Electron transfer reactions relevant to atom transfer radical polymerization

Nicolay V. Tsarevsky, Wade A. Braunecker, Krzysztof Matyjaszewski *

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

Abstract

The continuous development of more active and stable catalysts in atom transfer radical polymerization (ATRP) has increasingly required a thorough knowledge of concurrent electron transfer reactions that can affect catalyst performance. Special attention is provided in this short review to such processes, including disproportionation, most pronounced in Cu-mediated ATRP, the reduction of radicals to carbanions or oxidation to carbocations, and radical coordination to the metal catalyst resulting in the interplay of controlled radical polymerization mechanisms.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Atom transfer radical polymerization; Electron transfer; Disproportionation; Radical coordination

1. Introduction

Since the initial discovery of atom transfer radical polymerization (ATRP) 10 years ago, [1,2] materials research employing this technique has witnessed explosive growth and development [3–5]. Fundamental studies of the ATRP mechanism and components (illustrated in Scheme 1) have ultimately allowed for the synthesis of a vast array of polymeric products with controlled compositions, topologies, functionalities, and microstructures [6–10]. The full potential of this synthetic technique continues to be realized as current mechanistic research pushes the limits of ATRP in terms of decreasing catalyst concentration, increasing polymer molecular weight, extending the application of ATRP in protic and aqueous media, and expanding the range of polymerizable monomers [11,12].

In many cases, achieving these goals requires the development of more powerful catalysts that can appropriately shift the ATRP equilibrium in Scheme 1 from the dormant alkyl halide and transition metal activator ($Mt^z L_m$) to the actively propagating alkyl radical and transition metal deactivator ($XMt^{z+1}L_m$) [13]. Much research has focused on developing novel nitrogen-based ligands for Cu complexes in an effort to adjust the redox potential of the catalysts, and in turn, affect the position of the ATRP equilibrium (*vide infra*) [14–17]. Additionally, the range of transition metals employed in ATRP continues to be expanded in the search for more powerful catalysts and now includes Ti, [18] Mo, [19–22] Re, [23–25] Ru, [2,26–32] Fe, [33–41] Rh [26,42–45], Ni, [43,46–53] Pd, [54] Co, [55] Os, [56] and Cu [1,6,15,16,57–68]. As more catalysts are developed, their successful application will not only depend on a thorough understanding of the ATRP mechanism; knowledge of side reactions, particularly those involving electron transfer that can dramatically affect the outcome of the polymerization, will also be of key importance. This short review focuses primarily on three concurrent reactions involving electron transfer that may occur in metal catalyzed ATRP (Fig. 1; *E* is the redox potential of the couple shown in parentheses): (i) disproportionation of the ATRP activator (most common but not limited to Cu complexes), (ii) oxidation or reduction of organic radicals to carbocations or carbanions, respectively, and (iii) radical coordination to the ATRP catalyst. The main focus of this review will be Cu-mediated ATRP

---
* Corresponding author. Tel.: +1 412 268 3209; fax: +1 412 268 6897.
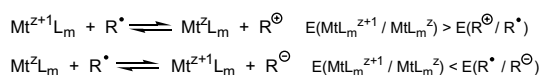*E-mail address:* km3b@andrew.cmu.edu (K. Matyjaszewski).
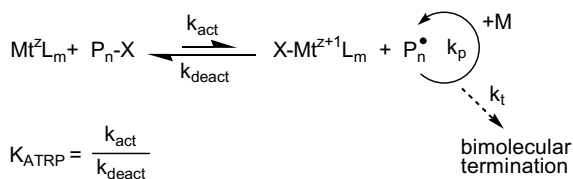
$$K_{ATRP} = \frac{k_{act}}{k_{deact}}$$
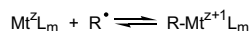
Scheme 1. ATRP mechanism.
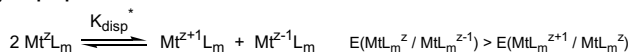
Fig. 1. Possible concurrent reactions involving electron transfer in ATRP.

but examples with other metal complexes will be provided where appropriate.

It was proposed [69] that the overall atom transfer equilibrium can be viewed as a combination of four simpler reversible reactions: (i) oxidation of the $Cu^I L_m$ complex (characterized by the equilibrium constant of electron transfer K_{ET}), (ii) reduction of a halogen atom to a halide ion (electron affinity K_{EA} of X), (iii) C–X bond homolysis (K_{BH}), and (iv) association of halide ion to $Cu^{II} L_m$ (termed *halogenophilicity* K_X) as shown in Scheme 2 and Eq. 1.

Although most Ru^{II} complexes are less reducing than Cu^I compounds, [70] their activity as ATRP catalysts are comparable. Scheme 2 suggests this may be attributed to a higher affinity of Ru^{III} complexes towards halide ions compared to Cu^{II} (i.e., larger association constant K_X). The higher K_X value would compensate for the smaller value of K_{ET} and would lead to an acceptable catalytic activity of Ru^{II} in ATRP.
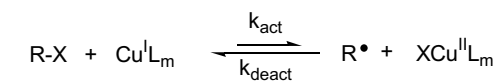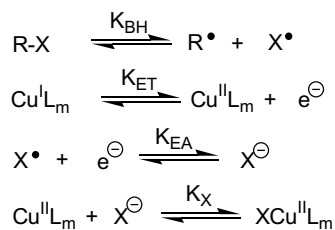
Scheme 2. Representation of atom transfer as a combination of a C–X bond homolysis of alkyl halide (RX), two redox processes, and a heterolytic cleavage of Cu^{II}–X bond. L represents a ligand [69].

$$K_{ATRP} = \frac{[XCu^{II}L_m][R^\cdot]}{[Cu^I L_m][RX]} = K_{BH}K_{ET}K_{EA}K_X \qquad (1)$$

2. Discussion

2.1. Catalyst performance and its evaluation

2.1.1. Experimental determination of the equilibrium constant K_{ATRP}

The catalyst activity is directly related to the value of K_{ATRP}. This can be determined either from polymerization kinetics data, in which case an apparent value is obtained ($K_{ATRP}/[XCu^{II}L_m]$), [14] or by measuring the accumulation of deactivator due to the persistent radical effect [71–73]. The classical equation predicted a linear dependence of the deactivator concentration on the cube root of time:

$$[XCu^{II}L_m] = (3K_{ATRP}^2 k_t[RX]_0^2[Cu^I L_m]_0^2)^{1/3}t^{1/3} \qquad (2)$$

If the termination rate constant is known, K_{ATRP} can be determined from the slope of the dependence $[XCu^{II}L_m]$ (determined spectrometrically) vs $t^{1/3}$ [69]. This method is useful only for low conversions of activator, $Cu^I L_m$, and alkyl halide. If these conditions are not met, the linear dependence (Eq. (2)) is not observed. The reason is that Eq. (2) was originally derived with the assumption that $k_{act}[Cu^I L_m]_0[RX]_0 = k_{deact}[R^\cdot][XCu^{II}L_m]$, i.e., that the concentrations of the activator and initiator do not change significantly during the experiment. This approach is valid only for time regimes in which the product $[R^\cdot][XCu^{II}L_m]$ remains nearly constant. This limits the application of the method, especially when active catalysts are being studied.

