

Recent mechanistic developments in atom transfer radical polymerization

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Abstract

Recent mechanistic innovations concerning catalyst development in atom transfer radical polymerization (ATRP) are described. The following topics will be discussed: structure–reactivity relationships of the polymerization catalyst, including correlating reaction parameters with catalyst, alkyl halide, and monomer structure; concurrent reactions that may occur during ATRP and will affect its efficiency, including oxidation/reduction of radicals to radical cations/anions, solvent, monomer, and radical coordination to the active catalyst, and side reactions particular to aqueous media. In addition, novel methods of fine tuning initiation, activation, and deactivation processes, including simultaneous reverse and normal initiation ATRP, activators generated by electron transfer ATRP, hybrid catalyst systems, and bimetallic ATRP will be presented.
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1. Introduction

Recent developments in controlled/“living” radical polymerization (CRP) processes have resulted in unprecedented control over the synthesis of many new well-defined (co)polymers with predictable molecular weights and narrow molecular weight distributions [1,2]. Among the available CRP techniques, atom transfer radical polymerization (ATRP) has proven particularly invaluable as a synthetic tool [3–5]. In addition to the extraordinary control that this technique has provided over polymeric materials with a plethora of topologies, compositions, microstructures, and functionalities [6–9], precise supramolecular control has been realized with ATRP that has led to the self-organization of many copolymers into regular nano-structured morphologies that in turn affects the macroscopic properties of these materials [10–13].

The basic working mechanism of ATRP involves homolytic cleavage of an alkyl halide bond R–X by a transition metal complex Mt^n to generate (with a rate constant k_{act}) the corresponding higher oxidation state metal halide complex $Mt^{n+1}X$ and an alkyl radical R^\bullet (Scheme 1) [14,15]. R^\bullet can then propa-

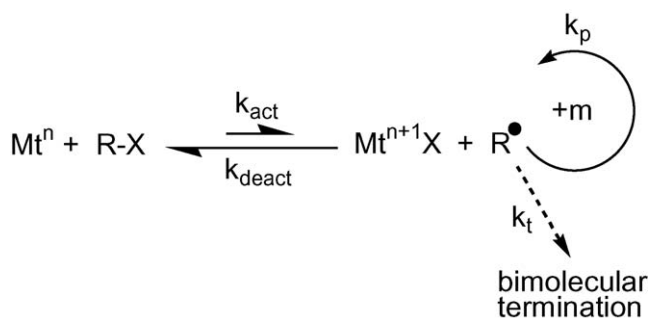
gate with a vinyl monomer (k_p), terminate by either coupling or disproportionation (k_t) [16], or be reversibly deactivated in this equilibrium by $Mt^{n+1}X$ (k_{deact}). Radical termination is diminished as a result of the persistent radical effect [17] that ultimately strongly shifts the equilibrium towards the dormant species ($k_{act} \ll k_{deact}$).

The efficient ATRP catalyst consists of a transition metal species which can expand its coordination sphere and increase its oxidation number, a complexing ligand, and a counterion which can form a covalent or ionic bond with the metal center. ATRP has been successfully mediated by a variety of metals, including those from Groups 4 (Ti [18]), 6 (Mo [19–21]), 7 (Re [22]), 8 (Fe [23–26], Ru [27,28], Os [29]), 9 (Rh [30], Co [31]), 10 (Ni [32,33], Pd [34]), and 11 (Cu [3,14]). Cu has proven by far the most efficient metal as determined by the successful application of its complexes as catalysts in the ATRP of a broad range of monomers in diverse media. Nitrogen-based ligands that are commonly used in conjunction with Cu include derivatives of bidentate bipyridine (bpy) [3,35] and phenanthroline (phen) [36], tridentate diethylenetriamine (DETA) [37] and terpyridine (tpy) [38], and tetradentate tris[2-aminoethyl]amine (TREN) [39], tetraazacyclotetradecane (CYCLAM) [40] and other branched multidentate ligands [41,42] (Fig. 1).

Control over polymerization molecular weight and molecular weight distribution in all CRP techniques is established

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Scheme 1. Mechanism for ATRP.

through a dynamic equilibrium between dormant species and propagating radicals. One advantage of ATRP over other CRP processes is that this equilibrium can be easily and appropriately adjusted for a given system by modifying the complexing ligand of the catalyst [14]. In this way, control has been established over the polymerization of a wide variety of monomers, including styrenics [43], (meth)acrylates [44–47], acrylonitrile [48,49], acrylamides [46,50] and others [14], over a broad range of temperatures.

This review will focus on mechanistic innovations concerning catalyst development in ATRP and will highlight those efforts which have optimized the overall catalytic process. Several facets are considered: finer components of the ATRP equilibrium; concurrent reactions that may occur during ATRP and will affect its efficiency; novel methods for fine tuning catalyst systems to alleviate handling problems and enhance efficiency.

