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Relationship between one-electron transition-metal reactivity and radical polymerization processes

Rinaldo Poli

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Prof. Rinaldo Poli
Laboratoire de Chimie de Coordination,
CNRS UPR 8241,
205 Route de Narbonne, 31077 Toulouse cedex (France)
Fax : +33-561553003
E-mail : poli@lcc-toulouse.fr

The achievement of controlled radical polymerization (CRP) has been one of the most spectacular advances of polymer chemistry in recent years, because materials where the architecture, average molecular weight, molecular weight distribution, and nature of chain-end functions are well defined have now become accessible by the use of a wide variety of polar monomers and “friendlier” polymerization techniques (e.g. unpurified organic solvents, emulsions, etc.). The key requirement to achieve this level of control is the ability to reduce to negligible levels the chances for two propagating radicals to encounter each other, leading to irreversible bimolecular terminations. There are many ways in which this condition has been achieved, but the method that has attracted the greatest attention is Atom Transfer Radical Polymerization (ATRP), following its discovery in 1995 in the laboratories of Matyjaszewski^[1] and Sawamoto.^[2]

The main interest and potential practical advantage of ATRP lies in the fact that a transition metal complex acts as a regulator of the radical concentration by reversibly transferring a halogen atom to the active radical, thereby transforming it into a halogen-terminated dormant species, without being incorporated itself into the polymer chain. Therefore, the metal complex acts merely as a catalyst and can potentially be recovered and recycled. The overall process boils down to a catalyzed sequential insertion of a certain (controlled) amount of monomer units into the carbon-halogen bond of a suitable alkyl halide initiator, see Scheme 1 (m = monomer), and can be considered as a natural extension of the metal-catalyzed atom transfer radical addition (ATRA).^[3] The catalyst, L_nM , activates the dormant species, $R(m)_x-Y$, by accepting its terminal halogen atom (Y) and generates the active radical, $R(m)_x\cdot$, plus an oxidized complex, L_nM-Y , the latter being related to the catalyst by an atom transfer, where the metal electronic configuration changes by one electron.

<Scheme 1>

Before the basic principles of ATRP were uncovered, however, transition metal complexes had already been shown capable to control the concentration of radical species and thereby to allow controlled chain growth for radical polymerization. The method is a particular example of the general concept of reversible addition-cleavage, see Scheme 2. In this scheme, I is a radical initiator producing R^{\bullet} as primary radical, like in classical free radical polymerization, while T is a reversible spin trap, namely a species capable to form relatively labile bonds with the propagating radical. Since T remains bound to the chain end in the polymer product, this is not a catalytic species. This procedure was first introduced by Otsu using the trityl radical as spin trap^[4] and subsequently developed with nitroxide radicals (nitroxide-mediated polymerization, or NMP). A stable but labile T-R compound may also be used as initiator (for instance, an alkoxylamine for NMP). However, Wayland extended this method to transition metal complexes as spin traps, demonstrating the ability of Co(porphyrin) complexes to control the polymerization of acrylates.^[5] In this case, the radical concentration is controlled by the reversible homolytic cleavage of the metal-carbon bond, a process closely related to the mechanism of action of vitamin B₁₂.^[6] This, like the atom transfer step in ATRP, is also a one-electron process. It is to be mentioned that this “reversible addition-cleavage” methodology has also been termed “Stable Free Radical Polymerization” (SFRP), on the basis on the notion that the spin trap T is often a stable radical, e.g. a nitroxide radical or a metallaradical. However, this is not strictly a requirement and, as we shall see later, other species (diamagnetic complexes, but also complexes whose spin state is triplet, quartet, etc.) may equally well assure this function. The term NMP, on the other hand, is specific for the reversible cleavage where T = organic nitroxide. Other specially coined terms have also been used for specific reversible addition-cleavage processes

(e.g. CMRP for “cobalt-mediated radical polymerization”).^[7] In this Minireview, we focus our attention on the reversible addition-cleavage phenomenon where T as a generic metal complex. We shall therefore use the term “organometallic radical polymerization” (OMRP), because it involves the reversible cleavage of a metal-carbon bond. We should also mention another important method for controlling radical polymerization, termed “reversible addition-fragmentation chain transfer” (RAFT), where the trapping function is exerted by dithioesters.^[8, 9] The latter methodology, however, combines the mechanistic paradigm of reversible addition-cleavage with a second one, namely that of degenerative transfer.^[10] It is important to underline that all the above mentioned methods differ in the nature of the “moderator” and the mechanism with which a dormant species is produced, but the monomer consumption always occurs via the same radical intermediates.

<Scheme 2>

This Minireview analyzes these two basic one-electron processes involving transition metals, ATRP (Scheme 1) and OMRP (Scheme 2, for T = transition metal complex), as well as other one-electron processes, as they relate to controlled radical polymerization. It will bring together very old knowledge from transition metal coordination chemistry and the more recent notions of metal-mediated controlled radical polymerization.

One-electron reactivity of transition metal complexes

In transition metal chemistry (especially containing metal-carbon bonds, i.e. organometallic chemistry), studies of chemical reactivity are mostly focused on two-electron processes such as ligand exchange, migratory insertion, oxidative addition, and so on, because of their close relevance to a variety of catalytic processes. However, one-electron reactivity

also plays a crucial role in many catalytic and stoichiometric reactions.^[11] The ubiquitous process, of prime relevance to this Minireview, is the one-electron oxidative addition of alkyl halides (Scheme 3), whereby one molecule of substrate splits homolytically to deliver the halogen atom to one metal complex molecule, and the alkyl radical to a second one. This process is favoured when the metal has the ability to expand its electron count and coordination number by only one unit.

<Scheme 3>

A seminal example involves the tetracyanocobaltate(II) ion, $[\text{Co}(\text{CN})_5]^{3-}$, yielding a 1:1 mixture of $[\text{Y-Co}(\text{CN})_5]^{3-}$ and $[\text{R-Co}(\text{CN})_5]^{3-}$ (Scheme 4a).^[12] A very early and relevant example is also the reaction of alkyl halides with aqueous Cr^{2+} (Scheme 4b), providing access to $[\text{R-Cr}(\text{H}_2\text{O})_5]^{2+}$, one of the earliest examples of stable alkyl derivatives of an open-shell transition metal, together with $[\text{X-Cr}(\text{H}_2\text{O})_5]^{2+}$.^[13] This reaction is quite general for complexes of Cr^{II} and has become the key part of one the workhorses of modern sophisticated organic synthesis, the Nozaki-Hiyama-Kishi reaction,^[14, 15] which has been rendered catalytic in chromium by Fürstner.^[16] The reaction shown in Scheme 4c is also an example of one-electron oxidative addition, although its intimate mechanism seems to involve two-electron steps.^[17] The $[\text{CpFe}(\text{CO})_2]_2$ complex does not react spontaneously with alkyl halides, but this process may also be relevant in controlled radical polymerization (*vide infra*). The mechanism of the one-electron oxidative addition reaction of alkyl halides has been quite firmly established as involving first the halogen atom abstraction step, followed by capture of the residual organic radical by the second transition metal complex molecule, according to Scheme 3.^[18, 19] The reactivity of organic radical with transition metal complexes has also been extensively investigated by Kochi,^[20] Espenson^[21, 22] and Meyerstein.^[23, 24] The reason

for the first event to be the M-Y formation, rather than the M-R formation, is related to the greater bond homolytic strength of the M-Y bond relative to the M-R bond. Thus, if we consider the process to ideally take place by homolytic rupture of the R-Y bond to yield R[•] and Y[•], the unsaturated metal complex finds a greater thermochemical advantage to form a bond with Y first. Note that the two steps of this process correspond to the two basic equilibria needed to accomplish a metal-mediated radical polymerization (ATRP and OMRP, respectively).

<Scheme 4>

It is quite ironic that the coordination chemists, who have known and understood the mechanism of this reaction for such a long time, have not realized its potential for controlled organic synthesis (ATRA) or polymerization (ATRP and/or OMRP). Conversely, in the opinion of this Author, the polymer scientists who have exploited ATRP to such a sophisticated degree have not yet fully explored its limitations in terms of the constraints imposed by the one-electron oxidative addition process. We shall explore these limits in this Minireview.

A bond dissociation energy approach to the study of one-electron processes

The concepts developed in this section are a logical deduction from generally accepted considerations and reasonable assumptions. They allow the rationalization of a wealth of experimental facts, as will be shown in the remainder of the article. We start by observing, from the phenomenological point of view, that an OMRP process where the organometallic complex is devoid of halogen atoms cannot enter the ATRP equilibrium. This is the case, for instance, for the Co(porphyrin) system. Unless halogen atoms are present in the coordination

sphere (*vide infra*), an OMRP is therefore uncontaminated by ATRP activation/deactivation equilibria. For systems that are set up under ATRP conditions, however, the situation may be more complicated. An analysis may be carried out using a variant of Scheme 3, where the active radical has already inserted a certain number (x) of monomer molecules, see Scheme 5. Once ML_n has accepted the halogen atom and generated the active radical $R(m)_x^\bullet$ (Scheme 5, first equilibrium), the latter may go back to the $R(m)_x-Y$ dormant species upon encountering the $Y-ML_n$ spin trap. On the other hand, the propagating radical may also encounter a second ML_n molecule, leading to $R(m)_x-ML_n$ (the OMRP dormant species), according to Scheme 5, second equilibrium. Thus, an ATRP process may be contaminated by the OMRP activation/deactivation equilibrium and ultimately by the one-electron oxidative addition process.