Recently, the equations describing the persistent radical effect were modified taking into account that the concentrations of both the activator and initiator change during the experiment [74]. If the activator and initiator are mixed in a 1:1 molar ratio, the reaction stoichiometry requires that $[RX]_0–[RX] = [Cu^I L_m]_0–[Cu^I L_m] = [XCu^{II}L_m]$. Using the assumption (justified by simulations) that the rate of generation of deactivator exceeds significantly the rate of consumption of radicals, new equations describing the time-dependence of $[XCu^{II}L_m]$ were obtained. A function $F([Cu^{II}L_m X])$ is defined whose values can be plotted against time, and K_{ATRP} is obtained from the slope of the linear dependence:

$$\begin{aligned}
F([XCu^{II}L_m]) &\equiv \frac{[Cu^I L_m]_0^2}{3([Cu^I L_m]_0 - [XCu^{II}L_m])^3} \\
&\quad - \frac{[Cu^I L_m]_0}{([Cu^I L_m]_0 - [XCu^{II}L_m])^2} \\
&\quad + \frac{1}{[Cu^I L_m]_0 - [XCu^{II}L_m]} \\
&= 2k_t K_{ATRP}^2 t + \frac{1}{3[Cu^I L_m]_0} \qquad (3)
\end{aligned}$$

In the case when $[\text{Cu}^I\text{L}_m]_0 \neq [\text{RX}]_0$, the time dependence of deactivator accumulation is more complex: [74]

$$
\begin{aligned}
F([\text{XCu}^{II}\text{L}_m]) &\equiv \left(\frac{[\text{RX}]_0[\text{Cu}^I\text{L}_m]_0}{[\text{Cu}^I\text{L}_m]_0 - [\text{RX}]_0}\right)^2 \\
&\times \left(\frac{1}{[\text{Cu}^I\text{L}_m]_0^2([\text{RX}]_0 - [\text{XCu}^{II}\text{L}_m])}\right. \\
&+ \frac{2}{[\text{RX}]_0[\text{Cu}^I\text{L}_m]_0([\text{Cu}^I\text{L}_m]_0 - [\text{RX}]_0)} \\
&\times \ln\left(\frac{[\text{RX}]_0 - [\text{X}Cu^{II}\text{L}_m]}{[\text{Cu}^I\text{L}_m]_0 - [\text{XCu}^{II}\text{L}_m]}\right) \\
&+ \left.\frac{1}{[\text{RX}]_0^2([\text{Cu}^I\text{L}_m]_0 - [\text{XCu}^{II}\text{L}_m])}\right) \\
&= 2k_t K_{ATRP}^2 t + \left(\frac{[\text{RX}]_0[\text{Cu}^I\text{L}_m]_0}{[\text{Cu}^I\text{L}_m]_0 - [\text{RX}]_0}\right)^2 \\
&\times \left(\frac{1}{[\text{Cu}^I\text{L}_m]_0^2[\text{RX}]_0}\right. \\
&+ \frac{2}{[\text{RX}]_0[\text{Cu}^I\text{L}_m]_0([\text{Cu}^I\text{L}_m]_0 - [\text{RX}]_0)} \\
&\times \left.\ln\frac{[\text{RX}]_0}{[\text{Cu}^I\text{L}_m]_0} + \frac{1}{[\text{RX}]_0^2[\text{Cu}^I\text{L}_m]_0}\right) \quad (4)
\end{aligned}
$$

The alkyl halide concentration decreases as the reaction proceeds and in some instances it is convenient to monitor the time dependence of RX consumption using chromatographic or spectroscopic techniques. In this case, equimolar or excess amount of the activating complex relative to initiator is used [16,74]. Values of K_{ATRP} measured with various alkyl halide initiators and Cu^I complexes that have been employed in ATRP are provided in Table 1. For different alkyl halides, the value of K_{ATRP} depends upon the degree of substitution (primary < secondary < tertiary). Alkyl halides with radical-stabilizing groups (such as α-cyano) are characterized by high activity. The K_{ATRP} values for alkyl bromides are higher than for chlorides with the same alkyl substituent, and for reactions mediated by the same complex. This is related to the higher bond dissociation energy of the C–Cl bond (Scheme 2). It should be noted that the strength of the C–Cl bond is higher by ca. 10 kcal mol^{-1} than C–Br and if this was the sole factor determining the values of K_{ATRP}, it is to be expected that K_{ATRP} for alkyl bromides should be several orders of magnitude larger than for the corresponding chlorides. However, the data in Table 1 shows that in reality the difference is less than an order of magnitude, which can be attributed to the higher electron affinity of chlorine compared to bromine [75–77]. K_{ATRP} can also be expressed as the ratio of the dissociation energies of the C–X and Cu^{II}–X bonds. The lower than expected difference between $K_{ATRP}(\text{RCl})$ vs $K_{ATRP}(\text{RBr})$, based only on BDE of C–X bonds, can be

attributed to the greater stability of the Cu^{II}–Cl compared to Cu^{II}–Br bond [78]. The ligand impact on K_{ATRP} is rationalized in the next section.

2.2. Factors determining the activity of the ATRP catalyst

The activity of the Cu-based ATRP catalyst is directly related to its reducing power, i.e. to the value of K_{ET} or the redox potential of the couple $\text{Cu}^{II}\text{L}_m/\text{Cu}^I\text{L}_m$. The redox potential is in turn related to the relative stabilization of the Cu^{II} vs the Cu^I state upon complexation with the ligand L. For ligands forming 1:1 complexes with copper ions, the following relation holds (E^0 is the standard potential of the $\text{Cu}^{II}/\text{Cu}^I$ couple): [81]
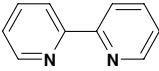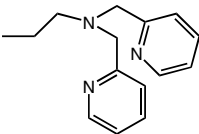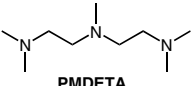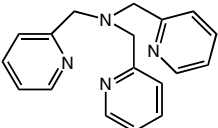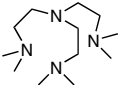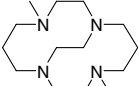
$$
\begin{aligned}
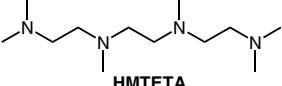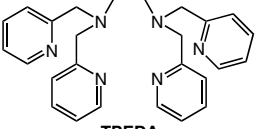E &= E^0 + \frac{RT}{F}\left(\ln\frac{[\text{Cu}^{II}]_{tot}}{[\text{Cu}^I]_{tot}} - \ln\frac{1 + \beta^{II}[\text{L}]}{1 + \beta^I[\text{L}]}\right) \\
&\approx E^0 + \frac{RT}{F}\left(\ln\frac{[\text{Cu}^{II}]_{tot}}{[\text{Cu}^I]_{tot}} - \ln\frac{\beta^{II}}{\beta^I}\right) \quad (5)
\end{aligned}
$$

where β^j is the stability constant of the Cu^jL complex. Thus, the knowledge of the readily measurable stability constants of Cu^{II}L and Cu^IL is sufficient to predict the catalytic activity of a given complex. Ideally, the value of K_X should be known as well, for it also contributes to the value of K_{ATRP}. Table 2 lists experimental values of β^{II}/β^I (in aqueous media) for copper complexes often used as ATRP catalysts along with the measured values of K_{ATRP} in the reaction of those complexes with ethyl 2-bromoisobutyrate in acetonitrile. Although the two sets of numbers were determined in two different solvents, the trend that higher values of β^{II}/β^I correspond to higher values of K_{ATRP} is clearly seen.

An important objective of many recent studies in ATRP has been the application of the technique to traditionally less reactive monomers like vinyl acetate, vinyl ethers, and α-olefins. In light of this goal, a thorough understanding of structure–activity relationships would aid in the development of more active ATRP catalysts [80]. Methods of electrochemical parametrization have been developed to help predict the redox potential of complexes with common stereochemistry, oxidation state, and spin state [86,87]. However, the application of such techniques are rather limited when multi-dentate ligands are employed that introduce varying degrees of distortion from ideal geometries.

