

A Silver Bullet: Elemental Silver as an Efficient Reducing Agent for Atom Transfer Radical Polymerization of Acrylates

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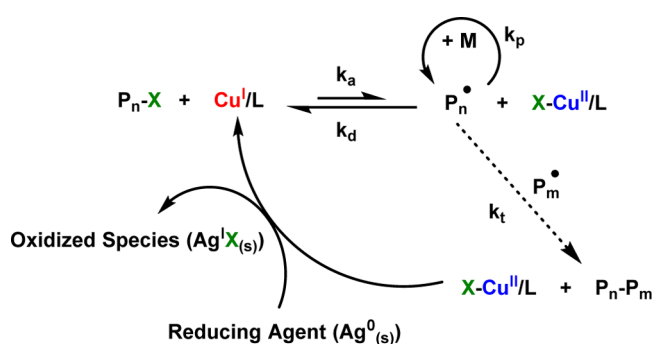
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S Supporting Information

ABSTRACT: Elemental silver was used as a reducing agent in the atom transfer radical polymerization (ATRP) of acrylates. Silver wire, in conjunction with a CuBr₂/TPMA catalyst, enabled the controlled, rapid preparation of polyacrylates with dispersity values down to $\bar{D} = 1.03$. The silver wire in these reactions was reused several times in sequential reactions without a decline in performance, and the amount of copper catalyst used was reduced to 10 ppm without a large decrease in control. A poly(*n*-butyl acrylate)-*block*-poly(*tert*-butyl acrylate) diblock copolymer was synthesized with a molecular weight of 91 400 and $\bar{D} = 1.04$, demonstrating good retention of chain-end functionality and a high degree of livingness in this ATRP system.

Since the conception of reversible deactivation radical polymerization (RDRP) in the 1990s, these types of methodologies have revolutionized polymer chemistry.¹ Particularly, RDRP techniques have allowed for the synthesis of polymers with very narrow molecular weight distributions (MWDs), predetermined molecular weights (MWs), and remarkable conservation of chain-end functionality, previously only achievable via ionic polymerization.² Atom transfer radical polymerization (ATRP) is among the most commonly utilized RDRP methods.³ In addition to nitroxide-mediated polymerization⁴ and reversible addition–fragmentation chain transfer polymerization,⁵ ATRP achieves its control of polymer chain growth and architecture through a transition metal-catalyzed activation/deactivation redox cycle of alkyl halides and alkyl radicals, respectively.⁶ Traditionally, a large concentration of transition metal catalyst was required to successfully conduct an ATRP due to unavoidable radical termination resulting in a buildup of deactivator species, consistent with the persistent radical effect.^{6a,7} However, within the past decade, the use of reducing agents has allowed for a decrease in the initial amount of metal catalyst necessary for an efficient ATRP down to the ppm level.⁸ Regeneration of the activator species from a deactivator complex is facilitated through a variety of different methods, including the addition of azo radical initiators (Initiators for Continuous Activator Regeneration, ICAR ATRP)⁹ or chemical reducing agents (Activator Regenerated by Electron Transfer, ARGET ATRP),¹⁰ use of electrical current (*e*ATRP)¹¹ or light (photoATRP),¹² or addition of zerovalent metals (Supplemental Activator and Reducing Agent, SARA ATRP) (Scheme 1).¹³ Zerovalent metals were

Scheme 1. Proposed Mechanism of ATRP in the Presence of Ag⁰



first applied to ATRP processes in 1997,¹⁴ where Cu⁰ (or Fe⁰) was used to both reduce Cu^{II} deactivator complexes to Cu^I activator species via comproportionation and directly activate alkyl halide species in solution. In SARA ATRP (also known as SET-LRP), Cu⁰ plays an active role in radical generation and plausible radical termination.^{13a,15} Therefore, a reducing agent that acts via single-electron transfer and is inert to radical generation and termination has long been sought after, but other metals such as Fe⁰, Mg⁰, or Zn⁰ operate via a SARA mechanism.¹⁶ We report here the use of Ag⁰ as a previously unexplored ARGET reagent.

