

Copper(I)-Catalyzed Atom Transfer Radical Polymerization

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Introduction

Over the past few decades, controlled/living polymerization methodology has steadily expanded to include all of the chain-growth polymerization methods: cationic, anionic, transition metal-catalyzed, and, most recently, free-radical polymerizations. In the strictest sense, a living polymerization is a chain-growth polymerization that proceeds in the absence of irreversible chain-termination and chain-transfer steps.¹ Thus, once a chain is initiated, it will grow until the monomer supply is depleted and will remain active either until more monomer is added, in which case chain growth will resume, or until a terminating agent is deliberately introduced. Provided that initiation is complete and exchange between species of various reactivities is fast, the final average molecular weight of the polymer can be adjusted by varying the initial conditions ($DP_n = \Delta[\text{Monomer}]/[\text{Initiator}]_0$, where DP_n = degree of polymerization) while maintaining a narrow molecular weight distribution ($1.0 < M_w/M_n < 1.5$, where M_w = weight-averaged molecular weight and M_n = number-averaged molecular weight).^{2–5} In a living poly-

merization using a monofunctional initiator, there is one site of chain growth per polymer chain, and consequently the resulting macromolecule can be used as a polymeric building block.⁶ Living polymers can be assembled into macromolecules that have different structures and compositions and display novel properties. In practice, it is difficult to control the chemistry of reactive chain ends such that chain-transfer and chain-termination reactions do not occur. Many times, though, the rates of these side reactions are sufficiently slow that polymerization conditions may be found in which well-defined polymers may be prepared. In such cases, the polymerizations are termed “controlled polymerizations”⁷ to indicate that, while chain transfer or chain termination may occur to some degree, the polymerizations are still as synthetically useful as true living polymerizations.

The Persistent Radical Effect in Free-Radical Addition Reactions

The rate constants for bimolecular radical coupling and disproportionation for most organic free radicals are near the diffusion-controlled limit, and these processes present a unique challenge in developing selective free-radical addition reactions. The concept of controlling fast radical reactions through an equilibrium between dormant adducts and their corresponding transient and persistent radicals was originally described in Fischer’s seminal 1986 publication.⁸ Daikh and Finke⁹ reported the first quantitative analysis of a highly selective free-radical reaction in 1992. The “persistent radical effect” occurs when concentrations of transient and persistent radicals are formed at equal rates in a single step. Because the transient radicals can undergo fast termination via coupling and/or disproportionation, their concentration decreases, and the concentration of the persistent radical builds up. Eventually, the concentration of persistent radical is sufficiently large that the rate at which the propagating radicals react with the persistent radicals in a deactivation (or reversible termination) step is much faster than the rate at which the propagating radicals react with each other in an irreversible termination step. Thus, addition chemistry can be performed involving free-radical intermediates that is highly selective for addition over radical coupling and disproportionation. It is interesting to note that in both publications the authors surmised that the persistent radical effect could find wide application in improving the selectivities of synthetic methods that involve free-radical intermediates.

One of the more useful synthetic methods involving free-radical addition chemistry is atom transfer radical addition (ATRA), which utilizes atom transfer from an organic halide to a transition-metal complex to generate the intermediate radicals. In ATRA (Scheme 1), a copper(I)

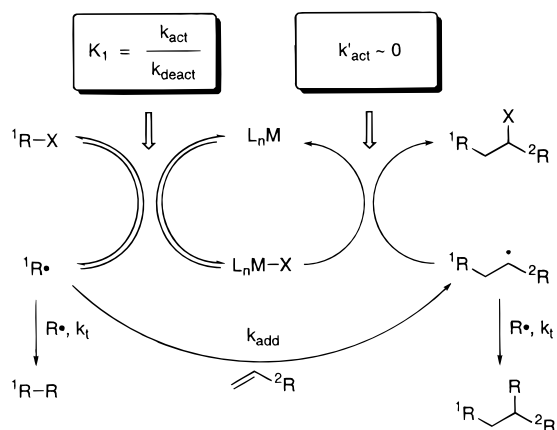
Timothy E. Patten was born in New York in 1967. He received his B.A. in chemistry from La Salle University in 1989 and a Ph.D. in chemistry from the University of California, Berkeley, in 1994 under the supervision of Bruce M. Novak. After doing postdoctoral research with Krzysztof Matyjaszewski at Carnegie Mellon University from 1995 to 1996, he joined the Department of Chemistry at the University of California, Davis, in 1996, where he is currently an Assistant Professor. His research is focused on developing methods for the preparation of well-defined polysaccharides and their analogues and on applying controlled/“living” radical polymerization methodologies to the synthesis of hybrid organic/inorganic nanoparticle materials.