Nevertheless, some generalizations can be made concerning the redox potentials of Cu complexes with various ligand morphologies. As complexes of Cu^I are typically tetrahedral while Cu^{II} species are more stable in tetragonal or square pyramidal geometries, [88] ligand morphologies that force a more planer geometry tend to stabilize Cu in its +2 oxidation state [89]. The result is a higher ratio of β^{II}/β^I and hence a more active ATRP catalyst. This is especially true of constrained macrocyclic ligands and was recently demonstrated with a derivative

Table 1
Values of K_{ATRP} measured in MeCN at 22 °C

Ligand	Cu^{I}X	Initiator[a]	K_{ATRP}	Ref.
bpy	Cu^{I}Br	EBriB	3.93×10^{-9}	[74]
BPMPrA	Cu^{I}Br	EBriB	6.2×10^{-8}	[16]
PMDETA **HMTETA**	Cu^{I}Br Cu^{I}Br Cu^{I}Br Cu^{I}Br Cu^{I}Cl	EBriB BPN PEBr EBriB PECl	7.46×10^{-8} 5.89×10^{-7} 2.9×10^{-9} 8.38×10^{-9} 7.9×10^{-10}	[74] [74] [79] [80] [79]
TPEDA	Cu^{I}Br	EBriB	2.0×10^{-6}	[16]
TPMA	Cu^{I}Br Cu^{I}Br Cu^{I}Cl Cu^{I}Br Cu^{I}Br Cu^{I}Cl	EBriB PEBr PECl BnBr MBrP MClP	9.65×10^{-6} 4.58×10^{-6} 8.60×10^{-7} 6.78×10^{-7} 3.25×10^{-7} 4.28×10^{-8}	[74]
Me$_6$TREN	Cu^{I}Br Cu^{I}Cl	EBriB MClAc	1.54×10^{-4} 3.3×10^{-6}	[74] [17]
DMCBCy	Cu^{I}Cl	MClAc	9.9×10^{-5}	[17]

[a] EBriB, ethyl 2-bromoisobutyrate; PEBr, 1-(bromoethyl)benzene; PECl, 1-(chloroethyl)benzene; BnBr, benzyl bromide; MBrP, methyl 2-bromopropionate; MClP, methyl 2-chloropropionate; BPN, 2-bromopropionitrile; MClAc, methyl chloroacetate.

of cross-bridged cyclam [17]. The application of electron donating substituents on the ligand will also result in a more reducing complex, [90–92] with the possible exception that added steric constraints may distort the geometry and destabilize a particular oxidation state of the complex [89].

Table 2
Correlation between the ratio β^{II}/β^{I} and K_{ATRP} for various Cu^I complexes used as ATRP catalysts

Catalyst	β^{Ia}	β^{IIa}	β^{II}/β^{Ia}	Ref.	K_{ATRP}[b]
Cu^IBr/bpy	8.9×10^{12c}	4.5×10^{13c}	5.0	[82]	3.93×10^{-9} [74]
$Cu^IBr/HMTETA$	1×10^{11}	3.98×10^{12}	39.8	[83]	8.38×10^{-9} [80]
$Cu^IBr/PMDETA$	$<1 \times 10^{8}$	1.45×10^{12}	$>1.45 \times 10^{4}$	[83]	7.46×10^{-8} [74]
$Cu^IBr/TPMA$	7.94×10^{12}	3.89×10^{17}	4.90×10^{4}	[84]	9.65×10^{-6} [74]
Cu^IBr/Me_6TREN	6.3×10^{8d}	2.69×10^{15}	4.3×10^{6d}	[85]	1.54×10^{-4} [74]

[a] Measured in aqueous solution.
[b] Reaction with EBriB in CH_3CN at 22 ± 2 °C.
[c] The values of β_2^{II} and β_2^{II} and their ratio are reported.
[d] This work.

Concerning donor atoms, the stability of Cu^{II} complexes typically increases according to thioether sulfur < aromatic nitrogen < carboxylic oxygen < aliphatic nitrogen [93]. The equilibrium constant of electron transfer may span more than 15 orders of magnitude for Cu complexes with these ligands; for example, the nitrogen analogues of tetradentate macrocyclic sulfur-based ligands form Cu complexes that are more reducing by as much as one volt [89]. If the activity of an ATRP catalyst is not appropriately matched with the reactivity of a given monomer, a successful controlled polymerization is unlikely.

It should be noted that activity of an ATRP catalyst (in terms of the position of the thermodynamic equilibrium), or the magnitude of the polydispersity index attainable, are not necessarily related to the rate at which the inner sphere redox process of atom transfer is catalyzed. It has been proposed that the degree of structural reorganization accompanying the inner sphere redox process might be correlated with rates of activation and deactivation in ATRP [88]. A similar proposition has been made concerning the kinetics of outer sphere electron transfer among Cu centers [94]. However, more studies will be necessary before it is possible to accurately predict rates of atom transfer based purely on catalyst structures.

3. Concurrent reactions in ATRP related to electron transfer

3.1. Disproportionation of Cu-based activating complexes in aqueous media

The compounds of Cu^I are able to participate in a bimolecular redox process termed *disproportionation*, which yields a Cu^{II} compound and elemental copper (Eq. (6)).

$$Cu^I + Cu^I \underset{}{\overset{K_{disp}}{\rightleftharpoons}} Cu^{II} + Cu^0 \qquad (6)$$
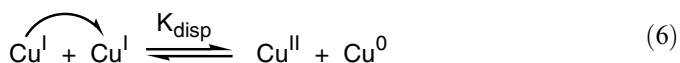
The extent to which a Cu^I compound disproportionates in a certain medium is related to both the value of K_{disp} (or K_{disp}^*, *vide infra*) and the concentration. Fig. 2 shows the dependence of the relative amount of Cu^{II} generated by disproportionation of Cu^I on both the disproportionation equilibrium constant and the initial concentration of Cu^I.
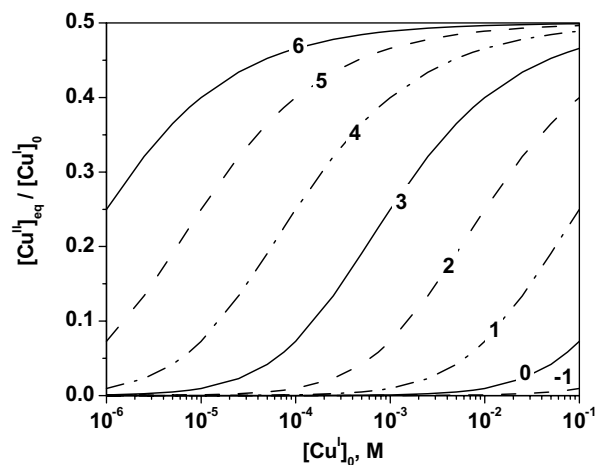
Fig. 2. Dependence of Cu^{II} generated via disproportionation of Cu^I upon the value of disproportionation equilibrium constant ($\log K_{disp}$ is shown at each curve) and the initial Cu^I concentration.

It should be noted that complete disproportionation corresponds to a fraction $[Cu^{II}]_{eq}/[Cu^I]_0 = 0.5$ (Eq. (6)).

The equilibrium constant K_{disp} is related to the difference of the redox potentials of the couples Cu^I/Cu^0 and Cu^{II}/Cu^I, according to Eq. (7), where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature, and F is the Faraday constant (96,500 C mol^{-1}).

$$\log K_{disp} = \frac{E^0(Cu^I/Cu^0) - E^0(Cu^{II}/Cu^I)}{2.303RTF^{-1}} \qquad (7)$$

K_{disp} depends strongly upon the nature of the medium, i.e., its polarity, as well as solvation and coordination ability. Table 3 lists values of K_{disp} for Cu^I ions in various solvents.

The values of K_{disp} have also been determined in mixed solvents containing water and DMSO, [104] DMF, [98] MeOH, [109] or MeCN [110]. As shown in Fig. 3, the disproportionation becomes significantly more prominent as the amount of water in the medium increases.

