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Inner Sphere and Outer Sphere Electron Transfer Reactions in Atom Transfer Radical Polymerization

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Abstract: The participation of electron transfer (ET) processes in atom transfer radical polymerization (ATRP) is discussed. Inner sphere electron transfer process (atom transfer) is the inherent part of ATRP. It includes the homolytic cleavage of C-halogen bond in dormant macromolecular alkyl halides species by the Cu(I) activator with the rate constant $k_{act} \approx 10^{0\pm1}$ $M^{-1}s^{-1}$. This process is reversible and the deactivation of growing radicals by X-Cu(II) species is very fast with the rate constant of deactivation $k_{act} \approx 10^{7\pm1}$ $M^{-1}s^{-1}$. However, in addition to the atom transfer process (inner sphere ET), outer sphere ET may also occur. Growing radicals can either be oxidized by Cu(II) species to carbocations or reduced by Cu(I) species to carbanions. These reactions were observed in the polymerization of p-methoxystyrene and initiation with 2-bromomalonates, respectively. In order to avoid these side reactions the catalyst structure should be fine tuned for the particular monomer and the range of targeted molecular weights. In addition, some side reactions can be avoided by slow addition of initiator (e.g. for benzhydryl halides), catalyst (for malonates and CCl_4 as initiators) and by reducing polymerization temperature.

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INTRODUCTION

Controlled radical polymerization is one of the most rapidly developing fields in synthetic polymer chemistry because it enables preparation of new materials which could not be previously prepared. There are several approaches towards controlled radical polymerization which employ dynamic equilibration between growing radicals present in minute amounts and dormant chains (Ref. 1). The most robust and most versatile methods seem to be nitroxide mediated polymerization and atom transfer radical polymerization (ATRP). The latter polymerization proceeds via a reversible redox process between alkyl halide and transition metals and involves electron transfer reactions. The contribution of inner sphere and outer sphere electron transfer reactions is of paramount importance and defines control of molecular weights, polydispersities and end-functionalities. This paper is focused on the assessment of the electron transfer processes in ATRP and on various methodologies to improve control of ATRP.

RESULTS AND DISCUSSION

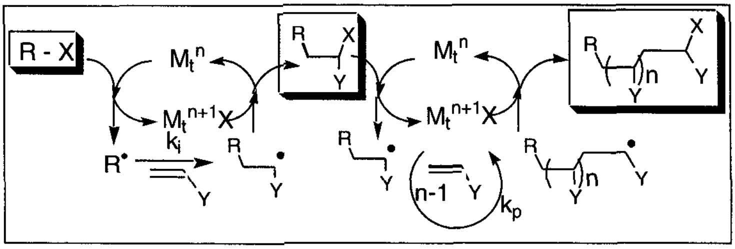
Atom Transfer Radical Addition (ATRA) and Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical addition employs atom transfer from an organic halide to a transition-metal complex to generate the substrate radical. This radical then adds to an alkene followed by the back-transfer of the halogen from the transition metal to the product radical, resulting in the final product (cf. left part of Scheme 1) (Ref. 2). In this reaction (which formally resembles Kharasch addition) (Ref. 3) a metal catalyst, usually a complex of a copper(I) halide and 2,2'-bipyridyl (Ref. 4, 5, 6) (although Ni (Ref. 7, 8), Pd (Ref. 9), Ru (Ref. 10), Fe (Ref. 11, 12) and other metals (Ref. 13) have been used as well), undergoes a one-electron oxidation with simultaneous abstraction of a halogen atom from a substrate. This inner-sphere electron transfer process reversibly generates an organic radical and a copper(II) complex (Ref. 14). After the back-transfer, the copper(I) complex is reformed along with alkyl halide, completing the catalytic cycle. The substrates are typically chosen such that if addition occurs, then the newly formed radical is much less stabilized relative to the initial radical and will essentially react irreversibly with the copper(II) complex to form an inactive alkyl halide product. Therefore, in ATRA, only one addition step should occur.

Initially it was not clear whether the intermediates were free-radicals, in a solvent cage, or coordinated to the metal center, but the most plausible mechanism based upon experimental evidence involves free-radicals. Initial doubts on the involvement of radical intermediates were related to unusually high selectivities of these reactions (>90 %), which are not observed in conventional free radical reactions. However, the high selectivities were elegantly explained by the existence of persistent radicals which reduce the stationary concentration of reacting radicals and minimize the contribution of termination (Ref. 15).