<Scheme 5>

In order to deepen this analysis and understand all possibilities and limitations, it is useful to consider the thermochemistry of the two equilibria in terms of the homolytic bond dissociation energies. The OMRP equilibrium is simply the homolytic rupture of the metal-carbon bond, thus $\Delta H_{\text{OMRP}} = \text{BDE}[L_nM-(m)_xR]$. The ATRP equilibrium formally involves the homolytic rupture of the $R(m)_x-Y$ bond and the formation of the $Y-ML_n$ bond, therefore $\Delta H_{\text{ATRP}} = \text{BDE}[R(m)_x-Y] - \text{BDE}(L_nM-Y)$.

From the point of view of an OMRP system, since this is uncontaminated by ATRP, its capability to control the radical polymerization is simply related to $\text{BDE}[L_nM-(m)_xR]$. Thus, if the metal-carbon bond is too weak, the ML_n species has an insufficient ability to trap the radicals and the resulting OMRP equilibrium leads to too high a radical concentration, which translates into a significant proportion of bimolecular terminations and to an uncontrolled

process. If, at the other extreme, the $R(m)_x-ML_n$ bond is too strong (namely, the equilibrium is too displaced toward the dormant species), no significant amount of radicals will be generated and there will be no polymerization. Finally, when the bond strength is “just right”, a controlled polymerization will take place, see Figure 1. All of this is valid, of course, when there are no halogens in the system, thus no radical trapping by the ATRP equilibrium may occur (but see more about this further down).

<Figure 1>

A brief parenthesis is in order, to comment on the meaning of “just right”. Obviously, more than a single value of the metal-carbon BDE will be suitable for a controlled radical polymerization process. Intuitively, a stronger bond will lead to a lower equilibrium radical concentration and therefore to a slower polymerization, but at the same time to a better control. However, the so-called “persistent radical effect”^[25] insures that a controlled process will also occur when the system generates a rather high amount of free radicals initially. This is because the spin trap (ML_n) is stable and will accumulate in the system following the initial disappearance of the reactive radicals caused by the irreversible terminations. The result is a self-regulation of the OMRP equilibrium. This observation also serves to alert us about the importance of the dynamic radical *concentration*, i.e. the equilibrium *position*, which depends on the *free energy* and not on the enthalpy. Thus, looking merely at the thermochemistry is insufficient. In fact, the concentration of other species (e.g. ML_n which accumulates because of the irreversible terminations) is not the only factor playing an important role; the reaction entropy also affects the system ability to control the polymerization. Since the OMRP spin trapping reaction is obviously characterized by a negative reaction entropy, the $BDE[R(m)_x-ML_n]$ value overestimates the stability of the OMRP dormant species.

Looking now at a system which is set up under ATRP conditions, the outcome depends first of all on the value of ΔH_{ATRP} : if this enthalpy difference is too small, too large, or just right, the amount of free radicals generated by the atom transfer process will correspondingly be too large, too small, or just right (note that the ATRP equilibrium involves the same number of molecules on either side and thus $\Delta S_{\text{ATRP}} \approx 0$ or $\Delta G_{\text{ATRP}} \approx \Delta H_{\text{ATRP}}$). In this case we also need to consider, however, the effect of the coupled OMRP equilibrium. Since the ATRP equilibrium will generally be shifted toward the combination of ATRP catalyst (ML_n , which is also the OMRP spin trap) and dormant species (R-Y), a fair concentration of OMRP spin trap will be available. The simplest case to examine is that in which ΔH_{ATRP} is too large (Figure 2). Since the equilibrium amount of radicals will be too small, there will be essentially no polymerization. Under these conditions, the value of ΔH_{OMRP} is irrelevant.

<Figure 2>

Under the opposite circumstances (ΔH_{ATRP} too small), the free radicals will not be efficiently trapped and the only possible regulation of their concentration may be provided by the OMRP equilibrium, see Figure 3. If ΔH_{OMRP} is also too small (case *a*), no efficient trapping is possible and the polymerization will be uncontrolled. If, at the opposite extreme (case *c*), ΔH_{OMRP} is too large, all radicals generated by the ATRP equilibrium will be irreversibly trapped by the OMRP equilibrium. The overall result is an irreversible one-electron oxidative addition and no polymer is formed. Finally, if ΔH_{OMRP} is just right (case *b*), a controlled polymerization will take place. Note, however, that the control is insured by the OMRP equilibrium, even though the system is set up under ATRP conditions. The thermochemistry of the overall one-electron oxidative addition ($\Delta H_{\text{Ox.Add.}}$, Scheme 5) favors the combination of oxidized complexes. Therefore, when the ATRP process is set up starting

from a 1:1 $ML_n/R-Y$ ratio (which is often the chosen stoichiometry), the resulting polymer will contain a 1:1 mixture of ML_n and Y end-functionalized chains. However, only one half of the ML_n complex exerts its regulating function (the polymer chain capping complex, by the OMRP mechanism), because the other half is sequestered in the L_nM-Y complex, a poor spin trap for the ATRP mechanism.

<Figure 3>

Finally, we need to examine the situation in which ΔH_{ATRP} is just right, see Figure 4. The meaning of “just right” is identical here to the OMRP situation examined above (the persistent radical effect operates in this case too). Under these circumstances, in the limiting situation where ΔH_{OMRP} is too small (case *a*) there is no efficient trapping of the active radical by the ATRP catalyst to yield the organometallic dormant species, but trapping still takes place by the oxidized L_nM-Y complex to yield the halogen-capped dormant species $R(m)_x-Y$, therefore a controlled polymerization process takes place. This is a pure ATRP. When ΔH_{OMRP} is also just right (case *b*), both trapping events will occur simultaneously. In this case, the polymerization will be controlled and the two mechanisms, ATRP and OMRP, will cooperate. A better control (and a slower polymerization) is expected relative to the case where ΔH_{OMRP} is too small, because the OMRP equilibrium contributes to further lower the concentration of propagating radicals. Finally, when ΔH_{OMRP} is too large (case *c*), trapping by ML_n will be irreversible. Therefore, even though the ATRP equilibrium is suitably placed to provide a controlled polymerization process, no polymerization will be possible and the reagents will lead to the products of the one-electron oxidative addition quantitatively.

<Figure 4>

The bond energy criteria elaborated above illustrates the thermochemical conditions to insure the possibility to achieve a controlled radical polymerization by either (or both) mechanisms. However, before going on to the next section, it is important to underline that these are necessary but not sufficient conditions to insure that the polymerization is well controlled. We must also add a crucial kinetic condition: the trapping rates must be fast relative to the propagation rates (low energy for the transition states leading to the dormant species).

Relevance to controlled radical polymerizations: interplay of ATRP and OMRP

The conditions examined in Figure 4 are quite important to all researchers practicing radical polymerizations under ATRP conditions. Generally, situation *a* is implicitly assumed since the vast majority of published ATRP studies reporting new catalysts only make reference to a mechanistic scheme such as that of Scheme 1. Very few studies have explicitly challenged this dogma, asking the specific question of whether the ATRP catalyst could generate an organometallic dormant species. One such example is the interaction of Cu^I complexes with the growing radical chains of polystyrene and poly(methyl acrylate). It was found that the CuBr/(4,4'-di-5-nonyl-2,2'-bipyridine) and CuOTf/(4,4'-di-*tert*-butyl-2,2'-bipyridine) systems have no effect on the rate of styrene polymerization (e.g. initiated by the AIBN thermal decomposition) but significantly slow down the rate of MA polymerization.^[26] This shows that there is a reversible interaction between the propagating methyl acrylate-derived radicals (but not the styrene-derived radicals) and the Cu^I metal center. However, the authors note that the interactions are very weak and neither improve the molecular weight and polydispersity control, nor affect tacticities which are the same as in conventional free radical polymerization without copper complexes. They conclude that “control in ATRP does not

originate in interactions of growing radicals with copper complexes but in the reversible halogen atom transfer". However, the same situation may not be valid in other cases. We were the first to report a system that is capable to control radical polymerization (in the case of styrene) under both ATRP and OMRP conditions. The system in question is $\text{CpMoCl}_2\text{L}_2$, a cyclopentadienylmolybdenum(III) system where L_2 could be bis(diphenylphosphino)ethane, dppe, of $(\text{PMe}_3)_2$, or η^4 -butadiene.^[27] Later, we found the same phenomenon when L_2 is $\text{ArN}=\text{CH}-\text{CH}=\text{NAr}$ (Ar = 2,6-diisopropylphenyl).^[28] Since the Mo^{III} complex is capable of reversibly trapping the propagating radical under OMRP conditions and since its concentration remains large under ATRP conditions, it is evident that both trapping mechanisms occur simultaneously, as illustrated by case *b* of Figure 4.

