Structure-Reactivity Correlation in Atom Transfer Radical Polymerization

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Summary: Kinetics of atom transfer radical polymerization (ATRP) with the special emphasis on dynamics of activation and deactivation is discussed. Various mechanistic features of ATRP related to electron transfer processes are presented. Elementary reactions of ATRP process are analyzed.

Introduction

The basic theory of free radical polymerization correlates structure of monomers and free radicals with the rate constants of propagation and cross-propagation. In general more reactive monomers form less reactive free radicals. Although free radicals do not bear charge, they can be polarized and have electrophilic or nucleophilic character. Electrophilic radicals are usually more reactive than nucleophilic radicals.[1] There is a tendency for cross-propagation and electrophilic radicals prefer to react with monomers which form nucleophilic radicals and vice versa. Thus, in copolymerization of styrene and methyl methacrylate both reactivity ratios are smaller than unity. It is anticipated that nearly all rules observed in conventional free radical polymerization apply to Atom Transfer Radical Polymerization (ATRP). This includes chemoselectivity, regioselectivity and stereoselectivity of propagation, transfer and termination steps. There might be a small caveat in some cases such as diffusion phenomena, incompatibilities, chain length dependent termination, additional side reactions with a ligand or complex but otherwise a general picture remains the same.

The only difference between ATRP and conventional process is the presence of reversible atom transfer steps responsible for the overall control of the process, shown in Scheme 1.

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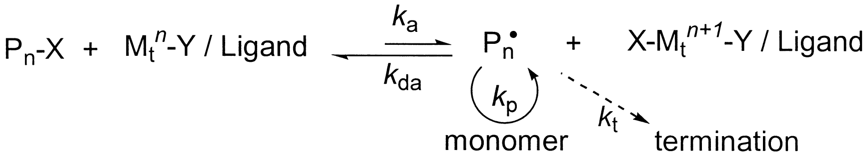
Scheme 1. General scheme of transition metal catalyzed ATRP.



The radicals, i.e. the propagating species P_n^*, are generated through a reversible redox process catalyzed by a transition metal complex (activator, M_t^n-Y/Ligand, where Y may be another ligand or the counterion) which undergoes a one-electron oxidation with concomitant abstraction of a (pseudo)halogen atom, X, from a dormant species, P_n-X. Radicals react reversibly with oxidized metal complexes, X-Mt^{n+1}/Ligand to reform the dormant species and the activator. This process occurs with a rate constant of activation, k_a, and deactivation k_{da}, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Other side reactions may additionally limit the achievable molecular weights. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, non-stationary stage of the polymerization. This process generates oxidized metal complexes as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages.[2] A successful ATRP will not only have a small contribution of terminated chains but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid reversible deactivation.

For example, Eq. 1 illustrates how the polydispersity index in ATRP in the absence of chain termination and transfer (otherwise polydispersity increases with conversion) relates to the concentrations of initiator (RX) and deactivator (D), the rate constants of propagation (k_p) and deactivation (k_{da}), and the monomer conversion (p).[3]

$$\frac{M_w}{M_n} = 1 + \left(\frac{([RX]_o - [RX]_t)k_p}{k_{da}[D]} \right)\left(\frac{2}{p} - 1 \right) \qquad \text{(Eq. 1)}$$

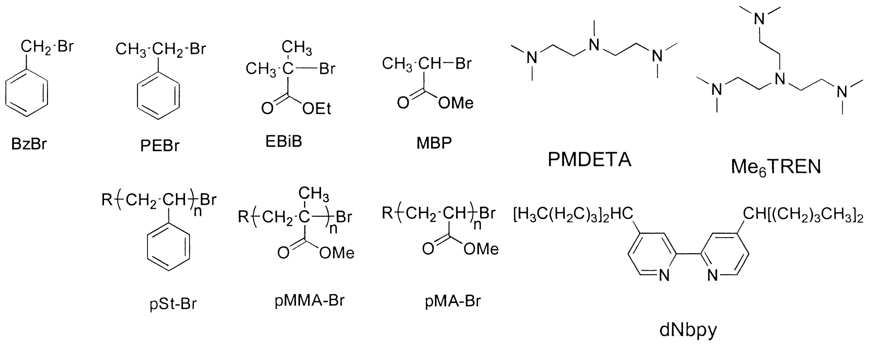
Thus, for the same monomer, a catalyst that deactivates the growing chains faster will result in polymers with lower polydispersities (smaller k_p/k_{deact}). Alternatively, polydispersities decrease with an increasing concentration of deactivator, although at the cost of slower polymerization rates. For example, the addition of a small amount of Cu(II) halides in the copper-based ATRP lead to better controlled polymerizations with decreased polymerization rates.[4, 5] Higher polydispersities are usually found for polyacrylates than for polystyrene or polymethacrylates due to a much higher k_p for acrylates.[6] Other predictions from Eq. 1 include higher polydispersities for shorter chains (higher $[RX]_o$) and a decrease of the polydispersity with monomer conversion.