The use of elemental silver as a reducing agent is attractive for many reasons. Silver has only two readily attainable oxidation states (0 and +1), so reduction with Ag⁰ would likely be a single-electron process.¹⁷ Both Ag⁰ and the proposed oxidized species (Ag^IX) are insoluble in most reaction media, which would simplify purification processes and lessen product contamination by transition metals, as well as open the possibility of application on an industrial scale.¹⁸ Lastly, Ag⁰ is relatively inert toward typical polymerization reagents, which could minimize or eliminate undesirable radical generation or termination events that are commonly observed in SARA ATRP and other reduced-catalyst techniques.^{13a} Herein, we report the first use of Ag⁰ as a heterogeneous reducing agent for copper-mediated ATRP.

The rate-determining step in many ATRP processes with low catalyst loading is the (re)generation of a low-valent activator

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species.⁹ Therefore, it is of great importance to determine the efficiency of this (re)generation process in new ATRP systems. To achieve this, the heterogeneous reduction of $\text{CuBr}_2/\text{TPMA}$ ($\text{TPMA} = \text{tris}(2\text{-pyridylmethyl})\text{amine}$)¹⁹ by Ag^0 in polymerization media was monitored as a function of time. Alkyl halide initiator was excluded from these reactions to allow for simple and quantitative determination of reduction rates. As one of the most commonly used ligands for Cu-mediated ATRP, TPMA was chosen for the high activity and stability of its copper complexes under these reaction conditions. It was observed that Ag^0 readily reduced $\text{Cu}^{\text{II}}\text{Br}_2/\text{TPMA}$ to the Cu^{I} activator species, which could then enter into the ATRP equilibrium in the presence of alkyl halide initiator (Scheme 1).⁹ In the absence of initiator, equilibrium between $\text{Ag}^0/\text{Cu}^{\text{II}}$ and $\text{Ag}^{\text{I}}/\text{Cu}^{\text{I}}$ was achieved after 90 min (Supporting Information (SI), Figure S1). It should be noted that copper complexes with both Me_6TREN and PMDTA as ligands ($\text{Me}_6\text{TREN} = \text{tris}[2\text{-(dimethylamino)ethyl}]\text{amine}$; $\text{PMDTA} = N,N,N',N',N''\text{-pentamethyldiethylenetriamine}$) were successfully reduced by Ag^0 as well, highlighting the large scope of this new methodology. To establish the efficacy of Ag^0 as a heterogeneous reducing agent for ATRP, the polymerization of *n*-butyl acrylate (BA) was carried out at 50 °C. Under these conditions, 62% monomer conversion was observed after 2 h at 200 ppm initial $\text{CuBr}_2/\text{TPMA}$ catalyst loading (SI, Figure S2). MW was in very good agreement with theoretical values throughout the reaction, increasing linearly with conversion, and at 62% monomer conversion, gel permeation chromatography (GPC) analysis revealed a very low dispersity value of $\bar{D} = 1.03$, among the lowest reported for copper-mediated ATRP of acrylates. At higher conversion, a decrease in reaction rate was observed, but good control over polymerization was maintained at all reaction times (SI, Figure S3). This low dispersity value likely indicates that Ag^0 is not active in the generation or termination of radicals, and rather acts solely as a reducing agent. Accordingly, polymerization of BA in the absence of CuBr_2 did not occur over 2 h, whereas, in the presence of $\text{CuBr}_2/\text{TPMA}$, 50% monomer conversion was attained after 2 h. Thus, if activation occurred with Ag^0 , it was slow enough relative to Cu^{I} activation to be kinetically negligible. Additionally, although radical–radical termination reactions are unavoidable in any RDRP, it is possible that the presence of Ag^0 may suppress alternative termination pathways such as Cu^{I} catalytic radical termination, which has been shown to be a dominant mode of radical termination in some Cu-based ATRP reactions of acrylates.^{15a}

