide (TMAB), sodium chloride (NaCl), potassium bromide (KBr).

The tetraalkylammonium salts demonstrated higher activity in shuttling the transition metal ligand due to their finite solubility in both phases, thus allowing it to shuttle between phases. On the other hand, the inorganic salts exhibited inactivity due to their failure to penetrate the micelle, making them ineffective. Polymerizations performed with TBAB demonstrated higher molecular weights and lower D (<1.20). The polymerization starts with a monomer-swollen micelle in a solution of 1:4 acetone/water, a ratio that offered optimal results. The ATRP transition metal catalyst (Cu^{II}-Br₂/TPMA), TBAB, and hydrophilic ATRP initiator N-(2-aminoethyl)-2bromo-2-methylpropanamide (OBr) are also dissolved in the aqueous continuous solvent. Initiation by OBr is thought to occur in the aqueous phase, producing oligomeric PMMA, which is then absorbed into the micelle or transported via the phase transfer agent.

Molecular weights for polymerizations with both TBAC and TBAB are very similar in the lower concentration range with M_n for 30 and 50 mM being 68,000 and 73,000 g/mol, respectively (Figure 1A). Although the final molecular weights are similar within this lower range of salt concentrations, the polymer dispersities were significantly different with TBAC displaying D above 1.6, while D with TBAB was below 1.2 (Figure 1B). When salt concentrations reached 100 mM, MMA polymerization rates for TBAB continued within the same molecular weight range (~74,000 g/mol) as the lower concentration TBAB reactions (Figure 1A). The dispersities of the resulting polymers with 100 mM TBAB remained quite low ($D \approx 1.14 - 1.17$) throughout the polymerization, indicative of a fast exchange between active sites and the dormant species (Figure 1B). On the contrary, at 100 mM TBAC, the rate dramatically decreased giving a final molecular weight of \sim 55,000 g/mol after a 6 hour polymerization.

Letter



Figure 1. (A) Effect of halide salt concentration (30, 50, 100, and 300 mM) on molecular weight of PMMA (ascorbic acid feeding rate = 23 nmol/min). (B) Dispersity of MMA polymerization as a function of TBAC and TBAB concentrations. $[M]_0 = 0.518$ M, $[I]_0 = 1$ mM, $[CuBr_2] = 0.075$ mM. All polymerizations were conducted at 30°C for 6 h.

The high stability of the C–Cl bond at the chain end produces an inefficient propagator in mini ME emulsion polymerization compared to the C–Br bond. Because of this slower rate, not all the chain ends are available to propagate simultaneously, thus broadening the dispersity. On the other hand, because the C–Br bond is less stable, propagation is faster and the accessibility of the monomer to the chain end is higher leading to fast but simultaneous propagation of the chain ends. The dispersity is thus controlled by the availability of monomer to the chain end where propagation occurs. If the chain end is inaccessible to monomer, not only does a reduced reaction rate occur, but control will be lost during the polymerization.

As salt concentrations were increased from 100 mM to 300 mM, the polymerization rates decreased giving a final molecular weight of ~55,000 g/mol for MMA polymerizations at 300 mM TBAB with a slightly higher D (<1.34; Figure 1B, Table S1). Alternatively, rates steadily decreased with a more dramatic effect in polymerizations with TBAC showing a final molecular weight of ~48,000 g/mol at 300 mM TBAC with a D > 3.0 (Figure 1B, Table S1). De Paoli et al.²⁰ observed a similar phenomenon of a decrease in rate of polymerization with increasing concentration of either Cl⁻ and Br⁻ in their ATRP

polymerizations. It was shown that the real activator in ATRP is the Cu^IL⁺ species and Cl⁻ and Br⁻ have different affinities to this activator. They explained that the effect of Br⁻ on K_{act} is smaller than the effect of Cl⁻ and is related to the speciation of Cu^I, which, for any given concentration of X⁻, produces a higher fraction of the activator in the presence of Br- than Cl^{-.20} The overall decrease in rates with increasing X⁻ concentrations are attributed to the production of inactive species (Figure 1A).