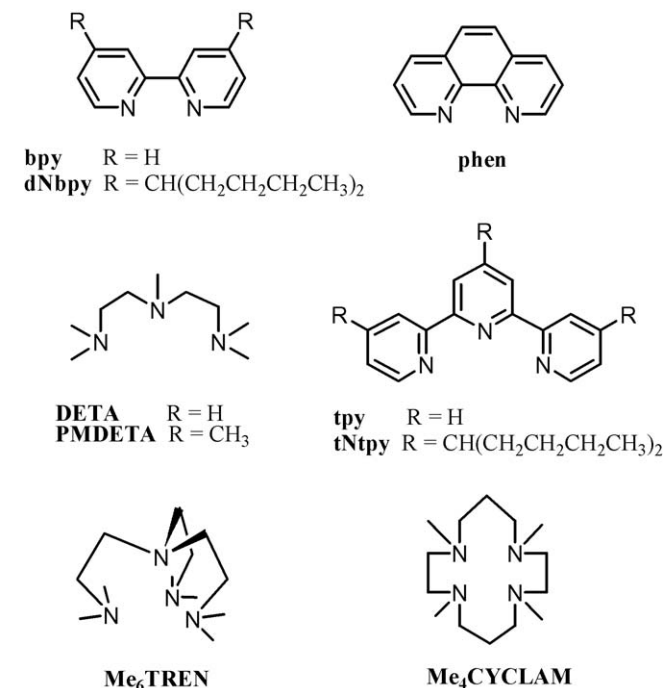


Fig. 1. Common nitrogen-based ligands employed in Cu mediated ATRP.

2. Recent developments

2.1. Confirming the radical nature of ATRP

ATRP originates from and is mechanistically similar to atom transfer radical addition (ATRA), a widely used reaction in organic synthesis [51,52]. ATRA exploits atom transfer from an organic halide to a transition metal complex to generate reacting radicals, followed by back-transfer of the atom from the transition metal to the product radical species. Although the most plausible mechanism for this reaction based upon experimental evidence involves free radicals, it has been debated as to whether the intermediate radicals are truly free radicals, in a solvent cage, or coordinated to the metal center. Indeed, it has been proposed for some systems that radicals produced in ATRA are somehow under the influence of the metal center [53,54]. If this were indeed true, it would have profound implications on structure–reactivity relationships in ATRP.

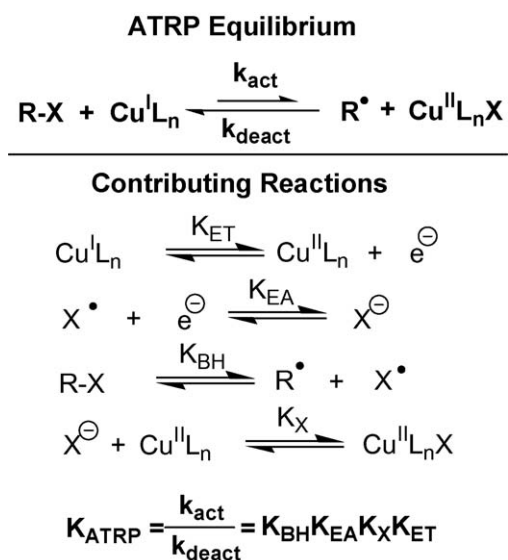
Numerous criteria have been used to determine the nature of the propagating species in ATRP. These include similarities between the reactivity ratios in conventional free radical and atom transfer radical copolymerization [55–60], the effect of added reagents, such as protic solvents, radical scavengers, and transfer reagents, the stereoselectivity or tacticity of the resulting polymers, and the concurrent formation of Cu^{II} species during the reaction [61]. Additional support for a radical mechanism has been the development of reverse ATRP, where the ATRP equilibrium in Scheme 1 is established from the right with a conventional free radical initiator and the higher oxidation state metal halide catalyst (Section 2.4) [62].

Despite recent suggestions that copper-mediated living radical polymerization is not a simple free radical process [63], further observations concerning similar rates of racemization, exchange, and trapping reactions [64], the identical reactivities of radicals in metal catalyzed and conventional free radical addition reactions [65], and the direct ESR observation of radicals during ATRP gelation experiments [66] all provide convincing evidence that the dominant intermediates in these processes are truly free radicals. Recent studies also revealed indistinguishable ¹³C kinetic isotope effects between free radical polymerization initiated by AIBN and ATRP initiated by ethyl 2-bromoisobutyrate using Cu^IBr/(bpy)₂ as the catalyst, further reinforcing a free radical mechanism of chain extension in ATRP [67].

2.2. Components of the ATRP equilibrium

2.2.1. Sub-equilibria

The overall ATRP equilibrium constant (K_{ATRP}) can be expressed as a combination of four reversible reactions: oxidation of the metal complex, or electron transfer (K_{ET}), reduction of a halogen to a halide ion, or electron affinity (K_{EA}), alkyl halide bond homolysis (K_{BH}), and association of the halide ion to the metal complex, or “halogenophilicity” (K_{X}) (Scheme 2) [68]. In a general effort to understand catalyst structure–reactivity relationships, many recent studies have focused on correlating these individual reactions with K_{ATRP} .



Scheme 2. Representation of ATRP equilibrium [68].

It is important to realize that these equilibrium constants, especially K_{EA} and K_{X} , are very solvent dependent. The values of K_{EA} are expected to be relatively high in protic solvents as halide anions are stabilized in such media [69]. K_{X} will likewise be affected with changes in solvent polarity and solvation of ions. Quantification of Br^- coordination to commonly used $\text{Cu}^{\text{II}}/\text{L}$ complexes in ATRP ($\text{L} = \text{bpy}$, PMDETA , and Me_6TREN) has revealed that K_{X} for these complexes is approximately five orders of magnitude greater in CH_3CN than in H_2O , attributed to efficient solvation of ions in aqueous media [70]. These measurements suggest that the majority of the halogen from the deactivating species will be dissociated from the metal under these conditions in water, which has direct implications on the degree of control that will be attainable in aqueous media with these catalysts. Additional studies have correlated K_{X} , directly measured in mixed protic solvents, with observed rates of polymerization and attainable degrees of control in aqueous ATRP [71].