Because silver is a relatively expensive reducing agent as compared to alternatives such as copper or ascorbic acid, minimization of the amount of Ag^0 wire used is highly desired. Five separate experiments were conducted with varying amounts of silver wire: 10, 5, 2, 1, and 0.5 cm (silver surface area-to-solution volume ratio (SA/V) = 0.64, 0.32, 0.13, 0.07, and 0.04 cm^{-1} , respectively). Figure 1a illustrates the polymerization kinetics of these five reactions. As the surface area of silver was decreased, the rate of polymerization similarly declined, suggesting the involvement of silver in the rate-determining step of the reaction. MW increased linearly with conversion (Figure 1b) and was nearly identical to theoretical molecular weight. MWDs were independent of silver surface area and remained low, with $\bar{D} = 1.02$ at 75% monomer conversion (2 cm Ag^0 wire). Importantly, because reaction rate was dependent on the SA/V and not on the total amount of silver used, the reaction rate could feasibly be increased by

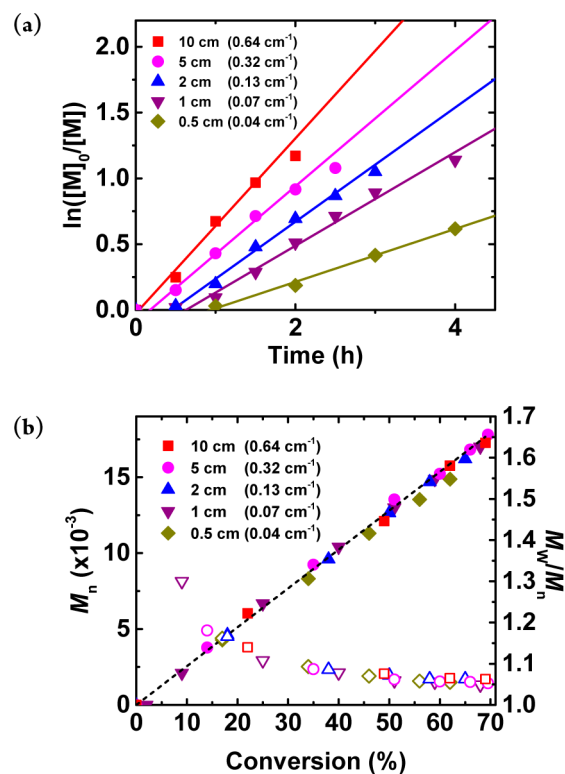


Figure 1. (a) Kinetics and (b) evolution of M_n and M_w/M_n with conversion in the ATRP of BA with various SA/V of silver. Reaction conditions: $[\text{BA}]_0:[\text{EBiB}]_0:[\text{CuBr}_2]_0:[\text{TPMA}]_0 = 200:1:0.04:0.08$ with $[\text{BA}]_0 = 3.49$ M in DMF at 50 °C, in the presence of 0.5–10 cm Ag^0 wire ($d = 2$ mm, $\text{SA} = 0.4\text{--}6.4$ cm^2 ; $V_{\text{tot}} = 10$ mL; $\text{SA}/V = 0.04\text{--}0.64$ cm^{-1}).

either increasing the surface area of silver or decreasing the total reaction volume.

Fortunately, use of large amounts of silver is still experimentally reasonable due to the high reusability of the metal. Indeed, one of the greatest advantages of a heterogeneous system is the potential reusability of the reagents,¹⁸ as demonstrated below. A single piece of silver wire was used without treatment in five sequential polymerizations of BA, and results are illustrated in Figure 2. The rate of polymerization does not change significantly over each cycle, and MW values match up well to theoretical values over all cycles. Most importantly, a high degree of control over polymerization was consistently maintained, with $\bar{D} = 1.05$ in all reactions. This result suggests that coating of the silver surface by either polymer or initial reagents is minimal and does not notably affect subsequent reactions.

It is also desirable to decrease the amount of catalyst necessary for reaction, so five different polymerizations were run with various initial $\text{CuBr}_2/\text{TPMA}$ catalyst loadings (Figure 3).²⁰ As observed previously,²¹ decrease of catalyst concentration resulted in a reduction of reaction rate and a slight broadening of MWD. However, at all catalyst concentrations linear increase of M_n with conversion was observed, with experimental values matching up well to theoretical. Additionally, with catalyst loadings of down to 10 ppm of CuBr_2 , at 62% monomer conversion $\bar{D} = 1.27$, indicating remarkably good control relative to comparable low-catalyst systems.