To assess the effect the cation has on the reaction mechanism, two inorganic halide salts were utilized, KBr and NaCl. When these salts were employed, polymerization did not occur (Table S2). Figure 2 (inset: left) illustrates an image of a



Figure 2. Fourier Transform Infrared Spectroscopy (FTIR) of polymerizations of MMA with TBAB or NaCl as halide salt in Pluronics F-127 surfactant (inset: mini ME emulsion with NaCl (left) and TBAB (right)).

reaction mixture when NaCl was used and its appearance did not change from when the reaction commenced. Figure 2 (inset: right) illustrates when the polymerization was conducted with TBAB. The solution transforms from cloudy and colorless to blue and transparent. This blue scattering is due to the Tyndall effect as the polymeric particles produced in the dispersed phase remained extremely small. The inability to produce PMMA when the inorganic salts are used is likely due to the localization of these salts in the aqueous phase and their limited ability to enter the micellar phase. As there is a large excess of salt compared to the CuBr₂, ligand, and initiator ATRP components, these components will also likely remain in the aqueous phase with the salt, therefore, impeding the polymerization.

Figure 2 further confirms the ineffectiveness of the inorganic salts (KBr and NaCl) in the polymerization of PMMA with mini ME emulsions. The carbonyl peak at 1728 cm⁻¹ associated with PMMA is not present after purification when mini ME emulsions are done with NaCl. When TBAB is utilized, the strong carbonyl peak is apparent after purification. Unswollen micelles were measured to have a diameter of 11 nm using dynamic light scattering measurements (DLS; Figure 3A), while monomer swollen micelles were measured to be 21 nm (Figure 3B). The final particle size was measured as 54 nm using DLS (Figure 3C). The reaction medium was viewed under an optical microscope before the start of the polymerization and revealed few small sparsely dispersed monomer droplets (~2 μ m; Figure S3). This indicates that, although monomer droplets exist in this emulsion system, most of the monomer is either in the aqueous phase or in monomer swollen micelles.



Figure 3. Particle size distribution of (A) Pluronics F-127 micelle alone, (B) monomer swollen micelle, and (C) polymer particle after mini Me emulsion polymerization occurred. Ascorbic acid feeding rate = 23 nmol/min, $[M]_0$ = 0.518 M, $[I]_0$ = 1 mM, $[CuBr_2]$ = 0.075 mM, [TBAB] = 100 mM. All polymerizations were conducted at 30°C for 6 h.

To compare the diffusion rate of the phase transfer catalyst in mini ME emulsion reactions, a less bulky cation on the phase transfer salt, TMAB, was employed. Polymerizations in which TMAB was utilized as the halide salt produced polymer with lower molecular weights and higher D than those done with TBAB; however, the polymerizations were more controlled than those with TBAC (Table S1). Plots of $\ln([M]_0/[M])$ versus time were obtained and used to compare phase transfer salts at 100 mM concentrations (Figure S1B). This plot demonstrates the relative linearity of polymerizations with TBAB, as also shown in Figure 4A, and the nonlinear nature of the polymerizations in 100 mM TBAC and TMAB. The bulkiness of the cation is pivotal, as the diffusion into the micelle appears to be faster with TBAB than with TMAB. This rate of diffusion becomes the limiting step of the polymerization. If the diffusion of the halide into the micelle is slow, such as in the case of TMAB, the overall polymerization rate slows and is associated with higher dispersity.

Figure 4B demonstrates a plot of $\ln([M]_0/[M])$ for MMA polymerizations with 100 and 300 mM TBAB and TBAC. The linearity of MMA polymerizations with TBAB indicates that the number of propagating species remains constant as described by the persistent radical effect (PRE).²¹ This linearity starts to deviate as the concentration of the salt increases; a very similar mechanism to that mentioned previously with TBAC. These plots demonstrate that faster polymerization rates and exchange result in polymers with *D* lower than 1.2 in a mini ME ARGET ATRP emulsion system.

Finally, the effect of acetone on the polymerization was evaluated and the results are summarized in Table S2. In 1979, John Ugelstad developed a seeded emulsion polymerization involving the addition of a low molecular weight water-soluble solvent, such as acetone, to "activate" or allow transport of monomer through the aqueous phase to swell a seed particle due to a designed-in increased entropy of mixing in the particles. Acetone was then removed, effectively trapping the water-insoluble monomer in the seed particles, thereby localizing the monomer where it could be polymerized in the oil phase (more than $100 \times$ the initial seed volume).¹⁶

As a control experiment in our studies using TBAB, acetone was not added to the reaction vessel at the start of the