It was shown that for a limited number of solvents, the values of K_{disp} could be correlated with the solvent polarity. For instance, the Cu^I disproportionation is significantly more pronounced in the very polar water ($\log K_{disp} \approx 6$, $\varepsilon(H_2O) = 78.54$), than in solvents of lower polarity such

Table 3
Disproportionation equilibrium constant of Cu^I ions in various solvents

| Solvent	$\log K_{disp}$ [a]	Ref.
H_2O	5.9–6.2 (0.05–3)	[95–97]
DMF	4.26	[98]
MeOH	3.6 (0.08)–3.8 (0.1)	[99,100]
AcOH	2.7 (0.11–0.26 (0.01–0.16 M $HClO_4$))	[101]
EtOH	0.56 (0.01–0.08)	[99]
Me_2SO	0.2–0.3 (0.1–1)	[102–104]
Me_2CO	−1.50	[105]
Pyridine	−13.97 (0.1)	[106]
EtCN	−19.59 (0)	[107]
PhCN	−19.97 (0)	[107]
MeCN	∼−21 (0–0.1)	[107,108]

[a] The number in parentheses is the ionic strength of the medium (in mol L^{-1}).

as methanol ($\log K_{disp} = 3.55$, $\varepsilon(MeOH) = 32.63$), ethanol ($\log K_{disp} = 0.55$, $\varepsilon(EtOH) = 24.30$), and acetone ($\log K_{disp} = -1.50$, $\varepsilon(Me_2CO) = 20.70$). The value of the disproportionation constant depends upon the dielectric constant of the medium ε (i.e., $\log K_{disp}$ decreases linearly as $1/\varepsilon$ increases) [105]. The correlation cannot be extended to solvents that coordinate strongly to copper ions such as pyridine, sulfoxides, [111] and nitriles [112,113].

In the presence of a complexing agent L that stabilizes Cu^I and Cu^{II} to a different degree, the disproportionation process is influenced and is characterized by a new equilibrium constant, K_{disp}^*, which can be named *conditional disproportionation constant*, in analogy with other conditional equilibrium constants used in coordination chemistry [114,115]. K_{disp}^* is defined in the same way as K_{disp} (in the absence of complexing agents) but using the total concentrations of Cu^I and Cu^{II} species ($[Cu^j]_{tot} = [Cu^j] + [Cu^jL_m] + \cdots$). The ability of Cu^I complexes to disproportionate (Eq. (8)) is determined by the stability constants of both the Cu^I and Cu^{II} complexes with the ligand L, according to Eq. (9) [80,83,116,117].

$$Cu^IL_m + Cu^IL_m \underset{}{\overset{K_{disp}^*}{\rightleftharpoons}} Cu^{II}L_m + Cu^0 + m\,L \qquad (8)$$
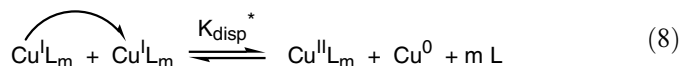
$$K_{disp}^* = \frac{[Cu^{II}]_{tot}}{[Cu^I]_{tot}^2} = \frac{1 + \sum_{j=1}^{m} \beta_j^{II}[L]^j}{\left(1 + \sum_{j=1}^{m} \beta_j^I[L]^j\right)^2} K_{disp};$$

$$\text{for} \quad 1:1 \text{ complex}: \quad K_{disp}^* = \frac{1 + \beta^{II}[L]}{(1 + \beta^I[L])^2} K_{disp}$$

$$\approx \frac{\beta^{II}}{(\beta^I)^2[L]} K_{disp} \qquad (9)$$

Eq. (9) can be used to predict whether a ligand is suitable for the formation of a stable Cu^I complex (with respect to disproportionation) in any given reaction media, provided that the stability constants of Cu^I and Cu^{II} complexes with L are known in the same media. It should be kept in mind that the values of both β^I and β^{II} change with temperature, [118] likely to a different degree. This means that even if the disproportionation of a Cu^I complex is negligible at ambient temperature, it may become appreciable upon changing the temperature.

Close examination of Eqs. (5) and (9) leads to the conclusion that for ligands forming 1:1 complexes with copper ions, the activity of the catalyst is proportional to β^{II}/β^I whereas the tendency of the Cu^I complex to disproportionate (which should be minimized) depends on the ratio $\beta^{II}/(\beta^I)^2[L]$. A "map" can be constructed [80,117,119] that can be used to select an appropriate ligand producing a complex of high activity, yet stable towards disproportionation. In Fig. 4, the performance (in aqueous solution) of catalysts derived from various tri- and tetradentate N-based ligands, all forming 1:1 complexes with copper ions, is presented (TETA [83] = triethylenetetramine, DETA [83] = diethylenetriamine, cyclam [120] = 1,4,8,11-tetraazacyclotetradecane or [14]aneN₄). As seen from the map, the cyclam-derived Cu^I catalyst possesses considerable activity
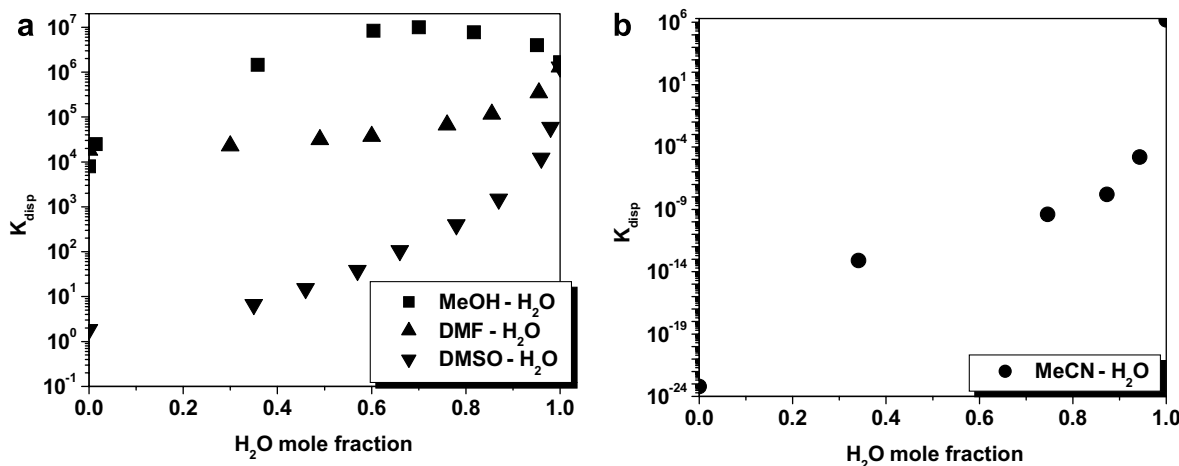

Fig. 3. Disproportionation of Cu^I in water-containing mixed solvents at room temperature.
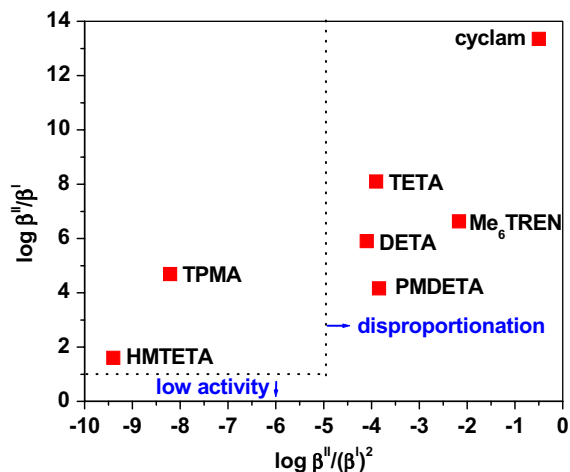
Fig. 4. Correlation between ATRP catalytic activity and disproportion-ation ability for several Cu^I complexes.