Scheme 1

General Concept of ATRA and ATRP



ATRA can be extended to atom transfer radical polymerization (ATRP) if the conditions can be modified such that more than one addition step is possible. Thus, if the radical species, before and after addition of the unsaturated substrate, possess comparable stabilization, then the activation-addition-deactivation cycle will repeat until all of the unsaturated substrate is consumed. This process results in a chain-growth polymerization.

Scheme 1 shows the mechanism of ATRP adapted from ATRA. The mechanism consists of phenomenologically related initiation and propagation processes. These sequences include an atom-transfer equilibrium along with radical addition to the monomer. Termination by radical coupling and disproportionation are also present; however, only a few percent of the polymer chains in ATRP undergo bimolecular termination and are not shown in Scheme 1. During one activation step several monomer molecules can be added to the growing radical; the degree of control is inversely proportional to this number. The presence of radical intermediates in the mechanism is consistent with experimental results from trapping experiments (Ref. 16,17), copolymerization reactivity ratios (Ref. 18,19), and the regio- and stereochemistry of the polymerization (Ref. 16). Thus, the net propagation sequence can be considered an "insertion" process proceeding via radical intermediates. A "reverse ATRP" experiment demonstrated that the proposed copper(II) complex formed after atom transfer is also an intermediate in ATRP. In reverse ATRP, the polymerization is entered from the right-hand side of the atom transfer by generating radicals from AIBN or BPO in the presence of $CuBr_2$ / 2 bipy and monomer (Ref. 20).

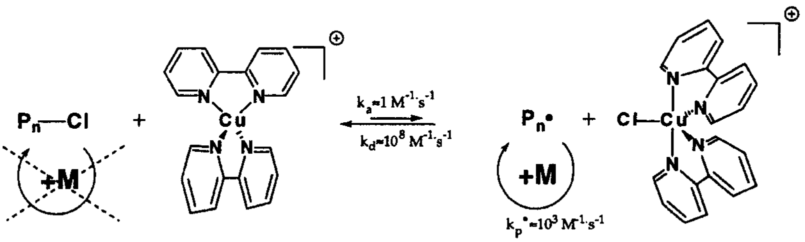
Polymerization systems utilizing this concept have been developed using Cu(I) (Ref. 16, 21, 22, 23, 24), Ni(II) (Ref. 25, 26), Ru(II) / $Al(OR)_3$ (Ref. 27) and Fe(II) (Ref. 28, 29, 30) complexes to catalyze the radical-forming equilibrium; however, in this paper we will primarily focus on copper-based ATRP.

Typical Features of ATRP

The simplified mechanism of copper based ATRP is shown in Scheme 2.

Scheme 2

Mechanism of ATRP



In agreement with some model reactions and estimates based on evolution of polydispersities with conversion, deactivation process in ATRP is very fast, nearly diffusion controlled, $k_d \approx 10^{7\pm1}$ M^{-1} s^{-1}. The equilibrium concentration of radicals is mainainted due to relatively fast activation process, $k_a \approx 10^{0\pm1}$ M^{-1} s^{-1}. The exact structure of Cu(I) and Cu(II) species in non-polar solvents is not precisely known but X-ray analysis suggests that Cu(I) is in the form of distorted tetrahedron with the weakly coordinating anion and Cu(II) is trigonal bipyramid with one halogen atom in the inner sphere, and other in the anionic form.

ATRP has been successfully used for the controlled polymerization of various substituted styrenes (Ref. 31), acrylates (Ref. 32), acrylonitrile (Ref. 33), methacrylates (Ref. 34), dienes and some other monomers(Ref. 28). Molecular weight of the resulting polymers can be controlled usually in the range of M_n=1,000 to 100,000, although well defined dimers (Ref. 4) as well as higher molecular weight polymers have also been prepared (Ref. 34). Polydispersities are usually well below $M_w/M_n<1.5$ which is the lower limit for conventional radical polymerizations and polymers with polydispersities as low as $M_w/M_n<1.05$ have been prepared (Ref. 22).