It is important to underline that the $\text{CpMoCl}_2\text{L}_2$ complexes contain halogen atoms in the coordination sphere. Therefore, after trapping the propagating radical to form a $\text{CpL}_2\text{Cl}_2\text{Mo}(\text{m})_x\text{R}$ dormant species, the latter could act, in turn, as an ATRP spin trap. If this happens, a mixture of $\text{R}(\text{m})_x\text{-Cl}$ and a new molecule, a Mo^{III} -capped polymer chain, $\text{R}(\text{m})_x\text{-MoClL}_2\text{Cp}$, would form. This means that the OMRP system would leak over to the ATRP mechanism. However, polymer analyses by ^1H NMR and MALDI-TOF revealed, in that particular case, no chlorinated end-functions.^[27] It can be imagined that a Cl atom transfer from a sterically encumbered $\text{R}(\text{m})_x\text{-MoClL}_2\text{Cp}$ complex to the propagating radical (itself a sterically hindered molecule) may be an unfavorable process relative to trapping by the less encumbered and more mobile $\text{CpMoCl}_2\text{L}_2$. Whether this phenomenon is true in general, however, is not known and the possible contamination by ATRP for a system set up under OMRP conditions, when the organometallic dormant species contains halogen, should always be considered as a possibility.

It is now pertinent to question whether other metal catalysts might display the same phenomenon of dual (ATRP/OMRP) control. A wide range of transition metal complexes

have been proven capable of controlling the radical polymerization of various monomers under typical ATRP conditions. These include $\text{Ti}^{\text{III}}\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}$),^[29] $\text{ReO}_2\text{I}(\text{PPh}_3)_2$,^[30] a variety of Fe^{II} coordination compounds,^[31-34] $\text{RuCl}_2(\text{PPh}_3)_3$,^[2] $\text{OsCl}_2(\text{PPh}_3)_3$,^[35] $\text{Co}(\text{O}_2\text{C}_7\text{F}_{15})_2$,^[36] $\text{RhCl}(\text{PPh}_3)_3$,^[37] $\text{Ni}(\text{PPh}_3)_4$,^[38] $\text{Ni}[o,o'(\text{CH}_2\text{NMe}_2)_2\text{C}_6\text{H}_3]\text{Br}$,^[39] $\text{Pd}(\text{OAc})_2/\text{PPh}_3$,^[40] and $\text{SmCl}_2/\text{lactic acid}$.^[41] For the particular case of Cp_2TiCl , it has been proposed that both ATRP and OMRP processes take place contemporarily (the reactions are carried out under “reverse” ATRP conditions, thermally decomposing AIBN in the presence of Cp_2TiCl_2).^[42, 43] A related system, involving a Cp_2TiCl -induced oxirane ring opening as initiation process, also seems to involve the reversible formation of a Ti^{IV} -capped dormant species.^[44, 45] The latter system is rather interesting because the initiation step is an ATRP-like activation, yielding $\text{Cp}_2(\text{Cl})\text{Ti}-\text{OCH}_2\text{CH}_2^\bullet$, which is however irreversible because of the high homolytic strength of the $\text{Ti}^{\text{IV}}-\text{O}$ bond, due to the titanium oxophilic character. The controlling function is assured by an OMRP-type trapping process by additional Cp_2TiCl .

Amongst the numerous reports of ATRP using Fe^{II} systems, none to the best of our knowledge addresses the possibility of simultaneous OMRP control through the formation of organometallic Fe^{III} dormant species. On the other hand, alkyl derivatives of Fe^{III} have been described in the literature, though these are relatively unstable compounds. For instance, Kochi has shown that the one-electron oxidation of stable $\text{Et}_2\text{Fe}(\text{bipy})_2$ yields $[\text{Et}_2\text{Fe}(\text{bipy})_2]^+$, which then decomposes in a variety of ways including Fe-C bond homolysis.^[46] Also, (porphyrin) Fe^{III} (alkyl) systems^[47, 48] were shown to readily undergo Fe-C bond homolysis.^[49] The generation of Fe^{III} alkyl species has been recently suggested as an event leading to catalytic chain transfer (CCT).^[50] This phenomenon will be further discussed in a later section. The radical trapping capability of $\text{RuCl}_2(\text{PPh}_3)_3$ has also not been considered, to the best of our knowledge.^[51] Quite recently, the osmium complex $\text{OsCl}_2(\text{PPh}_3)_3$ was shown to effectively control, like our $\text{CpMoCl}_2\text{L}_2$ system, the styrene radical polymerization under both

ATRP and OMRP conditions.^[35] Moreover, the reactions carried out under OMRP conditions did not reveal any chlorinated end-groups, whereas those carried out under ATRP conditions did not reveal any osmium-containing end-groups. Like with our $\text{CpMoCl}_2\text{L}_2$ complexes, the $\text{OsCl}_2(\text{PPh}_3)_3$ -controlled polymerization set up under OMRP conditions does not appear to be not contaminated by the ATRP process, whereas the polymerization set up under ATRP conditions must necessarily feature the OMRP trapping process. However, the system is energetically more stable as the sum of the Os^{II} catalyst plus the halogen-capped dormant species, leading to a polymer product capped only by halogen atoms under ATRP conditions. A given $\text{Os}^{\text{III}}\text{-C}$ bond is certainly expected to be stronger, in a homolytic sense, than the corresponding $\text{Ru}^{\text{III}}\text{-C}$ bond, but it would certainly be interesting to establish whether Ru^{II} complexes display any efficient trapping capability toward propagating radicals.

Until recently, Co(II) complexes had been proven effective only as OMRP spin traps and as chain transfer catalysts (see below). However, a recent report shows the ability of cobalt(II) perfluorooctanoate to control the polymerization of styrene initiated by (1-bromoethyl)benzene (BEB) – typical ATRP conditions.^[36] The same report shows the efficiency of the same system under typical OMRP conditions (thermal AIBN decomposition), although the authors incorrectly term this process “reverse ATRP” (no halogen is present, other than that of the CoCl_2 precursor, transformed to $\text{Co}(\text{O}_2\text{CC}_7\text{F}_{15})_2$ in situ by reaction with sodium perfluorooctanoate). A question remains, therefore, as to whether the $\text{Co}(\text{O}_2\text{CC}_7\text{F}_{15})_2/\text{BEB}$ process involves a combination of ATRP and OMRP (case *b* of Figure 4) or is a pure OMRP (case *b* of Figure 3). The authors indicate the presence of halogen end-groups (by NMR) and the absence of cobalt (by atomic absorption spectroscopy), suggesting formation of the ATRP dormant species (apparently, even for the polymer obtained under OMRP conditions!), but the evidence is not compelling since the polymer was treated in HCl -containing methanol before analysis. Another recent report shows the ability

of $\text{CoCl}_2/\text{Me}_6\text{TREN}$ to control the styrene and MMA polymerizations under typical ATRP conditions (2-EiBBBr initiator), although the resulting polymers show high polydispersities (1.6-1.8).^[52] The possible OMRP trapping is not mentioned in this report and the characterization of the chain-end functions (again, only by NMR) is not unambiguous. Interestingly, the control of these processes is improved by addition of a few percent of FeBr_3 or CuBr_2 . Under these conditions, obviously, a $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ or $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ -based ATRP mechanism, becomes operational. The authors propose that the higher oxidation state Fe or Cu complex traps more efficiently the growing radical chain and then is reoxidized by the $\text{Co}^{\text{III}}/\text{Me}_6\text{TREN}$ species. Thus, the process would remain controlled by the $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ pair through an ATRP mechanism. However, amine-supported low-spin Co(III) complex are not strong oxidants^[53, 54] and the redox equilibria shown in Scheme 6 are likely shifted to the side of the Co^{III} species and the more active Fe^{II} or Cu^{I} catalyst. It then appears that the improved control upon addition of FeBr_3 or CuBr_2 likely originates from a switch to a $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ or $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ ATRP mechanism.

<Scheme 6>

The effect of irreversible radical trapping on initiator efficiencies

The situation corresponding to case *c* of Figure 3 and Figure 4 merits further analysis. The considerations that will be developed here are in fact valid for any process where the propagating radical is trapped irreversibly by any reaction, not necessarily consisting of the irreversible formation of a metal-carbon bond. Namely, the propagating radical may also bind irreversibly to one of the ligands. Under these circumstances, as we concluded in a previous section, no polymerization should result. This is true, however, provided that the reaction products of the radical trapping reaction display no ability to get themselves involved in

radical controlling equilibria. Note that the one-electron oxidative addition reaction is characterized by a $ML_n/R-Y$ stoichiometry of 2:1 (Scheme 3). However, most ATRP processes are set up with a 1:1 stoichiometry, under the assumption that only the atom transfer equilibrium of Scheme 1 is operative (i.e., the first step of Scheme 3). Under these conditions, and if the reaction leads to the oxidative addition products $L_nM-Y + L_nM-R$ (or any other product of radical trapping), then 50% of the alkyl halide that was initially present remains unconsumed. At this point, a controlled polymerization may still take place, if the L_nM-Y molecule, or the L_nM-R molecule, or both, has the ability to function as ATRP catalyst. However, the initiator efficiency will be reduced, e.g. to 0.5 for this particular example of the 1:1 stoichiometry. The initiator efficiency is readily determined experimentally from the ratio of the theoretical and experimental molecular weights. For instance, when only half of the initiator molecules are able to give rise to growing polymer chains, the number average molecular weight for the polymer isolated at any given monomer conversion will be twice that calculated if the initiator had 100% efficiency.

