Controlled Radical Polymerization in the Presence of Oxygen

Krzysztof Matyjaszewski,* Simion Coca, Scott G. Gaynor, Mingli Wei, and Brian E. Woodworth

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Living polymerizations occur without termination or transfer reactions and have the advantage of being able to form well-defined polymers with predictable molecular weights and narrow polydispersities. The first examples of this were living anionic polymerizations,[1] which require the exclusion of moisture and oxygen and are run at low temperatures.

Radical polymerization methods have the advantage of being insensitive to the presence of water and have even been carried out in aqueous media. This allows for less rigorous reaction conditions and is convenient for industrial application. Free radical polymerizations typically have slow initiation and form a high molecular weight polymer limited by transfer and termination reactions leading to poorly controlled molecular weights and broad molecular weight distributions.[2] Also, in contrast to living ionic polymerization, it is very difficult to prepare well-defined homopolymers and block copolymers.

In recent years, radical polymerizations have been developed into controlled/"living" polymerizations yielding well-defined polymers. Currently, nitroxide-mediated,[3] metal-mediated,[4] and either ruthenium- or copper-catalyzed atom transfer radical polymerization (ATRP)[5] are at the forefront of controlled radical polymerizations. Improvements to these processes have been aimed toward application to new monomers, new initiators and new architectures, compositions, and functionalities.[6] In ATRP, recent advances have also been in the direction of new ligands[7] and new metals[8] which affect the activity and selectivity of the ATRP catalysts for various monomers. Also, improvements have been made in ATRP by the addition of small amounts of zerovalent metal.[9]

Up to this point, radical polymerizations need to be carried out in an oxygen-free environment. ATRP, in fact, requires less stringent conditions since O_2 can react with the catalyst as opposed to reacting with the free organic radicals which should be present in a much lower concentration. However, oxidation reduces the active catalyst concentration. For example, the Cu(I) catalyst is oxidized to a Cu(II) species which is not an active ATRP catalyst and can even be a deactivating species, if a halogen ligand is present, and further slow the polymerization.[7b]

In this communication, we report that controlled radical polymerizations with polymers having low polydispersities ($M_w/M_n < 1.2$) can be prepared *without* any removal of oxygen or inhibitor and does not require purging with inert gas, if a sufficient amount of zerovalent metal is present.

If Cu(I)Br/dNbpy complex is added (in excess), the polymerization occurs but at a slow rate. This is due
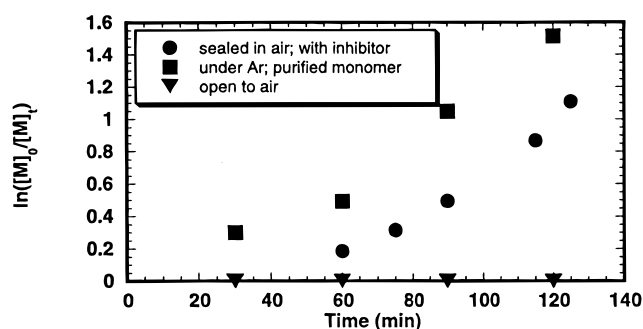

Figure 1. Kinetic plot of the bulk polymerization of styrene by ATRP with copper(0) powder at 110 °C under various conditions: styrene = 52.4 mmol; (1-bromoethyl)benzene = 0.525 mmol; $CuBr_2$ = 0.054 mmol; dNbpy = 0.262 mmol; Cu-(0) = 0.52 mmol.
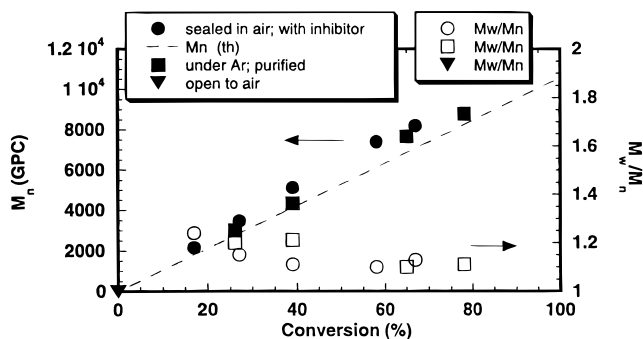

