Kinetics of Atom Transfer Radical Polymerization

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Abstract This review encompasses the fundamentals of kinetics of atom transfer radical polymerization (ATRP). ATRP is a versatile reversible-deactivation radical polymerization (RDRP) technique, frequently utilized to synthesize advanced functional materials. Detailed mechanistic investigations over the past two decades allowed for an in-depth understanding of the underlying processes and rational design of the reaction conditions. Various aspects of ATRP kinetics are reviewed such as initiation modes, methods allowing to decrease catalyst concentration, influence of the initiator, catalyst (transition metal, ligand, counterion), solvent, additives, type of monomer, and effect of temperature and pressure. Techniques utilized to determine kinetic parameters of catalytic systems are discussed. Finally, guidelines for synthesis of polymers with targeted architectures, predetermined molecular weights, narrow molecular weight distributions, and high retained chain end functionality are presented.

Keywords Controlled/Living Radical Polymerization, Reversible-Deactivation Radical Polymerization, Atom Transfer Radical Polymerization (ATRP), Mechanism, Kinetics.

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1. Introduction

Recent advances in polymer science have provided several procedures for targeted synthesis of functional materials, including specialty polymers for biomedical devices, microelectronics, cosmetics, paints, coatings, adhesives, or drugs with precise targeting. Until recently, materials with controlled architecture were primarily synthesized by living ionic or coordination polymerization. Despite benefits such as elimination of chain breaking reactions, i.e. transfer and termination, these techniques are very sensitive to contaminants, especially moisture. Alternatively, radical polymerization (RP) offers greater tolerance to impurities and functional groups. RP can be performed over a wide range of temperatures and in aqueous media. However, under typical RP conditions, the lifetime of a propagating radical is in the order of a fraction of a second, followed by irreversible termination. Consequently, due to the very short lifetime of radicals, control over the molecular structure of the polymers prepared by RP is extremely difficult and some architectures, e.g. block copolymers, are not easily accessible.

Over the past 25 years, the field of RP was revolutionized by introduction of the reversible deactivation radical polymerization (RDRP) procedures (also known as controlled radical polymerization (CRP) or living radical polymerization (LRP)). In these techniques, the lifetime of growing chains is significantly extended by insertion of periods of dormancy between short activity stages. In a typical example, the radical is allowed to propagate for 1 ms, before being reversibly deactivated and placed in dormancy for ~1 min. The total lifetime of the propagating radical species is still $1000 \times 1 \text{ ms} = 1 \text{ s}$, however with $1000 \times 1 \text{ min}$ inactive periods in between. This allows for the lifetime of a chain to be extended from ~1 s to ~1 day, providing improved control over the reaction. Moreover, the deactivated polymer chains can be isolated and reactivated in another reaction, e.g. to form block copolymers. Several different techniques were developed that exploit the reversible deactivation concept. The three most commonly used procedures are nitroxide-mediated polymerization (NMP),[1] reversible addition-fragmentation chain transfer polymerization (RAFT),[2] and atom transfer radical polymerization (ATRP).[3, 4]

ATRP is a very attractive RDRP technique due to the straightforward experimental setup and wide range of available monomers, solvents, and initiators. All of the components required

for ATRP are commercially available, rendering this technique readily applicable for the production of multiple functional materials. The initiator (generally an alkyl halide) can be monofunctional or multifunctional[5] and it can either be a free molecule, attached to a surface (nanoparticle, wafer, etc.)[6] or a biomolecule (protein, DNA).[7] This enables specificity in molecular design. ATRP can be used for preparation of stars, bottlebrushes, hybrid materials or (bio)materials. A prerequisite for synthesis of polymers with complex architectures is concurrent growth of all chains. In classical RP, a steady state concentration of radicals is established by balancing the rate of initiation and termination. In order to achieve sufficiently high degree of polymerization (DP), the rate of termination must be much slower than propagation. Consequently, the rate of initiation must be also much slower than propagation. In most RDRP techniques the concentration of radicals in the reaction media is established by the creation of a balance between rate of activation of the dormant species and the controlled deactivation of active propagating radicals. This removes the prerequisite of slow initiation, which can now be as fast as, or even faster, than propagation. This allows for synchronous growth of all chains, which enables synthesis of molecules with controlled composition or architecture such as stars, or bottlebrushes. The ability to synthesize (co)polymers with predefined molecular weight (MW), desired architecture, and narrow molecular weight distribution (MWD) has provided the ability to design molecules for multiple applications. Materials prepared by ATRP are used as sealants, adhesives, drug delivery carriers, coatings, membranes, anti-fouling surfaces, lubricants, blend compatibilizers, pigment dispersants, and in many other applications.[8-16]

In an ATRP control over polymer structure is achieved by forming a fast dynamic activation-deactivation equilibrium between radicals and dormant alkyl halides. This process is analogous to that known from NMP, though halide atoms, typically Br or Cl, are used instead of nitroxides. However, in contrast to NMP, significantly higher temperatures would be required to homolytically cleave a C–X bond. Therefore, ATRP employs a catalytic process. In a typical ATRP, a dormant (macro)alkyl halide (P_n-X) is activated by a transition metal catalyst in lower oxidation state, classically Cu^I/L , to generate a higher oxidation state halide complex ($X-Cu^{II}/L$) and a radical ($P_n^\bullet$) (**Scheme 1**). The radicals propagate, however typically after a single, or several monomer additions, they are deactivated back to reform dormant (macro)alkyl halides. Fast and efficient deactivation is essential in ATRP for synthesis of polymers with predefined MW and narrow MWD. Termination reactions are greatly suppressed due to the significantly

lower concentration of radicals present in the reaction medium, however, as in any radical polymerization including RAFT and NMP, they are unavoidable. Typically, the fraction of dead chains can be minimized and dormant polymer chains can be reused as (macro)initiators to form block copolymers or telechelic functional polymers.

Scheme 1. Mechanism of ATRP

2. Initiation Modes

2.1. Normal ATRP, Reverse ATRP, Simultaneous Reverse and Normal Initiation (SR&NI) ATRP, and Activators Generated by Electron Transfer (AGET) ATRP

In the original ATRP reactions reported in 1995 (often referred to as *normal* ATRP), a combination of an alkyl halide and a relatively high concentration of a transition metal catalyst in lower oxidation state ($\text{Cu}^{\text{I}}/2,2'$ -bipyridine) was used to initiate the polymerization.[3] This method is efficient and straightforward, however due to low oxidative stability of the Cu^{I} complex, it requires care in catalyst handling, as well as careful removal of oxygen from the reaction mixture. In order to avoid these limitations, a technique named *reverse* ATRP was developed.[4] In a reverse ATRP both the initiator and the activator complex are generated *in situ* by reaction of the oxidatively stable deactivator complex with radicals formed by thermal decomposition of a conventional free radical initiator, such as azobisisobutyronitrile (AIBN). This method also requires relatively high catalyst loadings and typically an equimolar amount of radical source which quickly dissociates. The schematic of reverse ATRP is presented on **Scheme 2**.

Scheme 2. Mechanism of Reverse ATRP. Reproduced with permission from Ref. [17]

At the onset of the reaction, generated radicals ($I^\bullet$) react with catalyst complex in the higher oxidation state to form alkyl halide initiators ($I-X$) and a catalyst complex in lower oxidation state. They can also initiate growth of a polymer chain, which is however quickly deactivated by higher oxidation state transition metal to form a dormant chain ($I-P_n-X$) and an ATRP activator. After the initial reduction process, the reaction proceeds as a normal ATRP. Reverse ATRP has number of advantages, including simplicity and ease in handling of the oxidatively stable catalysts. However, one of the major limitations of reverse ATRP is a restriction on the polymer architectures that can be prepared. Furthermore, limited functionalities can be introduced into the polymer chains, since usually monofunctional radicals are used as initiators. They are derived from decomposition of standard thermal radical initiators such as AIBN.

In order to resolve these challenges a procedure named *simultaneous reverse and normal initiation* (SR&NI) ATRP was developed (**Scheme 3**). In SR&NI ATRP the precursor of an active catalyst complex is introduced to the reaction in the higher oxidation state, similar to reverse ATRP. However, alkyl halide initiators are added to the starting reaction mixture, allowing the amount of thermal radical initiator to be reduced.[18] The ATRP activator is generated *in situ* by reduction of higher oxidation state catalyst complex, and majority of the chains grow from the initially added alkyl halide. Since SR&NI ATRP allowed for the use of more active catalysts, which could be employed at lower concentrations, this led to well-defined

products which were easier to purify. One limitation of SR&NI ATRP is the presence of small fraction of chains initiated by the free radical initiator.[19]

Scheme 3. Mechanism of SR&NI ATRP. Reagents supplied at the beginning of the reaction are marked in red. Reproduced with permission from Ref. [17]

Elimination of the additional chains initiated by the free radical initiator was achieved in the subsequently developed *activators generated by electron transfer* (AGET) ATRP.[20] AGET ATRP is in principle very similar to SR&NI ATRP. However, instead of thermal radical initiators, chemical reducing agents are utilized to quickly reduce the higher oxidation state catalyst complex and their oxidized products cannot initiate new chains. AGET ATRP can be employed with variety of reducing agents, including Sn^{II} compounds,[21] or ascorbic acid.[22, 23] Notably, it could also be conducted in the presence of limited amounts of air, as long as appropriately higher amounts of reducing agent were added.[23]

2.2. ATRP in the Presence of ppm Amounts of Catalyst

Normal ATRP utilized relatively large concentrations of the catalyst, i.e., about 10-100 mM, or 1000 – 10,000 ppm (expressed as the molar ratio of catalyst to monomer), which was introduced to the reaction in the lower oxidation state. In an attempt to reduce the cost of the reaction, and to simplify the purification of the products,[24] many efforts were dedicated to develop ATRP utilizing low concentrations of catalyst. The equation for rate of polymerization (R_p) in ATRP (**Equation 1**) suggests that in order to maintain a specific R_p , the ratio between

activator and deactivator complexes needs to remain constant. Therefore, the total amount of the catalyst could be decreased while preserving the original $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ ratio and consequently the rate of polymerization. However, in ATRP, as in every radical polymerization, radical termination reactions are unavoidable. This leads to an irreversible buildup of the deactivator species, i.e. the persistent radical effect (PRE),[25, 26] which slows down the reaction. However, if the concentration of catalyst is significantly lower than that of alkyl halides, termination reactions can lead to irreversible conversion of nearly all activator species into the deactivator complex, at which point the reaction essentially stops. For this reason, the simple reduction of the catalyst concentration in ATRP is not a viable solution.

$$R_p = k_p [M][P_n^\bullet] = k_p K_{\text{ATRP}} [M][P_n - X] \frac{[\text{Cu}^{\text{I}}/\text{L}]}{[\text{X}-\text{Cu}^{\text{II}}/\text{L}]}$$

Equation 1. Rate of polymerization in ATRP

Therefore, with the development of more active catalyst complexes, multiple strategies were invented that allowed for significant decrease of the catalyst concentration. Most commonly, an additional redox cycle is employed, which converts the deactivator formed via PRE back into the ATRP activator (**Scheme 4**). This can be achieved with chemical reducing agents (e.g., $\text{Sn}^{\text{II}}\text{R}_2$, ascorbic acid, Ag^0) in *activators regenerated by electron transfer* (ARGET) ATRP;[27] radical initiators (e.g., azobis(isobutyronitrile), AIBN) in *initiators for continuous activator regeneration* (ICAR) ATRP;[27] zerovalent metals (e.g., Cu^0 , Fe^0) in *supplemental activator and reducing agent* (SARA) ATRP;[28, 29] electric current in electrochemically mediated ATRP (*e*ATRP);[30] or light in photochemically mediated ATRP (photoATRP).[31, 32] In all of these methods, the deactivator complex formed by unavoidable radical termination reactions is reduced back to $\text{Cu}^{\text{I}}/\text{L}$ activator. This permits a significant reduction of the total catalyst concentration. This decrease is beneficial not only for economic and environmental reasons but also for minimizing catalyst induced side reactions with propagating (macro)radicals, which creates a boundary for the maximum achievable MW.[33]

Scheme 4. Mechanism of ATRP conducted with low catalyst concentrations. The $\text{Cu}^{\text{I}}/\text{L}$ activator complex is generated and then continuously regenerated by reduction of $\text{X}-\text{Cu}^{\text{II}}/\text{L}$.