There are several reports in the literature of unusually low initiator efficiencies, with no satisfactory interpretation being offered. In some cases, initiator efficiency values are not mentioned at all, but low values may be calculated as the ratio between the expected and the experimentally observed number-average molecular weights. We have reported ourselves a few systems that are characterized by quite low initiator efficiencies, for instance $f = 0.55$ for the styrene polymerization process shown in Figure 5.^[55] A similar behavior is observed for the analogous polymerization of methyl acrylate using the same catalyst ($f = 0.6$). Two main reasons are recognized as responsible for low initiator efficiencies. The first one is related to a slow activation rate relative to the propagation rate. Under these circumstances, only a fraction of initiator molecules will be activated at a particular time and will grow at regular rate, while another fraction has not yet been activated. This results in a broad polydispersity.

However, as time goes on, all initiator molecules will eventually be activated and the efficiency factor will tend to one, see Figure 6(a). A second reason leading to low initiator efficiencies is a slow deactivation of the propagating radicals, e.g. a small value of k_d in Scheme 1. In this case, the propagating radical concentration builds up to higher levels, inducing a significant amount of bimolecular terminations. This also results in a broad molecular weight distribution. In this case, the corresponding amount of initiator molecules is lost irreversibly and the initiator efficiency factor remains low throughout the polymerization process. However, the persistent radical effect will set in sooner or later, bringing back the process under control and the polydispersity will decrease with an increase of conversion, see Figure 6(b). Clearly, the process represented in Figure 5 does not belong to either of these situations, because the distribution is already rather narrow ($\overline{M}_w / \overline{M}_n < 1.2$) at the beginning of the polymerization and does not further decrease.

<Figure 5 and Figure 6>

The hypothesis of an irreversible one-electron oxidative addition as the factor reducing the initiator efficiency when using $\text{CpMoCl}_2(i\text{PrNCHCHNiPr})$ as ATRP catalyst is proven by the following observations:^[56] (a) the MA/ $\text{CpMoCl}_2(i\text{PrNCHCHNiPr})$ /AIBN system – typical OMRP conditions – leads to *no polymer whatsoever*, proving that all radicals generated by the initiator are irreversibly trapped by the metal complex; (b) whereas the MA/ $\text{CpMoCl}_2(i\text{PrNCHCHNiPr})$ / $\text{CH}_3\text{CHICOOEt}$ system (140:1:1; 30% in toluene) – typical ATRP conditions – yields PMA with an initiator efficiency of 0.6 (*vide supra*), the corresponding system with a 154:1:0.5 stoichiometry does not yield any polymer. However, after the addition of one more equivalent of $\text{CH}_3\text{CHICOOEt}$ (1.5 equivalents overall), the polymerization starts in a controlled fashion and the experimental molecular weights are close

to, in fact slightly smaller than, the theoretical ones (calculated on the basis of only the equivalent of initiator added later), see Figure 7. The fact that a polymerization still takes place, after one half of the initiator is irreversibly neutralized by the $\text{CpMoCl}_2(i\text{PrNCHCHN}i\text{Pr})$, means that the products of this irreversible reaction must themselves act as ATRP catalysts, generating polymer by the activation of the residual initiator.

<Figure 7>

The notion that the irreversible radical trapping may involve a ligand, rather than the metal center itself, is illustrated by a recent report of the cobaltocene (Cp_2Co) activity in the ATRP of MMA, initiated by $(\text{CH}_3)_2\text{CBrCOOEt}$.^[57] The authors propose, on the basis of well established organometallic chemistry, the transformations described in Scheme 7. However, they report an efficiency factor as low as 0.25 for a Co/RBr ratio of 1:1. Such a low value cannot be consistent with the suite of events described in Scheme 7, for which a minimum value of 0.5 should be observed for this particular stoichiometry (and, still, under the assumption that one of the two products are active ATRP catalysts). In addition, this schemes includes the hypothesis that the outer-sphere oxidation product, $[\text{Cp}_2\text{Co}]^+\text{Br}^-$, is an efficient radical trap. Other work, however, shows that outer sphere complexes are less efficient radical traps in ATRP.^[58, 59] On the basis of other known organometallic chemistry of cobalt, it seems possible to rationalize this very low efficiency factor in another way. It is possible to imagine that an additional fraction of available initiator further oxidatively add to the Co^{I} product of Scheme 7, yielding Co^{II} and/or Co^{III} products that could then operate as ATRP catalysts. Indeed, $[\text{CpCo}(\mu\text{-Y})]_2$ and $[\text{CpCoX}(\mu\text{-Y})]_2$ complexes have been described.^[60] The $[\text{Cp}_2\text{Co}]^+\text{Br}^-$ system, on the other hand, may well be a dead end, inactive complex.

Various tests could further probe the mechanism of this reaction (for instance, by use of $[\text{Cp}_2\text{Co}]^+\text{Br}^-$ under “reverse” ATRP conditions).

<Scheme 7>

Extension to “difficult” monomers.

A current challenge of CRP is the possibility to control the radical polymerization of monomers that generate more reactive radicals (e.g. vinyl acetate, vinyl chloride, vinylidene chloride, ethylene, ...). Much research effort has been devoted to the ATRP method, but success has remained very limited. The reason why these monomers are not easily controlled by ATRP is evident on the basis of the thermochemical considerations developed above and from the BDE values obtained for model R-Y molecules, see Table 1.^[61] These molecules may be considered as models of propagating radicals derived from the monomers indicated in the last column. Thus, relatively stabilized radicals such as those of styrene and methyl acrylate form weaker bonds with the halogen atoms, whereas more reactive radicals such as those of vinyl chloride, vinyl acetate, or ethylene form stronger bonds. Since $\Delta H_{\text{ATRP}} = \text{BDE}(\text{R-Y}) - \text{BDE}(\text{L}_n\text{M-Y})$ and the second term is constant for a given catalyst/halogen combination, the more reactive radicals will lead to more difficult activations for a given catalyst. The difference between styrene and vinyl acetate, for instance, is close to 10 kcal/mol for both Cl and Br derivatives. Clearly, these two monomers cannot be controlled by the same metal system. The BDEs of alkyl bromides are 8-10 kcal/mol weaker than those of the corresponding alkyl chlorides, but a similar differential is expected for the $\text{L}_n\text{M-Y}$ bonds, thus a change of halogen is not expected to provide a great variation of ΔH_{ATRP} .

<Table 1>

It is possible to imagine that a suitable solution may be found by changing other factors in the catalytic metal complex: the ligands, the metal oxidation state, or the type of metal. DFT calculations on model complexes have shown that the M-Y BDE decreases upon increasing the oxidation state, whereas it is much less dependent on the nature of two-electron (L-type) ligands.^[27] Therefore, it may be predicted that the radical polymerization of more difficult monomers may become controllable by using lower oxidation state catalysts. In this respect, the ubiquitous Cu^I system is rather limited, whereas more possibilities may exist for other metals, e.g. Ti, Mo, Re, ... However, the effect of the nature of one-electron (X-type) ligands, coordination geometry, electronic configuration and spin state has not yet been studied in detail. Much useful information may be anticipated by systematic studies in this area. Another useful argument is that BDE's usually increase within a group in the order $3d < 4d < 5d$. Thus, more difficult monomers may be controlled by changing the metal to a heavier congener (e.g. Mo to W, or Ru to Os). Systematic studies in this respect are also lacking.

There is, however, a potential problem with this approach. As M is changed in order to strengthen the M-Y bond, the M-R bond will strengthen too. Therefore, while the ΔH_{ATRP} is displaced toward the suitable range, ΔH_{OMRP} will correspondingly increase and this increase may be such to render the radical trapping process irreversible and lead to the one-electron oxidative addition products. This negative effect may be somewhat attenuated by playing on the ligand steric properties. Indeed, since propagating radicals occupy a larger cone angle in the metal coordination sphere relative to the halogen atoms, the $L_nM-(m)_xR$ BDE is expected to be more sensitive than the L_nM-Y BDE to the ligand steric bulk. Thus, the selection of a sterically more encumbering ligand shell, perhaps in combination with lower oxidation states

or with heavier metals, may hold some promise for matching the required ΔH_{ATRP} while maintaining a relatively low ΔH_{OMRP} when using reactive propagating radicals.