Figure 2. Dependence of number average molecular weight, M_n (closed symbols), and polydispersity, M_w/M_n (open symbols), vs percent conversion for the bulk polymerization of styrene by ATRP with copper(0) powder at 110 °C under various conditions.
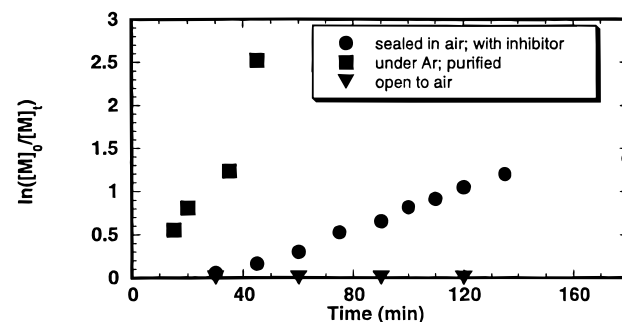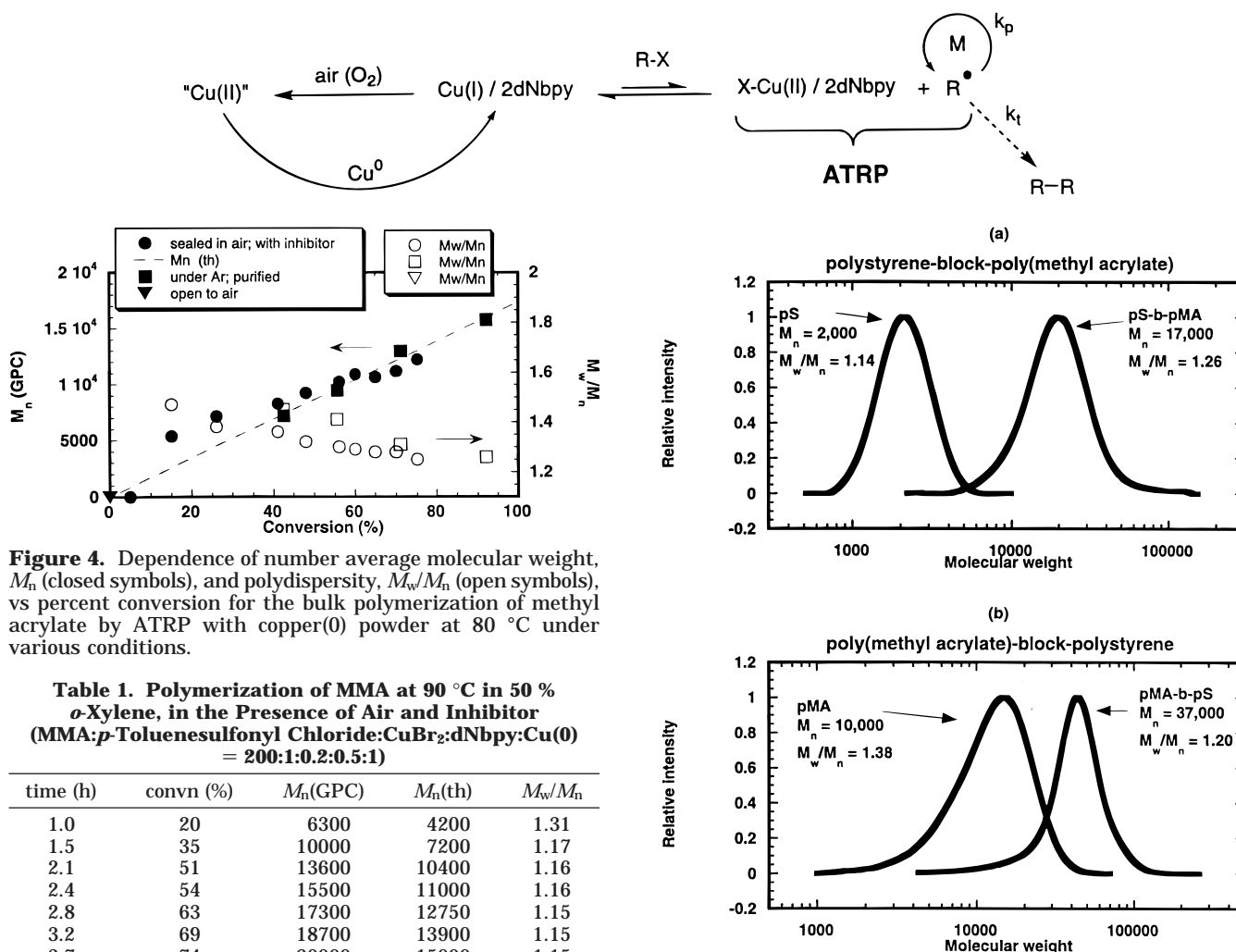