Table 4
Redox properties of radicals resembling polymeric radicals in MeCN

Radical	$E_{1/2}^{ox}$, V (vs SCE)	$E_{1/2}^{red}$, V (vs SCE)	Ref.
MeC˙(CO$_2$Et)$_2$		−0.03^{a}–0.45^{a,b}	[131,132]
MeC˙(CN)$_2$		0.16^{ab}	[131]
NCCH$_2$˙		−0.69^{c}	[133]
MeCH$_2$˙	<0.99	−1.36−−1.10	[129]
PhCH$_2$˙	0.73	−1.45	[134]
Me$_2$CH˙	0.47	−1.44	[129]
PhC˙HMe	0.37	−1.60	[134]
EtOC˙HMe	−0.45	(−1.2)	[134]
Et$_2$NC˙HMe	−1.12	(−2.0)	[134]

^{a} E_{irr}^{red}.
^{b} Measured in DMSO.
^{c} Measured in DMF.

but is unstable towards disproportionation. The catalysts derived from PMDETA and TPMA are of comparable activity, but the latter ligand is more appropriate for aque-ous ATRP since disproportionation of its Cu^I complex is appreciably less pronounced. Another conclusion from Fig. 4 is that N–H ligands, such as DETA and TETA, should form Cu-based catalysts of higher activity than their N-methylated analogues, PMDETA and HMTETA. In order to predict the performance of ATRP catalysts in media different from water, both β^I and β^{II} should be known in this media. There exists convincing evidence that the solvent composition can have a significant impact on complex stability [121,122]. Finally, it should be mentioned that since K_X is also responsible for the observed polymer-ization rate and control, its values may also be plotted on a separate axis to yield a three-dimensional catalyst selection map.

The complexes of other transition metals used to medi-ate ATRP can also disproportionate. For example, it has been shown that Ru^{III} complexes with N-based ligands disproportionate yielding a mixture of Ru^{II} and Ru^{IV} com-plexes [123–125]. Carbonyl compounds of monovalent metals such as Fe^I, [126] Ru^I, [127] and Os^I, [127] contain-ing phosphine ligands, have also been demonstrated to par-ticipate in this reaction.

3.2. Electron transfer between organic radicals and ATRP catalysts

The electrochemical properties of a large number of rad-icals have been studied and the redox potentials for both the reduction (leading to carbanions) and oxidation (lead-ing to carbocations) processes have been determined [128–130]. Table 4 lists the redox potentials of several low molecular weight radicals that structurally resemble polymeric radicals. Radicals with strong electron with-drawing α-substituents such as cyano or carboxy are highly oxidizing and are therefore very likely to accept electrons

from active, i.e., reducing, ATRP activators leading to the formation of carbanions which can quickly react with any protic compound (solvent or moisture). On the other hand, radicals with electron donating α-substituents (such as those derived from vinyl ethers or vinylamines) can be easily oxidized to carbocations by the ATRP deactivator, especially if it is a relatively strong oxidant. The carboca-tions may then lose a proton or combine with any basic or nucleophilic reaction component (solvent, monomer, polymer, etc.). Thus, both mentioned electron transfer reactions effectively "kill" the growing radicals.

Several electron transfer processes between carbon-cen-tered radicals and Cu complexes have been studied. For instance, one of the products of the reaction of benzyl chlo-ride with Cu^I complexes derived from aliphatic amine- and pyridine-based ligands was toluene, [135] which could be formed via the reduction of the initially formed benzyl rad-icals to carbanions followed by protonation. It was also shown that the reaction of acrylonitrile with benzyl bro-mide in the presence of the reducing Cu^I complex of TPMA lead to formation of 4-phenylbutyronitrile and 4-cyano-6-phenylhexanonitrile, [136] which were likely formed via addition of a benzyl radical to the monomer (in the latter case the formed radical reacted with two acrylonitrile mol-ecules) followed by reduction of the electrophilic α-cyano-radical to carbanion and subsequent protonation. In the reactions of 9-fluorenyl bromide and phenacyl chloride with the same complex in acetonitrile, the products of rad-ical reduction, fluorene and acetophenone, respectively, were produced [136].

The low conversion and limited molecular weights attainable in the ATRP of acrylonitrile [137] might be attributed to such electron transfer reactions that gener-ate carbanions from the electrophilic radicals. Similar results in terms of limited conversions and molecular weights were also observed when exceptionally reducing Cu-based catalysts derived from dimethyl cross-bridged cyclam were employed in the ATRP of n-butyl acrylate [17]. The application of ATRP techniques that decrease the amount of necessary metal catalyst can actually work to minimize electron transfer reactions between electro-philic radicals and extremely reducing Cu catalysts. For

example, using a technique known as activators regenerated by electron transfer (ARGET) ATRP, [138,139] wherein a small concentration of transition metal activator is continually regenerated when lost to the persistent radical effect with organic reducing agents, high molecular weight styrene-acrylonitrile copolymers can be prepared ($\sim$200 kg mol^{-1}) as compared to normal ATRP ($\sim$50 kg mol^{-1}) [140].

The oxidation of radicals by transition metal complexes, including those of Cu^{II}, was thoroughly studied throughout the 1960s and 1970s. Two general mechanisms for the radical oxidation were postulated: (i) electron transfer with formation of a carbocation that either loses a proton yielding an alkene or reacts with a nucleophile present in the system; and (ii) ligand-transfer [141,142]. Some early works worth mentioning include studies on alkyl radical oxidation by Cu^{II} compounds with both coordinating (carboxylate, halide and pseudohalide) and non-coordinating or weakly coordinating (tetrafluoroborate, triflate, and pechlorate) counterions in various solvents [143,144]. The oxidation of phenyl radicals formed in the thermal decomposition of benzoyl peroxide by various Cu^{II} compounds in acetic acid and its mixtures with acetonitrile was also studied [145]. The exact mechanism of oxidation depends upon numerous factors including the nature of the counterion/ligand and the solvent, as well as the redox potentials of both the radical and the Cu^{II} complex.

It has been shown that the Cu^{II} complex of 4,4′-di(5-nonyl)-2,2′-bipyridyl (dNbpy) most likely oxidizes 1-phenylethyl radicals (structural analogues of polystyrene propagating radicals) to the corresponding carbocations that are converted to styrene upon deprotonation [146]. Such a redox process would lead to loss of chain end functionality in the ATRP of styrene in the presence of relatively oxidizing Cu^{II} deactivators. Indeed, the chain end functionality of polystyrene prepared by ATRP mediated by the Cu complexes of dNbpy was studied [147,148]. It was shown that the Br end-group loss becomes pronounced at high monomer conversion, at which point a significant amount of deactivator is accumulated in the system due to the persistent radical effect. In addition, it was shown that in the ATRP of *p*-methoxystyrene that forms a radical even more nucleophilic than styrene, high molecular weight polymers are difficult to attain. This, again, can be attributed to formation of carbocations [149].

4. Radical coordination to the metal catalyst and the interplay of controlled radical polymerization mechanisms

One-electron oxidative addition processes between alkyl halides and transition metal species have been exploited in organic synthesis for many years, whereby homolytic cleavage of the alkyl halide in the presence of a metal complex ($Mt^z L_m$) yields one equivalent each of a metal halide ($XMt^{z+1}L_m$) and an organometallic species ($RMt^{n+1}L_m$). Of particular significance in this field are the Cr-catalyzed Nozaki–Hiyama–Kishi additions of organic halides to
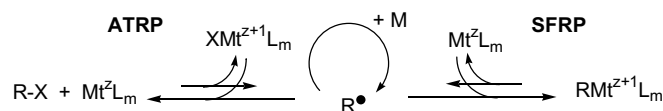
Scheme 3. Interplay between ATRP and SFRP mechanisms.

aldehydes that proceed via organometallic intermediates [150]. The reactions of organic radicals with Cu^I and Cu^{II} compounds may involve the formation of organocopper species [151,152]. While there is currently no experimental evidence which suggests organometallic Cu^{II}-R species are generated during Cu mediated ATRP, [153] recent studies have detailed the contribution of certain organomolybdenum species in mediating polymerization initiated by alkyl halides under ATRP conditions (Scheme 3) [20,154].