There is an interesting report that must be mentioned and commented at this point. Sawamoto has shown that the radical polymerization of vinyl acetate (VAc) can be controlled by $[\text{CpFe}(\text{CO})_2]_2$ in the presence of the iodide initiators $(\text{CH}_3)_2\text{C}(\text{I})\text{COOEt}$ or $\text{CH}_3\text{CH}(\text{I})\text{OCOCH}_3$, and the $\text{Al}(\text{O}i\text{Pr})_3$ co-catalyst in anisole at 60°C .^[62] This is a Fe^{I} catalyst and would therefore be expected to form stronger bonds with I (leading to $\text{Fe}^{\text{II}}\text{-I}$) relative to, say, Fe^{II} (leading to $\text{Fe}^{\text{III}}\text{-I}$). It is also a relatively unencumbered system, for which it is possible to envisage the formation of relatively strong $\text{Fe}^{\text{II}}\text{-alkyl}$ bonds. In addition, the metal-metal bonded dinuclear nature of the catalyst imposes the formation of the 17-electron and highly reactive $\text{CpFe}(\text{CO})_2$ metallaradical, right in the proximity of the propagating radical. It seems logical that a one-electron oxidative addition process should occur to yield a mixture of $\text{Cp}(\text{CO})_2\text{FeI}$ and $\text{Cp}(\text{CO})_2\text{Fe}(\text{VAc})_x\text{R}$, see Scheme 8. Indeed, stable alkyl derivatives such as $\text{CpFe}(\text{CO})_2\text{Et}$ are well known.^[63, 64] The experimental evidence that the initiator efficiency factor is close to 1 and that the isolated polymer contains iodo end groups shows that the one-electron oxidative addition equilibrium lies on the side of $[\text{CpFe}(\text{CO})_2]_2$ and $\text{R}(\text{VAc})_x\text{I}$. This is as expected since oxidative addition of alkyl halides to $[\text{CpFe}(\text{CO})_2]_2$ have not been reported. However, the control mechanism could well involve the active participation of the OMRP-type trapping process (case *b* of Figure 4). This could be easily checked by carrying out a radical polymerization under OMRP conditions, for instance from a suitable pre-synthesized $\text{CpFe}(\text{CO})_2\text{R}$ complex such as $\text{CpFe}(\text{CO})_2[\text{CH}(\text{Ph})\text{CH}_3]$,^[65, 66] or from $[\text{CpFe}(\text{CO})_2]_2$ and a radical initiator.

<Scheme 8>

The ultimate way to regulate the concentration of free radicals for highly reactive propagating radicals, however, is through the OMRP equilibrium. As discussed above, the OMRP activation relies only on the BDE of the metal-carbon bond in the organometallic dormant species. It is always possible in principle to design a metal complex, through an intelligent selection of ligands, metal centers, oxidation state, etc., leading to an organometallic dormant species with $\text{BDE}[\text{L}_n\text{M}-(\text{m})_x\text{R}] = \Delta H_{\text{OMRP}}$ in a suitable range for any monomer, since the OMRP equilibrium is not contaminated by other coupled equilibria (at least not in the absence of halogen atoms in the coordination sphere). In this respect, it is pertinent to underline the recent success in the controlled polymerization of vinyl acetate by this technique using $\text{Co}(\text{acac})_2$ as spin trap.^[7] This is in contrast to other Co^{II} systems (e.g. with porphyrines or Schiff bases as ligands), which irreversibly trap the propagating radicals of VAc (ΔH_{OMRP} too high), but control the polymerization of acrylates. Conversely, while the ΔH_{OMRP} $(\text{acac})_2\text{Co}-(\text{m})_x\text{R}$ is just right for $\text{m} = \text{VAc}$, it is too small for $\text{m} = \text{MA}$, leading to an uncontrolled process. There is, therefore, in the opinion of this Author, greater promise for the development of new controlled radical processes of the “difficult” monomers in OMRP than in ATRP. The difficulty associated to the formation of metal-capped polymers may be surmounted by subsequent transformations, which may allow the recovery and recycling of the metal complex. For instance, this is the case for the $\text{Co}(\text{acac})_2$ -capped PVAc, which may be converted to a R_2NO -capped polymer and $\text{Co}(\text{acac})_2$ by treatment with stable nitroxides.^[67]

The intervention of catalytic chain transfer (CCT)

Up until this point, we have neglected the catalyzed chain transfer, another phenomenon intimately related to the presence of transition metals capable of undergoing one-electron processes. Chain transfer can be catalyzed through the abstraction by ML_n of a β -hydrogen

atom from the propagating radical, to yield a hydride complex, L_nM-H , and a dead polymer chain with an unsaturated end-group, see Scheme 9.^[68]

<Scheme 9>

This phenomenon has its own practical relevance because it gives access to macromonomers with a controlled average molecular weight. Thus, considerable effort is devoted to a search of ML_n systems that exhibit high transfer rate constants (k_{tr} in Scheme 9) for a number of industrial applications.^[69] However, this phenomenon interferes with the chain growth process when “pseudo-living” polymerizations are sought via ATRP or OMRP methods. To resume, a L_nM complex apt to increase both its electron count and its coordination number by one unit has the potential to simultaneously exert three functions: ATRP catalyst, OMRP spin trap, and radical chain transfer catalyst. Our above mentioned study of the $CpMoCl_2L_2$ systems in the controlled polymerization of styrene has highlighted for the first time the interplay of these three functions.^[27] This phenomenon can be integrated in a general scheme which encompasses the metal-mediated radical generation and concentration regulation, the living chain grow, the chain transfer, and the one-electron oxidative addition, as depicted in Scheme 10.

<Scheme 10>

A first interesting consideration concerns which conditions are most appropriate for the manifestation of CCT. On the basis of the general energetic schemes in Figure 1 and Figure 4, the equilibrium concentration of the potential chain transfer catalyst will be low under OMRP conditions (the equilibrium is largely shifted toward the organometallic dormant

species), whereas it will be high under ATRP conditions (the equilibrium is largely shifted toward ML_n + halogenated dormant species). The latter statement is correct, obviously, provided that the OMRP trapping process does not predominate. Thus, we can readily conclude that CCT is favored under two circumstances: (a) under OMRP conditions, when ΔH_{OMRP} is too small, (case *a* of Figure 1); (b) under ATRP conditions, provided that the OMRP trapping process is not too important (e.g. case *a* of Figure 4). The most efficient catalytic processes are those carried out under OMRP conditions, with ML_n complexes that form very weak metal-carbon bonds. This is because both free radical and catalyst concentrations may be relative high at the same time. Under ATRP conditions, on the other hand, the ML_n concentration may be high, but the free radical concentration is kept low by the ATRP (and possibly also the OMRP) activation/deactivation equilibrium. The most active catalysts appear to be those based on cobaloximes, containing no halogen ligands in the system.^[70, 71] Catalytic activity, however, has also been shown for other systems such as $(C_5R_5)Cr(CO)_3$ ($R = H, Me, Ph$), $Cp^*Fe(CO)_2$, heavier analogues, the tris(pyrazolyl)borato derivatives $TpMo(CO)_3$ and $Tp^*Mo(CO)_3$,^[72-74] and certain (diimine)Fe systems.^[75]

The relative ability of a transition metal complex to abstract a β -H atom and to form a M-C bond obviously depends on the nature of the propagating radical. Certain radicals have a greater propensity than others to transfer a hydrogen atom. For a given radical, on the other hand, the type of metal complex affects the relative trapping/transfer ratio in ways that are not yet completely understood. Steric effects appear to be quite important to the extent that they have a greater effect on the formation of the organometallic dormant species than on the hydrogen atom transfer process yielding the hydride intermediate. Another potential side reaction consuming the chain transfer catalyst and equally disfavored by a greater steric encumbrance is the dimerization of ML_n . Recent work by Norton on $(C_5R_5)Cr(CO)_3$ -type

catalysts has shown that steric bulk enhances CCT activity by disfavoring the dimerization to M-M and the formation of M-R, in favor of the H-atom transfer reaction.^[74]

A recent study in our laboratory has shown that the complexes $\text{MoX}_3(\text{PMe}_3)_3$ ($\text{X} = \text{Cl}, \text{I}$) have a different trapping ability for free radicals generated under OMRP conditions: the trichloride complex significantly slows down the AIBN-initiated radical polymerization of styrene (though the observed molecular weight and $\overline{M}_w / \overline{M}_n$ are typical of an uncontrolled process), whereas the triiodide complex has essentially no effect.^[76] This is attributed to the greater steric bulk of the three iodide ligands relative to the corresponding number of chlorides. Consequently, when the polymerization is carried out under ATRP conditions [$\text{MoX}_3(\text{PMe}_3)_3$ + alkyl halide initiator], the equilibrium concentration of $\text{MoX}_3(\text{PMe}_3)_3$ during the polymerization process will be greater for $\text{X} = \text{I}$ than for $\text{X} = \text{Cl}$. This difference can rationalize the experimental observation of “living” growth in the trichloride case and CCT in the triiodide case. Incidentally, the $\text{MoX}_3(\text{PMe}_3)_3$ complexes are not “stable free radicals”, but rather contain three unpaired electrons (spin quartet state).