Letter



Figure 4. (A) First-order kinetic plot for polymerization of MMA in mini ME ARGET emulsion ATRP with 100 and 300 mM TBAB and TBAC. (B) Kinetic plot for polymerization of MMA with mini ME ARGET ATRP emulsion conducted with 100 mM of TBAB. $[M]_0 =$ 0.518 M, $[I]_0 = 1 \text{ mM}$, $[CuBr_2] = 0.075 \text{ mM}$ and ascorbic acid feeding rate at 23 nmol/min. All polymerizations were conducted at 30°C. Note: Lines were provided to guide the eye.

polymerization resulting in no polymer production. Another experiment was performed under the same conditions except acetone was added to the reaction vessel along with the preemulsified monomer swollen micelles. This mixture was stirred for 10 min and then acetone was evaporated. This experiment resulted in a lower molecular weight polymer (~40,000 g/mol) and a higher D (1.37) than under preferred conditions with TBAB, confirming the importance of using acetone as a shuttle system throughout the entire polymerization. Another control experiment involved the utilization of a hydrophobic initiator, methyl α -bromoisobutyrate, in lieu of the hydrophilic OBr initiator. The results of this experiment were similar to the previous control experiment with acetone evaporation. Polymer conversion was lower resulting in a molecular weight of 41,281 g/mol with a dispersity of 1.41, indicating that the location of initiation is pivotal to overall control of the polymerization.

In this work, an emulsion polymerization method based on ARGET ATRP was developed to polymerize MMA in an aqueous dispersion. Mini ME ARGET ATRP emulsion polymerization resulted in well-defined PMMA with dispersities as low as 1.14. By localizing the propagation and controlling the availability of monomer, we provide a framework that addresses the challenges of traditional miniemulsion and emulsion polymerizations. This was done by (a) the incorporation of acetone and (b) using a phase transfer agent. Acetone was used as an aid for reaction localization that helped lower molecular

weight dispersity. The presence and choice of halide in the phase transfer catalyst was also pivotal in the reaction rate and overall control of the polymerization. Introduction of bromide anion to the oil phase using TBAB was shown to provide excellent polymerization results with dispersities as low as 1.14 and $M_{\rm n}$ as high as 74,088 g/mol. A linear kinetic plot was obtained with polymerizations using TBAB thus suggesting a constant number of propagating species, proving it to be a facile method of PMMA polymerization. Polymerizations using TBAC as phase transfer agent generated polymer with much higher dispersities (D > 1.5) and slower polymerization rates. The use of inorganic salts in the emulsion process impeded polymerization due to a lack of transport into the oil phase micelle, while a less bulky cation (TMAB) offered weaker partitioning into the micelle, thus, lowering the rate and increasing D. It was concluded that faster rates of polymerization are associated with lower dispersities and higher molecular weights; these rates strongly depended on the phase transfer catalyst, the halide used, and the nature of the cation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacro-lett.8b00038.

Experimental section (PDF).

AUTHOR INFORMATION

Corresponding Author

*E-mail: cko3@cornell.edu.

ORCID 0

Roselynn Cordero: 0000-0002-6115-085X Richard A. Vaia: 0000-0003-4589-3423 Christopher K. Ober: 0000-0002-3805-3314

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the Air Force Office of Scientific Research (AFOSR FA9550-17-1-0038), and for prior support, the Air Force Research Laboratory (AFRL). This work made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF MRSEC Program (DMR-1719875).

REFERENCES

 Cunningham, M. F. Controlled/Living Radical Polymerization in Aqueous Dispersed Systems. *Prog. Polym. Sci.* 2008, 33 (4), 365–398.
 Asua, J. M. Emulsion Polymerization: From Fundamental Mechanisms to Process Developments. *J. Polym. Sci., Part A: Polym. Chem.* 2004, 42 (5), 1025–1041.

(3) Aizpurua, I.; Amalvy, J.; Barandiaran, M. J.; De La Cal, J. C.; Asua, J. M. Recent Developments in Miniemulsion Polymerization. In *Macromol. Symp.*; Wiley Online Library, 1996; Vol. 111, pp 121–131.
(4) Min, K.; Matyjaszewski, K. Atom Transfer Radical Polymerization

in Aqueous Dispersed Media. Open Chem. 2009, 7, 4.

(5) Wei, Y.; Liu, P.; Wang, W.-J.; Li, B.-G.; Zhu, S. Well-Controlled and Stable Emulsion ATRP of MMA with Low Surfactant Concentration Using Surfactant-ligand Design as the Copper Capture Agent. *Polym. Chem.* **2015**, *6* (15), 2837-2843.