2.2.1. Initiators for Continuous Activator Regeneration (ICAR) ATRP

In *initiators for continuous activator regeneration* (ICAR) ATRP the deactivator complex is slowly and continuously reduced back to the activator complex via a reaction with radicals formed by slow decomposition of a thermal radical initiator such as AIBN (**Scheme 5**).^[27] The rate of reduction can be tuned by type and amount of the initiator, and adjustment of the reaction temperature. Under typical polymerization conditions, decomposition is slow and a fraction of the AIBN remains until the end of the reaction since if all of the AIBN is depleted the reaction halts. Therefore, the kinetics of an ICAR ATRP resembles a conventional RP or RAFT, and depends on the rate of AIBN decomposition.^[34, 35] In ICAR ATRP, similar to SR&NI ATRP or RAFT, a small fraction of chains could originate from the added thermal initiator. Therefore, ICAR ATRP has to be used with caution if pure polymers with α -functionality introduced by (macro)alkyl halides are desired. Scale up of ICAR ATRP could be challenging due to the use of relatively large quantities of radical initiators. If the reaction temperature is not controlled in an accurate manner, the radical initiator might quickly decompose and lead to uncontrolled acceleration of polymerization and in consequence to a runaway reaction. This challenge was resolved by slow feeding of radical initiator in a process termed Ultimate ATRPSM.^[36]

Scheme 5. Mechanism of ICAR ATRP. A thermal radical initiator such as AIBN is used to continuously regenerate the $\text{Cu}^{\text{I}}/\text{L}$ activator complex via reduction of $\text{X-Cu}^{\text{II}}/\text{L}$.

2.2.2. Activators Regenerated by Electron Transfer (ARGET) ATRP

The caveats associated with ICAR ATRP, such as formation of polymers originating from the radical source, or possibility of runaway reactions, could be resolved with the use of chemical reducing agents that do not form radicals. This was accomplished in *activators regenerated by electron transfer* (ARGET) ATRP (**Scheme 6**). Typical reducing agents include $\text{Sn}^{\text{II}}\text{R}_2$ compounds,[37] glucose,[38] ascorbic acid,[39] Ag^0 , [40, 41] or hydrazine.[27] Additionally, certain monomers[42, 43] and ligands[44, 45] can be used as internal reducing agents. The rate of reduction, and thus rate of polymerization, can be adjusted by the type and amount of the reducing agent or by slow feeding.[35, 39] Selection of the appropriate additive is of great importance, since one needs to ensure that both reducing agent, and its oxidized product, does not interfere with the reagents added for the desired ATRP.[46] Examples of side reactions include complexation or reaction of ligand, monomer, or polymer with the reducing agent, complexation of reducing agent with the metal center of the catalyst complex, protonation of the ligand by acidic oxidation products, or nucleophilic substitution or elimination of halide chain ends.[47, 48] These reactions can lead to poor control (broad MWD, low chain end functionality), or entirely prevent the polymerization. In a specific example tin based reducing agents were shown to catalyze epoxide ring-opening of glycidyl methacrylate.[46]

Scheme 6. Mechanism of ARGET ATRP. A chemical reducing agent such as ascorbic acid is used to continuously regenerate the $\text{Cu}^{\text{I}}/\text{L}$ activator complex via reduction of $\text{X-Cu}^{\text{II}}/\text{L}$.

2.2.3. Supplemental Activator and Reducing Agent (SARA) ATRP

In *supplemental activator and reducing agent* (SARA) ATRP, a zerovalent metal, typically Cu^0 , but also Fe^0 , Zn^0 , or Mg^0 is employed.[49] In addition to the ATRP equilibrium between Cu^{I} and Cu^{II} , use of Cu^0 introduces additional slow reactions, i.e. supplemental activation of alkyl halides by Cu^0 , and reduction of Cu^{II} to Cu^{I} via comproportionation. The process gained attention due to simplicity in the reaction setup, ease of removal and reuse of the unreacted Cu^0 , and the ability to control the polymerization rate by adjusting the surface area of Cu^0 . Alternatively, inorganic sulfites such as $\text{Na}_2\text{S}_2\text{O}_4$ can be used.[50-52] The use of zerovalent metals in ATRP dates back to 1997, when Cu^0 and Fe^0 were used as direct activators of alkyl halides and reducing agents for the oxidatively stable deactivators.[53] However, in 2006 a different mechanism was suggested for the polymerization of acrylates in the presence of Cu^0 and tris[2-(dimethylamino)ethyl]amine (Me_6TREN) in polar solvents, initiated by alkyl halides.[54] It was proposed that alkyl halides were exclusively activated by Cu^0 via an outer sphere electron-transfer (OSET) process, with no contribution of Cu^{I} to the activation procedure. Instead, Cu^{I} generated by the exclusive Cu^0 activation process was postulated to instantaneously disproportionate to form Cu^0 and the Cu^{II} deactivator. Therefore, polymerization was claimed to be exclusively mediated by Cu^0 and Cu^{II} . This process was termed *single electron transfer living radical polymerization* (SET-LRP). It is worthwhile noting, that all of the components used in

this procedure (Cu^0 , alkyl halides, acrylates, polar solvents, and Me_6TREN) were previously used in ATRP.[55-59] The proposed mechanisms of SARA ATRP and SET-LRP are presented on **Scheme 7**. It is critical to note that all of the reactions involved in both mechanisms are identical except for the activation of the alkyl halides, which is proposed to occur by OSET in SET-LRP and by inner-sphere electron transfer (ISET) in SARA ATRP. However, their kinetic contribution to the system are dramatically different.

Scheme 7. The proposed mechanisms of a) SARA ATRP and b) SET-LRP. Arrow thickness denotes importance of the reactions, with bold arrows indicating major reactions, solid arrows indicating supplemental or contributing reactions and dashed arrows indicating reactions with negligible contributions to the polymerization procedure. $\text{Cu}^{\text{I}}\text{X/L}$ and $\text{Cu}^{\text{II}}\text{X}_2/\text{L}$ represent all Cu^{I} and Cu^{II} complexes, respectively, without particular speciation. Stoichiometrical balance is omitted for clarity. Reproduced with permission from ref. [29]

The main differences between the proposed mechanisms include: the major activator of alkyl halides (Cu^0 in SET-LRP vs. Cu^{I} in SARA ATRP); fate of the Cu^{I} (activation of alkyl halides in SARA ATRP vs. disproportionation in SET-LRP); and the mechanism of the activation of alkyl halides (OSET in SET-LRP and ISET in SARA ATRP).[28, 29] Kinetics of RDRP in the presence of Cu^0 was meticulously investigated via computational,[60] kinetic (both

experimental[61-67] and simulations[62, 68]), and electrochemical studies.[60, 69] It was demonstrated that majority of alkyl halides are activated by Cu^{I} , while contribution of Cu^0 to activation is only supplemental (<1%).[65] Both disproportionation and comproportionation processes are relatively slow in DMSO, with equilibrium shifted towards comproportionation.[64, 70] The time required for this process to reach equilibrium was in the order of 2 days, which suggests that the disproportionation and comproportionation equilibrium might be established long after the completion of a polymerization conducted under typical conditions.[62, 64] Interestingly, a similar situation was observed even in aqueous media, where disproportionation is thermodynamically favored.[62, 71] However due to the exceptional activity of Cu^{I} towards activation of alkyl halides, and high K_{ATRP} values, the actual concentration of Cu^{I} during polymerization is extremely low, thereby rendering a negligible rate of disproportionation, which depends on $[\text{Cu}^{\text{I}}]^2$. [62] Finally, activation of alkyl halides by both Cu^0 and Cu^{I} was shown to be ca. 9 orders of magnitude faster via ISET than via OSET.[60, 72] The values of activation rate coefficients calculated assuming the OSET mechanism were unrealistically low compared to the experimental values.[73]

Investigation of the mechanism of RDRP in the presence of Cu^0 in polar organic media and in water, revealed that under typical conditions, Cu^{I} activates alkyl halides more than 10^2 times faster than Cu^0 . Kinetics of the relevant processes dictate that the Cu^{I} species activates alkyl halides at least 10^7 times faster than they disproportionate, even in aqueous media, where disproportionation is thermodynamically favored. Consequently, none of the mechanistic features postulated in SET-LRP mechanism (fast and exclusive activation of alkyl halides by Cu^0 , instantaneous disproportionation of Cu^{I} , and activation via OSET process) could be verified experimentally, and RDRP in the presence of Cu^0 was shown to proceed via the SARA ATRP mechanism.

Similar to ARGET or ICAR ATRP, kinetics of SARA ATRP also resembles that of conventional RP. The rate of polymerization in SARA ATRP depends on the rate of radical generation (i.e. supplemental activation by Cu^0 and comproportionation), and S/V parameter of Cu^0 (cf. **chapter 3.2**).[74, 75]

2.2.4. Electrochemically Mediated ATRP (*e*ATRP)

In electrochemically mediated ATRP (*e*ATRP) regeneration of the Cu^{I} activator is achieved by application of an electrical current (**Scheme 8**).[30, 76, 77] *e*ATRP is similar to ARGET and ICAR ATRP in that it allows for the use of ppm amounts of catalyst. One of the advantages of *e*ATRP is the ability to precisely control the ratio of Cu^{I} to Cu^{II} by adjustment of the applied current, potential and total passed charge.[77, 78] After the reduction, the Cu complex in the form of the activator is distributed throughout the reaction mixture by vigorous stirring. The use of external stimuli introduces an additional level of control over the reaction, as polymerization can be stopped and restarted by applying anodic or cathodic current, i.e. converting the catalyst to Cu^{II} deactivator or Cu^{I} activator, respectively. Despite multiple “on-off” cycles the MW and MWD of the formed polymer typically remain uncompromised, demonstrating high retention of chain end functionality throughout the polymerization. *e*ATRP also allows for easy catalyst removal by electrodeposition of catalyst on the working electrode. The metallic Cu^0 can then be stripped into a fresh reaction mixture and reused in a subsequent polymerization.[77] The biggest challenges associated with *e*ATRP are the need for vigorous stirring in order to uniformly distribute the activator, which is (re)generated only at the electrode surface, the need to use supporting electrolytes, and, initially, a rather complex experimental setup.

Scheme 8. Mechanism of *e*ATRP. Application of anodic or cathodic current allows to oxidize or reduce the catalyst, respectively.

Originally, *e*ATRP was carried out with a constant applied potential. This requires utilization of a three-electrode system, consisting of a working electrode, a counter electrode, and

a reference electrode. However, recently, an alternative simplified system was developed, utilizing a sacrificial counter electrode (*se*ATRP) formed by direct immersion of an Al wire counter electrode in the reaction medium.[79] This allows for utilization of a galvanostatic process (i.e. constant applied current), which is simpler to implement than a potentiostatic one. Furthermore, in an effort to reduce the cost, the possibility of using an inexpensive, non-platinum cathode was investigated.[80, 81] *e*ATRP was shown to be an excellent tool for synthesis of polymers with complex architectures such as stars, brushes, or block copolymers,[82-87] and for some challenging monomers such as acrylamides[83, 88] and methacrylic acid.[89]

2.2.5. photoATRP and Metal-Free ATRP

In photoATRP, conducted in the absence of radical based photoinitiators,[90, 91] regeneration of the Cu^{I} activator is achieved by a photochemical reduction of excited Cu^{II} complexes by a free aliphatic amine, typically introduced in the form of excess ligand, via a reductive quenching mechanism (**Scheme 9**).[32, 92-94] In such a procedure the type of ligand selected and its molar ratio to $\text{X-Cu}^{\text{II}}/\text{L}$ plays an important role. PhotoATRP is similar to *e*ATRP in that the use of external stimuli allows for temporal control over the polymerization simply by switching the light off and on, without any negative influence on MW, MWD, and CEF.[31, 95] As in all other low-ppm ATRP methods, the rate of polymerization in photoATRP depends on the rate of radical generation, i.e. rate of reduction of Cu^{II} . This can be adjusted by varying light intensity (i.e. source brightness and distance from the reaction vessel), irradiation wavelength, and the concentration and ratio of Cu and ligand. PhotoATRP can be conducted utilizing inexpensive LEDs, nail polish curing UV lamps, or even under sunlight.[31] One challenge associated with the scale-up is associated with the limited depth of light penetration, i.e. the rapid decrease of the light intensity as it progresses toward the interior of the reaction vessel.