A recent report proposes an intriguing new pathway for CCT, apparently associated to changes of spin state: four-coordinate Fe^{II} complexes of type $\text{FeCl}_2(\text{RN}=\text{CHCH}=\text{NR})$ control the polymerization of styrene under ATRP conditions. However, whereas derivatives with $\text{R} = \text{alkyl}$ yield “living” chain growth, those with $\text{R} = \text{aryl}$ yield CCT.^[77, 78] This phenomenon correlates with the spin state of the atom transfer product, the Fe^{III} complex $\text{FeCl}_3(\text{RN}=\text{CHCH}=\text{NR})$ ($S = 5/2$ for $\text{R} = \text{alkyl}$, $3/2$ for $\text{R} = \text{aryl}$). The authors propose that the same relative spin state preference holds for the organometallic dormant species, whose formation would then be preferentially observed for the aryl-substituted complexes. Both Hartree-Fock calculations and the experimentally observed greater stability (higher decomposition temperature) of the aryl-substituted $\text{FeCl}_2(\text{CH}_2\text{Ph})(\text{RN}=\text{CHCH}=\text{NR})$ complexes are in support with this view. The organometallic dormant species would then

lead to chain transfer via a β -hydride elimination process, as shown in Scheme 11. Thus, this particular metal complex system appears to function by a combination of one-electron and two-electron processes, suitably orchestrated by the spin state. In this interesting variant of CCT mechanism, the catalytic ability is not related to the weakness of the M-R bond but rather to the availability of open coordination sites *cis* to the M-R function, capable to induce the β -hydride elimination process. It is worth to underline that the β -hydride elimination is mechanistically related to the olefin insertion into M-H and M-R bonds, i.e. the key step of olefin coordination polymerization. The accomplishment of both olefin coordination/insertion and homolytic bond cleavage using the same metal complex might open up new doors in polymer chemistry.

<Scheme 11>

In a previous study, we found that complexes $\text{CpMoCl}_2(\text{PMe}_3)_2$ and $\text{CpMoCl}_2(\text{dppe})$ lead to a “living” polystyrene chain growth under ATRP conditions, whereas the very similar complex $\text{CpMoCl}_2(\eta^4\text{-C}_4\text{H}_6)$, under identical conditions, leads to CCT.^[27] However, in this case we observed a “living” polymer growth (no CCT) when working under OMRP conditions, for all the above three complexes. This could be explained by invoking a lower concentration of the chain transfer catalyst under OMRP conditions. However, the reason for the different outcome of the different systems under ATRP conditions may not be so straightforward in this case. The attempted rationalization advanced in our original report was based on a greater steric impediment in the β -H transfer process for the more encumbered phosphine complexes. However, this impediment should be even stronger for the formation of the organometallic dormant species, yet there is control in all cases under OMRP conditions, showing that the metal-carbon bond is strong enough and forms rapidly for all

systems. If the steric factor is important for the generation of the organometallic dormant species, then ΔH_{OMRP} should be smaller for the bulkier phosphine system, resulting in a greater concentration of chain transfer catalyst, which is inconsistent with the experimental result. A CCT mechanism involving β -hydride elimination, like for the above-mentioned Fe system (Scheme 11) also appears unsuitable, because in that case more CCT should be observed under OMRP condition, contrary to the experimental result. Clearly, we have not yet achieved a complete understanding of the key parameters that regulate chain transfer vs. radical trapping.

Conclusions and outlook

A thorough understanding of one-electron transition metal reactivity is of fundamental importance for the correct interpretation of experimental results in metal-mediated radical polymerization processes. As we have shown in this Minireview, a variety of situations may result, depending on the thermodynamic parameters of the two fundamental steps of the one-electron oxidative addition process (Scheme 5) and on the kinetics of the catalyzed chain transfer (Scheme 9). The two fundamental steps of the one-electron oxidative addition correspond to the activation/deactivation equilibria of the two different metal-mediated controlled radical polymerization processes, ATRP and OMRP. These depend, from the thermochemical point of view, on the homolytic bond dissociation energies of three bonds: the L_nM-Y bond of the ATRP spin trap, the $R(m)_x-Y$ bond of the ATRP dormant species, and the $R(m)_x-ML_n$ bond of the OMRP dormant species. Knowledge of these three bond dissociation energies for a given system is essential to predict whether it will lead to an uncontrolled polymerization, to an irreversible one-electron oxidative addition, to no polymerization at all, or finally to a controlled polymerization and, in the latter case, whether the control will be insured solely by the ATRP activation/deactivation equilibrium, or solely

by the analogous OMRP equilibrium, or by a combination of both. We have shown that the interplay of the two equilibria, accompanied by an irreversibility of the OMRP-type radical trapping process, may lead to low initiator efficiency factors, provided the oxidative addition products are themselves active ATRP catalysts. We have explored the necessary conditions that must be met in order to achieve the controlled polymerization of monomers producing more reactive radicals. As we have argued, greater flexibility in terms of the radical controlling equilibrium position is provided under OMRP conditions by systems devoid of halogen atoms, although a drawback of this method is the necessary post-polymerization treatment to remove the metal from the chain ends. Finally, we have explored the conditions that regulate the extent of metal-catalyzed chain transfer, although a complete understanding of the parameters that regulate the relative extent of OMRP trapping and chain transfer events is still lacking.

Radical processes mediated by transition metal complexes will certainly continue to be heavily investigated in the future. These processes need complexes that are capable to increase both their electronic configuration and their coordination number by one unit, a condition that, given an appropriate coordination sphere (steric and electronic properties of the ligands, coordination geometry and spin state), can be satisfied for many different metals in a variety of different oxidation states. Further advance in this area will require a better understanding of how the above mentioned parameters (ligand properties, etc.) independently affect the three basic bond dissociation energies and the rate of β -H transfer. A key role in this game may be played by computational work.

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Captions for Figures and Schemes

Figure 1. Possibilities in OMRP, depending on the $\Delta H_{\text{OMRP}} = \text{BDE}[\text{R}(\text{m})_x\text{-ML}_n]$.

Figure 2. Possibilities in ATRP, when ΔH_{ATRP} is too large.

Figure 3. Possibilities in ATRP, when ΔH_{ATRP} is too small.

Figure 4. Possibilities in ATRP, when ΔH_{ATRP} is just right.

Figure 5. Experimental (squares) and theoretical (solid line) number average molecular weights (M_n) for the polymerization of styrene under ATRP conditions ($\text{CpMoCl}_2(i\text{PrNCHCHNiPr})/\text{Al}(\text{OiPr})_3/\text{CH}_3\text{CHICOOEt}$) in toluene solution (30% v/v) at 90 °C. The polydispersity index ($\overline{M}_w/\overline{M}_n$) is also shown as triangles. Data are taken from ref. [55].

Figure 6. Typical evolution of molecular weight (triangles) and polydispersity (hexagons) in the presence of low initiator efficiency: (a) slow initiation rate; (b) slow deactivation rate. The straight line represents the theoretical M_n for a living process ($f = 1$).

Figure 7. (a) kinetics; (b) evolution of the molecular weight (squares) and polydispersity index (triangles) as a function of conversion, for a PMA obtained in toluene (30% v/v) at 80°C with $\text{MA/CpMoCl}_2(i\text{PrNCHCHNiPr})/\text{Al}(\text{OiPr})_3$ ($\text{MA/Mo/Al} = 154:1:1$) and $\text{CH}_3\text{CHICOOEt}$ as initiator: 0.5 equiv initially, then 1 additional equivalent after ca. 30 h. The straight line represents the theoretical M_n for a living process ($f = 1$).^[56]

Scheme 1. Mechanism of action in ATRP

Scheme 2. Mechanism of action in reversible addition-cleavage polymerization

Scheme 3. The one-electron oxidative addition process in transition metal chemistry.

Scheme 4. Examples of one-electron oxidative addition processes.

Scheme 5. Interplaying ATRP and OMRP equilibria in controlled radical polymerization.

Scheme 6. Redox equilibria between different ATRP catalysts.

Scheme 7. Proposed mechanism for the cobaltocene-catalyzed ATRP of MMA.

Scheme 8. Oxidative addition of alkyl halides to $[\text{CpFe}(\text{CO})_2]_2$.

Scheme 9. Mechanism of catalyzed chain transfer (CCT).

Scheme 10. A global scheme for metal-mediated radical generation and one-electron processes.

Scheme 11. A proposed CCT pathway involving β -hydride elimination.