Since, the exchange process affects the control of ATRP, it is extremely important to correlate rate constants of activation and deactivation with the structure of involved reagents, including alkyl halides, transition metal centers, ligands and also external factors such as solvent and temperature.

Rate Constants of Activation and Deactivation

Recently there have been some reports on determination of these rate constants for model and macromolecular species. The structures of the corresponding reagents are shown in Chart 1 below.[7]

Chart 1. Ligands and model compounds mimicking polymeric chains used in kinetic studies.



The activation rate constants were measured using HPLC or GC under the kinetic isolation conditions achieved by trapping the generated radical with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as shown in Scheme 2.

Scheme 2. Model reaction for the activation rate constant measurements.

$$R\text{-}Br + Cu^{I}/L^{+} \xrightarrow{k_a} R^{\bullet} + BrCu^{2}/L^{+} \quad (1)$$

$$R^{\bullet} + Br\text{-}Cu^{2}/L^{+} \overset{k_{da}}{\dashrightarrow} R\text{-}Br + Cu^{I}/L^{+} \quad (2)$$

$$R^{\bullet} + T^{\bullet} \xrightarrow{k_c} R\text{-}T \quad (3)$$

$$R\text{-}T \overset{k_{dis}}{\dashrightarrow} R^{\bullet} + T^{\bullet} \quad (4)$$

$$R^{\bullet} + R^{\bullet} \overset{k_t}{\dashrightarrow} RR \quad (5)$$

Typical values of the activation rate constants measured at 35 °C are shown in the Table 1.[7]

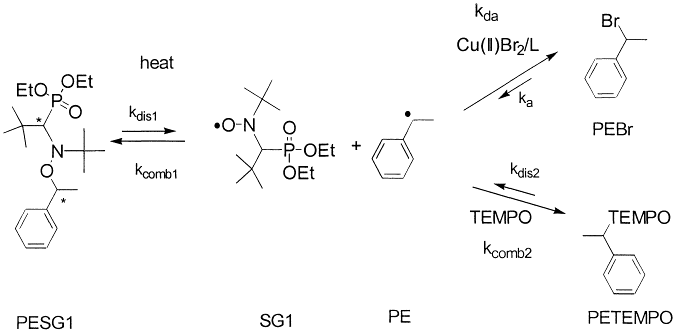
Table 1. Activation rate constants measured under various conditions at 35°C.

No.	**RX**	**Complex**	**Solvent**	k_a **[M^{-1}s^{-1}]**
1	PEBr	CuBr/2dNbpy	Acetonitrile	0.085
2	MBrP	CuBr/2dNbpy	Acetonitrile	0.052
3	EBriB	CuBr/2dNbpy	Acetonitrile	0.60
4	BzBr	CuBr/2dNbpy	Acetonitrile	0.043
5	PEBr	CuBr/PMDETA	Acetonitrile	0.12
6	MBrP	CuBr/PMDETA	Acetonitrile	0.11
7	EBriB	CuBr/PMDETA	Acetonitrile	1.7
8	PECl	CuCl/Me$_6$TREN	Acetonitrile	1.5
9	PEBr	CuBr/2dNbpy	Ethyl acetate	0.016
10	PECl	CuCl/2dNbpy	Acetonitrile	0.000056