Scheme 9. Mechanism of photoATRP. $\text{Cu}^{\text{I}}/\text{L}$ activator complex is regenerated via photochemical reduction of excited $\text{X-Cu}^{\text{II}}/\text{L}$ complex by a free aliphatic amine, herein introduced in the form of excess ligand (L).

Detailed investigation of photoATRP raised an important question: whether, and to what extent does photochemical process contribute to other ATRP reactions. Methods such as ICAR ATRP or ARGET ATRP are envisioned to be purely chemically controlled, however they are typically conducted under ambient lighting in the laboratory and thus level of involvement of photochemical processes in these reactions was quantified. Ambient lighting has a negligible effect on ICAR ATRP, suggesting that only decomposition of the thermal initiator (AIBN) contributes to activator regeneration.[96] Similar observations were found for ARGET ATRP.[97] In normal ATRP, however, ambient lighting resulted in an enhanced polymerization rate.[97] In order to further investigate the effect of light on activator regeneration, a method combining photochemical and chemical reduction was designed, termed PhICAR (photochemical plus ICAR) ATRP. The degree of involvement of photochemical reduction to the system strongly depended on the concentration of AIBN. At low $[\text{AIBN}]_0$ (0.035 equiv. to alkyl halide), contribution was higher (ca. 50%), while at high $[\text{AIBN}]_0$ (0.2 equiv. to alkyl halide), it declined to ca. 15%.[96]

Recently, a variety of organic molecules were reported to efficiently mediate photoATRP. Polymerization of methacrylate monomers was successfully conducted utilizing 10-phenylphenothiazine (PTZ), with good control over MW, MWD, and with temporal control.[98] PTZ and its derivatives were also applied to the synthesis of metal-free polyacrylonitrile with narrow MWD and predefined MW.[99] An extensive study was then conducted to elucidate the mechanism of metal-free ATRP (**Scheme 10**).[100] A number of PTZ

derivatives were investigated, all of which activated alkyl halide initiators that subsequently initiated polymerizations. However, only the use of *N*-aryl phenothiazine resulted in a controlled polymerization, which suggests that other PTZ derivatives were not efficient deactivators. The mechanism was proposed to proceed via an oxidative quenching cycle.

Scheme 10. Simplified mechanism of photoredox-mediated ATRP. Reproduced with permission from Ref. [100]

2.3. Surface Initiated ATRP (SI-ATRP)

The development of RDRP methods, in particular ATRP, has stimulated the growth of the field of organic/inorganic hybrid materials. A “grafting-from” ATRP process can easily be conducted from an initiator tethered to a solid surface such as a flat wafer, a sphere, or a cylinder (**Scheme 11**).^[6, 101-106] Grafting densities of up to 1 chain/nm² can be achieved. The grafting density can easily be controlled by decreasing the amount of initiator tethered to the surface, e.g. by introducing compounds that can be attached to the surface along with the ATRP initiator, but do not contain ATRP functionality. Controlling grafting density is of critical importance for the properties of the resulting materials. Brushes grafted from a flat surface with a lower grafting density tend to entangle and form mushroom-like structures.^[107] Densely grafted brushes cannot entangle and are highly extended, resulting in surfaces with exceptionally low friction properties.^[108-110] Entanglement regimes of brushes grafted from curved surfaces are highly dependent on the curvature of the surface.^[111]

Scheme 11. General principle of SI-ATRP. Interparticle termination can lead to formation of a gel.

Kinetically, SI-ATRP is analogous to ATRP methods proceeding in solution.[112, 113] However, due to particularly small amounts of initiator tethered to the surface, the deactivator complex cannot be formed via PRE in amounts needed for efficient deactivation.[114] Therefore, either an additional deactivator or a “sacrificial” initiator has to be added to the contacting reaction medium. Termination reactions between chains growing from flat surfaces are typically suppressed, since the chains have to be sufficiently close to each other, and in the form of radicals in order to terminate. However, radical centers can “migrate” through ATRP activation-deactivation cycles and eventually terminate[115, 116] Suppression of termination reactions is of utmost importance in SI-ATRP conducted from dispersed nanoparticles, since interparticle termination of chains can lead to formation of a gel (**Scheme 11**). Application of high pressure,[117] or reaction in a miniemulsion[118] helps to prevent or reduce the effect of interparticle termination reactions.

2.4. Control Over ATRP Using External Stimuli

External control over polymerization is attractive due to the possibility of fine-tuning of the reaction rate by adjustment of the properties of the stimuli. Additionally, the stimulus can be completely ceased and thus temporal control can be achieved, i.e. stopping and (re)starting of the polymerization by turning the stimuli off and on.

ATRP can be controlled by light (cf. photoATRP, **chapter 2.2.5**) or by electric current (cf. *e*ATRP, **chapter 2.2.4**). These methods have an additional advantage of not using additives such as reducing agents (as in ARGET ATRP) or thermal radical initiators (as in ICAR ATRP), eliminating potential associated side reactions. Although, additional external control over both ICAR ATRP and ARGET ATRP can be attained by feeding the reducing agent.[36, 39] Finally, a similar effect can be obtained in SARA ATRP, which can be stopped and restarted by lifting the Cu^0 wire out of the solution and subsequently re-immersing it.[119] Recently, a mechanically controlled ATRP initiated by ultrasound was reported.[120] Ultrasonication was also reported to improve homogeneity of the polymerization medium and diffusivity of the reactants. This led to enhanced control and increased livingness up to high monomer conversion in bulk ICAR ATRP of MMA.[121]

3. Kinetics of Atom Transfer Radical Polymerization

3.1. Kinetics of Normal ATRP

In ATRP, control over polymer structure is achieved by creating fast activation-deactivation equilibria. Alkyl halides ($\text{P}_n\text{-X}$) (or pseudohalides[122]) are activated by a transition metal complexes in a lower oxidation state (typically $\text{Cu}^{\text{I}}/\text{L}$) to generate radicals ($\text{P}_n^\bullet$) and a transition metal complex in higher oxidation state ($\text{X-Cu}^{\text{II}}/\text{L}$). Mechanistically, ATRP is an analogue of atom transfer radical addition (ATRA), which however incorporates reactivation of the formed alkyl halide adduct.[123] The generated radicals can propagate by adding one, or several monomers, before they are quickly deactivated back to the dormant (macro)alkyl halide. As in every radical polymerization, termination reactions are unavoidable. However, due to formation of a relatively low concentration of radicals, they are typically minimized. It should be noted that all kinetic considerations described in **chapter 3** for simplicity are based on the assumption that conventional biradical termination is the exclusive termination mode. However, in ATRP of acrylates, especially at high catalyst concentration (i.e. normal ATRP), catalytic radical termination (CRT) can account for the majority of terminated chains.[124] The extent of CRT depends on the ligand structure and the type of the radical, being significantly slower for styrene and methacrylates as compared to acrylates.[33] Detailed investigation of the influence of CRT on ATRP are underway.

In addition to experimental investigations, modeling techniques (both analytical methods and kinetic simulations) are a powerful approach to better understand the mechanism and optimize the reaction conditions.[125] These methods are especially valuable when elucidation of the contribution of respective reactions to the system is desired. Simulations of ATRP reactions were conducted using both stochastic-based approach, such as Monte Carlo method,[126-131] and kinetic-based (deterministic) approach.[132-135] Kinetic simulations have been extensively applied for simulations of both normal ATRP[35, 130, 135-140] as well as low-ppm methods, i.e. SARA ATRP,[62, 68, 141, 142] ICAR ATRP,[17, 134, 143] ARGET ATRP,[144, 145] photo ATRP, [92, 146] or eATRP.[147] A convenient tool for kinetic simulations of ATRP is PREDICI, which utilizes discrete Galerkin h-p-method for efficient treatment of the polymerization systems.[148, 149]

The rate of polymerization in ATRP (R_p) depends on the concentration of radicals ($[R^\bullet]$) and rate coefficient of propagation (k_p) (**Equation 2**) and can be measured by following consumption of monomer over time.[35]

$$R_p = -\frac{d[M]}{dt} = k_p[M][P_n^\bullet]$$

Equation 2. Rate of polymerization in radical polymerizations

Since an ATRP equilibrium is sustained in essentially all ATRP systems,[10] the concentration of radicals can be substituted with **Equation 3**, giving **Equation 1**.

$$K_{\text{ATRP}} = \frac{[X-Cu^{II}/L][R^\bullet]}{[Cu^I/L][RX]}$$

Equation 3. ATRP equilibrium constant (K_{ATRP})

Equation 1 indicates, that the overall rate of polymerization in an ATRP depends on the $[Cu^I]/[Cu^{II}]$ ratio and not on the total amount of the soluble Cu species present in the reaction medium. Kinetic simulations of a normal ATRP of methyl acrylate (MA) conducted for two distinct initial $[Cu^I]/[Cu^{II}]$ ratios and three different absolute concentrations of Cu species confirms this expectation.[35] **Figure 1a** shows that rate of an ATRP was independent of total amount of soluble Cu species but depended on the $[Cu^I]/[Cu^{II}]$ ratio, which remained constant throughout the polymerization. These results are consistent with **Equation 1**. Some small

deviations in kinetics could be observed at high monomer conversions, at higher $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ ratios and lowest $[\text{Cu}^{\text{I}}]+[\text{Cu}^{\text{II}}]$. This is due to the unavoidable radical termination reactions, which permanently transforms a fraction of Cu^{I} to Cu^{II} (i.e. the persistent radical effect, PRE[25, 26]), effectively changing the $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ ratio and thereby slowing down the polymerization.

Figure 1. (a) Kinetics of normal ATRP and evolution of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ ratio and (b, c) rates of propagation, activation, deactivation, and termination as a function of monomer conversion. Conditions: $[\text{MA}]:[\text{MBrP}]:[\text{Cu}^{\text{I}}\text{Br}]:[\text{Cu}^{\text{II}}\text{Br}_2]:[\text{Me}_6\text{TREN}] = 200:1:(x):(y):(x + y)$; 66% (v/v) MA in DMSO, $T = 25^\circ\text{C}$, where $x/y = 2.3$ (b) or 0.8 (c) and $x + y = 1, 3$, or 10 . Reproduced with permission from ref.[35]

Figure 1b and c show the rates of propagation (R_p), termination (R_t), and activation/deactivation (R_{a1}/R_{d1}) for all simulations. The only reactions with dependence on total concentration of soluble Cu species were the activation of alkyl halides by Cu^{I} (R_{a1}) and deactivation of radicals by Cu^{II} (R_{d1}). Additionally, these reactions were balanced throughout the

entire polymerization, demonstrating that ATRP equilibrium was maintained in all cases. While the rates of activation/deactivation had no influence on polymerization rate, they can influence MWD of the final product. Finally, faster polymerization also leads to increased termination due to higher concentration of radicals.

3.2. Kinetics of ATRP in the Presence of ppm Amounts of Catalyst

Every radical polymerization, including ATRP, is subject to unavoidable radical termination reactions. The termination of polymer chains leads to a gradual irreversible buildup of the deactivator species, i.e. the persistent radical effect (PRE).[25, 26] In normal ATRP, where the total concentration of Cu species is sufficiently high, this typically may only lead to a slight decrease in the polymerization rate (cf. **Figure 1**). However, when the catalyst concentration is significantly lower than that of the alkyl halide, termination reactions may lead to conversion of practically all Cu^{I} species into the deactivator state and halt of the reaction. For example, termination of 10% of chains in an ATRP with high catalyst concentration ($[\text{M}]_0:[\text{RX}]_0:[\text{Cu}^{\text{I}}/\text{L}]_0 = 200:1:1$, 5000 ppm Cu) leads to a slower polymerization. However, since the majority of Cu remains in the form of the activator complex, the reaction can still proceed, although at a reduced rate. In the case of low catalyst concentration, e.g. with a ratio of $[\text{M}]_0:[\text{RX}]_0:[\text{Cu}^{\text{I}}/\text{L}]_0 = 200:1:0.1$ (500 ppm Cu) the same 10% of terminated chains leads to an irreversible conversion of all Cu^{I} to Cu^{II} and a complete stop of the polymerization. This can happen at low monomer conversion. Therefore, activator regeneration methods were introduced to continuously reduce Cu^{II} formed by termination reactions, back to Cu^{I} activator (cf. **chapter 2.2**).

