

Zerivalent Metals in Controlled/"Living" Radical Polymerization

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Received August 19, 1997

Revised Manuscript Received September 17, 1997

The development of living polymerizations has grown rapidly in recent years as new methods to prepare novel materials have been explored.¹ Specifically, the search for a living radical polymerization system has received much interest in the past few years. Although termination reactions cannot be completely avoided in radical polymerizations, their contribution to the overall polymerization can be suppressed by establishing an equilibrium between active and dormant species.² Among the methods that have been explored to develop controlled/"living" radical polymerizations, such as TEMPO^{3–5} and metal-mediated⁶ polymerization systems, one of the most robust has been atom transfer radical polymerization (ATRP).^{7–22} ATRP has successfully polymerized styrenes,^{7–10,12} acrylates,^{8,23,24} methacrylates,^{11,18,20–22,25} and acrylonitrile^{13,26} to prepare polymers with predefined molecular weights and narrow molecular weight distributions. Also, polymers with novel architectures^{27,28} and compositions^{29,30} have been prepared.

ATRP establishes an equilibrium between active and dormant radicals by using a reversible redox reaction between a low oxidation state metal and an organic halide, Scheme 1. The halogen atom is homolytically transferred from the alkyl halide (R–X), with the rate constant k_a , yielding a carbon-centered radical (R•) and a metal whose oxidation state has increased by one (X–M_tⁿ⁺¹). This radical can then initiate the polymerization of the vinyl monomer(s) (M). The propagating radical reacts reversibly, with the rate constant k_d , with the metal halide to re-form the lower oxidation state transition metal and an oligomer with a halogen end group. This process can then repeat itself, resulting in the formation of a well-defined polymer. The rate of polymerization is defined by eq 1,¹⁰ where R_p is the rate

$$R_p = k_p K_{eq} [M][R-X]_0 \frac{[M_t^n]}{[X-M_t^{n+1}]} \quad (1)$$

of polymerization, k_p is the rate constant of polymerization, $K_{eq} = k_a/k_d$ is the equilibrium constant, $[M]$ is the concentration of monomer, $[R-X]_0$ is the initial concentration of initiator, $[M_t^n]$ is the concentration of the lower oxidation state metal, and $[X-M_t^{n+1}]$ is the concentration of the higher oxidation state metal.

The molecular weight control achieved by using ATRP, or any controlled/"living" radical polymerization, is obtained by the rapid and reversible deactivation of the propagating radicals, which results in a very low concentration of radicals, thus suppressing bimolecular termination. This is accomplished by the persistent radical effect,³¹ with the formation of deactivator in the reaction mixture, in this case X–M_tⁿ⁺¹. Although deactivator is necessary for a controlled polymerization, the system may produce more deactivator than is

Scheme 1. Equilibrium between Active and Dormant Species in Atom Transfer Radical Polymerization, ATRP

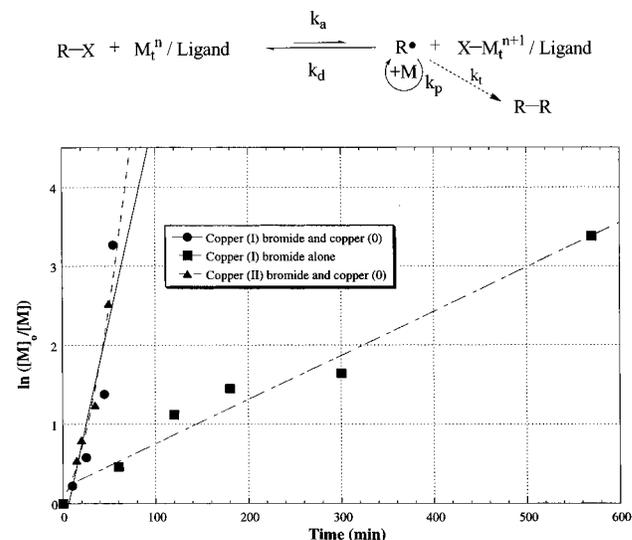


Figure 1. Kinetics of polymerization of methyl acrylate by atom transfer radical polymerization, ATRP. $[R-X]_0$ = methyl (\pm)-2-bromopropionate. $[MA]_0$ = 11.1 M, $[R-X]_0$ = 5.5 mM, $[Cu^I]$ = 1.1 mM, $[Cu^{II}]$ = 0.55 mM, $[dNbpy]$ = 2.2 mM, $[Cu^0]$ = 5.5 mM.