The relationship between one electron reactivity and controlled radical polymerization processes was recently discussed in a review paper that placed particular emphasis on the interplay of ATRP and stable free radical polymerization (SFRP) as depicted in Scheme 3 [155] The relative bond dissociation energies (BDEs) of the the R–X, Mt–X, and Mt–R bonds in such a system ultimately dictate whether polymerization is inhibited by the formation of a Mt–R bond, whether initiation efficiency might be reduced, or whether the entire polymerization initiated by an alkyl halide is actually mediated through the reversible formation of a Mt–R bond.

However, it is difficult to predict the role of the metal species in a polymerization based purely on calculated BDEs. It was recently demonstrated that $Os^{II}Cl_2(PPh_3)_3$ could mediate styrene polymerization under SFRP conditions (in the presence of a free radical initiator) as well as under ATRP conditions (with an alkyl halide initiator) [56]. The calculated relative BDEs of the R–X, Os^{III}–X and Os^{III}–R bonds suggested from an enthalpic standpoint that polymerization initiated by an alkyl halide would preferentially be mediated by SFRP (i.e., the equilibrium between ATRP and SFRP in Scheme 3 would shift predominantly towards SFRP) [156]. However, this was not observed experimentally, suggesting the Os^{III}–R bond need be much stronger to overcome the entropic penalty associated with its formation from an alkyl radical and metal species.

The identification of any $RMt^{z+1}L_m$ species generated during ATRP would have implications on optimization of the polymerization conditions, and as more and more non-Cu based ATRP catalysts are developed, such studies will become increasingly important. Complexes originally intended for use as ATRP catalysts might be optimized to make efficient SFRP spin traps. However, as polymerizations mediated by SFRP require a stoichiometric amount of mediating species per polymer chain, metal complexes that do readily form Mt–R bonds under ATRP conditions would not be expected to successfully mediate well-controlled polymerizations under conditions where sub-stoichiometric amounts of the metal species are

employed, as in the case of ICAR and ARGET ATRP [157].

5. Conclusions

The continuous development of more active and stable catalysts in ATRP has seen the recent application of many new catalyst/ligand combinations. Much research has been done to correlate catalyst structures with reactivity in ATRP, and now a thorough knowledge of concurrent electron transfer reactions that can affect catalyst performance is becoming increasingly important to realize further developments. Understanding disproportionation of the Cu^I-based ATRP activator, the oxidation/reduction of radicals to cations/anions, and radical coordination to the metal catalyst resulting in the interplay of controlled radical polymerization mechanisms may ultimately take ATRP to new dimensions.

Acknowledgements

References

[1] J.-S. Wang, K.J. Matyjaszewski, Am. Chem. Soc. 117 (1995) 5614.
[2] M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, Macromolecules 28 (1995) 1721.
[3] K. Matyjaszewski, J. Xia, J. Chem. Rev. 101 (2001) 2921.
[4] M. Kamigaito, T. Ando, M. Sawamoto, Chem. Rev. 101 (2001) 3689.
[5] K. Matyjaszewski, J. Spanswick, Mat. Today 8 (3) (2005) 26.
[6] T.E. Patten, L. Matyjaszewski, Acc. Chem. Res. 32 (1999) 895–903.
[7] V. Coessens, T. Pintauer, K. Matyjaszewski, Prog. Polym. Sci. 26 (2001) 337.
[8] K.A. Davis, K. Matyjaszewski, Adv. Polym. Sci. 159 (2002) 1.
[9] K. Matyjaszewski, Prog. Polym. Sci. 30 (2005) 858.
[10] K. Matyjaszewski (Ed.), Controlled/Living Radical Polymerization. From Synthesis to Materials (ACS Symp. Ser. 944);, ACS, Washington, DC, 2006.
[11] W.A. Braunecker, K.J. Matyjaszewski, Mol. Catal. A: Chem. 254 (2006) 155.
[12] W.A. Braunecker, K. Matyjaszewski, Prog. Polym. Sci. 32 (2007) 93.
[13] K. Matyjaszewski, T.P. Davis (Eds.), Handbook of Radical Polymerization;, Wiley, Hoboken, 2002.
[14] J. Qiu, K. Matyjaszewski, L. Thouin, C. Amatore, Macromol. Chem. Phys. 201 (2000) 1625.
[15] K. Matyjaszewski, B. Goebelt, H.-j. Paik, C.P. Horwitz, Macromolecules 34 (2001) 430.
[16] H. Tang, N. Arulsamy, J. Sun, M. Radosz, Y. Shen, N.V. Tsarevsky, W.A. Braunecker, W. Tang, K.J. Matyjaszewski, Am. Chem. Soc. 128 (2006) 16277.
[17] N.V. Tsarevsky, W.A. Braunecker, W. Tang, S.J. Brooks, K. Matyjaszewski, G.R. Weisman, E.H.J. Wong, Mol. Catal. A: Chem. 257 (2006) 132.
[18] Y.A. Kabachii, S.Y. Kochev, L.M. Bronstein, I.B. Blagodatskikh, P.M. Valetsky, Polym. Bull. 50 (2003) 271.
[19] J.A.M. Brandts, P. van de Geijn, E.E. van Faassen, J. Boersma, G.J. Van Koten, Organomet. Chem. 584 (1999) 246.
[20] E. Le Grognec, J. Claverie, R.J. Poli, Am. Chem. Soc. 123 (2001) 9513.
[21] F. Stoffelbach, J. Claverie, R. Poli, Compt. Rend. Chim. 5 (2002) 37.
[22] F. Stoffelbach, D.M. Haddleton, R. Poli, Eur. Polym. J. 39 (2003) 2099.
[23] Y. Kotani, M. Kamigaito, M. Sawamoto, Macromolecules 32 (1999) 2420.
[24] Y. Kotani, M. Kamigaito, M. Sawamoto, Macromolecules 33 (2000) 6746.
[25] H. Uegaki, Y. Kotani, M. Kamigaito, M. Sawamoto, ACS Symp. Ser. 760 (2000) 196.
[26] V. Percec, B. Barboiu, A. Neumann, J.C. Ronda, M. Zhao, Macromolecules 29 (1996) 3665.
[27] T. Ando, M. Kamigaito, M. Sawamoto, Tetrahedron 53 (1997) 15445.
[28] F. Simal, A. Demonceau, A.F. Noels, Angew. Chem., Int. Ed. 38 (1999) 538.
[29] F. Simal, S. Sebille, L. Hallet, A. Demonceau, A.F. Noels, Macromol. Symp. 161 (2000) 73.
[30] B. De Clercq, F. Verpoort, Tetrahedron Lett. 43 (2002) 4687.
[31] T. Opstal, F. Verpoort, Angew. Chem., Int. Ed. 42 (2003) 2876.
[32] M. Haas, E. Solari, Q.T. Nguyen, S. Gautier, R. Scopelliti, K. Severin, Adv. Synth. Catal. 348 (2006) 439.
[33] T. Ando, M. Kamigaito, M. Sawamoto, Macromolecules 30 (1997) 4507.
[34] K. Matyjaszewski, M. Wei, J. Xia, N.E. McDermott, Macromolecules 30 (1997) 8161.
[35] G. Moineau, P. Dubois, R. Jerome, T. Senninger, P. Teyssie, Macromolecules 31 (1998) 545.
[36] J. Xia, H.-j. Paik, K. Matyjaszewski, Macromolecules 32 (1999) 8310.
[37] M. Teodorescu, S.G. Gaynor, K. Matyjaszewski, Macromolecules 33 (2000) 2335.
[38] S. Zhu, D. Yan, Macromolecules 33 (2000) 8233.
[39] S. Zhu, D. Yan, G. Zhang, M. Li, Macromol. Chem. Phys. 201 (2000) 2666.
[40] V.C. Gibson, R.K. O'Reilly, W. Reed, D.F. Wass, A.J.P. White, D.J. Williams, Chem. Commun. (2002) 1850.
[41] V.C. Gibson, R.K. O'Reilly, D.F. Wass, A.J.P. White, D.J. Williams, Macromolecules 36 (2003) 2591.
[42] G. Moineau, C. Granel, P. Dubois, R. Jerome, P. Teyssie, Macromolecules 31 (1998) 542.
[43] D. Mecerreyes, G. Moineau, P. Dubois, R. Jerome, J.L. Hedrick, C.J. Hawker, E.E. Malmstrom, M. Trollsas, Angew. Chem., Int. Ed. 37 (1998) 1274.
[44] T. Opstal, J. Zednik, J. Sedlacek, J. Svoboda, J. Vohlidal, F. Verpoort, Coll. Czech. Chem. Commun. 67 (2002) 1858.
[45] J. Vohlidal, M. Pacovska, J. Sedlacek, J. Svoboda, J. Zednik, H. Balcar, NATO Sci. Ser., II: Math., Phys. Chem. 122 (2003) 131.
[46] C. Granel, P. Dubois, R. Jerome, P. Teyssie, Macromolecules 29 (1996) 8576.
[47] H. Uegaki, Y. Kotani, M. Kamigaito, M. Sawamoto, Macromolecules 30 (1997) 2249.
[48] H. Uegaki, Y. Kotani, M. Kamigaito, M. Sawamoto, Macromolecules 31 (1998) 6756.
[49] G. Carrot, J. Hilborn, J.L. Hedrick, M. Trollsas, Macromolecules 32 (1999) 5171.
[50] M. Husseman, E.E. Malmstrom, M. McNamara, M. Mate, D. Mecerreyes, D.G. Benoit, J.L. Hedrick, P. Mansky, E. Huang, T.P. Russell, C.J. Hawker, Macromolecules 32 (1999) 1424.
[51] G. Moineau, M. Minet, P. Dubois, P. Teyssie, T. Senninger, R. Jerome, Macromolecules 32 (1999) 27.
[52] C. Moineau, M. Minet, P. Teyssie, R. Jerome, Macromolecules 32 (1999) 8277.
[53] H. Uegaki, M. Kamigaito, M.J. Sawamoto, Polym. Sci.: Part A: Polym. Chem. 37 (1999) 3003.