Krzysztof Matyjaszewski was born in Poland in 1950. He received his Ph.D. from the Polish Academy of Sciences in 1976 under the supervision of Stan Penczek and received a Habilitation Degree from Lodz Polytechnic in 1985. Since 1985, he has been at Carnegie Mellon University, where he currently holds the J. C. Warner Professorship in Natural Sciences and served as Chemistry Department Head from 1994 to 1998. He has received a Presidential Young Investigator Award in 1989, the ACS Marvel Creative Polymer Chemistry Award in 1995, the Elf Chair of the French Academy of Sciences in 1998, and a Humboldt Senior US Scientist Award in 1999. He is the editor of *Progress in Polymer Science* and serves on the editorial boards of seven other polymer journals. His research is focused on developing new controlled/living polymerization techniques by radical and ionic mechanisms and the synthesis of novel well-defined organic and inorganic polymers. He has coauthored over 400 papers, 20 patents and 3 monographs.

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Scheme 1. General Mechanism for Atom Transfer Radical Addition (ATRA)

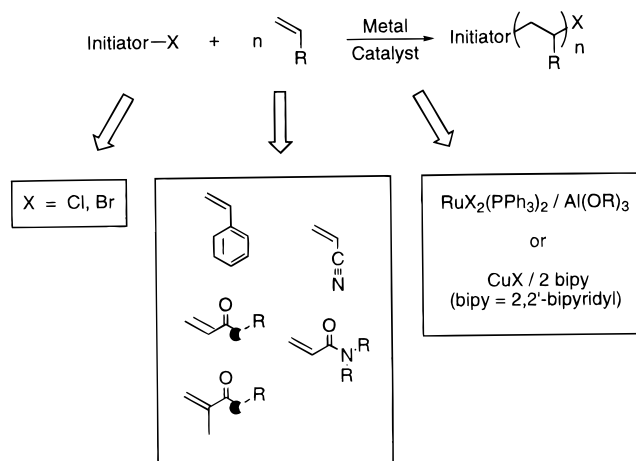


complex^{10,11} (although Ni,^{12,13} Pd,¹⁴ Ru,^{15,16} Fe,¹⁷ and other metal complexes¹⁸ have been used as well) undergoes a one-electron oxidation with concomitant abstraction of a halogen atom from a starting compound. This reaction generates an organic radical and a copper(II) complex, and substituents on the organic halide can facilitate the reaction by stabilizing the resulting radical. The organic radical can then add to an unsaturated group in an inter- or intramolecular fashion and then reabstract a halogen atom from the copper(II) complex to re-form the original copper(I) complex and to form the product (Scheme 1). Compounds derived from the self-reaction of radicals (i.e., termination) comprise very little of the product, because the copper(II) complex acts as a persistent radical and controls the concentration of the intermediate radicals. Substrates for this reaction are typically chosen such that if addition occurs, then the newly formed radical is much less stabilized than the initial radical and will essentially react irreversibly with the copper(II) complex to form an inactive alkyl halide product ($k_{\text{act}} \gg k'_{\text{act}}$). Thus, in ATRA, usually only one addition step occurs; however, if the starting and product alkyl halides possess similar reactivities toward atom transfer, then it should be possible to repeat the catalytic cycle and add multiple unsaturated groups as in a polymerization reaction.