Table 1. Computed (BP86/6-31G**) Bond Dissociation Energies (kcal/mol) of representative R-Y molecules as propagating radical models for the monomers shown.^[a]

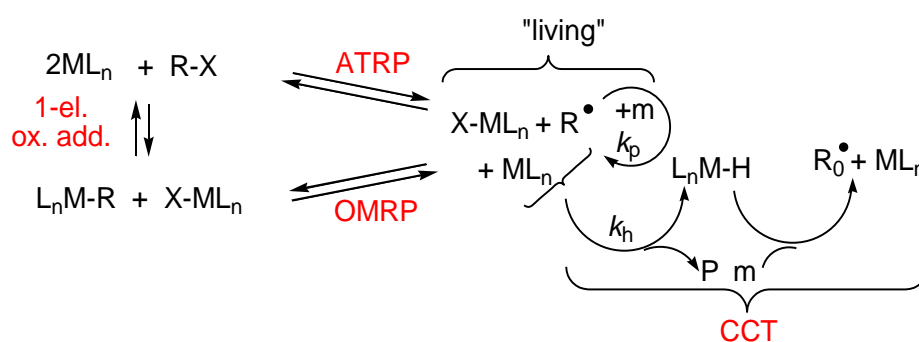
R	Y = Cl	Y = Br	monomer
CH ₃ CH ₂	83.1	73.1	ethylene
CH ₃ CH(OCH ₃)	82.2	73.3	vinyl ether
CH ₃ CH(O ₂ CCH ₃)	79.5	69.5	vinyl acetate
CH ₃ CH(Cl)	76.0	66.0	vinyl chloride
CH ₃ CH(COCH ₃)	71.0	62.9	vinyl ketone
CH ₃ CH(CO ₂ CH ₃)	69.9	61.4	methyl acrylate
CH ₃ CH(Ph)	68.5	59.9	styrene
(CH ₃) ₂ C(CO ₂ CH ₃)	66.9	58.9	methyl metacrylate
CH ₃ CH(CN)	65.9	57.2	acrylonitrile

^[a] Values taken from reference [61].

Text for Table of Contents

Controlled radical polymerization (CRP) has made giant steps after the development of efficient catalysts for Atom Transfer Radical Polymerization (ATRP). Another type of CRP process, which we term Organometallic Radical Polymerization (OMRP), uses the reversible formation of metal-carbon bonds. Finally, metals are also implicated in Catalytic Chain Transfer, involving H atom abstraction processes. This Minireview illustrates how one-electron transition-metal reactivity is crucial in metal-mediated CRP.

Table of Content Graphic



Figures and Schemes

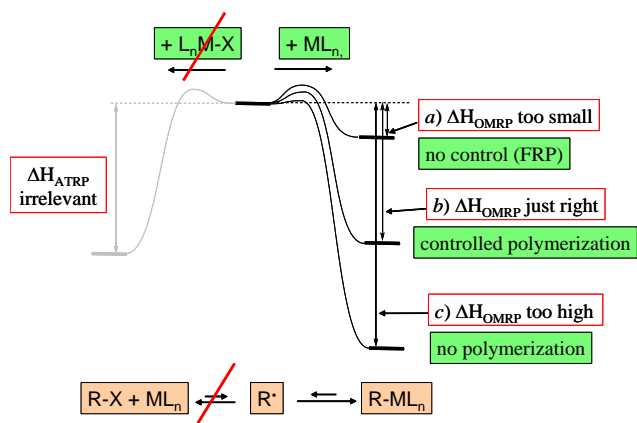


Figure 1

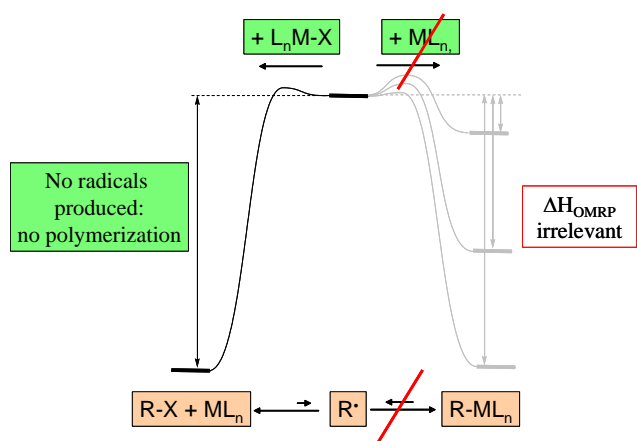


Figure 2

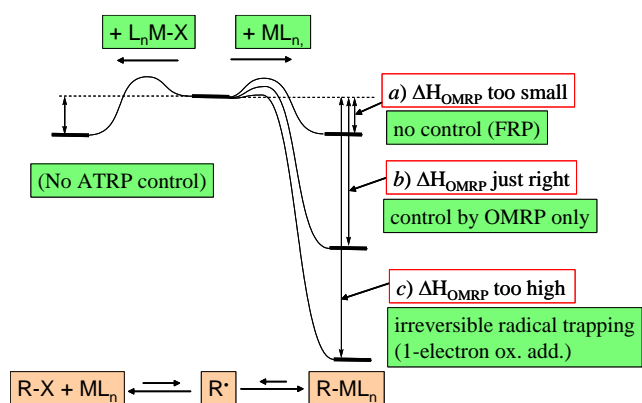


Figure 3

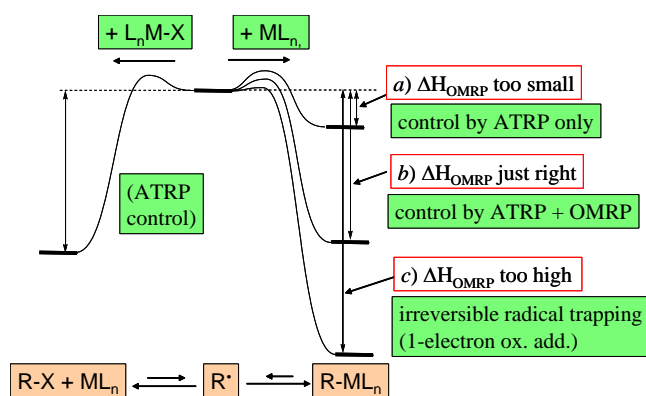


Figure 4

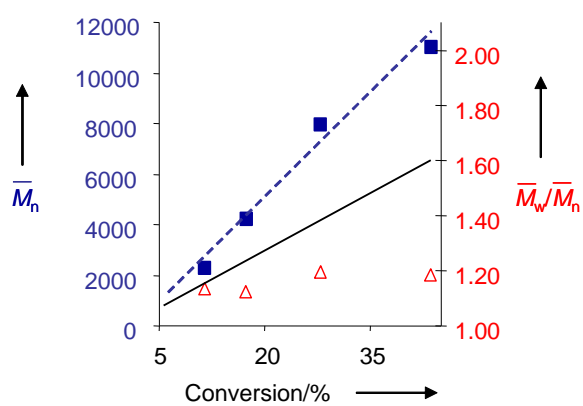


Figure 5

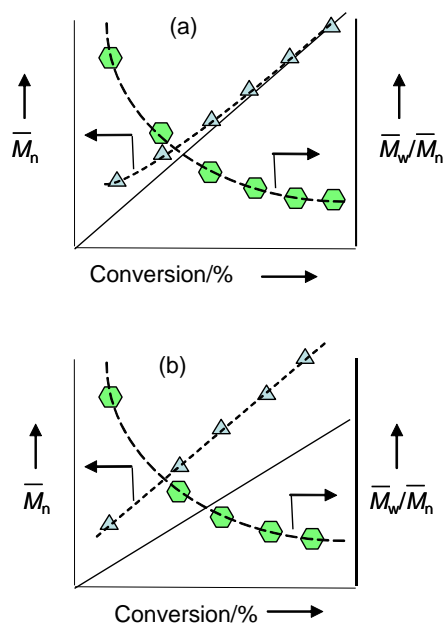


Figure 6

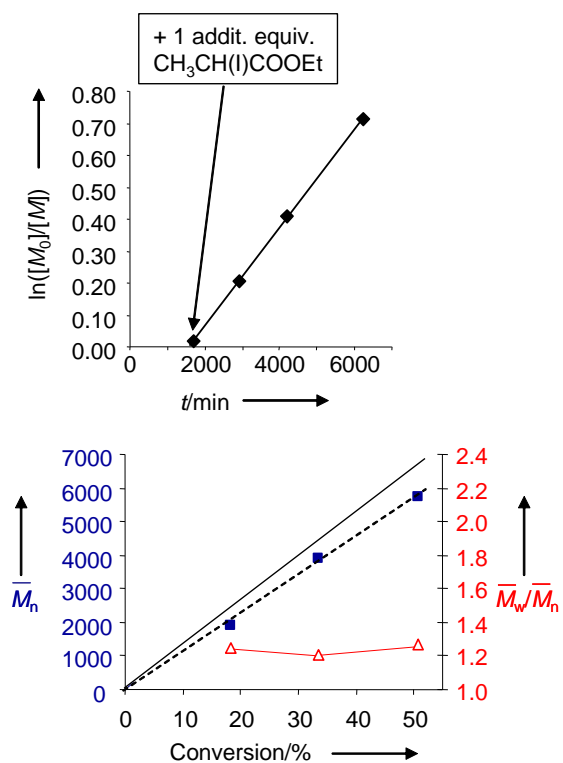
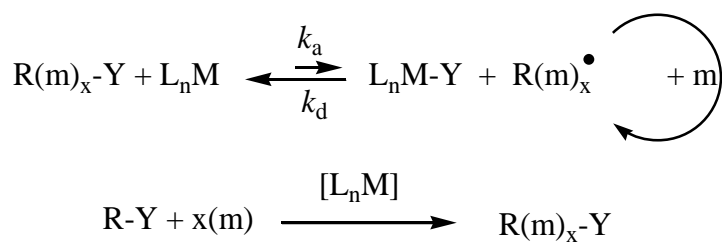
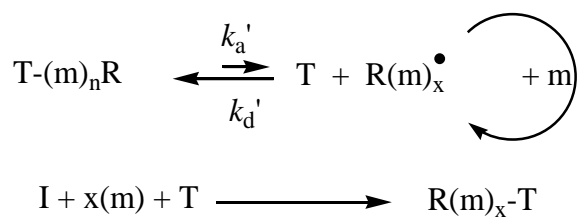


