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Competitive Equilibria in Atom Transfer Radical Polymerization

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Summary: With the recent development of new initiation techniques in atom transfer radical polymerization (ATRP) that allow catalysts to be employed at unprecedented low concentrations (∼10 ppm), a thorough understanding of competitive equilibria that can affect catalyst performance is becoming increasingly important. Such mechanistic considerations are discussed herein, including i) factors affecting the position of the ATRP equilibrium; ii) dissociation of the ATRP catalyst at high dilution and loss of deactivator due to halide dissociation; iii) conditional stability constants as related to competitive monomer, solvent, and reducing agent complexation as well as ligand selection with respect to protonation in acidic media; and iv) competitive equilibria involving electron transfer reactions, including the radical oxidation to carbocations or reduction to carbanions, radical coordination to the metal catalyst, and disproportionation of the Cu^I-based ATRP activator.

Keywords: atom transfer radical polymerization; catalysis; complex stability; competitive complexation; electron transfer

Introduction

Ten years of research has transformed atom transfer radical polymerization (ATRP) from a technique used to control polymer molecular weights and molecular weight distributions[1] into one where the composition, topology, functionality, and microstructure of a vast array of material products can also be controlled.[2–10] As the full potential of this synthetic technique continues to be realized, much effort is currently focused on making ATRP more viable on an industrial scale,[11] in particular by maximizing the efficiency of catalyst removal or recycling.[12–14] However, with the recent development of two initiation techniques known as activators regenerated by electron transfer (ARGET)[15,16] and initiators for continuous activator regeneration (ICAR),[17] ATRP can now be conducted with dramatically lower catalyst concentrations, where removal of the catalyst from the final product would not be necessary for many applications.

The following discussion highlights facets of the ATRP equilibrium that should be considered when conducting polymerization with the catalyst at very low concentration. After a brief discussion of the factors that determine this equilibrium, particular emphasis is paid to concurrent reactions that may occur during ATRP and will affect the efficiency of the technique, including dissociation of the catalyst, competitive complexation reactions, and equilibria involving electron transfer. Cu-mediated ATRP is described here but most of the concepts can be applied to polymerizations catalyzed by other metal complexes.

Factors Determining the Activity of the ATRP Catalyst

The ATRP mechanism involves homolytic cleavage of an alkyl halide bond R–X by a

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transition metal complex (typically $Cu^{I}L_m$ where L is a ligand, for example one of those shown in Figure 1) to reversibly generate the corresponding higher oxidation state metal halide complex ($XCu^{II}L_m$) and a propagating alkyl radical $R^{\bullet}$ (Scheme 1).[4,18] Typically, enough Cu catalyst is required (several thousand ppm) to ensure a sufficient concentration of Cu^{I} activator survives, as every act of radical termination results in the irreversible accumulation of Cu^{II} deactivator according to the persistent radical effect.[19–21] However, in ARGET and ICAR ATRP, organic reducing agents and radicals generated from free radical initiators reduce accumulated Cu^{II} back into Cu^{I}, effectively regenerating lost activator. This has ultimately allowed ATRP to be successfully conducted with ≤10 ppm of Cu catalyst.[17]

For convenience, it has been proposed that the ATRP equilibrium constant (represented in Scheme 1 as $K_{ATRP} = k_{act}/k_{deact}$) is 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).[22]

The relationship between several of these individual reactions and the overall position of the ATRP equilibrium has been clearly demonstrated in several studies. Alkyl halide bond dissociation energies for a series of ATRP monomers/initiators were found to correlate well with measured values of K_{ATRP}.[23] Additionally, K_{ATRP} and $E_{1/2}$ for a series of Cu^{I} complexes with different ligands were correlated, which illustrates that catalyst activity is dependent upon the reducing power of the complex.[24,25] These observations further indicate that under ideal conditions, where the predominant reactions in ATRP are those illustrated in Schemes 1 and 2, one can appropriately choose the catalyst/conditions for a given polymerization with a thorough understanding of these reactions. As an example, it is demonstrated herein how appropriate polymerization conditions can be selected in protic media with knowledge of K_X.

However, conducting ATRP with the catalyst at very low concentration can present new challenges. In many cases, competitive equilibria that could previously be neglected must now be considered as they may affect the position of the ATRP equilibrium. For example, ligands that are weakly bound to the metal ions may dissociate or be displaced by monomer or solvent, resulting in a new catalyst complex with a different value of K_{ATRP}. Such competitive equilibria and their relevance to catalyst selection are now discussed.