The activity of the catalyst in ATRP is also intrinsically dependent upon its redox potential. The linear correlation between K_{ATRP} and $E_{1/2}$ for a series of Cu^{I} complexes with nitrogen-based ligands and similar halogenophilicities clearly demonstrates this facet of the ATRP equilibrium [72–74]. However, it should be noted that different transition metals (i.e., Ru) are expected to have very different halogenophilicities [75]; thus, redox potential alone is not sufficient to compare K_{ATRP} between different metals [68]. However, these studies do provide a useful means for screening appropriate catalysts for a given system. Additionally, knowledge of the $E_{1/2}$ of a metal catalyst and an organic radical allows one to predict whether outer sphere electron transfer can occur as a side reaction to generate carbocations or carbanions (Section 2.3.1).

It can also be concluded that for a given catalytic system in the same solvent (where K_{ET} , K_{EA} , and K_{X} are essentially constant), K_{ATRP} should only depend upon the energetics of alkyl halide bond homolysis, or K_{BH} . Indeed, when the alkyl

halide bond dissociation energies were recently calculated for a series of ATRP monomers/initiators, they were found to correlate well with measured values of K_{ATRP} [76]. It was proposed that such calculations could also be used to predict equilibrium constants for unreactive monomers. Knowing K_{BH} as well as the rate constants of propagation for a given monomer, the rates of polymerization could be calculated for different monomers in ATRP under comparable conditions (same catalyst, constant K_{ET} , K_{EA} , and K_{X}). For example, if the ATRP of acrylonitrile would reach 90% conversion in 1 s, styrene would take 22 h and vinyl acetate 30 years to reach 90% conversion under the same conditions [76]. This calculation merely serves to demonstrate the necessity of choosing an appropriate catalyst for each monomer.

2.2.2. Activation and deactivation rates

The correlation of reaction parameters such as activation and deactivation in ATRP with catalyst, alkyl halide, and monomer structure, solvent composition and temperature, should ultimately lead to the development of more efficient catalysts. Furthermore, it is not possible to determine from K_{ATRP} alone whether a polymerization will be well controlled or not; fast activation and fast deactivation are required for good control. The determination of k_{act} is typically made by following the decay of R-X concentration when an alkyl radical R^\bullet formed by activation of an R-X bond is scavenged by a chemical agent, typically a nitroxide radical present in large excess [77].

In a recent thorough study, the activation rate constants for Cu complexes with a wide variety of nitrogen-based ligands were measured under the same conditions. The values of k_{act} for the different Cu complexes were observed to span more than seven orders of magnitude (Fig. 2). In general, the activity of the Cu -ligand complexes decrease in the following order: alkyl amine \approx pyridine $>$ alkyl imine \gg aryl imine $>$ aryl amine [78]. However, in some cases k_{act} is affected in a non-obvious way. For example, under identical conditions, the k_{act} of Me_6TREN is four orders of magnitude greater than that of Et_6TREN (Fig. 2).

Numerous other investigations have studied how k_{act} is affected by solvent, counterion, temperature, ligand/catalyst ratio, presence of monomer, effect of $[\text{Cu}^{\text{II}}]$, etc. [79–82]. When these studies were taken a step further and the k_{act} of certain dimeric alkyl halides were measured, it was discovered that the penultimate monomer unit can also have a dramatic effect on k_{act} [83], an observation of particular relevance in copolymerization. All of these aforementioned studies have provided a wealth of information that will ultimately serve as an excellent resource when considering appropriate conditions for a polymerization and when selecting/designing new ligands.

Deactivation rate constants have been much less studied, owing to the lack of efficient techniques for measuring the relatively fast process ($\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$). However, k_{deact} can be directly measured when generated radicals are trapped simultaneously by nitroxide radicals and the deactivator in a type of clock reaction [84]. Additionally, K_{ATRP} can be measured and k_{deact} determined knowing independently the value of k_{act} [65]. Determination of k_{deact} is important, as the degree of control over molecular weight distribution in a controlled radical poly-