The following conclusions can be drawn from the model studies. At 35 °C, 2-bromoisobutyrate is approximately 10 times more reactive than the other alkyl halides and 1-phenylethyl bromide is 10^3 times more reactive than the corresponding chloride. This difference dramatically decreases at higher temperatures due to the higher activation energy for the latter. PMDETA forms more reactive Cu(I) complexes than dNbpy. Me_6TREN is ~10^4 times more active than the dNbpy-based complex. The reaction is faster in acetonitrile than in ethyl acetate.[8]

The deactivation rate constants were determined by trapping 1-phenylethyl radicals using TEMPO in a competitive clock reaction (Scheme 3). The 1-phenylethyl radical was generated by the thermal decomposition of the 1-(N,N-(2-methylpropyl-1)-(1-diethylphosphono-2,2-dimethyl-propyl-1-)-N-oxyl)-1-phenylethane (PESG1) alkoxyamine.

Scheme 3. Model reaction for the deactivation rate constant measurements



Typical values of the activation rate constants measured at 75 °C are shown in the Table 2.[7]

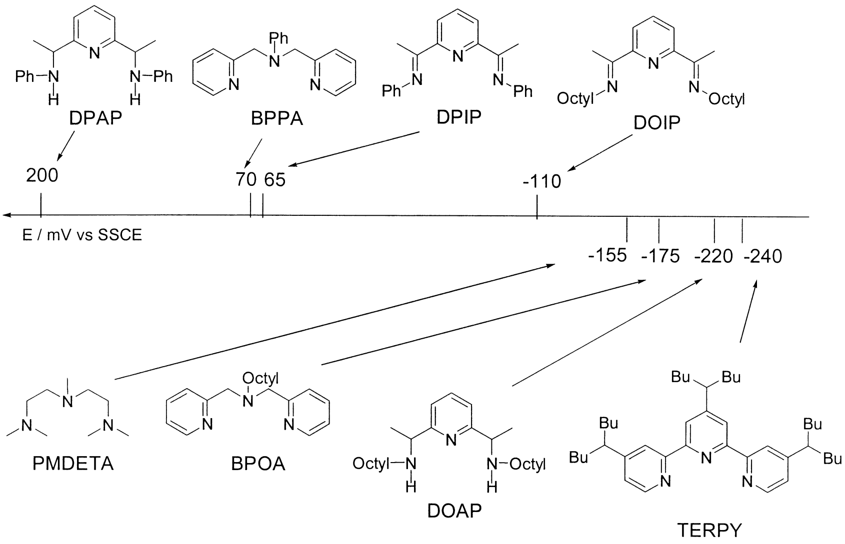
Table 2. Deactivation rate constant under various conditions at 75°C.

No.	Radical	Complex	Solvent	k_{da} [$M^{-1}s^{-1}$]
1	PE	$Cu(II)Br_2$/2dNbpy	Acetonitrile	2.5 10^7
2	PE	$Cu(II)Br_2$/PMDETA	Acetonitrile	6.1 10^6
3^c	PE	$Cu(II)Br_2/Me_6TREN$	Acetonitrile	1.4 10^7
4	PE	$Cu(II)Br_2$/2dNbpy	Ethyl acetate	2.4 10^8
5	PE	$Cu(II)Cl_2$/2dNbpy	Acetonitrile	4.3 10^6

In the deactivation process, the $CuBr_2$/dNbpy complex is more active in ethyl acetate than in acetonitrile. Deactivation is slower with $CuCl_2$ instead of $CuBr_2$. The reactivity of the $CuBr_2$/dNbpy complex is higher than with either the Me_6TREN or the PMDETA. Among the studied ligands, Me_6TREN appears to be most attractive since it promotes very fast activation but also sufficiently fast deactivation.

More systematic studies were performed with a series of N-based tridentate complexes shown in Chart 2 together with their reduction potentials.[9, 10]

Chart 2. Reduction potentials of the series of $CuBr_2$-complexes in CH_3CN, 500mV/s, 0.1 mol/L $[NBu_4][PF_6]$, E vs. SSCE.



The rate constants of activation and deactivation for 1-phenylethyl bromide and the corresponding radical correlate well with the reduction potentials of the Cu(II) complexes. The catalytic activity of the complexes decreases in the order: alkyl amine ≈ pyridine > alkyl imine >> aryl imine > aryl amine. The correlation between the activation and deactivation rate constants for copper complexes with bidentate (dNbpy) and tridentate ligands is approximately reciprocal, as shown in Figure 1.