[54] P. Lecomte, I. Drapier, P. Dubois, P. Teyssie, R. Jerome, Macromolecules 30 (1997) 7631.

[55] B. Wang, Y. Zhuang, X. Luo, S. Xu, X. Zhou, Macromolecules 36 (2003) 9684.

[56] W.A. Braunecker, Y. Itami, K. Matyjaszewski, Macromolecules 38 (2005) 9402.

[57] J.S. Wang, K. Matyjaszewski, Macromolecules 28 (1995) 7901.

[58] J. Xia, K. Matyjaszewski, Macromolecules 30 (1997) 7697.

[59] D.M. Haddleton, C.B. Jasieczek, M.J. Hannon, A.J. Shooter, Macromolecules 30 (1997) 2190.

[60] K. Matyjaszewski, Macromolecules 31 (1998) 4710.

[61] D.M. Haddleton, M.C. Crossman, B.H. Dana, D.J. Duncalf, A.M. Heming, D. Kukulj, A.J. Shooter, Macromolecules 32 (1999) 2110.

[62] J. Xia, K. Matyjaszewski, Macromolecules 32 (1999) 2434.

[63] M. Teodorescu, K. Matyjaszewski, Macromolecules 32 (1999) 4826.

[64] J. Xia, S.G. Gaynor, K. Matyjaszewski, Macromolecules 31 (1998) 5958.

[65] J. Xia, X. Zhang, K. Matyjaszewski, ACS Symp. Ser. 760 (2000) 207.

[66] J. Queffelec, S.G. Gaynor, K. Matyjaszewski, Macromolecules 33 (2000) 8629.

[67] Y. Inoue, K. Matyjaszewski, Macromolecules 36 (2003) 7432.

[68] S. Ding, Y. Shen, M.J. Radosz, Polym. Sci.: Part A: Polym. Chem. 42 (2004) 3553.

[69] T. Pintauer, B. McKenzie, K. Matyjaszewski, ACS Symp. Ser. 854 (2003) 130.

[70] T. Ando, M. Kamigaito, M. Sawamoto, Macromolecules 33 (2000) 5825.

[71] H.J. Fischer, Polym. Sci.: Part A: Polym. Chem. 37 (1999) 1885.

[72] H. Fischer, Chem. Rev. 101 (2001) 3581.

[73] A. Goto, T. Fukuda, Prog. Polym. Sci. 29 (2004) 329.

[74] W. Tang, N.V. Tsarevsky, K.J. Matyjaszewski, Am. Chem. Soc. 128 (2006) 1598.

[75] R.S. Berry, C.W. Reimann, G.N.J. Spokes, Chem. Phys. 37 (1962) 2278.

[76] R.S. Berry, C.W.J. Reimann, Chem. Phys. 38 (1963) 1540.

[77] J.D. Pandey, O.C.J. Saxena, Chem. Soc. (A) (1969) 397.

[78] M.B. Gillies, K. Matyjaszewski, P.-O. Norrby, T. Pintauer, R. Poli, P. Richard, Macromolecules 36 (2003) 8551.

[79] N.V. Tsarevsky, W.A. Braunecker, S.J. Brooks, K. Matyjaszewski, Macromolecules 39 (2006) 6817.

[80] N.V. Tsarevsky, W. Tang, S.J. Brooks, K. Matyjaszewski, ACS Symp. Ser. 944 (2006) 56.

[81] J.J. Lingane, Chem. Rev. 29 (1941) 1.

[82] Stability constants of metal–ion complexes. suppl. No 1. Special Publication No 25. The Chemical Society: London, 1971.

[83] N. Navon, G. Golub, H. Cohen, P. Paoletti, B. Valtancoli, A. Bencini, D. Meyerstein, Inorg. Chem. 38 (1999) 3484.

[84] E.A. Ambundo, M.-V. Deydier, A.J. Grall, N. Aguera-Vega, L.T. Dressel, T.H. Cooper, M.J. Heeg, L.A. Ochrymowycz, D.B. Rorabacher, Inorg. Chem. 38 (1999) 4233.

[85] G. Golub, A. Lashaz, H. Cohen, P. Paoletti, A. Bencini, B. Valtancoli, D. Meyerstein, Inorg. Chim. Acta 255 (1997) 111.

[86] A.B.P. Lever, Inorg. Chem. 29 (1990) 1271.

[87] A.B.P. Lever, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, Vol. 2, Elsevier, Amsterdam, 2004, pp. 251–268.

[88] T. Pintauer, K. Matyjaszewski, Coord. Chem. Rev. 249 (2005) 1155.

[89] P. Zanello, In: I. Bernal (Eds.), Stereochemical Control, Bonding and Steric Rearrangements, Vol. 4, Elsevier, Amsterdam, 1990, pp. 181–366.

[90] C.X. Zhang, S. Kaderli, M. Costas, E.-i. Kim, Y.-M. Neuhold, K.D. Karlin, A.D. Zuberbuehler, Inorg. Chem. 42 (2003) 1807.

[91] C.X. Zhang, H.-C. Liang, E.-i. Kim, J. Shearer, M.E. Helton, E. Kim, S. Kaderli, C.D. Incarvito, A.D. Zuberbuehler, A.L. Rheingold, K.D.J. Karlin, Am. Chem. Soc. 125 (2003) 634.

[92] L.Q. Hatcher, M.A. Vance, A.A.N. Sarjeant, E.I. Solomon, K.D. Karlin, Inorg. Chem. 45 (2006) 3004.