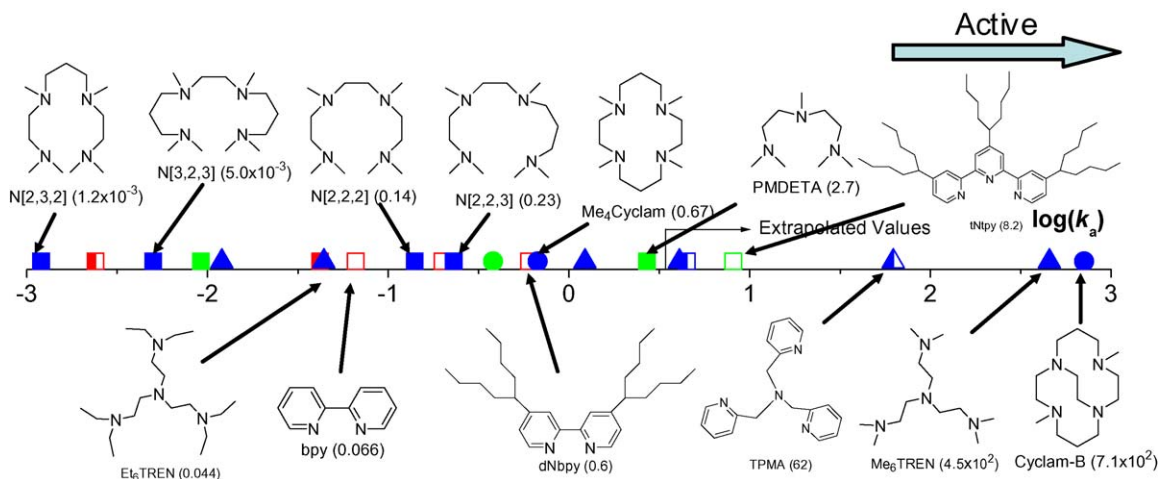


Fig. 2. ATRP activation rate constants for various ligands with EBriB in the presence of $\text{Cu}^{\text{I}}\text{X}$ ($\text{X} = \text{Br}$ or Cl) in MeCN at $35\text{ }^{\circ}\text{C}$ [78].

merization is limited by the rate of deactivation according to the relationship [85]:

$$\text{PDI} = \frac{M_w}{M_n} = 1 + \left(\frac{[\text{R-X}]_0 k_p}{k_{\text{deact}}[\text{X-Cu}^{\text{II}}]} \right) \left(\frac{2}{p} - 1 \right) \quad (1)$$

The Cu^{II} -halide bond length would be the simplest structural parameter that could be correlated with the rate of deactivation in ATRP. However, an analysis of this bond in complexes of Cu^{II} with dNbpy, tNtpy, PMDETA, Me_4Cyclam , and Me_6TREN found no direct correlation between Cu^{II} -Br bond length and the k_{deact} of these complexes [86]. It has further been proposed that the rate of structural reorganization of the Cu^{II} complex upon bromine abstraction by a radical in ATRP may be a determining factor affecting the observed rate of deactivation of the complex. However, further studies in this field will be needed to better understand these processes.

2.3. Exploring possible side reactions in ATRP

2.3.1. Outer sphere electron transfer

In addition to the atom transfer process (inner sphere electron transfer), in some cases an outer sphere electron transfer may also occur under typical ATRP conditions. On one hand, it is possible that ATRP catalysts may act as sufficiently strong Lewis acids to heterolytically cleave the R-X bond and produce carbocations; but depending on the redox potential of the organic radicals and the transition metal complex, the growing radicals may also be oxidized by Cu^{II} to carbocations (Fig. 3) [87]. The attempted polymerization of *p*-methoxystyrene under ATRP conditions catalyzed by CuBr/bpy has resulted predominantly in dimer formation. It was proposed that this dimer formation involved carbocationic intermediates as a result of the oxidation of these nucleophilic benzylic radicals [43,88]. A cationic process has also been observed to dominate over a radical one in a styrene polymerization catalyzed by $\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})_4\text{PF}_6$ [89].

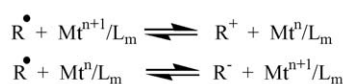
It should also be noted that the use of more active (i.e., more reducing) catalysts in ATRP can also result in the reduction of

electrophilic radicals. Indeed, Cu^{I} species have been observed to reduce malonate and trichloromethyl radicals to the corresponding anions [87]. These observations suggest that as more powerful Cu ATRP catalysts are developed, attention to side reactions such as reduction of radicals to carbanions should be considered.

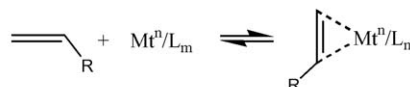
2.3.2. Monomer coordination

While π -coordination of vinyl monomers to many transition metal complexes has been extensively studied, including in complexes of Ru [90], Rh [91], Pt [92], Ni [93], and Cu [94,95], until recently very little had been studied on the effect of this coordination in ATRP. Based on solvent polarity and tem-

(a) Outer Sphere Electron Transfer



(b) Coordination of Olefin



(c) Formation of Organometallic Species



(d) Beta-Hydride Abstraction



(e) Disproportionation and/or Halide Dissociation

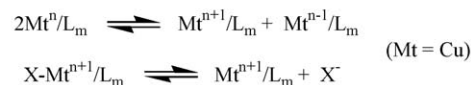
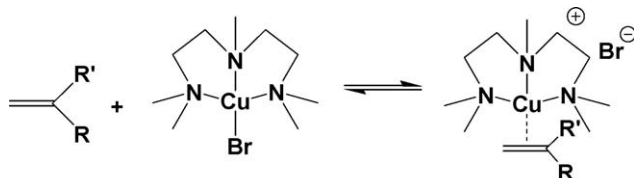


Fig. 3. Possible side reactions in metal catalyzed ATRP.



Scheme 3. Monomer coordination in ATRP.