Kinetics of ATRP in the presence of ppm amounts of catalyst resembles that of conventional radical polymerization (RP) and RAFT. This was demonstrated by kinetic simulations of two low-ppm ATRP systems: ICAR ATRP and SARA ATRP. These methods were chosen for their relative simplicity in computer modeling, since reduction kinetics in ARGET ATRP is more complex.[144, 145] However, analogous conclusions are applicable to other activator regeneration methods (ARGET ATRP, photoATRP, and eATRP).

The concentration of radicals in the steady state for low-ppm ATRP is determined from the equal rates of radical termination and radical generation. In ICAR ATRP formation of radicals is directly correlated with the rate of decomposition of the added thermal radical initiator

(e.g. AIBN). Therefore, concentration of radicals can be expressed by **Equation 4**, where f is initiator efficiency, k_{dc} is rate coefficient of decomposition, $[I_2]$ is concentration of initiator, and k_t is termination rate coefficient.

$$[R^\bullet] = \sqrt{\frac{fk_{dc}[I_2]}{k_t}}$$

Equation 4. Steady state concentration of radicals in ICAR ATRP.

Therefore, rates of polymerization in ICAR ATRP are governed by the concentration of thermal radical initiator and its rate of decomposition, and are independent of the concentration of soluble Cu species, unless it is very high. In such a case, ICAR ATRP switches to simultaneous reverse and normal initiation (SR&NI) ATRP procedure.

Kinetic simulations of ICAR ATRP for two different initial concentrations of Cu^{II} and I_2 are presented in **Figure 2**. **Figure 2a** shows that the polymerization rate was independent of $[Cu^{II}]_0$. Higher amounts of Cu^{II} resulted in a short induction period, associated with the necessity of producing a sufficient fraction of Cu^I activator. During this time Cu^{II} is gradually reduced to Cu^I until a steady concentration of radicals, and the associated $[Cu^I]/[Cu^{II}]$ ratio is achieved. This ratio adjusts based on the concentration of radicals given by **Equation 4** to fit the K_{ATRP} value, defined by **Equation 3**. The length of the induction period is dependent on the amount of Cu^{II} , the rate of the initiator decomposition, and the K_{ATRP} value. After the short induction period polymerization rates were equivalent for the same $[I_2]_0$, and $[Cu^I]/[Cu^{II}]$ ratio remained constant throughout the remaining polymerization period. Since the $[Cu^I]/[Cu^{II}]$ ratio depends on K_{ATRP} , the choice of ligand in ICAR ATRP is critical for maintaining narrow MWD. Nevertheless, the rate of polymerization is independent of the selected ligand.

It is worthwhile mentioning that during the initial induction period three distinct alkyl halide species may exist; one derived from I_2 ($I-X$), second from the added alkyl halide ($R-X$), and third, dormant polymer chains (P_n-X), all of which might have distinct K_{ATRP} values. Furthermore, small molecule radicals may add to the monomer with rate coefficients lower than the corresponding propagation rate coefficient (k_p). This can influence kinetic behavior of ICAR ATRP during the initial stages, in a manner similar to the “initialization” in a RAFT polymerization.

Figure 2. (a) Kinetics of ICAR ATRP and evolution of $[Cu^I]/[Cu^{II}]$ ratio, and (b) and (c) rates of propagation, activation, deactivation, and termination as a function of monomer conversion. Conditions: $[MA]:[MBrP]:[Cu^{II}Br_2]:[Me_6TREN]:[AIBN] = 200:1:(x):0.05:(y)$; 66% (v/v) MA in DMSO, $T = 25\text{ }^\circ\text{C}$, where $x = 0.002$ or 0.006 and $y = 0.3$ (b), or 0.05 (c). Reproduced with permission from ref.[35]

Rates of propagation (R_p), termination (R_t), and activation/deactivation (R_{a1}/R_{d1}) are presented in **Figure 2b and c**. The ATRP equilibrium was well maintained, with activation and deactivation rates depending on the total concentration of Cu. These rates did not impact rate of polymerization but can influence the MWD of the final product. As in a normal ATRP, faster polymerization also leads to increased termination due to the generation of a higher concentration of radicals.

In SARA ATRP generation of radicals is directly related to the supplemental activation by Cu^0 and comproportionation between Cu^0 and Cu^{II} . Therefore, the steady state concentration

of radicals can be expressed by **Equation 5**, where k_{a0} , k_{comp} , and k_t are the rate coefficients of activation of alkyl halides by Cu^0 , comproportionation, and termination, respectively, S is surface area of Cu^0 , V is the volume of the reaction medium, and $[\text{RX}]$ and $[\text{Cu}^{\text{II}}/\text{L}]$ are concentrations of (macro)alkyl halide and the Cu^{II} deactivator complex, respectively.

$$[\text{R}^\bullet] = \sqrt{\frac{k_{a0}(S/V)[\text{RX}] + k_{comp}(S/V)[\text{Cu}^{\text{II}}/\text{L}]}{k_t}}$$

Equation 5. Steady state concentration of radicals in SARA ATRP

The rate of polymerization in a SARA ATRP depends on the rate of radical generation and is proportional to the square root of the S/V parameter, as reported in the literature.[74, 75] **Figure 3** presents kinetic simulations of SARA ATRP for two different concentrations of Cu^{II} (0 or 50 ppm) and two lengths of Cu^0 wire (i.e. different S/V parameters). It should be mentioned that SARA ATRP can be conducted without the initially present soluble Cu species, as they can be generated *in situ* by activation of alkyl halides by Cu^0 and termination reactions. Nevertheless, often small amounts of Cu^{II} species are added at the onset of the reaction in order to facilitate deactivation and produce polymers with narrow MWD.[68]

Figure 3a shows that, similar to ICAR ATRP, higher initial $[\text{Cu}^{\text{II}}]$ led to generation of an induction period. Nevertheless, polymerization rates were only dependent on the S/V ratio. The $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ ratio adjusted to fit K_{ATRP} according to **Equation 3**, based on concentration of radicals, which is defined by **Equation 5**.

Figure 3. (a) Kinetics of SARA ATRP and evolution of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ ratio, and (b) and (c) rates of propagation, activation, deactivation, termination and Cu^0 activation as a function of monomer conversion. Conditions: $[\text{MA}]:[\text{MBRP}]:[\text{Cu}^{\text{II}}\text{Br}_2]:[\text{Me}_6\text{TREN}] = 200:1:x:0.1$; 66% (v/v) MA in DMSO, $T = 25^\circ\text{C}$, where $x = 0$ or 0.01 , with (b) $l = 10$ cm or (c) $l = 1$ cm of $d = 0.25$ mm Cu^0 wire ($S = 0.79$ cm² or 0.08 cm²), $V_{\text{total}} = 10$ cm³. Reproduced with permission from ref.[35]

Figure 3b and c shows rates of propagation (R_p), termination (R_t), activation of alkyl halides by Cu^0 (R_{a0}), activation of alkyl halides by Cu^{I} (R_{a1}), and deactivation of radicals by Cu^{II} (R_{d1}). As in other ATRP systems, the ATRP equilibrium was maintained throughout the reaction as R_{a1} and R_{d1} were balanced. Importantly, both of these rates progressively increased due to constant generation of soluble Cu species *via* activation of alkyl halides by Cu^0 and comproportionation. Activation of alkyl halides by Cu^0 was always much slower than by Cu^{I} . Additionally, an increase in R_{a0} led to an increase in soluble Cu species and thus to corresponding increase in R_{a1} . Finally, faster rates of polymerization led to faster termination.

3.3. Relation between Rate of Activation of Dormant Species and Overall Rate of ATRP

Interestingly, the same overall rate of ATRP can be achieved with dramatically different rates of activation of dormant species. Kinetic simulations of Normal, SARA and ICAR ATRP were designed to yield identical polymerization rates, implying identical concentration of propagating radicals (**Figure 4**). In all cases $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ was essentially equal, regardless of the regeneration mechanism (SARA, ICAR) or the initially set ratio (normal ATRP). However, the rates of activation of dormant species were significantly different, and in the case of SARA ATRP

additionally increased throughout the reaction (**Figure 4b**). This is because these rates depend on the absolute concentrations of Cu species, which are significantly higher in normal ATRP. Such analysis showed that there is no direct relationship between rate of activation of alkyl halides by Cu^{I} and rate of polymerization.

Figure 4. (a) Kinetics of Normal ATRP, ICAR ATRP, and SARA ATRP and evolution of $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ ratio, and (b) rates of propagation, activation, deactivation, termination and Cu^0 activation as a function of monomer conversion. Conditions:

Normal ATRP: $[\text{MA}]:[\text{MBrP}]:[\text{Cu}^{\text{I}}\text{Br}]:[\text{Cu}^{\text{II}}\text{Br}_2]:[\text{Me}_6\text{TREN}] = 200:1:0.7:0.3:1$;
 ICAR ATRP: $[\text{MA}]:[\text{MBrP}]:[\text{Cu}^{\text{II}}\text{Br}_2]:[\text{Me}_6\text{TREN}]:[\text{AIBN}] = 200:1:0.002:0.05:0.3$; SARA ATRP: $[\text{MA}]:[\text{MBrP}]:[\text{Cu}^{\text{II}}\text{Br}_2]:[\text{Me}_6\text{TREN}] = 200:1:0:0.1$ with $l = 10 \text{ cm}$ of $d = 0.25 \text{ cm}$ Cu^0 wire ($S = 0.79 \text{ cm}^2$). All reactions 66% (v/v) MA in DMSO, $T = 25^\circ\text{C}$, $V_{\text{total}} = 10 \text{ cm}^3$.

Reproduced with permission from ref.[35]

4. Molecular Weight

One benefit of ATRP, and other RDRP methods, is the ability to synthesize polymers with predetermined molecular weights (MWs), while maintaining narrow molecular weight distributions (MWDs). Similar to ionic living polymerizations, the average MW can be achieved by predefining the molar ratio between converted monomer(s) and initiating sites (alkyl halides). This ratio ($[\text{M}]_0/[\text{RX}]_0$) is often referred to as targeted degree of polymerization (DP_T). Both low-MW ($M_n \approx 1000$) and high-MW ($M_n > 1,000,000$)[117] polymers were successfully prepared by ATRP.

ATRP is a radical process, rendering it tolerant to many impurities and functionalities. Undesirable reactions, such as radical termination, are typically greatly minimized under appropriately selected conditions, however they are unavoidable and are always present to some extent. Additionally, they become more evident when targeting polymers with higher molecular weights. Deviation of MW from the theoretical values can be caused by several factors.

Slow and ineffective initiators lead to a distribution of initiation over time. In such a case, at the beginning the concentration of the active species is lower than theoretically expected, resulting in lower rate of monomer consumption (**Figure 5a**). Simultaneously, the ratio between the monomer and the active species is higher, resulting in a higher average MW (**Figure 5b**). After the full consumption of the initiator, the rate of polymerization should reach the same value as if slow initiation had not occurred, since the number of active species should now match the theoretical prediction. MW should also begin to approach theoretical values.[150] Therefore, for good control over MW a fast and efficient initiation is required to provide concurrent growth of all polymer chains. However, in normal ATRP the activity of the initiator should not be too high. This is because a very active initiator combined with high catalyst loading leads to a high concentration of radicals, which might result in early termination and loss of a fraction of the initiating sites. In such a case, a linear increase of MW is observed throughout the reaction, with MWs higher than the theoretical expectation. Such phenomenon can also stem from impurities in the initiator. An opposite case, i.e. linearly increasing MW with values lower than theory, is uncommon and can stem e.g. from monomer evaporation.

Figure 5. Effect of slow initiation and chain breaking reactions on (a) polymerization rate and (b) molecular weight

In the case of irreversible transfer, as the total number of chains progressively increases, average MW decreases (**Figure 5b**). However, transfer reactions should have no effect on the overall polymerization rate, provided that the rates of re-initiation from the newly formed chains are fast enough (**Figure 5a**).^[150] This is due to the constant number of active sites, since every transfer event leads to the formation of a new chain. It is worthwhile noting that for this reason living nature of the polymerization cannot be confirmed solely by a linear first-order kinetic plot. Linearity merely indicates a constant radical concentration.^[151]

Irreversible termination events lead to the increase in fraction of dead chains and decrease in the chain end functionality. Kinetically, termination leads to suppression of the polymerization rate, since active sites are gradually removed from the system (**Figure 5a**). The effect on MW depends on the mode of termination. In the case of termination by disproportionation, average MW should remain unaffected, since the total number of chains is constant. Therefore, linear evolution of MW with monomer conversion cannot alone be a definitive indicator of living nature of the polymerization.^[151] Termination by coupling leads to an increase in MW, as each termination of two radicals produces a single polymer chain, effectively reducing total number of chains (**Figure 5b**). This type of termination is especially challenging in the systems employing multifunctional initiators (e.g. stars, brushes, functionalized nanoparticles), as it can lead to undesirable crosslinking of the material.