The termini of the macromolecule are defined by the initiator used. The initial end-groups are generated by the alkylating part of the initiator which enables the introduction of a variety of functional groups such as allyl, hydroxy, epoxy, cyano, amino, vinyl and others (Ref. 35). The halogen atom from the initiator (or catalyst) occupies the other end of the macromolecule and can be easily displaced by azide and other nucleophiles (Ref. 36). Thus, ATRP is a very convenient method for the preparation of both symmetric and asymmetric telechelic macromolecules. Because radical polymerizations are tolerant to many functional groups, side functionalities have been incorporated by polymerization of hydroxyethyl (meth)acrylates, vinyl acrylate, trimethylsilyl (meth)acrylate and other functional monomers.

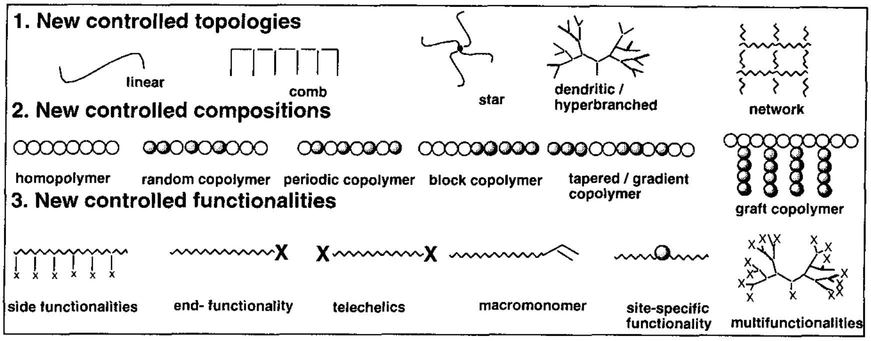
ATRP is a radical process and therefore it is possible to prepare various copolymers, much easier than using ionic copolymerization. The continuous growth of the chains with conversion is usually accompanied by the variation of the monomer feed composition in the simultaneous copolymerization. The drift in monomer feed is reflected by the continuous changes in the composition of all chains resulting in the formation of gradient copolymers (Ref. 18, 37). On the other hand, several segmented copolymers such as block and graft copolymers were prepared by sequential monomer additions (Ref. 38, 39).

Finally, ATRP allows for controlled (co)polymer topology leading not only to linear chains but also to stars, combs and hyperbranched structures (Ref. 39, 40, 41). A brief summary of new (co)polymers prepared by ATRP is shown in Scheme 3 below.

Of course, ATRP is not without limitations. These include the involvement of chain breaking reactions which set an upper limit for molecular weights; limitations on the structure of initiators which generate radicals either too slowly or too rapidly, and also limitations on the structure of catalysts which are either not reactive or not selective and participate in some side reactions. We will discuss potential improvements to these limitations in subsequent sections.

Scheme 3

Polymers with New Topologies, Compositions and Functionalities Prepared by ATRP



Increasing Molecular Weight Range

ATRP is a radical process and therefore, it will never be free from termination reactions. Proportion of terminated chains increases with the chain length and is determined by the concentration of radicals and the ratio of rate constants of propagation and termination. In order to reach higher molecular weights, the concentration of radicals should be reduced (polymerization should be slower) and the ratio k_p/k_t should be as high as possible. This ratio depends on a particular monomer but also on some external conditions such as temperature, viscosity, etc.

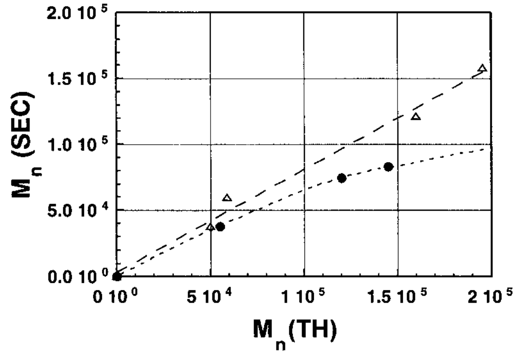


Figure 1. Correleation of experimental molecular weights with theoretical molecular weights for bulk polymerization of styrene at 110 (•) and 100 °C (Δ), intiated by 1-phenylethyl bromide and catalyzed by CuBr/2dNbipy.