However, behavior of Me_6TREN complex is quite unique. It activates much faster than expected from its redox potential but also it deactivates very fast. The deviation (indicated by arrows) from the correlation of rate constants of exchange with redox potential may be ascribed to very small entropic constraints in the passage from the X-Cu(II) to the Cu(I) state for the complex with bridged tetradentate ligand in comparison with complexes with tridentate ligands.

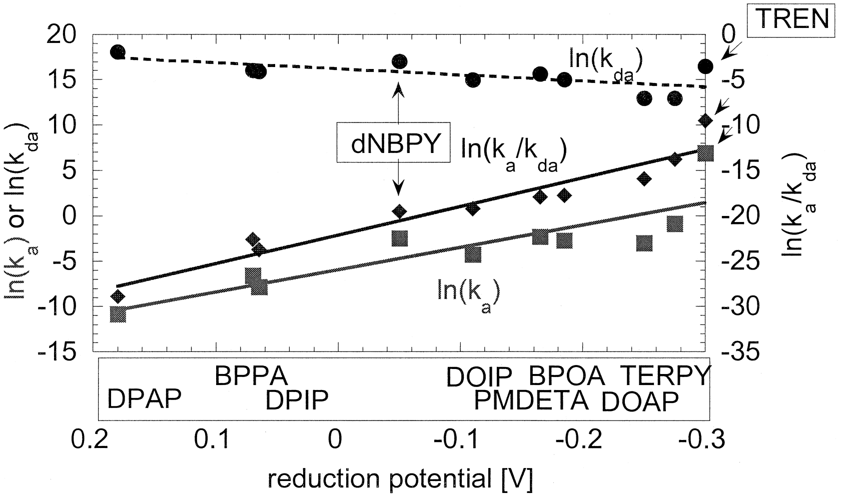


Figure 1. Dependence of the rate of activation for PEBr and deactivation for PE* radicals as well as their ratio (k_a/k_{da}) on the reduction potential of the Cu(II)-complexes. Rate constants of activation and deactivation were determined in acetonitrile at 35 °C and 75 °C respectively.

Knowing the values of the rate constants of all the elementary reactions involved in ATRP enhances the mechanistic understanding of ATRP, facilitates optimization of the reaction conditions for various monomers, and helps in selecting the proper initiator and catalyst structures. Without this knowledge, efficient catalysts such as Me_6TREN-based complexes,[11] may lead to poorly controlled ATRP processes as in the case of methyl methacrylate.[12]

Mechanism

The general mechanism of ATRP was shown in Scheme 1. The existence of free radical has been proposed in copper-mediated ATRP based on several experimental observations.[13]

(1). The ATRP equilibrium has been approached from both sides: RX/M_t^n and radicals/X-M_t^{n+1} species (reverse ATRP). Thus, successful polymerizations have been carried out using conventional free radical initiators, such as AIBN and BPO, as well as organic halides.[14, 15]

(2). Chemoselectivity is similar to that for conventional radical polymerizations. Typical radical inhibitors, such as galvinoxyl and TEMPO, inhibit the polymerization, and the polymerization is retarded by the presence of a small amount of oxygen. In addition, ATRP is converted into a system which displays conventional radical polymerization characteristics upon the addition of octanethiol as a chain transfer reagent.[16] Chain transfer in the BA polymerization also resembles the conventional radical process.[17] ATRP can be carried out in the presence of water[18, 19] or other protonogenic reagents, and is tolerant to a variety of functionalities.[20] Moreover, the reactivity ratios, which are very sensitive to the nature of the active centers, are nearly identical to those reported for the conventional radical polymerization but are very different from those for anionic, group transfer, and cationic systems.[21-27]

(3). Regioselectivity and stereoselectivity are similar to and do not exceed that for a conventional radical polymerization. All the polymers formed by ATRP have regular head-to-tail structures with the dormant species of the typical secondary/tertiary alkyl halide structures, as evidenced by NMR.[28, 29] In addition, polymers have the same tacticity as those prepared by a conventional free radical process.[15, 28] A recent racemization study using optically active alkyl halides also supports the radical intermediacy.[30]