5. Dispersity

Dispersity ($\bar{D}$) (formerly: polydispersity or PDI, term discouraged to use by IUPAC) in ATRP depends on the degree of polymerization, monomer conversion, and number of monomer units added within each intermittent activation/deactivation cycle, as shown in **Equation 6**.

$$\bar{D} = \frac{M_w}{M_n} = 1 + \frac{1}{DP_n} + \left(\frac{k_p [RX]_0}{k_d [Cu^{II}/L]} \right) \left(\frac{2}{p} - 1 \right)$$

Equation 6. Dispersity in ATRP. Herein DP_n is the number average degree of polymerization, p is monomer conversion, and k_p , k_a , k_d , are rate coefficients of propagation, Cu^I activation, and Cu^{II} deactivation, respectively.

With the provision of fast exchange, and in the absence of termination reactions, the value of $\bar{D}$ is expected to monotonically decrease with increasing monomer conversion (**Figure 6**). However, contrary to the prediction, often the $\bar{D}$ values increase with the progress of polymerization. In order for detailed quantification of the factors that influence the $\bar{D}$ value, recently a theory for MWD in ATRP was derived, utilizing an analogy to a series of continuous stirred tank reactors (CSTR).[152] It was confirmed that the value of $\bar{D}$ is a result of a balance between the number of activation/deactivation cycles and the fraction of terminated chains. Since the unavoidable radical termination reactions can have a large contribution to the system, recently a new equation was derived to account for the amount of dead chains (**Equation 7**).[153]

$$\bar{D} = \frac{M_w}{M_n} = 1 + \frac{1}{DP_n} + \left(\frac{k_p [RX]_0}{k_d [Cu^{II}/L]} \right) \left(\frac{2}{p} - 1 \right) + \left(\frac{k_t k_a [Cu^I/L]_0}{4k_p k_d [Cu^{II}/L]_0} \right) p$$

Equation 7. Dispersity in ATRP, including the amount of dead chains.

Figure 6. Evolution of dispersity ($\bar{D}$, M_w/M_n) with monomer conversion in Normal ATRP. Conditions used for kinetic simulation: $[M]:[RX]:[Cu^I/L]:[X-Cu^{II}/L] = 250:1:0.9:0.1$; $[M]_0 = 5$ M; $k_p = 1000 \text{ M}^{-1} \text{ s}^{-1}$, $k_t = 1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, $k_a = 1 \text{ M}^{-1} \text{ s}^{-1}$, $k_d = 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

$\bar{D}$ can generally be improved by targeting higher degrees of polymerization (with negligible termination) and stopping the reaction at lower conversion. Additionally, to provide polymers with narrow MWD efficient deactivation of the growing chains is required. This can be achieved by employing a higher loading of Cu^{II} deactivator complex in the initial reaction mixture. In low ppm ATRP techniques (cf. **chapter 2.2**) active ligands may be required to ensure that the majority of Cu species is in the form of Cu^{II}/L deactivator. This is because the Cu^I/Cu^{II} ratio adjusts to the steady state concentration of radicals, based on K_{ATRP} . For example, K_{ATRP} values for methyl 2-bromopropionate (MBrP) in acetonitrile (MeCN) are 1.3×10^{-10} , 4.0×10^{-9} , 3.2×10^{-7} , and 2.9×10^{-6} for 2,2'-bipyridine (bpy), N,N,N',N'',N'' -Pentamethyldiethylenetriamine (PMDETA), tris(2-pyridylmethyl)amine (TPMA), and tris[2-(dimethylamino)ethyl]amine (Me_6TREN) ligands, respectively.[154] Under typical polymerization conditions ($[RX]_0 = 25$ mM, $[R^\bullet] = 1 \times 10^{-8}$ M) this corresponds to the percentage of Cu^{II}/L deactivator $\approx 0.03\%$ for bpy, $\approx 1\%$ for PMDETA, $\approx 44\%$ for TPMA, and $\approx 88\%$ for Me_6TREN . Therefore, when conducting ATRP with low ppm of catalyst, ligands forming highly active catalysts are required for good control.

Specific applications may require polymers with different molecular weight distributions. Polymers with low $\bar{D}$ values were prepared by ATRP e.g. in the presence of Ag^0 ($\bar{D} = 1.03$),[40] inorganic sulfites ($\bar{D} = 1.05$),[51] or via photoATRP ($\bar{D} = 1.05$).[31] Polymers with designed

MWDs can be achieved e.g. by blending multiple polymers with various MWs. This leads to bi- or multimodal distributions of MW. Bimodal MWD of chains on a single polymer brush or polymer-nanoparticle hybrid material were achieved by intentional termination of a portion of active chains, e.g. by deactivation with TEMPO.[155, 156] Some degree of control over polymer dispersity was obtained by adjusting the amount of Cu^{II} deactivator and temperature in the low ppm ATRP systems.[157, 158] For example, when the polymerization of styrene was carried out with, 50, 5, and 1 ppm of Cu^{II} /L it resulted in $\bar{D} = 1.11$, 1.28, and 1.64, respectively.[37] Finally, designed dispersity, i.e. not only the value of $\bar{D}$ but also control over the shape of MWD was achieved in NMP by adjusting the rate of feeding of the initiator,[159] which could be extended to ATRP.

6. Preservation of Chain End Functionality

One of the critically important features of polymers prepared by RDRP methods is their “livingness”, i.e. preservation of high chain end functionality (CEF). The retention of a functional group at the ω -chain end allows for further functionalization or preparation of polymers with complex architectures, such as block copolymers, stars, brushes, etc.[160, 161] Therefore, synthesis of well-defined polymers requires identification and understanding of all chain-breaking reactions. ATRP, as any radical polymerization, is subject to the unavoidable radical termination reactions, which decrease CEF. Additionally, in the presence of Cu catalysts, propagating radicals can form R-Cu^{II} /L organometallic species, alike in organometallic-mediated radical polymerization (OMRP). The resulting organometallic species can terminate via catalytic radical termination (CRT).[33, 162, 163] Regardless of the proposed mechanisms, CRT leads to terminated polymer chains, effectively decreasing CEF.

High preservation of CEF is of critical importance, especially in synthesis of block copolymers, stars, brushes, and other complex architectures. A macroinitiator with a reduced CEF has a detrimental effect on the quality of the synthesized materials. It leads to the presence of a homopolymer impurity in block copolymers, or residual free arms in the synthesis of star polymers. During the preparation of homopolymers, high CEF should still be retained until the desired degree of polymerization is reached, and this is also of importance if end group functionalization is desired. Recently, it was stated that dispersity values of 1.1 or below are

associated with high retention of CEF in RDRP.[151] While generally true, this statement is not universally correct. If disproportionation termination events occur at high monomer conversion, CEF can be significantly lowered, while the influence on the shape of MWD and $\bar{D}$ value can be negligible.

GPC can be used as a straightforward method to illustrate preservation of CEF (**Figure 7**). The synthesized polymer can be precipitated, purified, dried, and reused as a macroinitiator in a chain extension reaction. When utilizing this technique, it is preferential to synthesize a “pseudo” block copolymer, i.e. perform a chain extension of the macroinitiator with the same monomer, effectively forming a higher MW homopolymer. This allows avoidance of potential issues arising from poor initiation and problems with the GPC detectors response to block copolymers. A clear shift of the entire peak towards high molecular weights validates high CEF in the macroinitiator (**Figure 7a**). However, when CEF is lower part of the macroinitiator remains unreacted (**Figure 7b-d**). The peak maximum of the block copolymer is shifted towards higher molecular weights when a higher fraction of inactive macroinitiator is present. This is because the amount of monomer in the chain extension step is constant in all cases, however the number of living chains that can be extended is progressively reduced. This alters the monomer/initiator ratio, i.e. the targeted degree of polymerization (DP_T) of the second block. Nevertheless, together with the constant number of all chains in the system, this leads to identical number average molecular weight (M_n) of the final product in all cases. However, $\bar{D}$ value increases with the amount of unreacted macroinitiator.

Figure 7. Simulated normalized GPC traces (log-normal distribution). Macroinitiators with (a) 100%, (b) 95%, (c) 85%, and (d) 70% CEF, before and after chain extension.

Termination reactions can be greatly minimized under well-designed ATRP conditions. This leads to a low dead chain fraction (DCF) and high preservation of CEF. However, miniscule changes in the CEF are challenging to measure by typical analytical methods such as NMR, GPC, or MS.[164-169] This is due to the relatively low signal-to-noise ratio arising from very low concentration of the end groups, compared to the amount of the polymer present in the final product. Alternatively, one can follow formation of the byproducts of the termination reactions. In ATRP, each radical termination event leads to the formation of Cu^{II} species. The principle of halogen conservation (PHC)[170] states that the amount of the halogen has to remain constant in the system. Therefore, each loss of CEF is associated with a transfer of the halogen atom to the Cu catalyst, or to the reducing agent. In normal ATRP, the buildup of $\text{X-Cu}^{\text{II}}/\text{L}$ can be measured

by UV-Vis spectroscopy which can be directly translated to the amount of lost halogen chain ends. Such measurements are simple to perform and accurate, even at very low DCF.

In low ppm ATRP methods, CEF can also be determined using PHC by additionally considering the amount of halogen atoms transferred in the reduction process. In ICAR ATRP, the amount of the decomposed thermal initiator can be measured. In *e*ATRP, the total amount of the reduced Cu^{II} equals the number of transferred electrons. Therefore, knowledge of the charge passed allows for determination of DCF. In ARGET ATRP, the amount of oxidation product of the reducing agent should be followed. Finally, in SARA ATRP, where the reducing agent is Cu⁰, total Cu concentration (Cu^I + Cu^{II}) should be measured. While determination of Cu^{II} concentration via UV-Vis is straightforward, Cu^I can also be measured indirectly, e.g. via oxidation to Cu^{II}, or can be calculated knowing the K_{ATRP} values.

CEF depends on several reaction parameters, such as concentration of propagating radicals (i.e. the rate of polymerization), structure of the monomer (i.e. rate coefficients of propagation and termination), concentration of monomer, targeted degree of polymerization, and monomer conversion. The fraction of dead chains, assuming exclusive termination via disproportionation (to maintain constant number of chains) is given by **Equation 8**.^[34]

$$\text{DCF} = 1 - \text{CEF} = \frac{[\text{T}]}{[\text{R} - \text{X}]_0} = \frac{2\text{DP}_T k_t [\ln(1 - p)]^2}{[\text{M}]_0 k_p^2 t}$$

Equation 8. Dead chain fraction (DCF) in ATRP, assuming exclusive termination via disproportionation. DP_T is the targeted degree of polymerization, p is monomer conversion, $[\text{M}]_0$ is the initial monomer concentration, t is time, and k_t and k_p are rate coefficients of termination and propagation, respectively.

