



# Iron-mediated reversible deactivation controlled radical polymerization



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## ABSTRACT

Metal-mediated reversible deactivation radical polymerization (RDRP) is now a cornerstone of functional polymer synthesis, dominated by copper complexes and the Atom Transfer Radical Polymerization (ATRP) moniker. A limitation of this approach is the contamination of the resultant polymers by the coloured copper complexes, thus requiring further purification, although protocols to reduce the amount of copper catalyst have been developed. Iron is an interesting alternative because of its low cost, low toxicity and reduced intensity of its optical absorption spectrum. Use of this metal in RDRP began in the late 90s and has continuously intensified. This review comprehensively covers all the work reported so far on RDRP mediated by iron complexes, organized according to ligand type, and discusses the specificities of this metal in terms of the multitude of accessible spin states and the interplay of different equilibria: atom transfer vs. direct radical trapping, associative vs. dissociative exchange, chain transfer by direct  $\beta$ -H atom transfer vs.  $\beta$ -H elimination from the dormant alkyl species.

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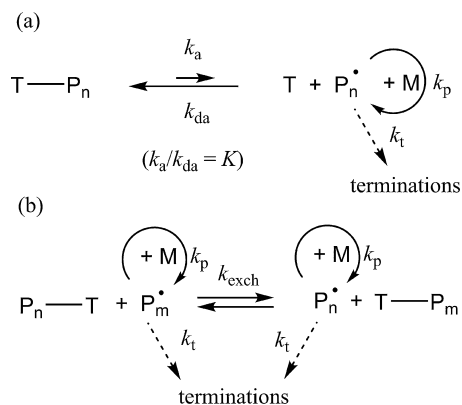
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## 1. Introduction

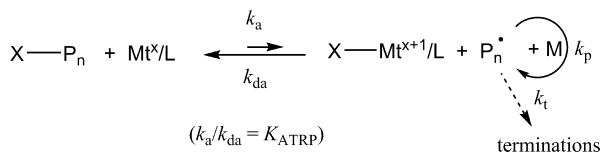
Since its development nearly 30 years ago [1–9], controlled radical polymerization has proven to be one of the most prolific contributions to modern polymer chemistry. Maintaining the functional group tolerance of conventional radical polymerization whilst offering control over molecular weight, dispersity ( $\mathcal{D}$ ) and macromolecular architecture has opened new avenues into a multitude of versatile advanced materials [10–29]. IUPAC generalizes the strategies to achieve this control as reversible-deactivation radical polymerizations (RDRP), but the individual techniques are commonly referred to by the specific strategy exploited to maintain control. Two general families of RDRP can be clearly distinguished, namely those involving dissociation of the reactive radical from a dormant species (Fig. 1a) and those involving associative exchange of the reactive radical with the dormant species, which also plays the role of transfer agent (Fig. 1b). In the former case a rapid, dynamic equilibrium between dormant and growing radical chains lowers the radical concentration, minimizing bimolecular termination reactions. These dissociative RDRP techniques benefit from the so-called “persistent radical effect” [30] (although the trapping reagent,  $T$ , need not be a “stable”, or persistent, free radical) and the polymerizations are slower than conventional free radical polymerizations, with an approximately first order rate law, although power laws have also been observed for some RDRP techniques [31]. In the second RDRP category there is no persistent radical effect. Rapid degenerative exchange



**Fig. 1.** General mechanisms of RDRP: (a) dissociative radical generation; (b) associative radical exchange.

in combination with a chain length-dependent termination rate ensures pseudo-living growth, as long as an influx of new radicals from a conventional radical initiator is maintained. The polymerization rate is regulated by the rate of radical production from the initiator, as in free radical polymerization.

Of these RDRP strategies, metal-mediated methods have developed into a powerful workhorse for scientists to produce specialized polymers due to their ease of use, advanced control over metal complex concentration, excellent end-group fidelity and monomer and initiator scope. Metal complexes can mediate RDRP in three different ways, with possible interplay between two or more different modes in certain cases [32]. A metal complex can act as the trapping species,  $T$ , in a reversible deactivation approach (Fig. 1a), yielding a dormant species that contains a metal–carbon bond (termed Organometallic Mediated Radical Polymerization, OMRP). Wayland reported the first example of OMRP in 1994, utilizing a cobalt porphyrin complex to mediate acrylate polymerization [6]. However, if the dormant species has a suitable structure, it can also act as a transfer agent for degenerative transfer polymerization (Fig. 1b) [33,34]. There are therefore two mechanistically distinct OMRP strategies, one dissociative (reversible termination, or RT-OMRP) and the other one associative (degenerative transfer, or DT-OMRP). The third metal-mediated RDRP method is Atom Transfer Radical Polymerization (ATRP), a dissociative-type mechanism where the trapping species,  $T$ , is an oxidized metal halide complex,  $X-Mt^{x+1}/L$ . Rather than forming a direct bond, however,  $T$  transfers a halogen atom and yields a halogen-terminated dormant species and a reduced metal complex,  $Mt^x/L$ , which is therefore a catalyst (Fig. 2). ATRP, first reported in 1995 by Matyjaszewski for a  $Cu^I/Cu^{II}$  system [7] and Sawamoto for a  $Ru^{II}/Ru^{III}$  system [8], also benefits from the persistent radical effect. ATRP can interplay with the dissociative RT-OMRP [32,35] and the two (associative and dissociative, DT and RT) OMRP methods may also operate for the same system [33,36].



**Fig. 2.** The ATRP mechanism.

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