(4). EPR studies have revealed the presence of X-Cu(II) species resulting from the persistent radical effect.[31-36] Additionally, the doubling of the molecular weight or cross-linking in multi-functional initiator systems as a result of radical-radical termination has been observed.[37]

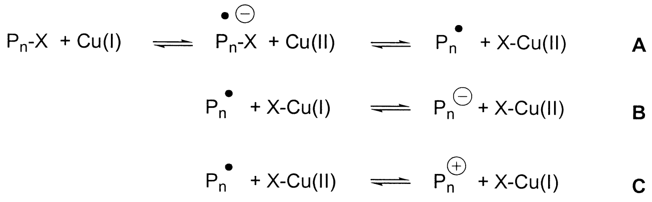
(5) Cross-exchange between different halogens and different polymerization systems (thermal and ATRP or nitroxide mediated and ATRP) demonstrates they have the same intermediates and supports the radical mechanism.[38] Thus, equimolar mixtures of initiators for the nitroxide-mediated polymerization and the ATRP lead to polystyrene with a unimodal molecular weight distribution (MWD).[39]

(6) Recently, propagating free radicals have been observed directly by EPR in the polymerization of dimethacrylates.[40]

However, not all alleged ATRP processes may in reality proceed via free radical processes. Involvement of organometallic species and/or ionic intermediates is also possible. The contribution of these species will depend on monomer, catalyst, anion, temperature, solvent, etc.

ATRP is typically described to proceed via an inner-sphere electron transfer (ISET) process; however, as an alternative to the inner-sphere process, outer-sphere electron transfer (OSET)[41, 42] may also occur. Scheme 4 illustrates several possible OSET processes that may occur in ATRP.

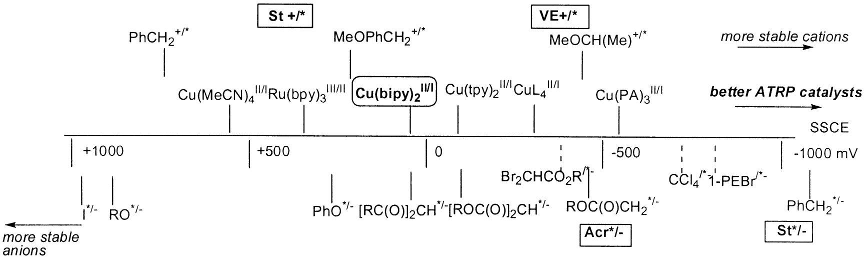
Scheme 4. Possible OSET processes in ATRP.



Path **A** concerns the formation of the intermediate radical anions followed by the halogen anion transfer to the oxidized metal. This would result in a two-step rather than a concerted inner sphere process for the generation of radicals from initiators or polymer dormant species. Preliminary correlation studies between rates of atom transfer reactions and R-X bond energies and electron affinities suggest the predominant concerted process for many initiating and propagating species. Thus, for adducts with the same radical-stabilizing substituent, tertiary alkyl halides are typically better initiators than secondary ones, which are better than primary alkyl halides. However, unexpectedly high rates even at the low temperatures found for some alkyl halides (e.g., haloacetonitrile) could indicate an outer-sphere electron transfer process. This may happen with initiators having very high electron affinities (e.g., diethyl 2-bromomalonate or CCl_4) and may sometimes lead to side reactions that reduce the initiation efficiency. In contrast, the formation of radical anions by the outer-sphere electron transfer process from Cu(I) to 1-phenylethyl bromide and other similar dormant species is not probable due to unfavorable redox potentials.

Chart 3 illustrates the interrelations between the electrochemical potentials of the copper complexes and the organic radicals as well as the propagating radicals in styrene and acrylate polymerizations. Depending on the redox properties of both the transition metal complex and the corresponding organic radicals, reduction of the growing radicals to carbanions (Scheme 4 Path **B**) or oxidation to carbocations (Scheme 4 path **C**) may happen under certain conditions and can sometimes become the dominant pathway.

Chart 3. Summary of electrochemical potentials of copper complexes and organic radicals.