necessary for the control of the polymerization, resulting in slower polymerizations. Removal of this "excess" amount of deactivator can result in faster reactions without sacrificing molecular weight control of the polymerization. This has been previously demonstrated in the TEMPO-mediated polymerization of styrene, when various acids, i.e., camphorsulfonic acid,³² or slowly decomposing initiators³³ were added to the reaction mixture to scavenge the excess TEMPO. The byproducts of the reaction of TEMPO with the acid, presumably, do not participate in the polymerization.

Here we report the use of zerovalent metals in conjunction with a suitable ligand to scavenge the excess metal halide. This provides a controlled/"living" radical polymerization with a significant reduction in the amount of catalyst required to obtain reasonable rates of polymerization, when compared to previous ATRP reactions. The reduction in catalyst concentration is a significant advancement in the development of controlled/"living" radical polymerization, as it may allow for the evolution of controlled radical polymerizations to commercially viable processes.

When a small amount of copper powder was added to the polymerization of styrene and (meth)acrylates by ATRP, a dramatic rate increase was observed. In Figure 1, the rates of polymerization for methyl acrylate under three different reaction conditions are shown. The first was the "normal" ATRP of methyl acrylate with a 1:0.2:0.4 ratio of initiator (methyl (\pm)-2-bromopropionate) to copper(I) bromide to ligand (4,4'-dinonyl-2,2'-bipyridine, dNbpy); the ratio of initiator to monomer was 1:200 for all three polymerizations. The reaction reached a conversion of 97% after 570 min. Next, the same initiating system was used in the same proportions, but for this reaction copper powder was added; the polymerization was nearly 10 times faster, with a conversion of 96% being obtained after 55 min. Finally, the polymerization was conducted in the presence of copper powder using copper(II) bromide in place of copper(I); the ratio of initiator to copper(II) was 1:0.1. As observed

Table 1. Results for the Polymerization of Various Monomers Using Copper-Based Catalysts in ATRP^a

monomer	R-X ^b	CuBr ₂	Cu ⁰	dNbpy ^c	time (h)	conv ^d	M _{n,th}	M _{n,SEC} ^e	M _w /M _n ^e
methyl acrylate (100)	1	0.1	0.2	0.2	1.2	0.92	8 000	8 150	1.13
	1*	0	1	2	7 (70 °C)	0.97	8 340	14 500	1.31
	0.1	0.1	0.2	0.2	3	0.48	35 300	40 700	1.38
methyl methacrylate (100)	1	0.1	0.2	0.2	1	0.95	9 600	8 970	1.21
	1	0	1	2	0.5	0.93	9 300	8 360	1.45
styrene (100)	1	0.1	0.3	0.5	2.5	0.57	6 110	5 890	1.10
	1	0	0.1	0.2	7	0.98	10 400	9 030	1.18
	1	0	0.1	0.1**	2	0.99	10 500	12 500	1.38
	0.1	0.1 ^f	0.2	1.1	6	0.57	61 100	57 800	1.33
	0.1	0.01	0.03	0.1	22	0.43	44 900	48 700	1.22

^a Values for monomer, initiator, metal, and ligand are the molar ratios to each other. All reactions were performed in bulk. Temperature: methyl acrylate, 90 °C; methyl methacrylate, 70 °C; styrene, 110 °C. ^b [R-X]: (methyl acrylate) methyl (±)-2-bromopropionate, * = diethyl 2-bromo-2-methylmalonate; (methyl methacrylate) *p*-toluenesulfonyl chloride; (styrene) 1-phenylethyl bromide. ^c dNbpy = 4,4'-bis(5-nonyl)-2,2'-bipyridine, ** = 1,1,4,7,10,10-Hexamethyltriethylenetetramine was used in place of dNbpy. ^d Conversion measured by gas chromatography. ^e Molecular weights determined by size exclusion chromatography (SEC) in THF with linear polystyrene standards. ^f Copper(I) bromide was used instead of copper(II) bromide.