(6) Kagawa, Y.; Zetterlund, P. B.; Minami, H.; Okubo, M. Atom Transfer Radical Polymerization in Miniemulsion: Partitioning Effects of Copper(I) and Copper(II) on Polymerization Rate, Livingness, and Molecular Weight Distribution †. *Macromolecules* **2007**, *40* (9), 3062– 3069.

(7) Schork, F. J.; Luo, Y.; Smulders, W.; Russum, J. P.; Butté, A.; Fontenot, K. Miniemulsion Polymerization. In *Polymer Particles*; Okubo, M., Ed.; Springer: Berlin, Heidelberg, 2005; Vol. 175, pp 129–255.

(8) Fantin, M.; Park, S.; Wang, Y.; Matyjaszewski, K. Electrochemical Atom Transfer Radical Polymerization in Miniemulsion with a Dual Catalytic System. *Macromolecules* **2016**, *49* (23), 8838–8847.

(9) Bombalski, L.; Min, K.; Dong, H.; Tang, C.; Matyjaszewski, K. Preparation of Well-Defined Hybrid Materials by ATRP in Miniemulsion. *Macromolecules* **2007**, *40* (21), 7429–7432.

(10) Rusen, E.; Mocanu, A. Atom Transfer Radical Emulsion Polymerization (Emulsion ATRP) of Styrene with Water-Soluble Initiator. *Colloid Polym. Sci.* **2013**, *291* (9), 2253–2257.

(11) Wang, Y.; Lorandi, F.; Fantin, M.; Chmielarz, P.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. Miniemulsion ARGET ATRP via Interfacial and Ion-Pair Catalysis: From Ppm to Ppb of Residual Copper. *Macromolecules* **201**7, *50* (21), 8417–8425.

(12) Cheng, C.; Shu, J.; Gong, S.; Shen, L.; Qiao, Y.; Fu, C. Synthesis and Use of a Surface-Active Initiator in Emulsion Polymerization under AGET and ARGET ATRP. *New J. Chem.* **2010**, 34 (1), 163–170.

(13) Elsen, A. M.; Burdyńska, J.; Park, S.; Matyjaszewski, K. Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization in Miniemulsion with 50 Ppm of Copper Catalyst. ACS *Macro Lett.* **2013**, *2* (9), 822–825.

(14) Kwak, Y.; Magenau, A. J. D.; Matyjaszewski, K. ARGET ATRP of Methyl Acrylate with Inexpensive Ligands and Ppm Concentrations of Catalyst. *Macromolecules* **2011**, *44* (4), 811–819.

(15) Simakova, A.; Averick, S. E.; Konkolewicz, D.; Matyjaszewski, K. Aqueous ARGET ATRP. *Macromolecules* **2012**, *45* (16), 6371–6379.

(16) Ugelstad, J.; Kaggerud, K. H.; Hansen, F. K.; Berge, A. Absorption of Low Molecular Weight Compounds in Aqueous Dispersions of Polymer-Oligomer Particles, 2. A Two Step Swelling Process of Polymer Particles Giving an Enormous Increase in Absorption Capacity. *Makromol. Chem.* **1979**, *180* (3), 737–744.

(17) Ugelstad, J.; El-Aasser, M. S.; Vanderhoff, J. W. Emulsion Polymerization: Initiation of Polymerization in Monomer Droplets. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11* (8), 503–513.

(18) Ugelstad, J.; Mfutakamba, H. R.; Mork, P. C.; Ellingsen, T.; Berge, A.; Schmid, R.; Holm, L.; Jorgedal, J.; Hansen, F. K.; Nustad, K. Prepartation and Application of Monodisperse Polymer Particle. *J. Polym. Sci., Polym. Symp.* **1985**, *72*, 225–240.

(19) Schork, F. J.; Luo, Y.; Smulders, W.; Russum, J. P.; Butté, A.; Fontenot, K. Miniemulsion Polymerization. In *Polymer Particles*; Okubo, M., Ed.; Springer: Berlin, Heidelberg, 2005; Vol. 175, pp 129–255.

(20) De Paoli, P.; Isse, A. A.; Bortolamei, N.; Gennaro, A. New Insights into the Mechanism of Activation of Atom Transfer Radical Polymerization by Cu(i) Complexes. *Chem. Commun.* **2011**, 47 (12), 3580.

(21) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101* (9), 2921–2990.