Equation 8 indicates that higher initial monomer concentration leads to lower DCF. In bulk polymerization of methyl methacrylate (MMA), at 80 °C, targeting $\text{DP}_T = 100$, at 70% monomer conversion, the DCF is 4.6% for bulk polymerization, but 6.9% and 9.2% for monomer/solvent ratios 2/1 and 1/1, respectively. Lower DCF can also be obtained, when targeting higher degree of polymerization and stopping the reaction at lower monomer conversion. For example, preparation of PMMA with $\text{DP} = 60$ can be achieved by targeting $\text{DP}_T = 75$, 100, or 150 and proceeding to 80%, 60%, or 40% conversion, respectively. Analysis of these conditions in bulk

polymerization of MMA at 80 °C shows that the three different reaction conditions would result in 12.3%, 5.3%, and 2.5% DCF, respectively.[34]

The reaction time required to reach a certain DP with highly preserved chain end functionality depends on the reactivity of the monomer. To preserve 90% CEF for poly(methyl acrylate) with $DP_T = 100$ at 90% monomer conversion, a ≈ 10 minute reaction is required. The same level of control in the polymerization of methyl methacrylate (MMA) or styrene (St) requires ≈ 17 h and ≈ 3.5 days, respectively.[34]

7. Monomers

A wide variety of monomers including styrenes[3], acrylates[171], methacrylates[171], acrylonitrile[172, 173], acrylamides[174, 175], methacrylamides[174, 175], and 4-vinyl pyridine[176] were polymerized by ATRP. Considering the large number of commercially available derivatives of these compounds, the number of monomers polymerizable by ATRP is vast. Some functional monomers include 2-hydroxyethyl (meth)acrylate,[177, 178] glycidyl (meth)acrylate,[179, 180] and dimethylaminoethyl methacrylate.[181, 182] ATRP was also successfully used for copolymerization of vinyl monomers with simple olefins.[183-186]

However, certain monomers polymerizable by conventional radical polymerization still present challenges for ATRP, e.g. vinyl acetate, vinyl chloride and *N*-vinylpyrrolidone, although examples of polymerizations were reported in the literature.[187-192] Often, the limitations arise from the inability to provide efficient reactivation of the dormant polymer chains. Polymerization of vinyl esters (e.g. vinyl acetate) remains elusive due to formation of relatively strong carbon-halogen bonds at the chain ends. Such dormant chains would require development of highly active catalysts. Additionally, polymerization of strongly coordinating monomers is challenging due to ligand displacement resulting in lower halophilicity of the deactivator complexes.

Polymerization of acidic monomers is also challenging due to the possible protonation of the ligand at low pH values,[78, 193] displacement of the halide anion from the Cu^{II} deactivator complex,[78] or competitive coordination of the carboxylate group to Cu.[193, 194] However, the main reason behind the inability to polymerize methacrylic acid via ATRP was recently

identified as lactonization, i.e. an intramolecular substitution at the chain end, leading to lactone-terminated chains. In order to overcome this undesirable side reaction, the –Br chain end was substituted with –Cl, a poorer leaving group, the pH was lowered to diminish the presence of carboxylate anions, and the polymerization reaction was accelerated. This allowed the synthesis of well-defined poly(methacrylic acid) via ATRP.[89]

ATRP was also used for polymerization of macromonomers to prepare star-like and bottlebrush structures, and for copolymerization of macromonomers with conventional monomers to form functional graft copolymers.[195-207] Macromonomers are typically based on styrene, acrylate, or methacrylate monomers, but contain long side chains or bulky side groups. Due to the high viscosity, steric hindrance, and relatively low concentration of the polymerizable vinyl groups, polymerization of macromonomers can be challenging and requires consideration of the thermodynamic limitations of the monomer, i.e., ceiling temperature (T_c) and equilibrium monomer concentration ($[M]_e$).[195, 208-211]

Careful optimization of reaction parameters is often required in ATRP in order to efficiently mediate the polymerization and obtain polymers with predefined MW, narrow MWD and high CEF. This includes selection of an adequate catalyst complex, initiator, solvent, temperature, and additives for polymerization of a particular monomer. However, recently universal conditions (methyl bromophenylacetate (MBPA), $\text{Br-Cu}^{\text{II}}/\text{PMDETA}$, isopropyl alcohol (IPA), Cu^0 wire) were successfully used for polymerization of acrylates, methacrylates, and styrene and required only adjustment of temperature.[212] Such universal conditions have to ensure that all selected monomers and polymers, as well as other reaction components are soluble in the chosen solvent. Furthermore, since ppm amounts of catalyst were used, sufficiently active ligands should be employed to ensure that the majority of soluble Cu species is in the form of $\text{X-Cu}^{\text{II}}/\text{L}$ to provide efficient deactivation.

8. Initiators

Alkyl halides (RX) are commonly utilized as initiators in an ATRP. The number of growing chains during the polymerization is determined by the amount of RX introduced to the polymerization medium, provided that initiation is fast and transfer and termination reactions are negligible. Therefore, rate of polymerization in ATRP has a first order dependence on the

concentration of RX (**Equation 1**). The range of available initiators is very broad. Examples of the structure of a variety of alkyl halide initiators are presented in **Figure 8**, along with their K_{ATRP} values for $\text{Cu}^{\text{I}}\text{X}/\text{TPMA}$ in MeCN at 22 °C. Typically, alkyl bromides or chlorides are utilized, however alkyl iodides and pseudo-halides ($-\text{SCN}$, $-\text{NCS}$, etc.) can also be employed.[213] Initiators can be monofunctional, bifunctional, or multifunctional, leading to linear, telechelic, and complex architectures, respectively. Initiators can also contain a multitude of functional groups, such as azide or alkyne,[214] enabling post-polymerization modification e.g. via click-chemistry, or they can contain a degradable group such as a disulfide,[215] allowing for degradation of the polymers. Initiators can be tethered to a surface of a silica wafer,[216] (nano)particles,[156 , 217-219] proteins,[7] DNA,[220] cyclodextrin,[82] glucose,[221] cellulose fibers,[222] and many other surfaces.

Figure 8. ATRP equilibrium constants for various initiators with $\text{Cu}^{\text{I}}\text{X}/\text{TPMA}$ ($\text{X} = \text{Br}, \text{Cl}$) in MeCN at 22 °C. Color key: (red) 3°; (blue) 2°; (black) 1°. Symbol key: (solid) R-Br; (open) R-Cl; (bottom-half-solid) R-I; (Δ) phenyl; (□) ester; (○) nitrile; (◇) phenyl ester; (☆) allyl. Reproduced with permission from ref. [154]

The activity of different ATRP initiators depends on several parameters such as the nature of the leaving group and stability of the formed radical, and is affected to a lesser degree by steric considerations.[213] Alkyl bromides are typically more active than chlorides due to the lower bond dissociation energy (BDE) of the C–Br bond compared to a C–Cl bond. The C–I bond has even lower BDE, which would imply much higher activity of alkyl iodides. However, the ATRP equilibrium constant (K_{ATRP}) depends on the bonding of halide to the Cu species,[213, 223, 224] and the affinity of I towards Cu is much lower than that of Br or Cl. Conversely, affinity of F to Cu is very high, however the C–F bonds have remarkably high BDE. This results in hampered (re)activation of alkyl fluorides, as well as poor deactivation efficiency, yielding low K_{ATRP} values.[225] Therefore, alkyl iodides and fluorides are rarely employed in ATRP. Nevertheless, many fluoropolymers were modified *via* grafting from method.[16, 226, 227] Alkyl iodides can be used in a degenerative transfer (DT) polymerization,[228-230] or in conjunction with organic catalysts in reversible complexation mediated polymerization (RCMP), which typically includes minor contribution of DT.[231-234] Activity of alkyl halides is also dependent on the degree of substitution of the formed radical. Alkyl halides yielding tertiary radicals are generally more active than their secondary counterparts and much more active than their primary counterparts. The reactivity is influenced by the substituents stabilizing the radicals, resulting in the observation that one of the most active ATRP initiators is ethyl bromophenylacetate (EBPA), a secondary initiator stabilized by both ester and benzyl groups.

In order to provide well-defined polymers with narrow molecular weight distribution (MWD) and high chain end functionality (CEF), an appropriate initiator should be selected for a particular monomer. Frequently, initiators are chosen such that they resemble the structure of the polymer. This results in the selection of 2-bromopropionitrile (BPN) for polymerization of acrylonitrile, methyl 2-bromopropionate (MBrP) for methyl acrylate, and 1-phenylethyl bromide (PEBr) for styrene. Following this reasoning, ethyl α -bromoisobutyrate (EBiB) could be used for polymerization of methyl methacrylate. However, due to the effect of the penultimate unit on the reactivity of the chain end it is not the best choice.[235, 236] Instead, BPN or EBPA can be used. Generally, in a normal ATRP (cf. **chapter 2.1**) the activity of the initiator should be equal to, or slightly higher than that of the polymer chain end. However, selection of a too active initiator, combined with a high loading of Cu catalyst leads to a high instantaneous concentration of radicals and thus to a high degree of radical termination at the onset of the reaction. This

restriction is not applicable to ATRP methods with activator regeneration (cf. **chapter 2.2**), where activity of the initiator should be much higher than that of the chain end. This allows for quick conversion of the entire initiator and concurrent growth of all polymer chains. In the opposite case, i.e. when the activity of polymer chain end is much higher than that of the initiator, polymer chain ends will be preferentially reactivated, leading to broad MWD.

Activity of initiators also has to be carefully considered during the synthesis of block copolymers. In such a case, at first a homopolymer is prepared, which is subsequently utilized as a (macro)initiator. Therefore, the order of monomer addition should be appropriately planned. More active monomers should be used for the synthesis of the macroinitiator in order to provide efficient transition to the second block yielding concurrent growth of all polymer chains, and in turn well-defined materials. In ATRP the reactivity of a specific monomer is based on a combination of steric and polar effects and follows the order: acrylonitrile > methacrylates > styrene $\approx$ acrylates > acrylamides.[237] Alternatively, a technique termed halogen exchange can be utilized to efficiently polymerize more active monomers starting from a less active macroinitiator.[238] In such a case, the first block is prepared using a bromide containing initiator, which is subsequently chain-extended using copper chloride catalyst. After first activation and monomer addition the macroradicals are reversibly deactivated with $-\text{Cl}$ instead of $-\text{Br}$. The higher activity arising from the structure of the second monomer is then compensated for by the lower activity of the $-\text{Cl}$ terminated chain end. Effectively, the remaining $-\text{Br}$ terminated macroinitiator can be preferentially activated, leading to higher initiation efficiency, thereby allowing all chains to grow simultaneously. The principle of halogen exchange reaction is illustrated on **Figure 9**.

Figure 9. Chain extension of polymers composed of less active monomers with a more active monomer using (a) normal ATRP and (b) ATRP with Halogen Exchange. Reproduced with permission from ref. [238]

9. Catalysts

ATRP can be conducted with a wide variety of transition metal catalysts, although Cu-based complexes are most frequently used. The metal center in an efficient ATRP catalyst must have two easily accessible oxidation states separated by one electron. Additionally, the catalyst must be able to accept the (pseudo)halogen, which requires a sufficiently high halogenophilicity.[239] Finally, the halidophilicity, i.e. the association of the halide anion to the catalyst in the higher oxidation state, should be sufficiently high to provide efficient deactivation. Examples of other metals successfully used in ATRP include Fe,[240] Ru,[241] Co,[242] Ti,[243] Ni,[244] Mo,[245, 246] Re,[247] Rh,[248] Pd,[249] and Os.[250]

Cu complexes are most commonly utilized in ATRP, owing to their availability, low cost, oxidative stability of Cu^{II} , and versatility of the formed catalyst complexes. Performance of a Cu catalyst can be easily tuned by the selection of the ligand. The activity of Cu complexes in ATRP spans over ca. 10 orders of magnitude, when the same conditions (solvent, initiator, temperature) are used, based solely on ligand selection. Historically, the first ATRP reactions were conducted using 2,2'-bipyridine (bpy) ligands.[3] Well-defined polystyrene, poly(methyl acrylate), poly(methyl methacrylate), and polyacrylonitrile were prepared.[3, 4, 172] Since $\text{Cu}^{\text{II}}/\text{bpy}$ has limited solubility in nonpolar solvents, it forms heterogeneous systems, which influences the control over the polymerization. Typically, homogeneous conditions are desired, as shown by very low dispersity polymers prepared using 4,4'-dinonyl-2,2'-dipyridine (dNbpy) ligand.[251, 252] However in certain cases in normal ATRP precipitation of excess $\text{Cu}^{\text{II}}/\text{L}$ complex formed

via the persistent radical effect might be beneficial for maintaining the rate of polymerization. This is because in normal ATRP the rate of polymerization depends on the $[\text{Cu}^{\text{I}}]/[\text{Cu}^{\text{II}}]$ ratio and not on the total amount of the soluble Cu species (cf. **chapter 3.1** and **Equation 1**). Solubility of the catalyst is also of critical importance in polymerizations conducted in heterogeneous media, e.g. miniemulsion.[19, 22, 23] In such a case, the ligand should be selected to ensure that the $\text{Cu}^{\text{II}}/\text{L}$ deactivator species is present in the same phase as the growing radicals for efficient deactivation.[118, 253-263]

After the initial discovery of ATRP using bpy as ligand, significant research was devoted to the synthesis of more active catalytic systems. Examples of the structure of a variety of ligands are presented in (**Figure 10**), along with their K_{ATRP} values determined with EBiB as initiator in the presence of $\text{Cu}^{\text{I}}\text{Br}$ in MeCN at 22 °C. Measurement of the ATRP equilibrium constants (K_{ATRP} , cf. **chapter 13.1**) and activation/deactivation rate coefficients ($k_{\text{act}}/k_{\text{deact}}$, cf. **chapter 13.2 and 13.3**) allowed for establishment of a structure-property relationship for efficient ligand design.[154] Notably, it was found that k_{act} contributes significantly more to the value of K_{ATRP} as compared to k_{deact} , which varies to a lower extent for most ligands. The activity of the catalytic system depends on several parameters: denticity, i.e. number of the nitrogen atoms, (tetradentate > tridentate > bidentate); nature of the nitrogen (pyridine ~ alkyl amine > alkyl imine > aryl imine > aryl amine); length of the linker between nitrogen atoms ($\text{C2} \gg \text{C3} > \text{C4}$); and topology of the ligand (bridged cyclic > branched > cyclic ~ linear).