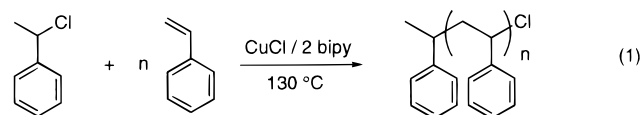
Atom Transfer Radical Polymerization

In 1995, a new class of controlled/"living" radical polymerization methods was reported independently by the groups of Sawamoto¹⁹ and Matyjaszewski:²⁰ atom transfer radical polymerization (ATRP, Scheme 2). While sharing many similar mechanistic features with other controlled/"living" polymerization techniques, ATRP differs through the use of reversible metal-catalyzed atom transfer to generate the propagating radicals rather than photochemically or thermally promoted homolytic cleavage. This Account pertains primarily to copper(I)-catalyzed ATRP, although references to studies on other metal ATRP systems have been made to illustrate correlations between the techniques. For copper(I)-catalyzed ATRP, conditions were found for atom transfer from 1-phenylethyl chloride

Scheme 2. General Conditions for Ruthenium(II)- and Copper(I)-Catalyzed Atom Transfer Radical Polymerization (ATRP)



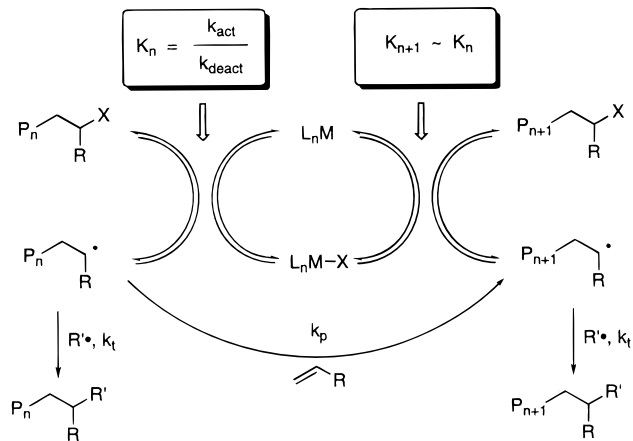
initiator (eq 1). After an activation–addition–deactivation



cycle in the presence of styrene, the resulting product possessed an α -phenylalkyl chloride moiety with a reactivity very similar to that of the starting 1-phenylethyl chloride. The catalyst could, therefore, reactivate the addition product, and the activation–addition–deactivation cycle of ATRA could be repeated until all of the unsaturated substrate present was consumed, resulting in a chain-growth polymerization. To demonstrate the process, styrene was polymerized at 130 °C using copper(I) chloride complexed with 2 equiv of 2,2'-bipyridine (bipy) and 1-phenylethyl chloride initiator.^{20,21} Monomer conversion obeyed first-order kinetics for several half-lives. Plots of molecular weight (M_n) as a function of conversion were linear up to high conversions, and the molecular weight distributions were smaller than the theoretical lower limit for free-radical polymerizations ($M_w/M_n < 1.5$). Additionally, when polymer isolated from these polymerizations was heated with styrene and CuCl/2bipy, quantitative extension of the polymer chains was observed. While this first report on copper(I)-catalyzed ATRP mainly described the polymerization of styrene, this method is applicable to a wide range of monomers, including styrenes, acrylates, methacrylates, substituted acrylamides, and acrylonitrile. Other ATRP systems have been developed using complexes of copper(I),^{22,23} ruthenium(II),^{24,25} Ni(II),^{26,27} and Fe(II)^{28,29} to catalyze the atom transfer equilibrium.

The mechanism of ATRP, as adapted from that of ATRA, is shown in Scheme 3. The steps are organized into an atom transfer equilibrium that generates and deactivates the propagating radicals from either an initiator or a polymer chain end, radical addition to monomer, and termination by coupling (or disproportionation). The initiation steps are omitted, but these are phenomenologically related to the propagation steps in Scheme 3. The

Scheme 3. General Mechanism for Atom Transfer Radical Polymerization (ATRP)



primary role of the initiator is to determine the number of dormant chains and to provide the structure of the initiating end of the polymer chain. After activation of a dormant chain, more than one monomer potentially can add to the chain, and the number of additions that occur before deactivation determines the polydispersity of the final polymer. Even though the persistent radical effect minimizes the total number of chains terminated by coupling or disproportionation to less than a few percent, irreversible termination is never completely eliminated in ATRP (or other controlled/living radical polymerizations).