Dissociation of the ATRP Catalyst

Dissociation Upon Dilution

Several factors should be considered when selecting the appropriate ligand for ATRP,

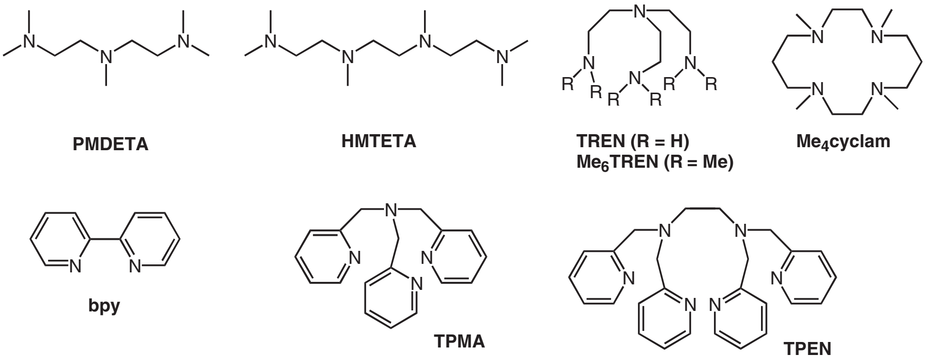
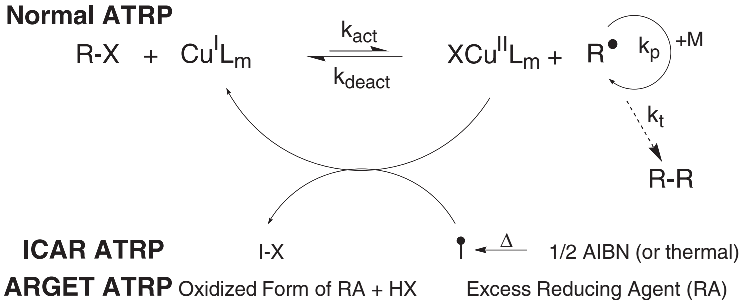


Figure 1.
N-based ligands used in ATRP.

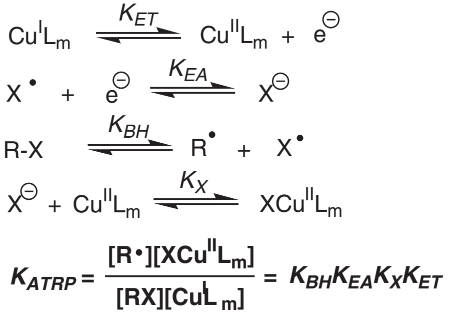


Scheme 1.
Representation of ATRP equilibrium.

especially for very dilute systems with respect to the catalyst. First, the catalyst should not dissociate appreciably at the low concentration used in processes such as ARGET or ICAR. The fraction of non-dissociated complex depends upon its stability (β^j; for definition, *vide infra*, eq (3)) and the dilution. If $[\mathrm{Cu^jL}]_0$ (j is the copper oxidation state and L is the ligand) is the initial concentration of catalyst, this fraction is given by eq (1).

$$\frac{[\mathrm{Cu^jL}]}{[\mathrm{Cu^jL}]_0} = 1 - \frac{\sqrt{1+4\beta^j[\mathrm{Cu^jL}]_0}-1}{2\beta^j[\mathrm{Cu^jL}]_0} \qquad (1)$$

Figure 2 shows the dependence (1), according to which, if 90% of the catalyst should remain in solution at a total concentration of 10^{-5} M (the low limit for ARGET or ICAR), the catalyst should have a stability constant larger than 10^7. This is true for both the Cu$^{\mathrm{I}}$ and Cu$^{\mathrm{II}}$ states of the catalyst. From this point of view, ligands commonly employed under normal ATRP conditions such as PMDETA, where $\beta^I < 10^8$ at room temperature,[26] are not suitable for ARGET or ICAR ATRP.