Figure 10. ATRP equilibrium constants for various N-based ligands with EBiB in the presence of $\text{Cu}^{\text{I}}\text{Br}$ in MeCN at 22 °C. Color key: (red) N2; (black) N3 and N6; (blue) N4. Symbol key: (solid) amine/imine; (open) pyridine; (left-half-solid) mixed; ($\square$) linear; (Δ) branched; ($\circ$) cyclic; Reproduced with permission from ref. [154]

The activity of the catalyst complex can be additionally tuned by incorporation of electron donating groups into the ligand. Incorporation of two *m*-Me and a *p*-MeO group on one, two, or three pyridine groups in a commonly used ATRP ligand, tris(2-pyridylmethyl)amine (TPMA) led to an increase of catalytic activity by 1, 2, and 3 orders of magnitude, respectively.[264] The redox potential of the catalyst complex provides an excellent correlation with activity of the catalyst in an ATRP (**Figure 11**). This allows for facile complex characterization using cyclic voltammetry.

Figure 11. Dependence of the ATRP equilibrium constant (K_{ATRP}) on the half-wave potential ($E_{1/2}$) of the $\text{Cu}^{\text{II}}\text{Br}_2/\text{L}$ complexes. Measured with ethyl α -bromoisobutyrate (EBiB) in MeCN. Data from ref. [154, 265] Structures of ligands are shown in **Figure 10** or explained in text.

The motivation behind synthesis of more active ligands was to enable polymerizations at lower catalyst concentrations, and to polymerize less active monomers with higher R-X bond dissociation energies (e.g. vinyl acetate, vinyl ethers, or olefins). The most active ATRP ligand to date, tris((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)amine (TPMA^{*3}), was successfully employed in an ICAR ATRP of acrylates utilizing only 5 ppm of Cu.[264] However, such ligands are typically not suitable for use in normal ATRP. High loading of highly active catalyst leads to a rapid radical formation and thus to fast termination at the onset of the reaction. Kinetic simulations of normal ATRP of methyl acrylate utilizing various ligands showed that the reaction rate initially increased with the activity of the catalyst, eventually decreasing for more active catalysts (**Figure 12**).[266] In an extreme case, for a hypothetical ligand 2-((bis((4-(dimethylamino)pyridin-2-yl)methyl)amino)methyl)-*N,N*-dimethylpyridin-4-amine (TPMA^{*N}), which is expected to be ca. 3 orders of magnitude more active than TPMA^{*3}, no polymerization was observed.

Figure 12. First-order kinetic plot for simulations of normal ATRP of MA with different catalysts under the conditions: $[M]:[RX]:[Cu/L] = 200:1:0.2$ in 50% (v/v) solvent, $T = 25\text{ }^{\circ}\text{C}$. Adapted with permission from Ref. [266] Structures of ligands are shown in **Figure 10** or explained in text.

In addition to participating in the ATRP equilibrium, active Cu complexes can react with propagating radicals, forming $R-Cu^{II}/L$ organometallic species, similar to organometallic-mediated radical polymerization (OMRP).[124, 162] This reaction is especially pronounced during polymerization of acrylates. The formed dormant $R-Cu^{II}/L$ can then undergo catalytic radical termination (CRT), producing terminated polymer chains and regenerating Cu^I/L complex.[33, 124] Indeed, it was shown that conventional radical polymerization was retarded in the presence of various Cu^I/L complexes.[162, 163] Although the intricacies of the CRT mechanism are yet to be determined, it depends on the structure of the ligand.[124] While both K_{ATRP} and rate coefficient of CRT (k_{CRT}^{app}) increases with the activity of the catalyst complex, the effect is much more pronounced for K_{ATRP} . This suggests that there is a possibility of designing highly active ATRP catalysts, with minimized influence of undesirable CRT.

The activity of a catalyst is proportional to the ratio between Cu^{II}/L and Cu^I/L complex stability constants (β^{II}/β^I) and thus it can be coarsely predicted by knowing the easily obtainable β^{II} and β^I values.[267] Complexes with $\beta^{II} > \beta^I$ are desired for high activity, i.e. the Cu^{II}/L complex is preferentially stabilized. However, high β^I is also favored, since the extent of

disproportionation of Cu^{I} complexes is proportional to the $\beta^{\text{II}}/(\beta^{\text{I}})^2$ ratio. These features allow for design of highly active non-disproportionating complexes (e.g. TPMA).[267] It is also critically important to consider speciation of the Cu/L complexes. $\text{Cu}^{\text{I}}/\text{L}$ complex requires a free coordination site in order to activate alkyl halides, rendering $\text{X-Cu}^{\text{I}}/\text{L}$ an ineffective activator. Conversely, $\text{X-Cu}^{\text{II}}/\text{L}$ requires a coordinated halide in order to deactivate growing radicals and a dissociated $\text{Cu}^{\text{II}}/\text{L}$ complex is an inefficient deactivator (**Equation 9**).[268] The extent of the dissociation (K_{X}) depends on the nature of the halide and the solvent. In aprotic solvents, the value $K_{\text{Br}}^{\text{II}}$ is in the order of 10^5 M^{-1} , [268, 269] but for $\text{Br-Cu}^{\text{II}}/\text{Me}_6\text{TREN}$ in H_2O it is only 4.4 M^{-1} . [270] This suggests that in aqueous ATRP a large part of deactivator is dissociated, leading to poor deactivation efficiency. The loss of $\text{X-Cu}^{\text{II}}/\text{L}$ can be compensated for by either high catalyst loading or by the addition of salts such as NaBr or TEABr, which shifts the dissociation equilibrium towards the deactivator species.[62] It is worthwhile noting that rate coefficients of alkyl halide activation by $\text{Cu}^{\text{I}}/\text{L}$ and radical deactivation by $\text{Cu}^{\text{II}}/\text{L}$ complexes are often expressed as apparent rate coefficients, without consideration of speciation.

Equation 9. Halidophilicity (K_{X}), i.e. association of the halide anion to the Cu/L complexes. The superscript ^I and ^{II} represents the Cu oxidation state and subscript _X represents halogen.

Halidophilicity of $\text{Cu}^{\text{II}}/\text{L}$ complexes follows the trend of $\text{F} > \text{Cl} > \text{Br} > \text{I}$. [225] $\text{F-Cu}^{\text{II}}/\text{L}$ is an inefficient deactivator due to the high strength of the $\text{Cu}^{\text{II}}\text{-F}$ bond, which results in a disfavored atom transfer to the propagating radicals. Conversely, the $\text{I-Cu}^{\text{II}}/\text{L}$ bond is very weak resulting in low K_{ATRP} values, despite typically low BDE of alkyl iodides. This can facilitate the polymerization to proceed e.g. *via* a degenerative iodine transfer mechanism.[229, 230] Therefore, Br and Cl based Cu catalysts are most widely used in ATRP, with Br prevailing due to typically higher K_{ATRP} values.

Iron based catalysts have attracted a considerable degree of attention due to being more biocompatible, environmentally friendly, abundant, and inexpensive.[271] A wide range of nitrogen,[240, 272] or phosphorus[45, 273, 274] based ligands were successfully used in Fe-based ATRP. Furthermore, polar solvents such as dimethylformamide (DMF) and acetonitrile

(MeCN) can be utilized as ligands.[275] Similar to Cu-catalyzed ATRP, the catalyst in the lower oxidation state, i.e. the activator Fe^{II} species, is sensitive to oxygen. Therefore, many efforts were devoted to develop procedures allowing for direct addition of the oxidatively stable Fe^{III} compounds to the reaction, e.g. AGET ATRP[276], ICAR ATRP,[277, 278] SARA ATRP,[279] or *e*ATRP.[280] Recently, photoATRP was employed to efficiently polymerize MMA using FeBr_3 as catalyst precursor in the absence of additional ligands, radical initiators, or reducing agents,[281] and even without conventional ATRP initiators, utilizing *in situ* formed alkyl halides.[282]

A series of small organic molecules with photoredox properties were also screened for their use in ATRP in the absence of metal-based catalysts. 10-phenylphenotiazine (PTZ) was reported to successfully mediate ATRP, with good control over molecular weights, narrow molecular weight distributions, and with temporal control, i.e. the ability to stop and restart polymerization by switching the external stimuli (380 nm irradiation) off and on.[98] The use of other organic photoredox catalysts, such as perylene,[283] fluorescein,[284] 5,10-diaryl-5,10-dihydrophenazine derivatives,[285] carbazolyl dicyanobenzene-based fluorophore,[286] and PTZ derivatives[99, 100] were also investigated. The possibility of synthesizing materials without a residual transition metal catalyst is particularly attractive for the preparation of functional materials targeting electronic applications.

10. Additives

ATRP in the presence of ppm amounts of catalyst (cf. **chapter 2.2**) requires continuous regeneration of the $\text{Cu}^{\text{I}}/\text{L}$ activator lost in radical termination reactions via the persistent radical effect (PRE).[25, 26] This can be achieved by direct reduction of the formed $\text{Cu}^{\text{II}}/\text{L}$ deactivator, formation of radicals that subsequently reduce $\text{Cu}^{\text{II}}/\text{L}$, or by supplemental activation. Chemical reducing agents utilized in ATRP include $\text{Sn}^{\text{II}}\text{R}_2$ compounds,[37] glucose,[38] ascorbic acid,[39] Ag^0 , [40, 41] or hydrazine.[27] Conventional thermal radical initiators such as AIBN can also be utilized.[27] Additionally, certain monomers[42, 43] and ligands[44, 45] can be used as internal reducing agents. Finally, inorganic sulfites[51] [52] or Cu^0 in multiple forms (tubes, wire, mesh, powder, etc.)[287] can be used to regenerate $\text{Cu}^{\text{I}}/\text{L}$ by both reduction of $\text{Cu}^{\text{II}}/\text{L}$ via comproportionation and by supplemental activation of alkyl halides.[29] The advantage of using the heterogeneous reducing agent is the ability to easily remove it from the polymerization

medium upon reaction completion. The rate of Cu^{II} reduction, and thus the rate of polymerization, can be adjusted by the type and amount of the reducing agent, temperature, or by slow feeding.[35]

When employing any additive in an ATRP reaction, their reactivity towards all components in the reaction medium has to be considered. In ARGET ATRP (cf. **chapter 2.2.2**), it must be ensured that both reducing agent and its oxidized product does not have a detrimental influence on the polymerization.[46] In ICAR ATRP (cf. **chapter 2.2.1**) thermal decomposition of conventional radical initiator leads to the formation of radicals which can reduce $\text{Cu}^{\text{II}}/\text{L}$, but can also initiate polymerization, resulting in decreased α -chain end functionality which can be introduced by substituted alkyl halides. The effect of the amount thermal radical initiators on the MW and livingness of the system was investigated in detail by Zhu, et al.[288] Alternatively, external stimuli such as light or electric current can be utilized as a “cleaner” solution. However, photoATRP still requires the use of an excess of ligand, or other free aliphatic amine, e.g. triethylamine, and *e*ATRP requires the use of salts to increase ionic conductivity. The addition of excess of ligand can be advantageous as it ensures complete complexation of the Cu catalyst. The addition of salts in *e*ATRP, especially in aqueous media can be beneficial, since added NaCl or NaBr can both increase conductivity and prevent deactivator dissociation (cf. **chapter 9** and **Equation 9**).