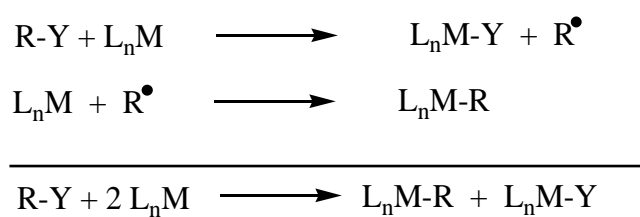
Figure 7



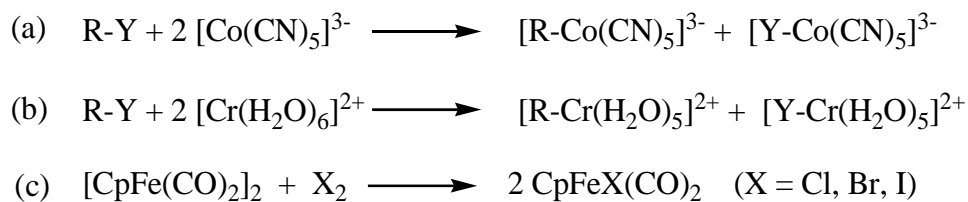
Scheme 1



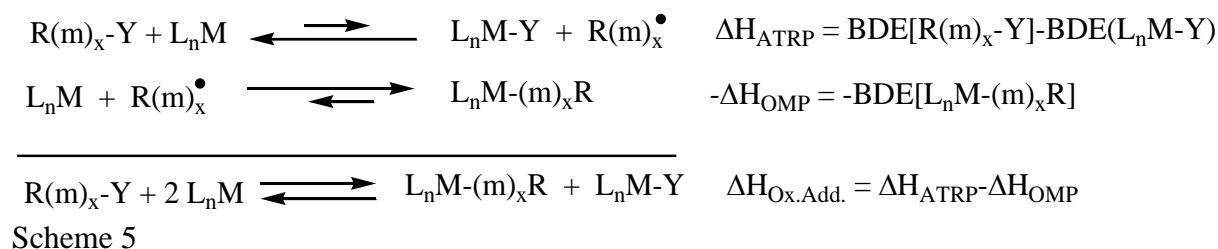
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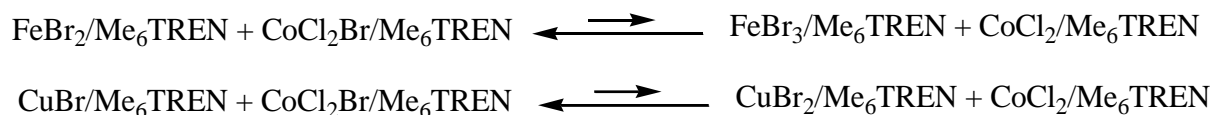
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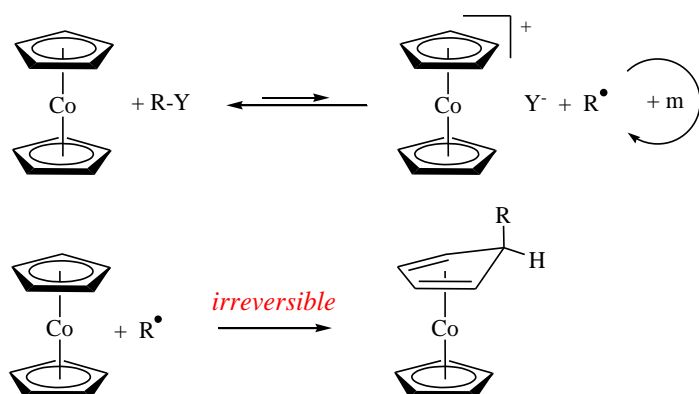
Scheme 4



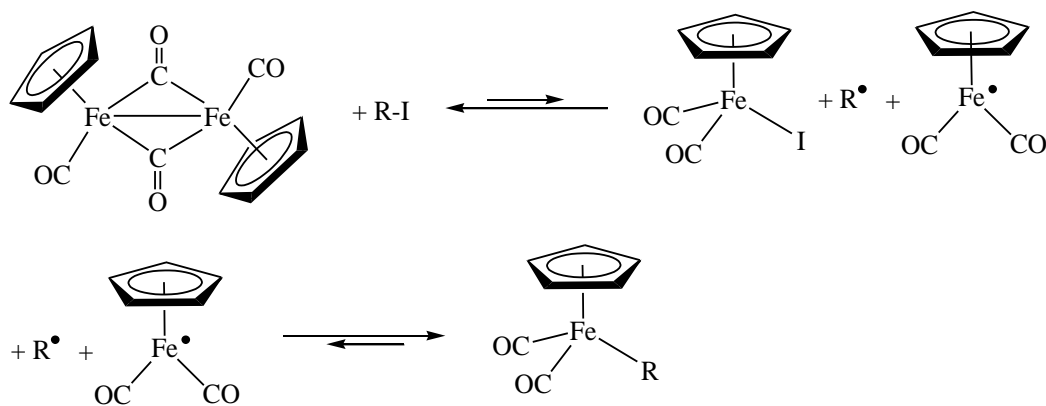
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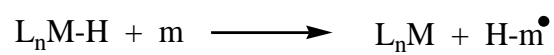
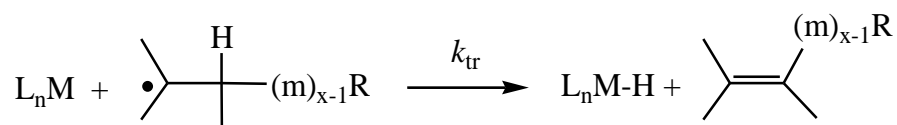
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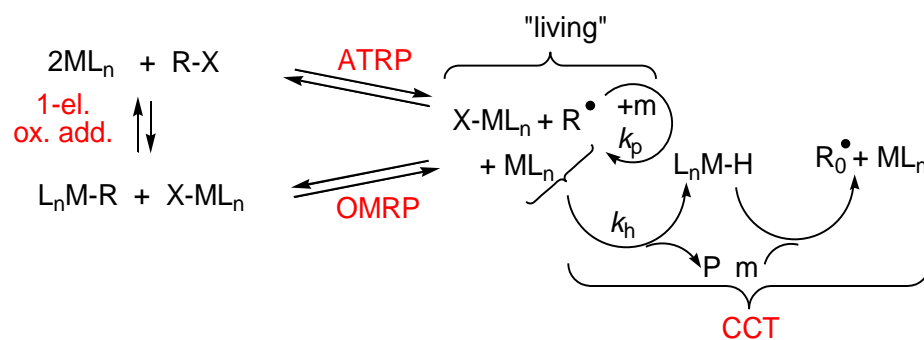
Scheme 7



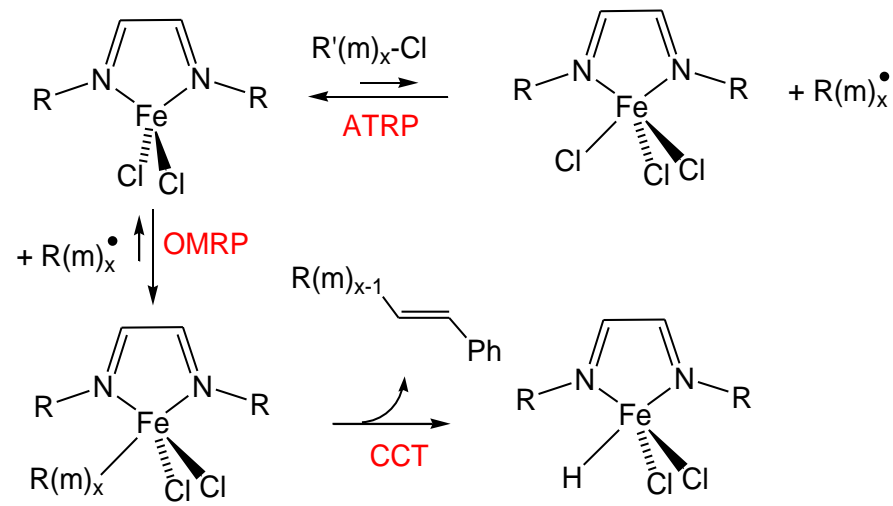
Scheme 8



Scheme 9



Scheme 10



Scheme 11