Figure 3. Kinetic plot of the bulk polymerization of methyl acrylate by ATRP with copper(0) powder at 80 °C under various conditions: methyl acrylate = 66.6 mmol; methyl (±)-2-bromopropionate = 0.33 mmol; $CuBr_2$ = 0.033 mmol; dNbpy = 0.166 mmol; Cu(0) = 0.33 mmol.

to two factors: first, the amount of Cu(I) is reduced by oxidation to Cu(II), second, the concentration of Cu(II), which is a deactivator, is increased further slowing the polymerization.[7b] Adding Cu(0) to the system, reduces the Cu(II) to Cu(I) and allows for a smaller concentration of catalyst to be added initially.

Also, the equilibrium Cu(II) + Cu(0) ⇌ 2Cu(I), which can be shifted to the right by stabilization of the Cu(I) with ligands,[10] enables the use of more convenient Cu-(II) complexes as starting materials.[9] They are more robust than their Cu(I) analogues and are more readily available.

Scheme 1

Figure 4. Dependence of number average molecular weight, M_n (closed symbols), and polydispersity, M_w/M_n (open symbols), vs percent conversion for the bulk polymerization of methyl acrylate by ATRP with copper(0) powder at 80 °C under various conditions.

Table 1. Polymerization of MMA at 90 °C in 50 %
***o*-Xylene, in the Presence of Air and Inhibitor**
(MMA:*p*-Toluenesulfonyl Chloride:CuBr$_2$:dNbpy:Cu(0)
= 200:1:0.2:0.5:1)

time (h)	convn (%)	M_n(GPC)	M_n(th)	M_w/M_n
1.0	20	6300	4200	1.31
1.5	35	10000	7200	1.17
2.1	51	13600	10400	1.16
2.4	54	15500	11000	1.16
2.8	63	17300	12750	1.15
3.2	69	18700	13900	1.15
3.7	74	20000	15000	1.15
4.2	81	21200	16500	1.16

Table 2. Polymerization of Styrene at 110 °C in Bulk, in
the Presence of Air and Inhibitor with FeBr$_3$/DNbpy/
Fe(0) (Styrene:1-Phenylethyl Bromide:FeBr$_3$:DNbpy:Fe(0)
= 100:1:0.2:0.6:2)

time (h)	convn (%)	M_n(GPC)	M_n(th)	M_w/M_n
1.5	0			
3.0	0			
4.0	18	3600	2100	1.47
5.0	41	6500	4450	1.27
6.0	64	9800	6800	1.16
7.0	81	11700	8600	1.16

For the polymerization of styrene,[11] an induction period of approximately 35 min occurred before monomer consumption was observed (Figure 1). This induction period is likely due to the removal of the oxygen present in the system via Scheme 1. Figures 1 and 2 show that aside from an induction period, the polymerization of styrene in the presence of air gave similar results to those performed under an inert atmosphere. Good agreement with the theoretical molecular weight and low polydispersities were observed (Figure 2). Similarly, for the polymerization of methyl acrylate,[12] an induction period was observed (Figures 3 and 4) and the control of the polymerization is comparable to that obtained under an inert atmosphere.