For example, the ATRP of *p*-methoxystyrene using Cu(I)/$(dNbpy)_2$ was unsuccessful.[43] The oxidation of the *p*-methoxystyryl radical to cations (Scheme 4 path **C**) was postulated, yielding cationic intermediates responsible for an elimination process. Similarly, the presence of a large amount of cupric triflate in the polymerization of styrene reduces the molecular weight and terminates the reaction, presumably through oxidation of the growing radicals via an outer-sphere electron transfer process.[44] The observed slow termination reaction in the ATRP of styrene was attributed to the same process.[45] In addition, the cationic polymerization may occur using $CuPF_6(CH_3CN)_4$ complexes for styrene polymerizations,[46] which can be ascribed to the much stronger oxidation (and weaker reducing) power of this complex in comparison with the $Cu(I)/(bpy)_2$ complex.[47]

As shown in Chart 3, more reducing catalysts are also more active in ATRP. The activity of the catalysts in ATRP depends not only on the redox potential, but also on the halogenophilicity of the transition metal complexes. Both parameters are affected by the nature of the transition metal and ligand, including the complexation constants, the nucleophilicity, back bonding, steric effects, etc. For a series of nitrogen-based ligands with C-2 links, in the Cu-based ATRP of methyl acrylate, a linear correlation between the polymerization rate (expressed by the apparent equilibrium constant, i.e. $K_{eq}^{app} = K_{eq}/[Cu(II)]$) and the redox potential of the complex in acetonitrile was found.[48] However, such correlations may fail by switching to ligands based on other heteroatoms (P, S, O), with different links between heteroatoms (C-3 or C-4), and especially for different transition metals which may have dramatically different halogenophilicities than Cu.

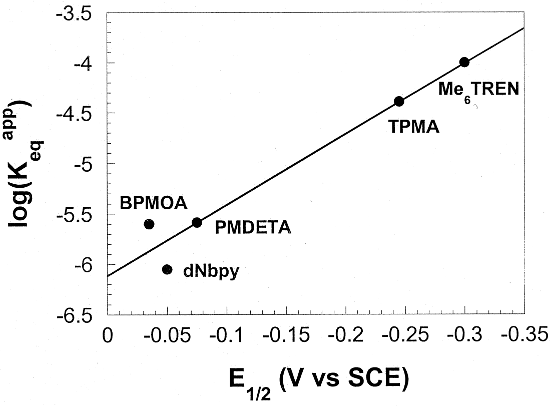


Figure 2. Correlation between the kinetics of the ATRP of MA and the redox potentials of the CuBr complexes in acetonitrile.

Some radicals may react reversibly with metal centers, forming organometallic species, as reported previously.[49, 50] This could happen with either the Cu(I) or the Cu(II) species, especially in the absence of ligand.[51] It seems that these reactions are not very important in the styrene polymerization, since the rates of the conventional radical polymerization initiated by azo compounds or peroxides are not strongly affected by the addition of $Cu(I)/(dNbpy)_2$ or $Cu(OTf)_2(dNbpy)_2$.[44] Cupric triflate was used in these experiments instead of cupric bromide because the latter acts as an efficient inhibitor and results in reverse ATRP. For MA, the addition of cupric salts has no effect on the rates and molecular weights when using conventional initiators. However, the reaction rates decrease in the presence of $CuBr(dNbpy)_2$ and $CuOTf(dNbpy)_2$. This observation can be explained either by the formation of organometallic R-Cu(II) species, providing an additional pathway of control and supplementing the atom transfer process, or by the reversible reduction of growing radicals to the enolate anions, as discussed previously. The contribution of these reactions is, however, relatively small, since the polymerization of 2-hydroxyethyl acrylate is well controlled either in bulk or in aqueous solution.[52] The selectivity of atom transfer over formation of organometallic species depends on the spin state of some transition metals. Low spin species should favor atom transfer and Mt-X bonding, whereas high spin species the formation of Mt-C bond and organometallic species.

Elementary Reactions

Similar to RP, the elementary reactions in ATRP consist of initiation, propagation, transfer and termination (Scheme 5). However, successful ATRP behaves quite differently than RP. Initiation in ATRP must be fast and completed at low monomer conversion. Termination should be suppressed and usually much less than 10% of all chains terminate. Rate and concentration of propagating radicals is established by equilibration between activation and deactivation steps and NOT via steady state as in RP in which rates of initiation and termination are essentially equal. Transfer in most cases may be neglected because polymers with relatively low molecular weights are targeted.