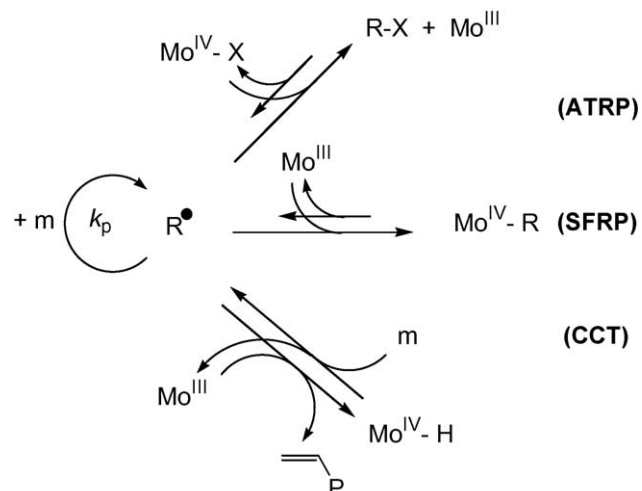
perature, the dissociation of a halide anion from a Cu^{I} ATRP catalyst could result in the coordination of a solvent molecule or vinyl monomer to the metal center. Indeed, several Cu^{I} complexes of the form $[\text{Cu}^{\text{I}}(\text{PMDETA})(\pi\text{-M})]^+$ (where M = vinyl monomer) have been isolated as model ATRP catalysts with the π -coordinated monomers methyl acrylate, methyl methacrylate, styrene, and 1-octene with BPh_4^- as the counterion [96]. While solid evidence has reinforced a free radical mechanism of chain extension in ATRP (vide supra), vinyl monomer coordination to Cu^{I} during ATRP could potentially alter the reactivity of the monomers in a polymerization (Scheme 3).

Vinyl monomer coordination to $\text{Cu}^{\text{I}}(\text{PMDETA})^+$ ATRP catalysts in the presence of BPh_4^- and Br^- was quantified using ^1H NMR and UV–vis techniques. It was determined that under typical ATRP conditions ($[\text{monomer}]/[\text{catalyst}] = 100/1$, bulk), as much as 10% of methyl acrylate could displace Br^- and coordinate to $\text{Cu}^{\text{I}}(\text{PMDETA})^+$ at room temperature [97]. However, when several copolymerization experiments were performed where the extent of monomer coordination was controlled by varying the counterion, it was ultimately concluded that monomer reactivity was not significantly affected by π -coordination to $\text{Cu}^{\text{I}}(\text{PMDETA})^+$ in radical copolymerization, and furthermore that this coordination plays no significant role in the chain extension step of ATRP [97].

2.3.3. Radical coordination and β -H abstraction

In stable free radical polymerization (SFRP), a SFR (or persistent radical) reversibly couples with a propagating alkyl radical to generate an equilibrium between a propagating and a dormant species that can result in a controlled polymerization. The persistent radicals capable of mediating SFRP, first developed as nitroxide mediated polymerization [98], have recently been expanded from organic species to include transition metal complexes such as Co [99–101] and now Mo [20]. While there is no experimental evidence to date which suggests there is any contribution from an SFRP mechanism in Cu mediated ATRP (i.e., radical coordination to Cu^{I}), recent studies of Mo mediated CRP have suggested there could be an interplay between ATRP and SFRP under certain conditions [20]. Furthermore, it was observed that subtle changes in the complexing ligands of these ATRP Mo catalysts promoted catalytic chain transfer polymerization [102] (Scheme 4).

Indeed, there has recently been a growing interest in the interplay of radical mechanisms. An investigation of $\text{Os}^{\text{II}}\text{Cl}_2(\text{PPh}_3)_3$ mediated polymerization suggested this complex could mediate both ATRP and SFRP [29]. It was also recently observed that diimine complexes of Fe^{II} could successfully mediate ATRP, but a slight modification of the substituents of the complexing lig-



Scheme 4. Interplay of radical polymerization mechanisms on Mo catalysts [20].

and converted the complex to a CCT catalyst [103]. These types of studies undoubtedly will become increasingly important as more non-Cu-based ATRP systems are developed.

2.3.4. Disproportionation of Cu^{I} in aqueous media

It has become increasingly desirable to conduct ATRP in aqueous media, primarily because this would allow for the controlled polymerization of many hydrophilic and ionic monomers that cannot otherwise be polymerized in organic media, but also because there has been a tendency in recent years to replace flammable and toxic organic solvents with more environmentally friendly ones [71]. However, an important side reaction of Cu-catalysts in aqueous media is disproportionation of Cu^{I} ions; indeed, the equilibrium constant for disproportionation of Cu^{I} is very large in water ($K_{\text{disp}} = 10^6$). Nevertheless, disproportionation can be effectively suppressed with ligands that stabilize the Cu^{I} versus Cu^{II} complexes [104] with overall stability constants β_i^{I} and β_j^{II} , respectively, defined as

$$\beta_k^m = \frac{[\text{Cu}^m\text{L}_k]}{[\text{Cu}^m][\text{L}]^k}, \quad m = \text{I or II} \quad (2)$$

Such ligands change the equilibrium constant of disproportionation to a conditional value, K_{disp}^* , which can be related to the concentration of ligand and the overall stability constants as

$$K_{\text{disp}}^* = \frac{1 + \sum_{j=1}^n \beta_j^{\text{II}}[\text{L}]^j}{(1 + \sum_{i=1}^m \beta_i^{\text{I}}[\text{L}]^i)^2} K_{\text{disp}} \quad (3)$$

Monomers such as 2-hydroxyethyl methacrylate and some carboxylate salts [105] have been successfully controlled in ATRP with no additives in pure water. These monomers stabilize Cu^{I} through complexation and effectively lower K_{disp}^* . With knowledge of the stability constants of pyridine with Cu^{I} and Cu^{II} [106], it was recently demonstrated that K_{disp}^* of Cu^{I} could be suppressed by more than 10 orders of magnitude in the presence of 1 M pyridine. Using pyridine as a co-solvent, the successful ATRP of several ionic monomers, which otherwise stabilized

Cu^{II} relative to Cu^I in pure water, was demonstrated for the first time [107].