Scheme 2.
Components of the ATRP equilibrium.[22]

Most of the stability constants reported in literature have been determined at room temperature. However, ATRP is often carried out at elevated temperatures, at which the stability of the Cu$^{\mathrm{I}}$ and Cu$^{\mathrm{II}}$ complexes decreases, and therefore their dissociation becomes more pronounced. The thermochemistry of polyamine complexes of metal ions, including Cu$^{\mathrm{II}}$, has been extensively studied.[27] The enthalpies of formation of Cu$^{\mathrm{II}}$ complexes of polyamines in aqueous solution are in the range of -40 to -80 kJ mol^{-1}. A temperature increase from 25 to 110 °C should lead to a decrease in the stability constant by 2–3 orders of magnitude. The dependence of β^{II} for the Cu$^{\mathrm{II}}$ complexes of PMDETA,[28] TREN,[29] Me$_6$TREN,[28] TPMA,[30,31] and TPEN[30,31] on temperature is presented in Figure 3.

Loss of Deactivator

ATRP reactions in aqueous solvents are usually fast, even at ambient temperature, and the polymerizations are accelerated as the amount of water in the solvent is increased. This could be due to the effect of water or similar protic solvents on k_p, K_{ATRP}, and/or deactivator concentration [XCu$^{\mathrm{II}}$L$_{\mathrm{m}}$]. The solvent can also change the nature of the catalytic species. Specific solvation of

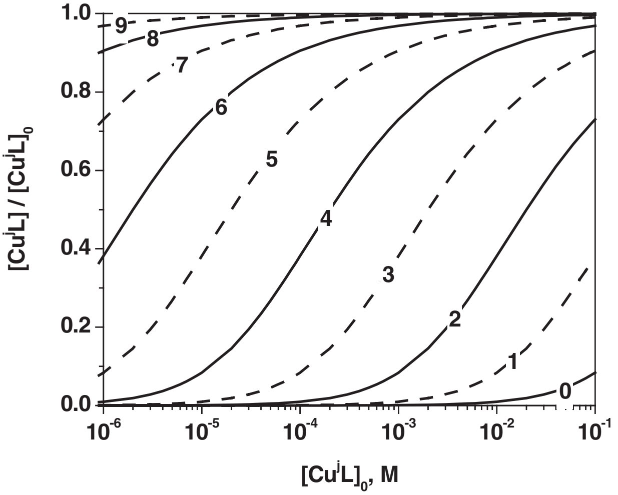


Figure 2.
Dependence of remaining, non-dissociated complex as a function of its initial concentration and its stability ($\log\beta^j$ is shown at each curve).

some polar monomers able to form hydrogen bonds with protic solvents does indeed lead to a small increase in k_p.[32–34] It was demonstrated[35] that copper-based ATRP deactivators ($XCu^{II}L_m$) are relatively unstable in protic media and tend to dissociate forming the complex $Cu^{II}L_m$ that cannot deactivate radicals. The concentration of deactivator actually present in the system depends upon the value of the halogenophilicity of the Cu^{II} complex, K_X, and upon the total concentrations of Cu^{II} complexes and halide ions, according to eq (2) (charges are omitted for simplicity).

$$[XCu^{II}L_m] = \frac{F - \sqrt{F^2 - 4K_X^2[Cu^{II}]_{tot}[X]_{tot}}}{2K_X} \qquad (2)$$

$$(F \equiv 1 + K_X[Cu^{II}]_{tot} + K_X[X]_{tot})$$

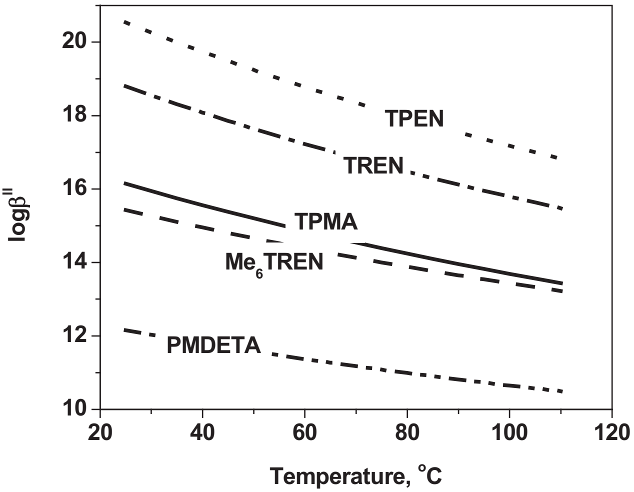


Figure 3.
Stability of Cu^{II} complexes with N-based ligands in aqueous solution as a function of temperature.