For a well-controlled ATRP, initiation should be fast and quantitative. The apparent initiation rate constant ($k_i^{app} = k_i K_o$, where k_i and K_o refer to the absolute rate constant of addition of the initiating radical to the alkene and the atom transfer equilibrium constant for the initiating species, respectively) should be at least comparable to the apparent propagation rate constant ($k_p^{app} = k_p K_{eq}$, where k_p and K_{eq} refer to the absolute rate constant of propagation and the atom transfer equilibrium constant for the propagating species, respectively). If $k_i^{app} << k_p^{app}$, polymers with higher molecular weights than the theoretical values and higher polydispersities will be obtained. This behavior is based on the assumption that the system is equilibrated or there was deactivator added initially. The situation is more complex when the amount of the deactivator is small and the rate determining step of initiation is only activation. If initiation is too fast and a lot of radicals are generated during the initiation step, irreversible radical termination will reduce the initiator efficiency and slow down the polymerization. A general guideline for choosing a suitable ATRP initiator is that the initiator should have a chemical structure similar to the dormant polymer species.

Scheme 5. Elementary reactions in ATRP.

Initiation

$$\text{R-X} + \text{M}_t^{n}\text{-Y / Ligand} \xrightleftharpoons[k_{da}^{o}]{k_a^{o}} \text{R}\bullet + \text{X-M}_t^{n+1}\text{-Y / Ligand}$$

$$\text{R}\bullet + \text{M} \xrightarrow{k_i} \text{P}_1\bullet$$

Propagation

$$\text{P}_n\text{-X} + \text{M}_t^{n}\text{-Y / Ligand} \xrightleftharpoons[k_{da}]{k_a} \text{P}_n\bullet + \text{X-M}_t^{n+1}\text{-Y / Ligand}$$

$$\text{P}_n\bullet + \text{M} \xrightarrow{k_p} \text{P}_{n+1}\bullet$$

Termination

$$\text{P}_n\bullet + \text{P}_m\bullet \xrightarrow{k_t} \text{P}_{n+m} \text{ or } \text{P}_n^{=} + \text{P}_m^{H}$$

These rules also apply to cross-propagation step in block copolymerization. We refer to reactivities of monomer in ATRP in terms of k_p^{app}, which does not scale with the true k_p values. Efficient crossing in block copolymerization requires $k_{cross}^{app} > k_p^{app}$, unless halogen exchange is employed.[38]

Polymer chains propagate by adding new monomer units to the growing chain ends. To obtain well-defined polymers with low polydispersities, it is crucial to rapidly deactivate the growing chains to form dormant species. Termination occurs through combination or disproportionation pathways and is most significant at the beginning of the polymerization. After a sufficient amount of the higher oxidation state metal complex has been built up by the irreversible termination reaction, the persistent radical effect predominates and radical termination is minimized.[2, 53] It has been proposed that termination rate coefficients are chain length dependent and decrease during the polymerization to result in a steady rate of polymerization.[54] This helps to form well-defined polymers at higher conversions. However, when the monomer concentration becomes very low, propagation slows down but termination and other side reactions may still occur with the usual rate. Thus, there is a certain window of concentrations and conversions where the polymerization is well controlled.

In ATRP there might be additional side reactions, not present in RP. They may include loss of activity by OSET, heterolytic cleavage of R-X bond, loss of HX at elevated temperatures in polar solvents, nucleophilic displacement of X by basic solvents and additives (or monomers), supplementary transfer with ligands and complexes and some others. Proper choice of reaction conditions and understanding of the physical organic chemistry associated with those side reactions may reduce their contribution.

ATRP is a complex process based on several elementary reactions. Success depends on controlling all of them as well as on controlling the concentrations and reactivities of the involved species. The rate constants of radical propagation are systematically being evaluated by pulsed laser polymerization techniques[6]. The rate constants of termination are less accessible, as they depend on the chain length and the viscosity of the medium.[6] As discussed before, in ATRP perhaps most important are the rate constants for the activation and deactivation steps. They depend on the structure of monomer (i.e. the radical and the dormant species), on the halogen and, obviously, on the transition metal complexes. The values of the rate constants of some of these reactions have been reported for the polymeric species and some for the model systems, which mimic the structure of the dormant/active species.[7, 55, 56]

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