2.3.5. Dissociation of halide ligand/solvent coordination

In addition to disproportionation, another ATRP side reaction that occurs to a significant extent in water is hydrolysis of the Cu^{II}–halide complex. A recent EXAFS study of typical ATRP deactivators in aqueous media demonstrated the marked heterolytic dissociation of Cu^{II}–Br bonds [108]. Because H₂O solvates Br[−] ions much better than organic solvents such as CH₃CN, reversible dissociation of the halide anion from the higher oxidation state metal complex will be much more significant in aqueous media. Indeed, quantification of Br[−] coordination to various Cu^{II} complexes revealed that the equilibrium constant of formation for Cu^{II}Br is approximately five orders of magnitude greater in CH₃CN than in H₂O [70]. This dissociation, which is presumably followed by coordination of water to Cu^{II}, ultimately lowers the concentration of available deactivator during ATRP. This is consistent with the observation that ATRP reactions are typically much faster and less controlled in aqueous and protic media [71]. However, the deactivator solvolysis can be suppressed and control over the polymerization of hydrophilic polymers can be achieved with the addition of extra halide salts to the reaction [71].

2.3.6. Additional side reactions

Several other noteworthy side reactions in ATRP mostly involve the polymer chain end. These include transfer reactions associated with the complexing ligand, in particular replacement of the halogen chain end atoms by hydrogen atoms, which become especially significant when excess complexing ligand is used [109–111]. A loss of chain end functionality during ATRP can also result from hydrolysis of the R–X bond and subsequent accumulation of acid, particularly for styrenic monomers [112]. β-Hydrogen elimination reactions can be induced by the Cu^{II} deactivator [113]. Additional side reactions peculiar to nitrogen containing monomers such as 4-vinyl pyridine involve reactions of the alkyl bromide chain end with pyridine units in the monomer and polymer (or pyridinolysis) that lead to the formation of branched polymeric structures, a reaction that evolves much slower with alkyl chloride chain ends [114]. Such studies have in many cases proven critical to preserving chain end functionality in ATRP.

2.4. Novel modes of initiation/activation/deactivation

Much research has been devoted to the development of more active catalysts which could be used to reduce the total amount of catalyst needed and/or to polymerize less reactive monomers with strong alkyl–halide bond strengths [115]. However, such systems are inherently less oxidatively stable, as the catalysts are more reducing. These systems often require special handling procedures to remove all oxygen and oxidants so as to avoid forming the redox conjugate of the catalyst that will shift the ATRP equilibrium in Scheme 1 towards the dormant state and significantly reduce the rate of the reaction.

Reverse ATRP (Scheme 5b) could be a convenient method for avoiding this problem. In this technique, the ATRP initiator and lower oxidation state transition metal activator (Cu^I) are generated in situ from conventional radical initiators and the higher oxidation state deactivator (Cu^{II}) [62,116]. The initial polymerization components are less sensitive to oxygen, and yet the same equilibrium between active and dormant species can ultimately be established. This technique would therefore be more compatible with commercial processes.

However, there are several drawbacks associated with reverse ATRP: (1) because the transferable halogen atom or group is added as a part of the copper salt, the catalyst concentration must be comparable to the concentration of initiator and therefore cannot be independently reduced; (2) block copolymers cannot be formed; (3) Cu^{II} complexes are typically much less soluble in organic media than those complexes of Cu^I, often resulting in a heterogeneous (and poorly controlled) polymerization; (4) very active catalysts must be used at lower temperatures where the gradual decomposition of thermal initiators results in slow initiation and consequently poor control. The following will describe the evolution of efficient methods to circumvent these and related problems in the development of ATRP catalytic systems.