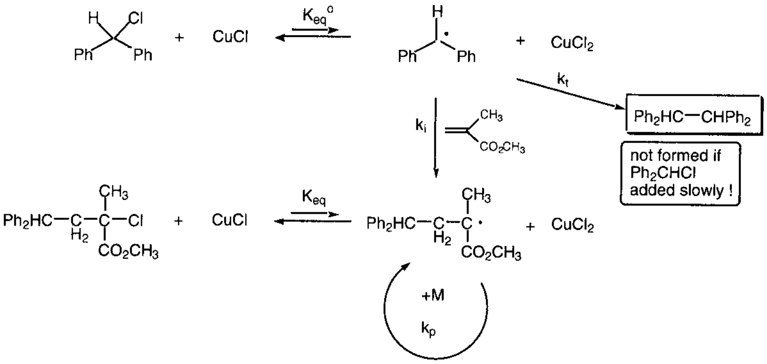
As will be demonstrated later, there are other side reactions in ATRP. These may include outer sphere electron transfer with reduction/oxidation of growing radicals, transfer reactions (to monomer, polymer) and possibly the formation of new organometallic species. It appears that the contribution of some of these reactions depends on temperature as shown in Figure 1; progressively higher molecular wieght polystyrenes can be prepared at lower temperatures. At 110 °C, the upper limit for the initiating system consisting of alkyl bromide and CuBr/bipy is in the range of $M_n \approx 80{,}000$, whereas at 100°C, polystyrenes with $M_n > 150{,}000$ were prepared.

Initiation with Benzhydryl Halides

Polymerization of MMA initiated by diphenylmethyl chloride (benzhydryl chloride) leads to polymers with very low polydispersities ($M_w/M_n < 1.1$) but with molecular weights nearly twice larger than predicted from the $\Delta[M]/[I]_0$ ratio. In addition, the polymerization is much slower than using other alkyl halides as initiators. When solid benzhydryl chloride is introduced to the reddish brown reaction mixture containing monomer and catalyst (CuBr/dNbipy), an immediate color change to dark green indicates formation of Cu(II) species. This indicates that the initiating radicals quicker dimerize, reducing the efficiency of initiation and slow down the reaction by irreversibly producing a large excess of deactivator ($CuBr_2$). Indeed, 1,1,2,2-tetrahenylethane is formed quantitatively within 5 minutes when benzhydryl chloride is added to an excess CuBr/dNbipy in the absence of monomer.

Scheme 4

Increasing Inititiation Efficiency by Slow RX Addition



However, control can be significantly improved by slow addition of a solution of benzhydryl chloride to the reaction mixture over 5 to 10 minutes. Under such conditions, an excess of radicals is not produced and the contribution of bimolecular termination is much smaller (Scheme 4). The resulting reaction is faster (Figure 2) and initiator efficiency approaches 100%.

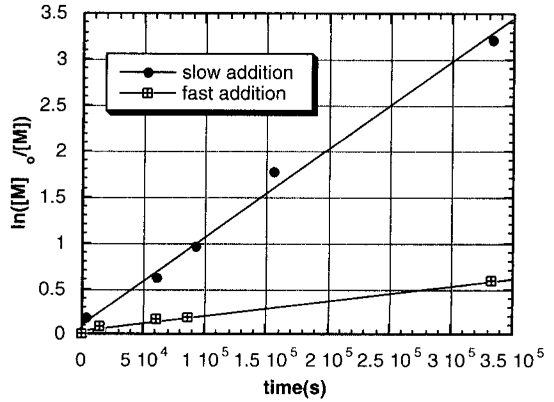


Figure 2. Semilogarithmic kinetic plots for solution polymerization of MMA in 50% diphenyl ether at 90°C for slow and fast addition of benzhydryl chloride. For slow addition, the initiator solution was added during 5min. [benzyhydryl chloride]$_o$ = 0.023M, [CuX]$_o$ = 0.0115M, [dNbpy] = 0.023M.

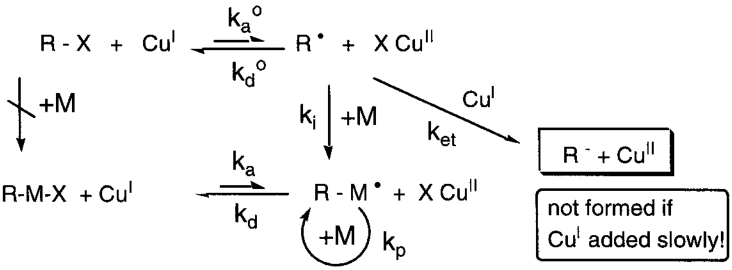
Initiation with Bromomalonates and Carbon Tetrachloride

Carbon tetrachloride has been used successfully as an initiator for the polymerization of several monomers using the heterogeneous catalytic system CuBr/bipy. However, CCl_4 was inefficient as an initiator for the homogeneous catalysis using CuBr/dNbipy in styrene polymerization. The same observation was made when using diethyl 2-bromomalonate as initiator. After addition of the initiator an immediate change of color from brownish red to dark green indicated formation of $CuBr_2$/dNbipy species. Slow addition of the initiator failed to improve this system.