Kinetic,^{30–33} EPR,^{34–36} inhibition,^{20,37–39} UV–visible,³⁰ GC–MS,³⁰ and NMR experiments³⁰ lend support to the mechanism in Scheme 3. The intermediacy of free radicals in ATRP, as opposed to an oxidative addition–insertion–reductive elimination mechanism, was supported by the following evidence.⁴⁰ The regiochemistry and tacticity of poly(methyl methacrylate) [PMMA] formed using ATRP are similar, within experimental error and to stereo-sequences as large as pentads, to those of compounds formed in a classical free-radical polymerization. The presence of stable free radicals, such as galvinoxyl, in these polymerization systems effectively inhibits polymerization. Additionally, the chemoselectivity of ATRP (i.e., reactivity ratios and the reactivity toward transfer agents) is quite similar to that of free-radical polymerizations, except in situations in which the functional group of interest reacts with the metal center. Both EPR and UV–visible measurements have been used to detect and quantify the formation of Cu(II) that would be expected if the persistent radical effect were operating in these polymerizations.

The possibility exists that the intermediate radicals in ATRP can coordinate to the copper(I/II) metal centers to form metal–alkyl intermediates. However, model free-radical polymerizations conducted in the presence of copper(I) and -(II) complexes indicated that, even if present, such species do not contribute significantly to the process that is responsible for polymerization control.⁴¹ Furthermore, ATRP is inert toward many relatively acidic additives, such as alcohols and phenols, that would normally react with transition metal–alkyl bonds. All of the above experimental data, considered in aggregate,

support the conclusion that ATRP mediated by copper(I)/bipyridine complexes proceeds via free-radical intermediates. However, this mechanism need not hold for ATRP catalyzed by other metal/ligand systems, as these polymerizations might involve ionic or coordination mechanisms. Such polymerizations should also be examined for the intermediacy of free radicals.

Advances Resulting from Understanding the Mechanism of ATRP

From the very early stages in the development of ATRP, progress in understanding the mechanism of polymerization allowed for advancements in molecular weight control, in adaptation of the method to different conditions, and in the design and synthesis of polymeric materials. Discussed below are a few such advances, and it is expected that further progress in understanding ATRP will further expand the scope and utility of this method.

Narrow Molecular Weight Distributions. Initially, bipy was used as the ligand for ATRP, and its complexes with copper(I) halides were sparingly soluble in the nonpolar polymerization media. The very first ligand modifications reported were the addition of solubilizing, long alkyl groups to the 4,4'-positions of bipy.^{42,43} The resulting polymerizations yielded polymer with much narrower molecular weight distributions. The reason for this improvement derived from an enhanced solubility of the corresponding copper(II) complex, or deactivator, that increased the rate of deactivation relative to propagation. Because the molecular weight distribution has a direct dependence upon the ratio k_p/k_{deact} (eq 2, where p is conversion and D represents deactivator, i.e., X–Cu(II), and R–X = alkyl halide end group), a noticeable improvement in molecular weight distributions was observed (i.e., $1.0 < M_w/M_n < 1.15$ for substituted 2,2'-bipyridines versus $1.2 < M_w/M_n < 1.5$ for bipy).

$$\frac{M_w}{M_n} = 1 + \left(\frac{2}{p} - 1\right) \left(\frac{([RX]_0 - [RX]_p)k_p}{k_{deact}[D]} \right) \quad (2)$$

Acceleration of Polymerization Rate. Based upon the rate law for ATRP (eq 3),

$$R_p = k_{app}[M] = k_p[P^*][M] = k_p K_{eq} [In] \frac{[Cu(I)]}{[Cu(II)X]} [M] \quad (3)$$