2.4.1. Simultaneous reverse and normal initiation (SR&NI) ATRP

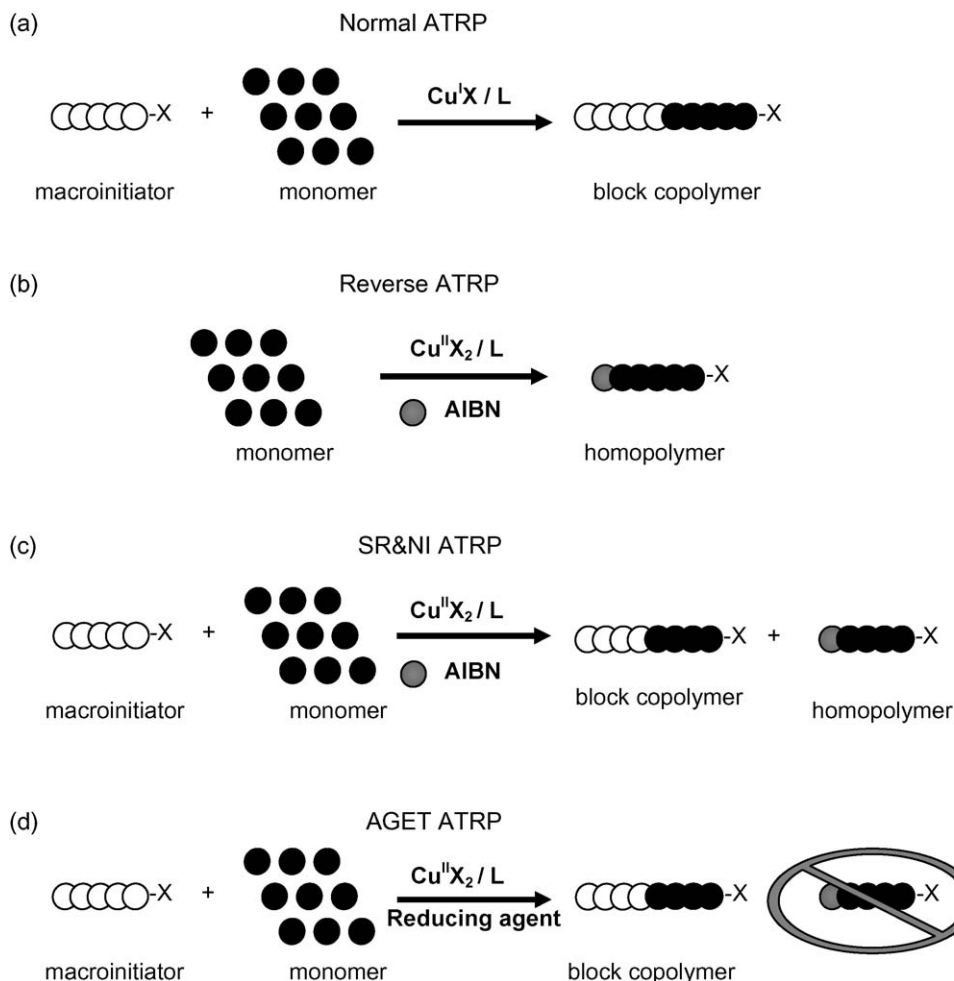
In contrast to reverse ATRP, SR&NI ATRP utilizes a dual initiation system comprised of standard free radical initiators and the higher oxidation state metal complex as well as initiators with a transferable atom or group (Scheme 5c) [117]. This provides the advantage of allowing highly active catalyst complexes to be added to the reaction as the higher oxidation state catalyst in lower concentration relative to the initiator, unlike in reverse ATRP, because the transferable atom is not solely apart of the catalyst salt. The radicals generated by the free radical initiator are deactivated by a Cu^{II}X/L complex forming Cu^I/L and some halogenated chains. The Cu^I/L can then activate the alkyl halide initiator (which may be present in excess) and concurrently mediate normal ATRP.

SR&NI ATRP has successfully produced well-defined homopolymers in bulk, solution, emulsion, and heterogeneous polymerization from surfaces [118]. The technique has also found application in miniemulsion systems where addition of the catalyst precursor as an oxidatively stable salt prior to sonification simplified the procedure [119,120].

However, there are some limitations to this method, particularly with the production of block copolymers. Because a conventional free radical initiator is used to form radicals that reduce the Cu^{II} complex, homopolymer chains initiated by these radicals will always be present, which can lead to a partial loss of control over functionality and topology in the synthesis of block copolymers.

2.4.2. Activator generated by electron transfer (AGET) ATRP

In this technique, electron transfer rather than organic radicals are used to reduce the higher oxidation state transition metal



Scheme 5. Methods for conducting ATRP [121].

complex (Scheme 5d). This way, no homopolymers are produced during block copolymerization as in SR&NI ATRP. Many of reducing agents could theoretically be used, provided that the reduction occurs without formation of intermediates which could act as new initiators. The principle was demonstrated with a number of Cu^{II} complexes using tin(II) 2-ethylhexanoate [121] and ascorbic acid [122] as the reducing agents, which reacted with the Cu^{II} complex to generate the Cu^{I} ATRP activator. Normal ATRP then proceeded in the presence of alkyl halide initiators or macromonomers. Oxidatively stable catalyst precursors that allow the synthesis of pure copolymers can now be easily prepared, stored, and shipped to be used in AGET ATRP.

2.4.3. Activators regenerated by electron transfer (ARGET) ATRP

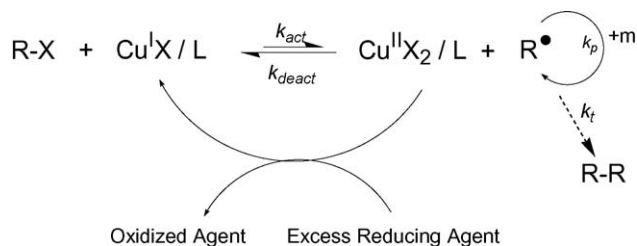
Perhaps the most recent industrially relevant development in the field of CRP was the realization of ARGET ATRP to lower the amount of transition metal catalyst necessary to achieve controlled polymerizations [123]. In principle, the absolute amount of copper catalyst can be reduced under normal ATRP conditions without affecting the polymerization rate, a rate which is governed by a ratio of the concentrations of Cu^{I} to Cu^{II} species

according to Eq. (4):

$$R_p = k_p[M][P^*] = k_p[M]K_{\text{ATRP}}[R-X] \frac{[\text{Cu}^{\text{I}}]}{[\text{X}-\text{Cu}^{\text{II}}]} \quad (4)$$

However, because the Cu^{II} deactivator accumulates during ATRP due to radical termination reactions according to the persistent radical effect, if the initial amount of copper catalyst does not exceed the concentration of those chains which actually terminate, no Cu^{I} activating species will remain, and polymerization will halt.