On the other hand, the polymerization was successful when the catalyst was added slowly to the reaction mixture. Presumably, the malonate and trichloromethyl radicals react not only with alkenes via the addition pathway but also can be reduced to the corresponding anions by Cu(I) species (Scheme 5). When the concentration of Cu(I) is significantly reduced, radicals are still formed but they can react more selectively with alkenes since the outer sphere electron transfer process is less probable.

Scheme 5

Increasing Initiation Efficiency by Slow Catalyst Addition



After the first addition to alkene, the probability of the electron transfer is much lower due to the difference in reduction potential between the substrate and product radicals (cf. Scheme 6). At this stage more Cu(I) species can be added to continue the propagation at the usual rate. (Figure 3).

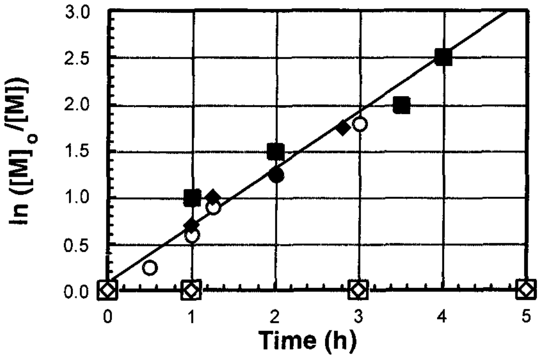


Figure 3. Semilogarithmic kinetic plots for bulk polymerization of styrene at 110°C for slow (filled symbols) and fast addition (empty symbols) of CuBr/2dNbipy. For slow addition, the catalyst solution was added during 5 min. $[RX]_o = 0.09$ M, $[CuBr/2dNbipy]_o = 0.09$ M. Initiators: 1=phenylethyl bromide (o), dimethyl 2-bromomalonate (□ ■), CCl_4 (◇◆).

In the polymerization of MMA, the malonate radicals apparently do not add to MMA fast enough, even when the catalyst is added slowly. However, diethyl 2-bromo-2-methylmalonate is an efficient initiator for MMA, presumably because the electron donating methyl group reduces possibility of the electron transfer by destabilizing the potential carbanion.

Polymerization of p-Methoxystyrene

Several substituted styrenes have been polymerized successfully using CuBr/bipy and CuBr/dNbipy as catalysts, resulting in polymers with low polydispersities and with degrees of polymerization defined by the $DP=\Delta[M]/[I]_o$ ratio. Only p-methoxystyrene, although consumed with a "normal" rate, predominantly resulted in dimer formation (Ref. 42). The structure of the dimer suggests involvement of carbocationic intermediates. Thus, in contrast to the reduction of the electrophilic malonate radicals discussed in the previous section, the oxidation of the nucleophilic benzyl radicals, stabilized by the electron donating p-methoxy group seems plausible.

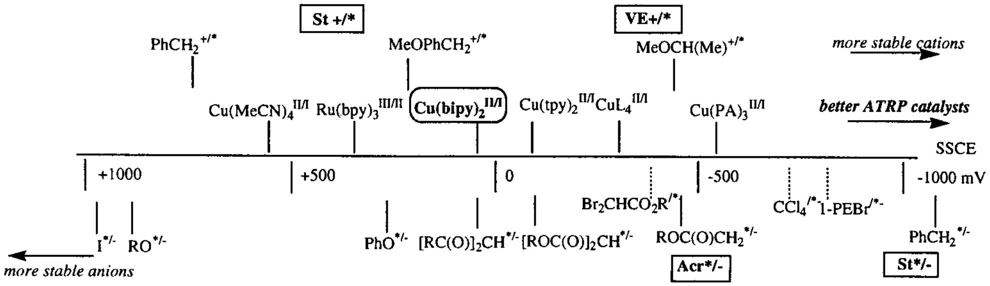
It has been previously reported that even in the styrene polymerization by a $CuPF_6/(CH_3CN)_4$ complex, the cationic process dominates over the radical one (Ref. 43). It is possible that some ATRP catalysts may act as sufficiently strong Lewis acids to cleave R-X bond heterolytically producing carbocations, rather than homolytically generating radicals. Nevertheless, the growing radicals could be oxidized by a Cu(II) species to the same cations, depending on the redox potential of the organic radicals and the transition metal complexes.