To expand the scope of this methodology, polymerizations of *tert*-butyl acrylate (*t*BA) and methyl acrylate (MA) were carried

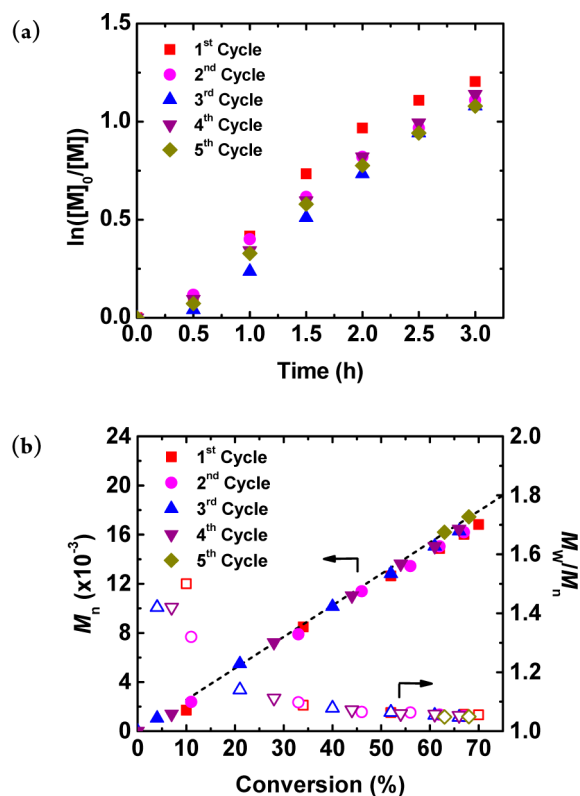


Figure 2. (a) Kinetics and (b) evolution of M_n and M_w/M_n with conversion in the ATRP of BA with the same silver wire in five sequential reactions. Reaction conditions: $[BA]_0:[EBiB]_0:[CuBr_2]_0:[TPMA]_0 = 200:1:0.04:0.08$ with $[BA]_0 = 3.49$ M in DMF at 50 °C, in the presence of 5 cm Ag^0 wire ($d = 2$ mm, $SA = 3.2$ cm²; $V_{tot} = 10$ mL).

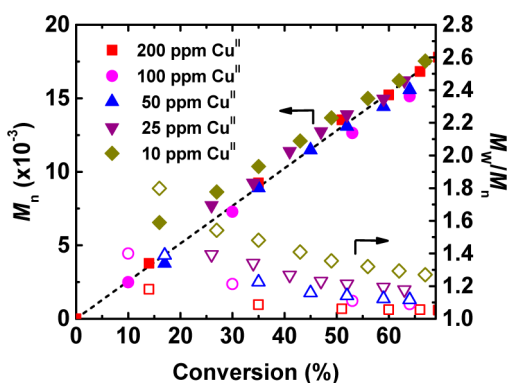


Figure 3. Evolution of M_n and M_w/M_n with conversion in the ATRP of BA with various initial concentrations of $CuBr_2$. Reaction conditions: $[BA]_0:[EBiB]_0:[CuBr_2]_0:[TPMA]_0 = 200:1:x:2x$ ($x = 0.04, 0.02, 0.01, 0.005, 0.002$) with $[BA]_0 = 3.49$ M in DMF at 50 °C, in the presence of 5 cm Ag^0 wire ($d = 2$ mm, $SA = 3.2$ cm²; $V_{tot} = 10$ mL).