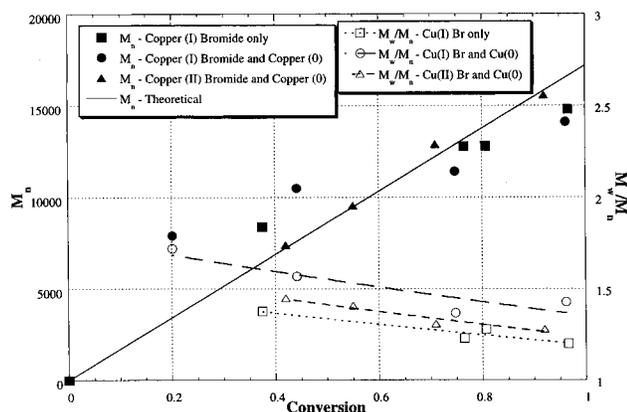


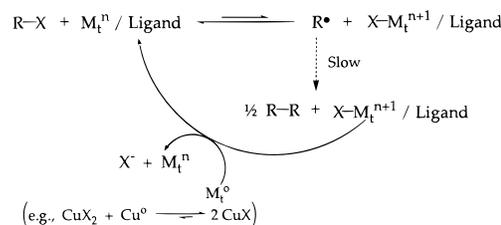
Figure 2. Dependence of number average molecular weight, M_n (closed symbols), and polydispersity, M_w/M_n (open symbols), versus conversion for the polymerization of methyl acrylate by ATRP in the presence and absence of zerovalent copper powder.

in Figure 1, the reaction rate was similar to that obtained using twice as much copper(I) than copper(II), in the presence of copper(0). In addition, the color of the reaction mixture turned from dark green, typical of copper(II), to dark red, indicating reduction of copper(II) to copper(I).

Even with the faster rates of polymerization in the presence of copper(0), the control of the polymerization was maintained, as can be seen in the plots of number average molecular weight (M_n) and polydispersity (M_w/M_n) versus conversion, Figure 2. The molecular weights followed the theoretical line as predicted by $M_n = MW(\Delta[M]/[R-X]_0)$ (solid line); MW is the molecular weight of methyl acrylate, 86. The final polydispersities of the copper(II)/copper(0) catalyst system approached those of the copper(I) only catalyst system, which were the lowest. The copper(I)/copper(0) system provided polymers with molecular weights initially higher than predicted and with the highest polydispersities. The benefits of enhanced rate and controlled molecular weights were observed for the polymerization of methyl methacrylate and styrene, Table 1.

It was also possible to use copper(0) alone, without added copper(I) or copper(II), however with less satisfactory results. It must be stressed that it was necessary to add ligand, i.e., dNbpy, to the reaction mixture, to solubilize the resulting copper(I) and -(II) species (vide infra) and to also affect the equilibrium between the two. Previously, it had been reported that free radical polymerizations could be initiated by alkyl halides in the presence of various zerovalent metals without added

Scheme 2. Equilibrium in ATRP and the Removal of Excess High Oxidation State Metal Halide by Reaction with Zerovalent Metal



ligand, but the polymerizations were uncontrolled.^{34–36} This was most likely due to the low solubility of the X-M_t^{n+1} species and, therefore, slow deactivation of the propagating radical.

A plausible explanation for the dramatic rate increase by simply adding copper metal is as follows. The copper(II) that is generated in the equilibrium reaction between copper(I) and the activated alkyl halide is necessary for the controlled polymerization, Scheme 1.¹⁰ The copper(II), although allowing for greater control of the polymerization, i.e., lower polydispersities, retards the polymerization as the rate is inversely proportional to the concentration of copper(II), eq 1.