It should also be noted that methyl methacrylate can also be polymerized by the method described here to form polymers with narrow molecular weight distribu-

(a)
polystyrene-block-poly(methyl acrylate)

pS
$M_n = 2,000$
$M_w/M_n = 1.14$

pS-b-pMA
$M_n = 17,000$
$M_w/M_n = 1.26$

(b)
poly(methyl acrylate)-block-polystyrene

pMA
$M_n = 10,000$
$M_w/M_n = 1.38$

pMA-b-pS
$M_n = 37,000$
$M_w/M_n = 1.20$

Figure 5. Size exclusion chromatography traces of (a) polystyrene-*block*-poly(methyl acrylate) and (b) poly(methyl acrylate)-*block*-polystyrene.

tions ($M_w/M_n < 1.2$). The M_n's obtained were 20−30% higher than the theoretical values, possibly indicating termination of propagating chains at early stages of the polymerization (Table 1).

This process is not specific to copper: Fe^{III}Br$_3$/dNbpy, in the presence of iron powder, allowed for the controlled polymerization of styrene in the presence of air and inhibitor. After an induction period of about 4 h, linear kinetic plots were observed; however, M_n's were higher than theoretical values. Polydispersities decreased with increasing conversion; at 80% conversion, $M_w/M_n = 1.16$ (Table 2).

The synthesis of block copolymers where both segments were polymerized by the method described in this communication were attempted. A homopolymer of polystyrene was synthesized and isolated ($M_n = 2000$; $M_w/M_n = 1.14$). Methyl acrylate was then polymerized from the halogen-terminated polystyrene chain to yield a polystyrene-*block*-poly(methyl acrylate) copolymer ($M_n = 17000$; $M_w/M_n = 1.26$) (Figure 5a). Analogously, the poly(methyl acrylate) homopolymer ($M_n = 10\,000$; $M_w/M_n = 1.38$) was used to initiate the ATRP of styrene to form a poly(methyl acrylate)-*block*-polystyrene copolymer ($M_n = 37\,000$; $M_w/M_n = 1.20$) (Figure 5b). It should be noted that the size exclusion chromatography results are based on polystyrene standards and do not take

changes in hydrodynamic volumes or refractive indices of the copolymers into account. Regardless, block copolymers are formed efficiently using this process, indicating that a majority of the halogen chain ends remain intact.

This discovery enables the preparation of well-defined polymer from certain vinyl monomers which have been previously available only by living anionic or controlled/ "living" polymerization methods after the strict removal of oxygen and inhibitor. Still, these reactions cannot be carried out with continuous exposure to air, but it is sufficient to close off the reaction flask with a septum to prohibit the free introduction of air. The adventitious oxygen in the solution and in the headspace above the solution is effectively scavenged by the process described in Scheme 1 where enough copper(0) powder is present to recycle Cu(II) to the active Cu(I) catalyst. The amount of oxygen in the solution and in the headspace above the solution are important factors in this system. With an unlimited headspace (vessel not capped), the polymerization does not occur. With a minimal headspace, the polymerization occurs after a short induction period due to the consumption of oxygen in the system. The length of the induction period depends on the volume of the headspace: the more headspace above the solution, the longer the induction period, with more copper(0) powder necessary. Oxygen in the reaction mixture presumably will both react with the Cu(I) catalyst and the propagating radicals (P$^{\bullet}$) but will not react with the dormant species (P–X). However, since the concentration of Cu(I) is much greater than the concentration of propagating radicals (i.e. 10^{-1}M $\gg$ 10^{-8}M), and the concentration of dormant polymer chain is much greater than the concentration of propagating radicals (i.e. 10^{-1}M $\gg$ 10^{-8}M), few of the polymer chains become terminated allowing for a controlled polymerization with the ability to form block copolymers.