Electrochemical "Master Scheme" for ATRP

Scheme 6 presents some approximate values for redox processes for the previously discussed metal complexes, together with the estimated potentials for the oxidation and reduction of selected organic radicals (Ref. 44, 45, 46, 47, 48). Although most of these values were determined in acetonitrile, and some were only roughly estimated, they provide a general picture of some plausible electron transfer processes.

Scheme 6

Redox Potential for Various Organometallic Complexes and Various Organic Radicals



The upper row presents the oxidation potential of radicals with substituents stabilizing carbocations. Also, the oxidation potential for radicals in polymerization of styrene and vinyl ethers are estimated (boxes). The bottom row refers to the values of reduction potentials of some electrophilic radicals together with the estimated values for reduction potentials for radicals in polymerization of acrylates and styrene (boxes). The broken lines refer to the reduction of some alkyl halides to the corresponding radical anions.

There are several important conclusions to be made from he inspection of Scheme 6. It appears that poor ATRP catalysts may participate in an outer sphere electron transfer process to oxidize some organic radicals, including styryl radicals. Indeed, the $^{+}Cu(MeCN)_4$ complex leads to cationic styrene polymerization (Ref. 43). As mentioned before, p-methoxystyrene also forms carbocations when $CuBr/(dNbipy)_2$ is used (Ref. 31) and the radical homopolymerization of vinyl ethers has been unsuccesful for the same reason. Thus, it may be predicted that using more powerful catalysts, which better stabilize higher oxidation states of the metal (like CuX with aliphatic polyamines) the radical polymerization of some of these monomers may be successful.

On the other hand, a better catalyst may reduce the electrophilic radicals such as those present in the polymerization of acrylates or acrylonitrile. $CuBr(dNbipy)_2$ can already reduce malonate, acetylacetonate and trichloromethyl radicals under the appropriate conditions. More powerful catalysts may increase the proportion of side reactions for electrophilic redicals. It seems that $Cu/bipy_2$ is a relatively universal catalyst, which may be used for many but not all monomers. Further development of new ATRP catalysts may require specific design for each group of monomers in order to prevent an outer sphere electron transfer reaction and the side reactions due to either carbocations or carbanions:

$$\mathbf{R^{\bullet} + Cu(II) \rightleftharpoons R^{+} + Cu(I)} \quad \textbf{\textit{side reactions due to carbocations}}$$

$$\mathbf{R^{\bullet} + Cu(I) \rightleftharpoons R^{-} + Cu(II)} \quad \textbf{\textit{side reactions due to carbanions}}$$

The data in Scheme 6 indicate that reduction of alkyl halides to generate radical anions by outer sphere electron transfer is not very likely and that the radicals are generated by the direct inner-sphere electron transfer process which is consistent with the proposed mechanism for atom transfer radical polymerization.

CONCLUSIONS

Electron transfer processes are an inherent part of ATRP. The predominant pathway involves an inner-sphere electron transfer process which is based on the homolytic cleavage of a C-halogen bond in a dormant macromolecular alkyl halides species by the Cu(I) activator with the rate constant $k_{act} \approx 10^{0\pm1}\ M^{-1}s^{-1}$. This process is reversible and the deactivation of growing radicals by X-Cu(II) species is fast with the rate constant of deactivation $k_{act} \approx 10^{7\pm1}\ M^{-1}\ s^{-1}$. However, in addition to the atom transfer process (inner sphere ET), the outer sphere electron transfer may also occur. Growing radicals can either be oxidized by Cu(II) species to carbocations or reduced by Cu(I) species to carbanions. In order to avoid these side reactions the catalyst structure should be fine tuned for each particular monomer and the range of targeted molecular weights. In addition, some side reactions can be avoided by slow addition of initiator, catalyst or by reducing polymerization temperature.

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