The value of K_X is lower in protic media than in "conventional" solvents. Typical values of K_X in aprotic solvents (hydrocarbons, ethers, ketones, DMF, etc.) are on the order of 10^4–10^5 M^{-1},[36] whereas in protic solvents, these values are two or more orders of magnitude lower (10–10^3 M^{-1}).[35] Knowledge of the precise values of K_X is crucially important, for it determines both the ATRP catalyst activity (Scheme 2) and the amount of deactivator present in the system (eq (2)) and therefore the degree of polymerization control.[37] The equilibrium constant of halide anion coordination can be measured by spectroscopic means,[38] as described in the literature for bpy-based ATRP deactivators in several protic solvents.[35] The refined values can be easily determined using programs such as Hyperquad.[39] The halogenophilicity of $[Cu^{II}(bpy)_2]^{2+}$ towards both Br^- and Cl^- was studied in various water-containing mixed solvents, and it was shown that in all cases the values of K_X decreased significantly as the amount of water in the mixtures increased (Figure 4).[35,40]

Thus, dissociation of the $XCu^{II}L_m$ complex is very pronounced in protic media, particularly in water-rich solvents, and the lower deactivator concentration leads to increased polydispersity.[41]

There are three general ways to improve the control over polymerization in protic media: i) select ATRP catalysts that possess high values of K_X (this value should depend upon the nature of the ligand L and the metal), ii) employ catalyst containing large initial amounts of deactivator (sometimes up to 80 mol % of the total catalyst), or iii) add extra halide salts to the system. The utility of the last two methods has been demonstrated.[35,42,43]

Conditional Stability Constants and Catalyst Destabilization by Competitive Complexation

In ATRP, various processes may interfere with the formation of the catalyst, both in the lower and higher oxidation states, resulting in a decrease in the corresponding stability constants. Typical side reactions include formation of additional complexes of the central atom with the solvent, monomer or other reaction components and the protonation of the ligand (especially important when the ligand is a

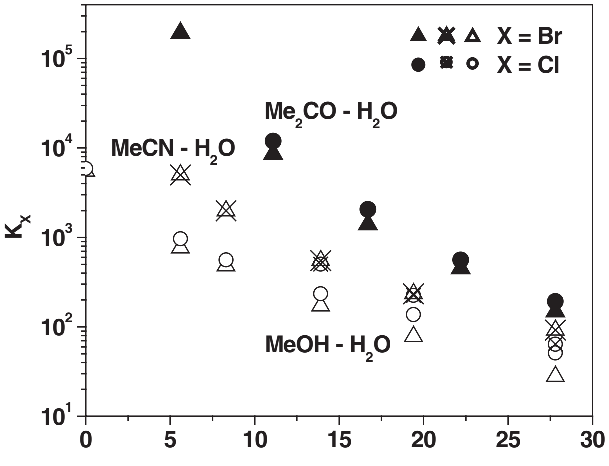


Figure 4.
Dependence of halogenophilicity, K_{Br} or K_{Cl}, of $[Cu^{II}(bpy)_2]^{2+}$ upon the concentration of water in mixtures of acetone (filled symbols), acetonitrile (crossed symbols), and methanol (open symbols) with water.[40]

relatively strong base). The complex formation of interest is now characterized by an apparent or, as Schwarzenbach[44] termed it, *conditional stability constant*, denoted by K^* (stepwise) or β^* (overall stability constant). Conditional stability constants have been widely utilized in analytical chemistry and have proven very useful for the understanding of equilibrium reactions in complex systems containing various metal ions and ligands.[44–49]

Consider the formation of the complex CuL (oxidation state is omitted for simplicity) in the presence of acids, which can protonate the ligand L yielding HL, $H_2L, \ldots, H_rL$, and in the presence of another ligand L′. The latter can react with the metal center giving the complexes CuL′, $CuL'_2, \ldots, CuL'_p$. The stability constants of the complexes formed between Cu and the ligand L′ are designated as $\beta_{1,L'}, \beta_{2,L'}, \ldots, \beta_{p,L'}$ and acidity constants of the protonated ligand L are $K_{a,1}, K_{a,2}, \ldots, K_{a,r}$:

$$\beta_{k,L'} = \frac{\left[CuL'_k\right]}{[Cu][L']^k} \quad (k = 1, 2, \ldots, p) \tag{3}$$

$$K_{a,h} = \frac{[H][H_{r-h}L]}{[H_{r-h+1}L]} \quad (h = 1, 2, \ldots, r) \tag{4}$$