References and Notes

(1) Szwarc, M. *Nature* **1956**, *178*, 1168.

(2) Moad, G.; Solomon, D. H. *The Chemistry of Free-Radical Polymerization*; Pergamon: Oxford, England 1995.

(3) (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US 581,429, 1985. (b) Georges, M. K.; Veregin, R. P. N.; Dazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987. (c) Hawker, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 11185.

(4) Wayland, B. B.; Pszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.

(5) (a) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721. (b) Wang, J. S.; Maty-jaszewski, M. *J. Am. Chem. Soc.* **1995**, *117*, 5614. (c) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970. (d) Haddle-ton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.

(6) Matyjaszewski, K.; Gaynor, S. G. *ACS Symp. Series* **1998**, *685*, 396.

(7) (a) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866. (b) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674. (c) Haddleton, D. M.; Crossman, M. C.; Hunt, K. H.; Topping, C.; Waterson, C.; Suddaby, K. G. *Macromolecules* **1997**, *30*, 3992. (d) Destarac, M.; Bessière, J.-M.; Boutevin, B. *Macromol. Rapid Commun.* **1997**, *18*, 967. (e) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697.

(8) (a) Uegaki, H.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 2249. (b) Lecomte, Ph.; Drapier, I.; Dubois, Ph.; Teyssié, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 7631. (c) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576. (d) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665. (e) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507. (f) Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules* **1997**, *30*, 8161. (g) Moineau, G.; Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1998**, *31*, 1.

(9) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348.

(10) (a) Ogura, T. *Inorg. Chem.* **1976**, *15*, 2301. (b) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843. (c) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 856.

(11) Bulk polymerization of styrene/1-phenylethyl bromide/CuBr$_2$/Cu(0) in the presence of air and inhibitor: To a sample vial (approximately 7 mL in volume) was added Cu(0) (99% pure, copper for organic synthesis (Aldrich)) (33 mg; 0.52 mmol), CuBr$_2$ (12 mg; 0.054 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (107 mg; 0.262 mmol), 1-phenylethyl bromide (71.6 μL.; 0.525 mmol), and styrene (6 mL; 52.4 mmol) followed by 0.6 mL of chlorobenzene as an internal reference. All manipulations were performed in air. The styrene was unpurified and contained inhibitor (10−15 ppm 4-*tert*-butylcatechol). The sample vial was charged with a stir bar and then fitted with a rubber septum. The vial was then immersed in an oil bath and held by a thermostat at 110 °C with vigorous stirring. At various times, samples were taken via syringe and quenched with THF. The volume lost by sample removal was replaced with argon. The samples were used to monitor percent monomer conversion relative to the internal reference (GC) and molecular weight (SEC).

(12) Bulk polymerization of methyl acrylate/methyl (±) 2-bromopropionate/CuBr$_2$/Cu(0) in the presence of air and inhibitor: To a sample vial (approximately 7 mL in volume) was added Cu(0) (99% pure, copper for organic synthesis (Aldrich)) (21 mg; 0.33 mmol), CuBr$_2$ (7.4 mg; 0.033 mmol), 4,4′-di(5-nonyl)-2,2′-bipyridine (68 mg; 0.166 mmol), methyl (±)-2-bromopropionate (37 μL; 0.33 mmol) and methyl acrylate (6 mL; 66.6 mmol) followed by 0.6 mL of chlorobenzene as an internal reference. All manipulations were performed in air. The methyl acrylate was unpurified and contained stabilizer (200 ppm hydroquinone monomethyl ether). The sample vial was charged with a stir bar and then fitted with a rubber septum. The vial was then immersed in an oil bath and held by a thermostat at 80 °C with vigorous stirring. At various times, samples were taken via syringe and quenched with THF. The volume lost by sample removal was replaced with argon. The samples were used to monitor percent monomer conversion relative to the internal reference (GC) and molecular weight (SEC).