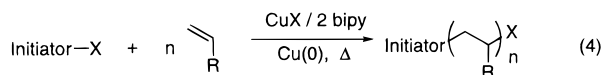
where

$$K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{[P^*][Cu(II)X]}{[Cu(I)][PX]}$$

improvements in the rate of polymerization can be gained either by increasing the equilibrium constant for atom transfer or by reducing the concentration of deactivator (i.e., copper(II)). The former has been achieved through changes in the ligand systems.^{44,45} Altering the σ -donation and π -accepting abilities of the ligands on the copper center changes the redox potential for the copper half-reaction in the atom transfer equilibrium and, conse-

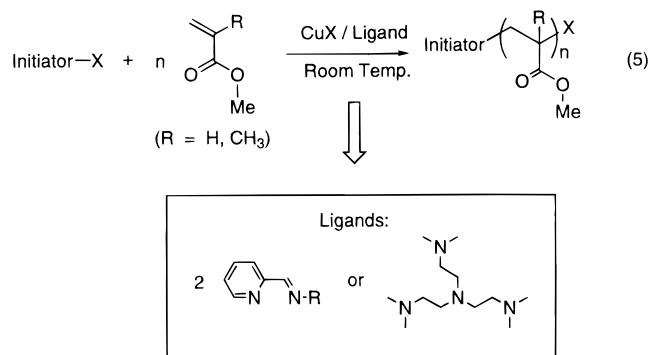
quently, the value of the equilibrium constant. Polymerizations using aliphatic polyamines are faster than polymerizations using 2,2'-bipyridines, presumably because the poorer π -accepting ability of the former ligands results in less stabilization of the copper(I) oxidation state than for the latter ligands.

Recently, it was discovered that the addition of copper metal to ATRP produced significant rate enhancements (eq 4).^{46,47} As discussed above, the deactivator, or the

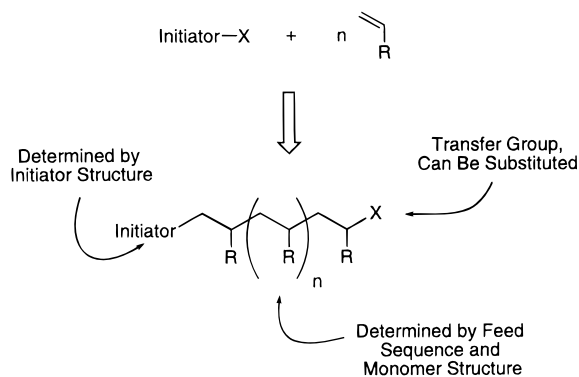


copper(II) species, is important for molecular weight control in ATRP. However, because the rate of polymerization is of inverse order with respect to the concentration of copper(II), too high a concentration of this reagent will lead to rather slow rates of polymerization. Upon addition of copper metal to the polymerizations, a disproportionation of the copper(0) and the copper(II) species re-forms the starting copper(I) complex. This equilibrium reaction probably is driven by the presence of the bipyridyl ligands, which serve to stabilize copper in its 1+ oxidation state. Thus, the addition of copper metal to ATRP regulates the amount of deactivator and keeps its concentration to the minimum necessary for polymerization control. The net result is a maximization of the observed rate of polymerization. An additional advantage to using copper metal in ATRP is that any copper(II) species formed from the oxidation of copper(I) by dioxygen will also be removed via disproportionation with copper(0). In this manner, ATRP can be conducted without prior degassing, provided that the reaction vessel is closed and that copper metal is present to scavenge the dioxygen present.⁴⁸

Conducting Polymerizations at Lower (and Ambient) Temperatures. Thermal energy must be added to the polymerization for the atom transfer equilibrium to generate a sufficient concentration of radicals. Thus, conducting polymerizations at lower temperatures usually results in very small concentrations of radicals and very long polymerization times. However, for monomers whose rate constants of radical propagation (k_p) are large, such as acrylates, fast polymerizations at lower temperatures have been achieved through modifications of both the charged and uncharged ligands on the copper(I) center (eq 5).^{45,49} Altering the structure of the ligands affects the redox