The conditional stability constant of the complex of interest CuL is defined using the concentrations of the metal and ligand in all species except CuL, rather than only the concentrations of free metal and ligand:

$$\begin{aligned} \beta^*(CuL) &= \frac{[CuL]}{\left([Cu]_{tot} - [CuL]\right)\left([L]_{tot} - [CuL]\right)} \\ &= \frac{[CuL]}{([Cu] + [CuL'] + \ldots + [CuL'_p])([L] + [HL] + \ldots + [H_rL])} \end{aligned} \tag{5}$$

Schwarzenbach[44] also introduced *alpha-coefficients*, which are related to the extent to which side reactions occur, including the formation of complexes as well as ligand protonation). These coefficients are defined as follows:

$$\begin{aligned} \alpha_{Cu} &\equiv \frac{[Cu]_{tot} - [CuL]}{[Cu]} \\ &= \frac{[Cu] + [CuL'] + \ldots + \left[CuL'_p\right]}{[Cu]} \\ &= 1 + \frac{[CuL']}{[Cu]} + \ldots + \frac{\left[CuL'_p\right]}{[Cu]} \\ &= 1 + \beta_{1,L'}[L'] + \ldots + \beta_{p,L'}[L']^p \\ &= 1 + \sum_{k=1}^{p} \beta_{k,L'}[L']^k \end{aligned} \tag{6}$$

$$\begin{aligned} \alpha_L &\equiv \frac{[L]_{tot} - [MtL]}{[L]} \\ &= \frac{[L] + [HL] + \ldots + [H_rL]}{[L]} \\ &= 1 + \frac{[HL]}{[L]} + \ldots + \frac{[H_rL]}{[L]} \\ &= 1 + \sum_{h=1}^{r} \frac{[H]^h}{\prod_{g=r-h+1}^{r} K_{a,g}} \end{aligned} \tag{7}$$

In the absence of side reactions, the alpha-coefficients are equal to unity, but can become large if side reactions occur, depending on the stability of the complexes CuL′, $CuL'_2, \ldots, CuL'_p$, the strength of the acids HL, $H_2L, \ldots, H_rL$, and the concentrations of the ligand L′ and protons. Equation (5) can be rewritten as:

$$\beta^*(CuL) = \frac{[CuL]}{[Cu][L]} \frac{1}{\alpha_{Cu}\alpha_L} = \frac{\beta(CuL)}{\alpha_{Cu}\alpha_L} \tag{8}$$

Organic compounds with double or triple carbon-carbon bonds are known to form complexes with various transition metals, including copper.[50–53] A number of Cu^I–olefin complexes have been studied and

Table 1.

Formation constants of Cu(PMDETA)(π-M)$^+$ complexes[a] [56]

Monomer	K_M/M^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J mol^{-1} K^{-1}
MA	760	−30.2 (±2.8)	−46.0 (±9.4)
Sty	250	−22.7 (±0.4)	−30.5 (±1.6)
Oct	320	−26.2 (±0.8)	−40.0 (±2.8)
MMA	6	−25.4 (±0.5)	−70.2 (±1.8)

[a] Thermodynamic information was calculated from formation constants measured over a 40 °C range; K_M is reported at 25 °C.

even structurally characterized, and some of them have considerable stability.[54] The coordination of several monomers such as styrene, 1-octene, methyl acrylate, and methyl methacrylate to the Cu^I/PMDETA complex with non-coordinating anions was recently reported.[55,56] Formation constants for these complexes (Table 1) were determined from variable temperature ^{1}H NMR experiments monitoring the free and complexed vinyl proton resonances. The complexation is comparatively weak relative to halide ions and nitrogen based ligands, but at large monomer concentrations and especially at low catalyst concentration it may lead to a destabilization of the catalyst. These effects are compounded with difunctional monomers such as 4-vinylpyridine, whose coordination to Cu-based ATRP catalysts has been studied by electrochemistry.[57]

In the special case of ATRP of acidic monomers, or in processes where acid is generated throughout the polymerization as in ARGET ATRP,[17] significant ligand protonation may take place, reflected by a large α_L value. Figure 5 shows the dependence of $\beta^{II,*}$ (eq (8)) upon the medium pH for the Cu^{II} complexes of various N-based ligands, for which the protonation constants have been measured, including Me$_4$cyclam,[58] HMTETA,[58] Me$_6$TREN,[58] PMDETA,[26] and TPMA.[59]