In ARGET ATRP, the relative concentration of catalyst to initiator can be reduced much lower than under normal ATRP conditions because a reducing agent (such as tin(II) 2-ethyl hexanoate or ascorbic acid) is used in excess to constantly regenerate the Cu^{I} activating species according to Scheme 6. This technique has effectively reduced the amount of Cu catalyst necessary to achieve control in a polymerization from typical values around 1000 ppm down to approximately 10 ppm. The economical and environmental implications of this development are obvious; additionally, the catalyst and excess reducing agent can effectively work to scavenge and remove dissolved oxygen from the polymerization system, an added benefit of industrial relevance.



Scheme 6. Proposed mechanism for ARGET ATRP [123].

While polymers of styrene with $M_n > 60,000$ g/mol and $M_w/M_n < 1.2$ have been produced using this technique with only 10 ppm of Cu catalyst [123], the degree of control over polymerization molecular weight distribution will always be limited in ATRP by the ratio of propagation to deactivation rate constants and the concentration of deactivator according to Eq. (1).

2.4.4. Hybrid and dual catalyst systems

As one of the perceived limitations of ATRP is the difficulty in removal of the transition metal catalyst after polymerization (a difficulty which has been alleviated with the development of ARGET ATRP), immobilized-supported catalysts were developed to aid in catalyst separation [124–129]. However, polymers prepared with these immobilized catalysts typically exhibited high molecular weights and broad molecular weight distributions as a result of diffusion limitations [84]; i.e., while activation occurs readily when an initiator molecule diffuses to the surface of the immobilized catalyst to initiate polymerization, deactivation cannot occur until the propagating chain slowly diffuses back to the surface.

Controlled polymerization with an immobilized catalyst can be achieved with the addition of a small amount of a soluble efficient deactivator (<3 mol% relative to immobilized Cu^{I}) which accelerates the rate of deactivation of the growing radical chain [130]. After the soluble Cu^{II} species in this “hybrid” system deactivates the growing radical chain in solution, it can diffuse to the supported catalyst without a significant diffusion barrier and be reconverted to Cu^{II} through a halogen exchange redox reaction with the immobilized Cu species that initiated polymerization (Scheme 7). The major fraction of the active transition metal complex in this system is thus immobilized and can be easily removed from the product by simple filtration, leaving only a small amount of soluble catalyst present in low ppm concentration in the resulting polymer [131].

A similar concept was used in the development of a halogen free neutral Cu^{I} ATRP catalyst, which proved to be an efficient activator of dormant chains but a poor deactivator [132]. The

addition of 3 mol% (versus the neutral Cu^{I} complex) of an efficient deactivator ($\text{Cu}^{\text{II}}\text{Br}_2/\text{Me}_6\text{TREN}$) was sufficient to dramatically increase control in the reaction. The proposed mechanism is similar to that of the immobilized “hybrid” catalyst, where the majority of chains are activated and deactivated by $\text{Cu}^{\text{I}}/\text{L}$ and $\text{Cu}^{\text{II}}\text{Br}_2/\text{Me}_6\text{TREN}$, respectively (Scheme 7).

2.4.5. Bimetallic ATRP

Our group is currently working to extend the concept of dual metallic catalysis to bimetallic ATRP systems in an effort to utilize economically and environmentally attractive metals (such as Fe) as activators of polymerization in the presence of a small amount (<5 mol% relative to activator) of an efficient Cu-based deactivator. This concept is fundamentally different from known bimetallic ATRA catalysts consisting of single, binuclear catalytic species [133] in that the two independent catalytic species have proposed separate roles of activation and deactivation.

Indeed, we have observed that several inexpensive Fe^{II} catalysts can initiate the polymerization of styrene and (meth)acrylates, but control in these systems is poor ($\text{PDI} \sim 1.8$). Upon addition of 5 mol% of a Cu^{II} -based deactivator, a dramatic increase in control over the polymerization is observed ($\text{PDI} < 1.3$) [134]. Further studies are being conducted to verify that the majority of chains are activated by Fe^{II} and deactivated by Cu^{II} , after which these two complexes are regenerated by a reaction between their respective redox conjugates (in parallel to the reaction proposed in Scheme 7).

3. Conclusions

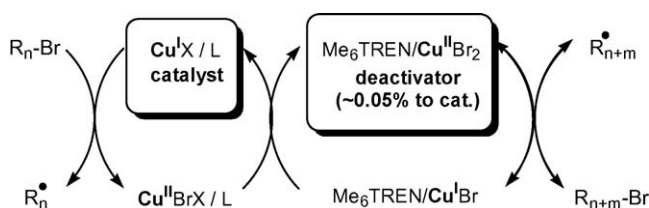
Most ATRP research is commercially, environmentally and/or economically driven. Much research has been done to correlate reaction parameters with catalyst, alkyl halide, and monomer structure, identify concurrent reactions that may occur during ATRP and will affect its efficiency, and fine tune methods of initiation, activation, and deactivation in ATRP. But whatever the motivation or incentive – whether it be developing more powerful catalysts that allow the polymerization of less reactive monomers, or facilitating the polymerization of hydrophilic monomers in aqueous media, or developing methods that streamline the catalytic process – a fundamental knowledge of the many facets of the ATRP equilibrium will be absolutely necessary to push ATRP into new dimensions.

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Scheme 7. Proposed mechanism for dual catalyst systems.

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