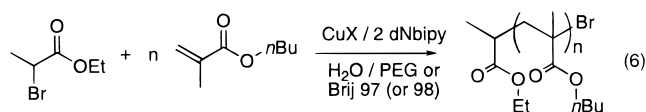


Scheme 4. Structural Features of a Polymer Chain That Can Be Controlled Using ATRP



potential of the copper center and can provide larger concentrations of radicals at lower temperatures, thus facilitating polymerizations at ambient and subambient temperatures. Presumably the design, synthesis, and use of new ligands or additives likewise will allow for the polymerization of other monomers at lower temperatures. For radical polymerizations, better ratios of k_p/k_t usually are obtained at higher temperatures, but some side reactions may occur at such high temperatures. Thus, the discovery of ATRP systems that function at lower temperatures will allow for the optimization of reaction conditions to prepare precisely defined polymers.

Water-Borne Polymerization Using ATRP. It was demonstrated that ATRP was tolerant of water in the polymerization medium,³⁰ which suggested that applying ATRP to emulsion systems might be feasible. Early attempts at emulsion polymerizations using ATRP were unsuccessful, though, due to the solvolysis and displacement of the halide ligand on the copper(II) centers by the alkylsulfonate surfactants. Because the most important aspect of the ATRP mechanism is the transfer of a halogen atom to and from the copper center, the loss of halide ligands from the copper(II) centers constituted an irreversible termination step. With a change to nonionic surfactants, the resulting emulsion polymerizations were successful and retained a high degree of molecular weight control (eq 6).⁵⁰ A range of monomers, including acrylates,



methacrylates, and styrenes, were polymerized successfully using emulsion ATRP systems.

Design and Synthesis of Polymeric Materials. By understanding the mechanism of ATRP and the roles of the individual components, one can use this methodology to prepare macromolecules with novel architectures and functionality.⁵¹⁻⁵⁴ In ATRP, there are three parts of the final macromolecule that can be modified via changes in the polymerizations components: the initiating end group, the terminating end group, and the intervening repeat unit sequence (Scheme 4). The initiator provides the structure

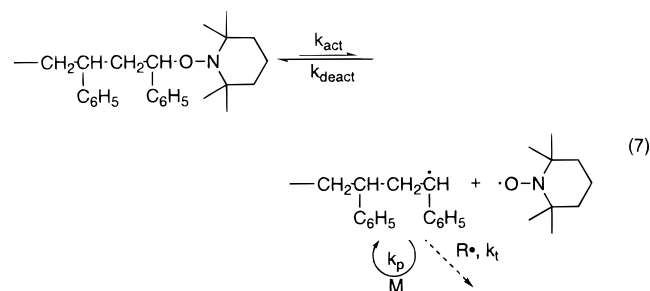
of the initiating end of the polymer chains and the halogen-transfer group that resides at the terminating end of the dormant chain. The initiator can be a small molecule, a polyfunctional small molecule, or a macromolecule, which would produce end-functional polymers, star polymers, and graft copolymers, respectively. To elaborate the composition of the terminating end of the polymer chains, the halogen end groups must be transformed into other functional groups. Depending upon the feed sequence of the polymerization, the intervening repeat units can have compositions ranging from random to tapered to block sequences. For a recent account of the various types of polymeric materials that have been prepared to date using ATRP, the reader is directed to recent reviews.^{51,52,54,55}