The complexes of basic ligands, especially when their stability constants in the absence of protonation are relatively low (e.g., Cu^{II} complex of HMTETA) are very much destabilized in acidic media. The complex of the basic Me$_6$TREN is markedly more destabilized in acidic media than the complex of the less basic ligand TPMA. From this point of view, TPMA is a promising candidate for ARGET and ICAR reactions. The complex of Me$_6$TREN can also be used but in conjunction with excess base (or excess free ligand) that will trap the acid generated during the redox process.[17] In the presence of side reaction, the amount of catalyst actually present in the system

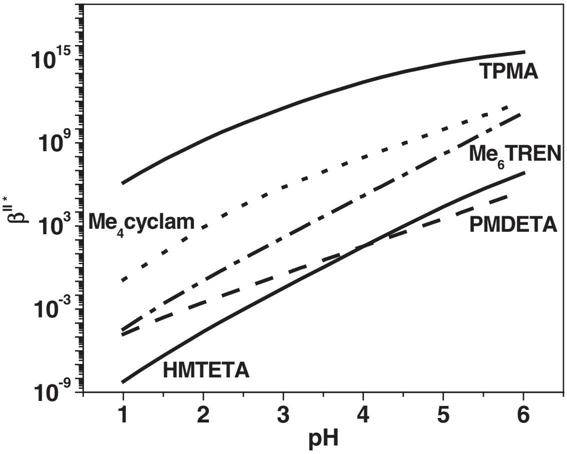


Figure 5.

Dependence of the conditional stability constant of Cu^{II}L complexes used as ATRP catalysts on pH of the medium.

can be calculated using eq (1), but with $\beta^{j,*}$ instead of β^{j}.

Coordination of alkyl halides to Cu^{I} complexes may also occur;[60,61] the $Cu^{I}(PPh_3)_3Cl$ complex of benzyl iodide was even isolated in the solid state.[61] However, there is not enough evidence that these reactions contribute to the destabilization of the ATRP catalyst.

Competitive Equilibria Involving Electron Transfer

Reduction/Oxidation of Organic Radicals

Inner sphere electron transfer is generally considered the predominant redox process that occurs in ATRP. However, outer sphere electron transfer (OSET) may also occur between organic radicals and transition metal complexes whereby growing radicals are oxidized to carbocations by Cu^{II} or reduced to carbanions by Cu^{I}.[62] The extent to which OSET occurs in ATRP is dictated by the relative redox potentials of the species involved.

The redox potentials of various organic radicals have been measured[63–65] and it is well-established that radicals with α-electron-withdrawing substituents (cyano, carboxy, etc.) are rather electrophilic or oxidizing. In other words, the radicals formed during the ATRP of acrylonitrile or acrylates are likely to oxidize very reducing (i.e., very active) ATRP catalysts. Active catalysts have been observed to reduce electrophilic radicals to their corresponding carbanions, and it is this side reaction that is believed responsible for limiting the attainable conversion and molecular weight of polyacrylonitrile prepared by ATRP.[66–68] Similarly, limited conversions were attained in the ATRP of n-butyl acrylate mediated by an exceptionally active and reducing Cu-based catalyst derived from dimethyl cross-bridged cyclam.[69] Interestingly, the application of ICAR ATRP under high dilution may actually work to minimize OSET between electrophilic radicals and extremely reducing Cu catalysts. The majority of the Cu catalyst under these conditions is present as the higher oxidation state complex, in contrast to normal ATRP, where the majority of the catalyst is in the lower oxidation state. Therefore, under ICAR conditions, very little Cu^{I} would be available to reduce such radicals to carbanions.

The Cu^{II} deactivator can also catalyze electron transfer reactions that result in a loss of halide chain end functionality during the ATRP of styrenic type monomers. HBr can be evolved from alkyl radicals and $Cu^{II}Br_2/L$ to give unsaturated chain ends and $Cu^{I}Br/L$.[70–72] This side reaction has thwarted the production of well-defined high molecular weight polystyrene in ATRP, with upper limits between 30,000 and 50,000 g mol^{-1}. However, the use of ARGET and ICAR ATRP that minimize Cu concentrations could allow high molecular weight polymers to be produced as side reactions between the chain end and the catalyst should be minimized. Indeed, high molecular weight styrene (co)polymers (200,000 g mol^{-1}) with narrow molecular weight distributions ($M_w/M_n < 1.2$) have been synthesized with just 10 ppm of Cu catalyst using these new techniques.[73]