The addition of the zerovalent metal, copper powder, slowly removed excess deactivator, copper(II), by a simple electron transfer process, Scheme 2.³⁷ Removal of small amounts of copper(II) enhanced the rate, yet there was still a sufficient concentration of copper(II) to maintain control of the polymerization. Reduction of copper(II) by copper(0) regenerated copper(I), further enhancing the rate of polymerization. In the polymerization system using only copper(I)/copper(0), the early stages of the polymerization were not well controlled, due to the low concentration of copper(II), cf. Figure 2. By producing copper(I) in situ, i.e., using copper(II) and copper(0) as the only added metals, the best control of the molecular weight and low polydispersity was observed, due to the initial presence of a small amount of deactivator. The use of copper(0) resulted in a significant increase in the rate of polymerization, with a relatively small increase in the polydispersity of the final polymer. This may indicate that the polydispersities were affected not only by deactivation and termination reactions but also by slowly occurring side reactions, whose contribution was diminished in the faster polymerization system.

It should be noted that the polymerization was initiated by RX in the presence of copper(0) alone, without added copper(I) or -(II). This would indicate

Table 2. Results of Iron-Based Catalysts in ATRP^a

monomer	R-X ^b	FeBr ₂	Fe ⁰	dNbpy	time (h)	conv ^c	M _{n,th}	M _{n,SEC} ^d	M _w /M _n ^d
styrene (100)	1	1	0	2	21	0.64	6840	6470	1.27
	1	1	1	2.0	3.5	0.81	8640	8960	1.19
	1	1	1.1	15 ^e	17	0.86	9130	9860	1.22
	1	0.7 ^f	2	2.1	2	0.81	8570	8240	1.15
(200)	1	0.2	0.2	0.6 ^g	19	0.65	13700	13200	1.17

^a Values for monomer, initiator, metal, and ligand are the molar ratios to each other. All reactions were performed at 110 °C in bulk. ^b R-X: 1-phenylethyl bromide. ^c Conversion was determined by gas chromatography. ^d Molecular weights determined by SEC in THF with linear polystyrene standards. ^e *N,N*-dimethylformamide was used in place of dNbpy. ^f Iron(III) bromide was used in place of iron(II) bromide. ^g Tris(*n*-butyl)amine was used in place of dNbpy.

that the alkyl halide/polymer chain also reacts with the copper(0) directly to form the radical and copper(I). This process is irreversible since radicals do not react with copper(I) to form copper(0).¹⁰ The copper(I) can then react with R-X to reversibly generate radicals and start the controlled polymerization. The contribution of the reaction between copper(0) and R-X to its overall effect on the control/kinetics of the polymerization is not yet known and is currently being studied.

The addition of zerovalent metals to lower the concentration of the higher oxidation state metal in the reaction was not limited to just the copper-based catalyst systems. When iron powder was used in conjunction with iron(II), an increase in the rate was observed. Similar to the use of copper(II)/copper(0), iron(III) halides were also used in the presence of iron(0) to prepare iron(II) in situ. The results for the iron catalyst systems are summarized in Table 2.

Although the rate enhancements obtained by simply adding basic metals has been demonstrated, the systems have not yet been optimized. Also, improvements may be made by using different forms of the metal, such as varying the size of the powder or using metal wire or sheets. Other factors, such as temperature, use of a solvent, stirring rate, etc., may also play a role in optimization.

In summary, well-defined polymers were prepared by adding simple metals to an ATRP initiating system. This process is faster than previously reported systems where metal salts alone had been used. This advancement in the development of controlled/"living" radical polymerization is significant in that the amount of catalyst required for reasonable rates may be lowered.

Acknowledgment. This research was supported by the industrial members of the Atom Transfer Radical Polymerization Consortium at Carnegie Mellon University. These members include: Akzo-Nobel, Asahi, Bayer, BF Goodrich, Ciba, DSM Research, Elf Atochem, Geon, Kaneka, Japan Synthetic Rubber Co., PPG, and Rohm & Haas. The authors are grateful to Dr. Atsushi Kajiwara for the ESR measurements.

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