Understanding how the polymerization conditions will affect the ultimate structure of the macromolecule is equally as important to materials syntheses as knowing how the polymerization components can be assembled in new ways. For example, in the synthesis of macromolecules that possess multiple sites of growth, such as star polymers and hyperbranched polymers, the concentration of radicals affects the rates of polymerization and structures of the final polymer. In self-condensing vinyl polymerization leading to hyperbranched polymers,^{56–62} the concentration of initiator sites is much greater than in ATRP leading to linear polymers. Consequently, a greater amount of copper(II) will be formed to establish the persistent radical effect. If ligands are used for which the resulting copper(II) complex is soluble in the polymerization medium and if the concentration of copper(I) is much less than the concentration of alkyl halide groups, then most of the copper(I) will be converted to copper(II), and the rate of polymerization will be exceedingly slow. If Cu(0) is added to these polymerizations to reduce the concentration of deactivator, then the syntheses are successful.⁶¹ Using ligands for which the resulting copper(II) complex is much less soluble in the polymerization medium is also an effective strategy for preparing branched and hyperbranched polymers, because these less soluble catalysts provide for both a sufficiently fast rate of radical deactivation for controlled polymerization and a fast rate of polymerization.⁵⁸ Another example of how the reaction conditions in ATRP impact the structure of the final polymer can be found in the synthesis of star polymers^{63–65} and graft polymers.^{66–68} In ATRP leading to linear chains, there is a finite probability that two macromolecules will terminate via coupling. When several chains, N , are grown from a single core, this small, yet finite, probability that two macromolecules may couple is magnified N times. Thus, these polymerizations must be limited to low conversions to minimize the proportion of coupled macromolecules in the product, or one can use conditions that reduce the steady-state concentration of radicals (i.e., lower initiator concentration, lower temperature, less catalyst, etc.).

Comparison of the Various Methods for Controlling Radical Polymerizations

The first examples of radical polymerizations controlled using stable or persistent radicals actually date back to 1969⁶⁹ and 1979,⁷⁰ although it was not recognized until later that the persistent radical effect was the operative mechanism in these polymerizations. Other early examples involved the use of dithiocarbamates⁷¹ and stable nitroxyl radicals⁷² to effect polymerization control. In 1993, Georges et al.⁷³ revisited Solomon and co-workers' work and developed a system using 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) to obtain low-polydispersity polystyrene. This work spurred a great deal of recent work on developing new controlled/"living" radical polymerization systems and on applying these polymerization systems to the synthesis of new polymeric materials. Presently, the three most efficient controlled/"living" radical polymerization methods are nitroxyl radical-mediated polymerizations,⁷⁴ reversible addition–fragmentation transfer polymerization (RAFT),⁷⁵ and ATRP. Each of these methods has relative advantages and disadvantages with respect to the range of polymerizable monomers, reaction conditions, terminating end groups, and additives (i.e., catalysts, accelerators, etc.).

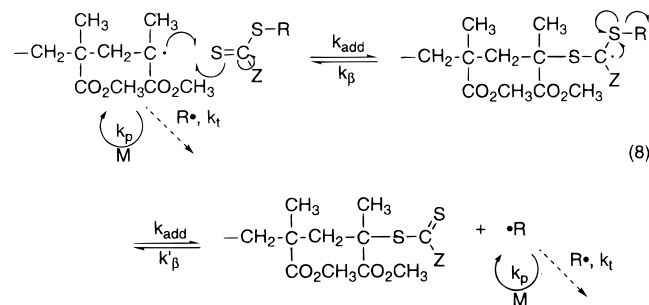
Most nitroxyl radical-mediated polymerization systems use TEMPO as the persistent radical (eq 7). The initiating



systems consist of either a combination of a conventional radical initiator with TEMPO (the optimum ratio is apparently 1.3:1) or a preformed alkoxyamine. The reaction times for these polymerizations are typically on the order of 24 h, but rate accelerators, such as acids and acyl compounds, can reduce these times. The terminating end group of a dormant chain is an alkoxyamine, and presently few methods for the substitution of the nitroxide at the chain end are known. Quite high degrees of polymerization can be attained in the polymerization of styrene and its copolymers, and the polymerizations can be conducted in bulk, solution, dispersion, and emulsion. The TEMPO-mediated polymerization of acrylates and methacrylates yields mostly uncontrolled polymerization or unsaturated oligomers, due to the abstraction of chain-end β -H atoms. Other nitroxyl radicals with higher equilibrium constants for radical formation, such as phosphate-containing nitroxyl radicals, have been applied successfully to the polymerization of acrylates and methacrylates.⁷⁶ Some alkoxyamines are not yet commercially available and need to be synthesized, and they are relatively expensive. The chief advantages of this polymerization method are its

simplicity and the fact that it does not require a catalyst, just elevated temperatures.