out, and for both acrylates, 60% monomer conversion was achieved in under 2 h (SI, Figure S9). MW was in good agreement with theoretical values, indicating a high degree of livingness and preservation of chain-end functionality. A sample of *PtBA* ($M_n = 3600$; $\bar{D} = 1.17$) was further studied by ¹H NMR spectroscopy and indicated $97 \pm 3\%$ retention of chain end functionality (SI, Figure S10). This result suggested the possibility of facile and precise block copolymer synthesis, so chain extension from poly(*n*-butyl acrylate) (PBA) was carried

out. PBA-Br ($M_n = 6600$, $\bar{D} = 1.08$) was synthesized and purified according to the procedure given in the SI, and used as a macroinitiator in the subsequent polymerization of *tBA*. Monomer conversion as a function of time revealed pseudo-first-order kinetics, suggesting that a constant concentration of radicals was maintained throughout the reaction. Additionally, a linear increase in MW with conversion was observed while maintaining very narrow MWD, with $\bar{D} = 1.04$ (SI, Figure S11). The GPC traces of chain extension shown in Figure 4 reveal

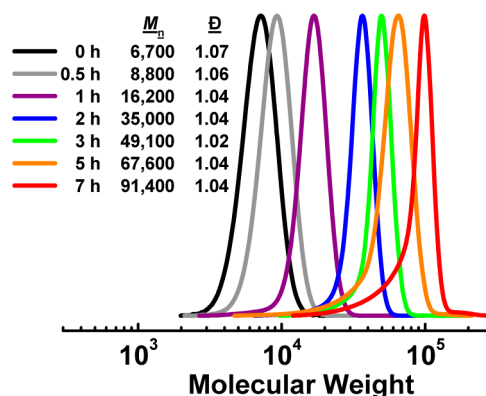


Figure 4. GPC traces for the chain extension from PBA-Br with *tBA*. Reaction conditions: $[tBA]_0:[PBA-Br]_0:[CuBr_2]_0:[TPMA]_0 = 1000:1:0.2:0.4$ with $[tBA]_0 = 3.49$ M in DMF at 50 °C, in the presence of 5 cm Ag^0 wire ($d = 2$ mm, $SA = 3.2$ cm²; $V_{tot} = 10$ mL).

very narrow MWD with minor low-molecular-weight tailing at higher conversions, typical for this type of chain extension.²² However, it should be noted that at lower monomer conversion (>50%), \bar{D} actually decreased upon chain extension from the PBA-Br macroinitiator, from $\bar{D} = 1.07$ to $\bar{D} = 1.02$ at 40% conversion. Thus, copper-catalyzed ATRP with Ag^0 is a very powerful method for the preparation of highly defined block copolymers.

In conclusion, a new copper-catalyzed ATRP system with elemental silver as the reducing agent was developed. Good control over polymerization of BA, *tBA* and MA was demonstrated with this methodology, with MW dispersity down to $\bar{D} = 1.03$. Monomer conversions of 60% were achieved in 1.5–2 h with 200 ppm of $CuBr_2$ /TPMA catalyst loading, and MW of the resulting polymers were in good agreement with theoretical values. The same silver wire could be used for several sequential polymerizations without adverse effects on the polymer produced, and treatment of the silver was not required after each reaction. The amount of silver wire used in each reaction could be reduced to $l = 0.5$ cm, corresponding to a surface area-to-volume ratio of 0.04 cm⁻¹, without decrease in control. Polymerization of BA with 10 ppm of $CuBr_2$ /TPMA catalyst loading afforded PBA with MW in excellent agreement with theoretical values and $\bar{D} = 1.29$. Chain extension of a PBA-Br macroinitiator with *tBA* exhibited high chain-end functionality, and a PBA-*b*-*PtBA*-Br diblock copolymer was synthesized with $\bar{D} = 1.02$.

The use of silver as a reducing agent in ATRP represents a significant advance. As silver is a one-electron heterogeneous reductant, the side reactions that often hinder the efficacy of conventional ARGET ATRP reactions are minimized, and in contrast to the Cu^0 used in traditional SARA ATRP reactions, Ag^0 does not engender a buildup of reactive Cu^I through the course of reaction. As evidenced by the low \bar{D} values and high

livingness observed here, silver likely does not act to generate nor terminate radicals in the system, thereby eliminating the side reactions observed in other ATRP processes, which have previously led to some loss of chain-end functionality. As such, silver is an excellent reducing agent for highly controlled ATRP.

■ ASSOCIATED CONTENT

📄 Supporting Information

Full experimental details and additional characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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