Radical Coordination

One and two electron oxidative addition processes that involve electron transfer between alkyl radicals and transition metal species have been exploited in organic synthesis for many years.[74] These reactions can ultimately result in the formation of stable metal-alkyl complexes. The formation of such organometallic species during ATRP would have several implications on the role of the catalyst. The relative bond dissociation energies of the the Mt–R, Mt–X, and R–X bonds would ultimately dictate whether polymerization would be inhibited by the formation of a Mt–R bond, whether initiation efficiency might just be reduced, or whether the entire polymerization could be mediated through the reversible formation of such a Mt–R bond (as in stable free radical polymerization, or SFRP).[75]

While there is currently no experimental evidence that suggests any organometallic Cu^{II}–R species are formed during Cu-mediated ATRP,[76] several recent studies have suggested that certain Mo^{III} complexes initiate polymerization from alkyl halide ATRP initiators but then proceed to mediate polymerization through the reversible formation of a Mo^{IV}–R species as in SFRP.[77] This is a particularly important mechanistic observation in light of the new ICAR and ARGET processes. As polymerizations mediated by SFRP require a stoichiometric amount of metal species per polymer chain, such a Mo catalyst would not be expected to successfully mediate polymerization under ARGET or ICAR ATRP conditions where sub-stoichiometric amounts of the metal species are employed.

Disproportionation

Compounds of Cu^I are able to participate in a bimolecular redox process termed *disproportionation*, which yields a Cu^{II} compound and elemental copper according to eq (9).

$$\overset{\curvearrowright}{\mathrm{Cu^{I} + Cu^{I}}} \xrightleftharpoons{K_{disp}} \mathrm{Cu^{II} + Cu^{0}} \qquad (9)$$

While conducting ATRP in aqueous media has both economic and environmental advantages, the equilibrium constant for disproportionation of Cu^I is very large in pure water ($K_{disp} = 10^6$), resulting in a loss of the Cu^I activator.

However, disproportionation can be suppressed with the choice of appropriate ligands based on knowledge of the overall stability constants of the complexes for the Cu^I and Cu^{II} oxidation states (β_j^I and β_j^{II}).[14,26,37] The equilibrium constant of disproportionation is changed in the presence of complexing ligands to a new conditional value, K^*_{disp}, which is related to the concentration of ligand and its overall stability according to eq (10).

$$K*_{disp} = \frac{1+\sum_{j=1}^{m} \beta_j^{II}[\mathrm{L}]^j}{\left(1+\sum_{j=1}^{m} \beta_j^{I}[\mathrm{L}]^j\right)^2} K_{disp} \qquad (10)$$

The activity of a catalyst with ligands forming 1:1 complexes with copper ions is proportional to the relative binding constants of the ligand to the higher and lower oxidation state of the metal species (β^{II}/β^{I}).[37] The tendency of a Cu^I complex to disproportionate depends on the ratio $\beta^{II}/((\beta^{I})^2[\mathrm{L}])$, as expressed in eq 10. Knowledge of these stability constants in aqueous media can therefore be used to screen catalysts that will have both appropriately high activity in ATRP but will also be stable towards disproportionation.[14] For example, knowing the binding constants[78] of the two oxidation states of Cu with bpy,[79] PMDETA,[26] and TPMA,[59] one can predict that while Cu^I complexes with bpy would not be very active in ATRP, they would be stable towards disproportionation; Cu^I(PMDETA) would be more active, but would not be stable towards disproportionation; and Cu^I(TPMA) would both be active and stable towards disproportionation.

Conclusions

Several of the side reactions encountered in ATRP, such as catalyst dissociation and competitive monomer complexation, become more pronounced when the catalyst is used at very low concentration. These and other undesirable reactions, such as catalyst disproportionation or radical coordination to the metal center, can often be avoided with the appropriate choice of transition metal and complexing ligands. Still other side reactions, such as electron transfer between alkyl radicals and the metal catalysts, can actually be minimized by using low catalyst concentrations. This work aimed to demonstrate that with a thorough knowledge of the components of the ATRP equilibrium and a general awareness of potential side reactions under certain conditions, ATRP catalysts can be rationally selected and conditions optimized for very diverse polymerization systems.

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