Presently, RAFT polymerization is applicable to a wide range of monomers, including styrenes, acrylates, methacrylates, and acrylamides (eq 8), and can be carried out in bulk, solution, dispersion, and emulsion.⁷⁵ The initiat-



ing system consists of a standard free-radical initiator and a dithioester-transfer agent, and the reaction times are typically on the order of hours. During the polymerization, the radical concentration is supplied by the radical initiator, so some of the end groups will have a different structure than provided by the dithioester-transfer agent. The terminating end groups of the dormant polymer chains are dithioesters, which are colored and can give off an odor for low molar mass species. Chemical manipulations might be desirable for removal or displacement of the end group, or new generations of transfer agents can be developed to replace these end groups. The chief advantages of RAFT are its simplicity and the fact that no catalyst is required. A potential disadvantage of RAFT, and degenerative transfer polymerization methods in general, is that a concentration of low molecular weight radicals is always present and available for termination reactions. In contrast, at sufficient conversions, both ATRP and nitroxyl radical-mediated polymerization systems have only high molar mass radicals, and therefore, termination is much slower.

As discussed above, ATRP has been used successfully for a large range of monomers, although the polymerizations of vinyl esters, acrylic acid, and acrylamide have not yet been successful. ATRP has been carried out in bulk, solution, dispersion, and emulsion at temperatures ranging from -20 to 130 °C, and a degree of tolerance to oxygen has been reported in the presence of zero-valent metals. The transition-metal catalyst regulates both the rate of polymerization and the polydispersities, and via halogen exchange it can facilitate cross-propagation in the synthesis of difficult block copolymers.⁷⁷ An advantage of ATRP is that the transfer group is a simple halogen atom, and it becomes the end group of the dormant polymer chains, which is especially important fact for low molar mass chains that have a high proportion of end groups. The halogen-containing initiators can be derived from a range of commercially available compounds, and the halogen end groups can be displaced with other useful functional groups using S_N2 , S_N1 , radical, and other chemistries.⁷⁸ A disadvantage of ATRP is the fact that, after

the polymerization, the copper(I) catalyst must be removed or recycled from the final polymerization product.

Future Directions for ATRP

In the near future, there are several important directions for the study of ATRP. First, there is still much room for advancement in understanding the chemistry of the metal complexes in these polymerizations. Specifically because the atom-transfer equilibrium is the governing mechanistic step in ATRP, more in-depth knowledge concerning the metal catalysts will allow for better control over end-group structures, an expansion of monomer types that can be polymerized using ATRP, and an extension of molecular weight control to even higher molar masses. More efficient catalysts will also reduce the amount of transition-metal complex needed for these polymerizations, and different catalyst designs will lead to easily recyclable ATRP catalysts or even solid-supported ATRP catalysts.

Second, because this method is tolerant of polar functional groups, water, and many impurities, ATRP and other controlled/living polymerization methods are optimally suited for application to materials synthesis. To date, most such work using ATRP has involved the preparation of organic polymeric materials with novel structures and compositions. Further work is needed in broadening the range of specialty polymers (i.e., polar thermoplastic elastomers, branched polymers, amphiphilic block copolymers, etc.) that can be prepared using ATRP, since this is one of the areas of advantage for controlled/"living" radical polymerizations over conventional free-radical polymerization methods. A less explored application of ATRP is its use in the modification of inorganic materials.^{64,79–84} Many novel materials can be envisioned that combine the magnetic, optical, and mechanical properties of well-defined inorganic phases with the array of properties that well-defined organic polymer phases display. Because of the demonstrated synthetic versatility of ATRP and other controlled/living radical polymerization methods, such applications of these methods appear to be a rich area for exploration.

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