[93] A.W. Addison, Inorg. Chim. Acta 162 (1989) 217.

[94] D.B. Rorabacher, Chem. Rev. 104 (2004) 651.

[95] F.J. Fenwick, Am. Chem. Soc. 48 (1926) 860.

[96] G. Anderegg, Helv. Chim. Acta 46 (1963) 2397.

[97] L. Ciavatta, D. Ferri, R.J. Palombari, Inorg. Nucl. Chem. 42 (1980) 593.

[98] J. Malyszko, M.J. Scendo, Electroanal. Chem. 269 (1989) 113.

[99] J.E.B.J. Randles, Chem. Soc. (1941) 802.

[100] J.P. Desmarquest, C. Trinh-Dinh, O.J. Bloch, Electroanal. Chem. 27 (1970) 101.

[101] A.I. Molodov, L.A. Yanov, D.V. Golodnitskaya, Elektrokhimiia 13 (1977) 300.

[102] A. Foll, M. Le Demezet, J.J. Courtot-Coupez, Electroanal. Chem. 35 (1972) 41.

[103] S. Ahrland, P. Blauenstein, B. Tagesson, D. Tuhtar, Acta Chem. Scand. A 34 (1980) 265.

[104] J. Malyszko, M. Scendo, Monatsh. Chem. 118 (1987) 435.

[105] D. Datta, Indian J. Chem. 26 A (1987) 605.

[106] S. Ahrland, S. Ishiguro, I. Persson, I. Acta Chem. Scand. A 40 (1986) 418.

[107] A. Lewandowski, J. Malinska, Electrochim. Acta 34 (1989) 333.

[108] S. Ahrland, K. Nilsson, B. Tagesson, Acta Chem. Scand. A 37 (1983) 193.

[109] L.A. Yanov, A.I. Molodov, Elektrokhimiia 11 (1975) 1112.

[110] P. Singh, I.D. MacLeod, A.J.J. Parker, Solution Chem. 11 (1982) 495.

[111] M. Calligaris, O. Carugo, Coord. Chem. Rev. 153 (1996) 83.

[112] R.A. Walton, Quart. Rev. Chem. Soc. 19 (1965) 126.

[113] B.N. Storhoff, H.C. Lewis Jr., Coord. Chem. Rev. 23 (1977) 1.

[114] G. Schwarzenbach, Die Komplexometrische Titration, second ed., Enke, Stuttgart, 1956.

[115] A. Ringbom, Complexation in Analytical Chemistry, Interscience, New York, 1963.

[116] G. Golub, H. Cohen, P. Paoletti, A. Bencini, L. Messori, I. Bertini, D.J. Meyerstein, Am. Chem. Soc. 117 (1995) 8353.

[117] N.V. Tsarevsky, K. Matyjaszewski, ACS Symp. Ser. 937 (2006) 79.

[118] P. Paoletti, L. Fabbrizzi, R. Barbucci, Inorg. Chim. Acta Rev. 7 (1973) 43.

[119] N.V. Tsarevsky, K.J. Matyjaszewski, Polym. Sci.: Part A: Polym. Chem. 44 (2006) 5098.

[120] M.M. Bernardo, M.J. Heeg, R.R. Schroeder, L.A. Ochrymowycz, D.B. Rorabacher, Inorg. Chem. 31 (1992) 191.

[121] S. Ahrland, N.O. Bjork, Coord. Chem. Rev. 16 (1975) 115.

[122] A. Lewandowski, J. Malinska, New J. Chem. 20 (1996) 653.

[123] D.P. Rudd, H. Taube, Inorg. Chem. 10 (1971) 1543.

[124] R.A. Binstead, L.K. Stultz, T.J. Meyer, Inorg. Chem. 34 (1995) 546.

[125] E. Masllorens, M. Rodriguez, I. Romero, A. Roglans, T. Parella, J. Benet-Buchholz, M. Poyatos, A.J. Llobet, Am. Chem. Soc. 128 (2006) 5306.

[126] M.J. Therien, C.L. Ni, F.C. Anson, J.G. Osteryoung, W.C.J. Trogler, Am. Chem. Soc. 108 (1986) 4037.

[127] L. Song, W.C.J. Trogler, Am. Chem. Soc. 114 (1992) 3355.

[128] D. Griller, D.D.M. Wayner, Pure & Appl. Chem. 61 (1989) 717.

[129] D.D.M. Wayner, A. Houmam, Acta Chem. Scand. 52 (1998) 377.

[130] K. Daasbjerg, S.U. Pedersen, H. Lund, General Aspects of the Chemistry of Radicals, in: Z.B. Alfassi (Ed.), Wiley, Chichester, 1999, pp. 385–427.

[131] J.M. Kern, P. Federlin, Tetrahedron 34 (1978) 661.

[132] M.E. Niyazymbetov, Z. Rongfeng, D.H.J. Evans, Chem. Soc., Perkin Trans. 2 (1996) 1957.

[133] A.A. Isse, A.J. Gennaro, Phys. Chem. A 108 (2004) 4180.

[134] D.D.M. Wayner, D.J. McPhee, D.J. Griller, Am. Chem. Soc. 110 (1988) 132.

[135] K. Wada, H. Hashimoto, Bull. Chem. Soc. Jpn. 41 (1968) 3001.

[136] R.R. Jacobson, Z. Tyeklar, K.D. Karlin, Inorg. Chim. Acta 181 (1991) 111.

[137] K. Matyjaszewski, S.M. Jo, H.-j. Paik, S.G. Gaynor, Macromolecules 30 (1997) 6398.

[138] W. Jakubowski, K. Matyjaszewski, Angew. Chem., Int. Ed. 45 (2006) 4482.
[139] W. Jakubowski, K. Min, K. Matyjaszewski, Macromolecules 39 (2006) 39.
[140] J. Pietrasik, H. Dong, K. Matyjaszewski, Macromolecules 39 (2006) 6384.
[141] J.K. Kochi, Science 155 (1967) 415.
[142] J.K. Kochi, Acc. Chem. Res. 7 (1974) 351.
[143] C.L. Jenkins, J.K.J. Kochi, Am. Chem. Soc. 94 (1972) 843.
[144] C.L. Jenkins, J.K.J. Kochi, Am. Chem. Soc. 94 (1972) 856.
[145] K. Wada, J. Yamashita, H. Hashimoto, Bull. Chem. Soc. Jpn. 40 (1967) 2410.
[146] K. Matyjaszewski, K. Davis, T.E. Patten, M. Wei, Tetrahedron 53 (1997) 15321.
[147] J.-F. Lutz, K. Matyjaszewski, Macromol. Chem. Phys. 203 (2002) 1385.
[148] J.-F. Lutz, K.J. Matyjaszewski, Polym. Sci.: Part A: Polym. Chem. 43 (2005) 897.
[149] J. Qiu, K. Matyjaszewski, Macromolecules 30 (1997) 5643.
[150] A. Fuerstner, N.J. Shi, Am. Chem. Soc. 118 (1996) 12349.
[151] M. Freiberg, D.J. Meyerstein, Chem. Soc., Chem. Comm. (1977) 127.
[152] G. Ferraudi, Inorg. Chem. 17 (1978) 2506.
[153] K. Matyjaszewski, B.E. Woodworth, Macromolecules 31 (1998) 4718.
[154] R. Poli, F. Stoffelbach, S. Maria, Polym. Prepr. 46 (2) (2005) 305.
[155] R. Poli, Angew. Chem., Int. Ed. 45 (2006) 5058.
[156] W.A. Braunecker, B. Morelli, W.C. Brown, R. Poli, K. Matyjaszewski, in preparation.
[157] K. Matyjaszewski, W. Jakubowski, K. Min, W. Tang, J. Huang, W.A. Braunecker, N.V. Tsarevsky, Proc. Natl. Acad. Sci. USA\ 103 (2006) 15309.