11. Solvents

Due to its radical nature ATRP can be conducted in a wide range of solvents.[289] In addition to common organic solvents, water,[39, 177, 290] ionic liquids,[291-293] alcohols,[289] supercritical CO_2 ,[294] or poly(ethylene oxide)[295] were used. ATRP was also shown to work at low pH, provided that appropriate ligands are employed.[89] ATRP can also be carried out in heterogeneous media[19, 22, 23, 118, 253] if precautions are made to guarantee the presence of radicals and the $\text{Cu}^{\text{II}}/\text{L}$ deactivator species in the same phase, to ensure efficient deactivation (cf. **chapter 11.1**).[253]

Solvent effects are typically insignificant in conventional radical polymerization. They usually arise from the changes of propagation rate coefficient.[296, 297] However, the presence of water might accelerate polymerization of certain monomers such as (meth)acrylic acid,[297]

or acrylamides.[298, 299] Additionally, termination rate coefficient can be affected due to changes of reaction viscosity upon addition of solvent.[300] This effect is of particular importance during the polymerization of macromonomers, where solvation of the growing polymer chains can play a significant role on the termination reaction.[195, 301]

When conducting ATRP reactions, one needs to consider solubility of all involved components in the reaction medium, i.e. the initiator, monomer, growing polymer, and both oxidation states of the catalyst. For example, $\text{Cu}^{\text{II}}/\text{bpy}$ has limited solubility in nonpolar solvents, which leads to precipitation of excess of the deactivator complex. This can cause limited control over the polymerization. Typically the amount of solvent added to the reaction should be minimized in order to preserve high chain end functionality (cf. **Equation 8** and **chapter 6**).[34] However, under some circumstances the presence of solvent is required, e.g. to lower the viscosity or to ensure homogeneity of the reaction medium. For instance, bulk polymerization of acrylonitrile is unfeasible, due to insolubility of high MW polyacrylonitrile in its own monomer.[302, 303] Bulk polymerization of MMA up to high monomer conversions is challenging due to the depletion of the monomer and transition of the polymer into the glassy state.[288, 304] Progressively increasing viscosity of the reaction mixtures may lead to diffusional limitations of ATRP elemental reactions. Due to the very high reactivity of radical species, biradical termination reactions are typically diffusion controlled. However, other fast reactions such as deactivation of radicals by $\text{X}-\text{Cu}^{\text{II}}/\text{L}$ complexes might also face similar diffusional limitations as viscosity of the medium increases. This can lead to a loss of control over the polymerization. In some cases, when the system becomes glassy, even the propagation reaction can become diffusion controlled. Since termination, deactivation, and propagation are competitive reactions, the diffusional limitations can significantly influence the outcome of the polymerization.[304] Therefore, presence of a solvent is often desired to overcome these limitations. On the other hand, removal of the solvent from the product might be difficult and costly.

If ATRP is conducted at an elevated temperature, boiling point of the solvent has to be considered. In polymerization of macromonomers, or monomers with bulky functional substituents, initial monomer concentration should be carefully designed due to the possible proximity to the equilibrium monomer concentration.[195] Furthermore, the chosen solvent

should not interfere with the reaction. Solvents that could induce transfer, or could be active in an ATRP (e.g. CHCl_3) should be avoided.

Despite the minor influence of solvents on standard radical reactions, a significant acceleration of ATRP was observed in the presence of polar organic solvents, e.g. DMSO.[289] This can be attributed to the preferential stabilization of the more polar $\text{Cu}^{\text{II}}/\text{L}$ complexes, over the less polar $\text{Cu}^{\text{I}}/\text{L}$ counterparts. The effect of solvents on the K_{ATRP} is presented in **Figure 13**. Faster polymerization rates are particularly pronounced in the presence of water.[78, 305] However, aqueous media present several challenges that have to be considered. First, the values of both activation rate coefficients (k_{act})[62, 306] and ATRP equilibrium constants (K_{ATRP})[137] are very high in the presence of water. This leads to a high concentration of radicals and thus high rate of termination. Therefore, in normal ATRP, large amounts of $\text{Cu}^{\text{II}}/\text{L}$ relative to $\text{Cu}^{\text{I}}/\text{L}$ should be added to suppress radical generation. In low ppm ATRP techniques (cf. **chapter 2.2**), highly active ligands should be used to ensure that the majority of the Cu species is present in the form of the $\text{Cu}^{\text{II}}/\text{L}$ deactivator. Additionally, to slow down generation of radicals, instead of adding reducing agents at the onset of the reaction, they can be continuously fed into the reaction mixture to generate and maintain a low concentration of the $\text{Cu}^{\text{I}}/\text{L}$ complex.[39]

Figure 13. Predicted vs. Experimental values of $\log(K_{\text{ATRP}})$ in the presence of various solvents. Reproduced with permission from ref. [289]

Furthermore, halidophilicity, i.e. association of the halide anion to the Cu^{II} complex, is typically low in aqueous media (cf. **chapter 9** and **Equation 9**). Finally, Cu^{I} complexes are

prone to disproportionate in aqueous media. Generally, disproportionation is more favored in more polar solvents, with several exceptions. Solvents that bond to Cu^{I} , such as sulfoxides (e.g. DMSO), or nitriles (e.g. MeCN) effectively prevent disproportionation.[64] The extent of the disproportionation can also be tuned by the choice of ligand. Complexes with high $\text{Cu}^{\text{I}}/\text{L}$ and $\text{Cu}^{\text{II}}/\text{L}$ stability constants (β^{I} and β^{II} , respectively) can form active and non-disproportionating ATRP catalysts (e.g. TPMA). This is because activity of the catalyst is proportional to $\beta^{\text{II}}/\beta^{\text{I}}$, while the extent of disproportionation is proportional to $\beta^{\text{II}}/((\beta^{\text{I}})^2[\text{L}])$. [267] The latter relationship also means that disproportionation can be tuned not only by the type, but also by the amount of the free ligand. Despite these challenges, multiple aqueous ATRP techniques have been shown to be efficient methods to obtain well-defined polymers in a short time frame.[39, 62, 83, 88, 95]

11.1. ATRP in Dispersed Media

In addition to a wide variety of solvents, including water, ATRP was successfully applied in aqueous dispersed media. Such processes are of particular interest for industrial applications, since they offer lower reaction viscosity, improved heat dissipation, and an environmentally friendly alternative to volatile organic solvents.[255, 307] Nonetheless, conducting ATRP in dispersed media possesses additional challenges and requires cautious reaction planning. Most notably this involves issues with partitioning of the catalyst between the organic and aqueous phase, which in addition may be different for $\text{Cu}^{\text{I}}/\text{L}$ and $\text{Cu}^{\text{II}}/\text{L}$. [253, 308] Ligands commonly utilized for homogeneous low catalyst concentration ATRP, such as Me_6TREN or TPMA, are typically unsuitable for dispersed media, because their $\text{X}-\text{Cu}^{\text{II}}/\text{L}$ complexes show much higher affinity towards aqueous phase. Migration of the deactivator species out of the organic phase results in an inefficient radical deactivation and thus in an uncontrolled reaction. Therefore, more hydrophobic ligands such as bis(2-pyridylmethyl)octadecylamine (BPMODA) were employed for dispersed media. They contain long alkyl chains, effectively reducing catalyst solubility in aqueous phase. Moreover, it has to be ensured that all additionally introduced components, e.g. surfactants or stabilizers do not interfere with the polymerization process, while simultaneously forming stable dispersions. Finally, the reducing agent should be able to rapidly and efficiently reduce $\text{Cu}^{\text{II}}/\text{L}$ back to the $\text{Cu}^{\text{I}}/\text{L}$ activator.

Well-defined latexes were prepared by ATRP in emulsion,[261, 309-313] miniemulsion,[19, 22, 23, 118, 253, 308, 314-317] and microemulsion.[257, 259, 260] Further development of miniemulsion systems allowed to obtain polymers with very high MW[318] and to significantly reduce catalyst concentration *via* an appropriate ligand design.[253] ATRP was also successfully carried out in suspension[319, 320] and in inverse miniemulsion.[321, 322] Most recently, electrochemical control over ATRP in miniemulsion was achieved.[323] This was realized by a dual catalyst system, comprising of both aqueous and organic phase catalyst. Such approach allowed to efficiently transfer electrochemical stimulus through the continuous aqueous phase to the organic monomer droplets. Interestingly, the reaction rates in the dual catalyst system were dictated not by the catalyst redox potential but by the hydrophobicity and partition coefficient of the aqueous phase catalyst.

12. Copolymerization

ATRP and other RDRP methods provide a versatile toolbox that expands the compositional capabilities for the preparation of copolymers. In contrast to the conventional radical polymerization (RP), which typically offers only homopolymers and statistical copolymers, ATRP allows for synthesis of block, periodic, and gradient structures. Cross-propagation of monomers in ATRP and RP are essentially the same, i.e. reactivity ratios of comonomers are nearly identical.[324, 325] However some minor differences have been observed in copolymers prepared via ATRP and RP, which are typically attributed to competitive equilibria.[326]

Block copolymers are prepared by synthesis of a first block, which subsequently is used as a (macro)initiator for a second block. This can be done both with a purification step between the two steps, or in one pot by sequential monomer injection, provided that the initial polymerization reaches high monomer conversion. Otherwise, the sequentially formed block would be a statistical copolymer of the leftover monomer from the first block and newly introduced monomer. Synthesis of block copolymers requires high preservation of chain end functionality (cf. **chapter 6**) as well as efficient reinitiation (cf. **chapter 8**). Thus, reactivity of the chain end has to be considered. In ATRP the reactivity is based on a combination of steric and polar effects and follows the order: acrylonitrile > methacrylates > styrene $\approx$ acrylates > acrylamides.[237] If this order of the monomers cannot be followed, a technique named halogen exchange can be

used (cf. **chapter 8** and **Figure 9**).[238] This allows efficient preparation of block copolymers starting from a less active macroinitiator and a more active monomer. The potential of ATRP for production of segmented copolymers was recently highlighted by the preparation of multiblock structures, e.g. a decablock copolymer.[327, 328]

ATRP can also be efficiently combined with other polymerization or post-polymerization methods for preparation of copolymers with complex architectures.[329-331] Click chemistry was successfully employed for preparation of a variety of macrocyclic, block, star, and graft copolymers.[161, 332-340] Concurrent or consecutive ATRP and ring-opening,[341-344] ring-opening metathesis,[345] or cationic[346, 347] polymerization reactions were reported. Furthermore, ATRP can be conducted from macroinitiators prepared via different methods: step-growth,[348] cationic,[349] anionic,[200, 350, 351] coordination,[352] ring opening,[202, 353] conventional radical polymerization,[196] or utilizing two RDRP methods.[354]

The preparation of gradient copolymers is also possible using ATRP.[355] The requirements are efficient initiation, concurrent growth of all polymer chains, and effortless cross-propagation: features provided only by the RDRP methods. In gradient copolymers, the polymer composition varies continuously from one chain end to the other.[130, 356] This can be achieved either in a spontaneous manner, basing solely on the reactivity ratios of the comonomers,[357, 358] or in a forced way, by continuously feeding of one of the monomers into the reaction medium.[315, 359] The latter method is often preferred due to the higher degree of control over the polymer microstructure by programming the comonomer feed ratios.[360, 361] Due to their very broad glass transition temperatures, gradient copolymers find applications as sound or vibration dampening materials.[362]

13. Measuring Parameters of Catalytic Systems

The kinetic parameters of the system have to be determined in order to understand the fundamentals of the ATRP mechanism. Since ATRP reactions involve multiple components, and often competitive equilibria,[326] simultaneous measurement of all of the reaction rate coefficients is difficult. However, the contributing reactions can be isolated and studied separately in order to obtain kinetic parameters. Afterwards, all components can be combined into a compound, comprehensive model. Such a methodology was previously shown to allow for

an in-depth understanding of the underlying processes and their contributions to the ATRP reaction.[17, 35, 62, 68, 115, 116, 134-136, 144, 361, 363-368]

13.1. ATRP Equilibrium Constants (K_{ATRP})

The value of ATRP equilibrium constant ($K_{\text{ATRP}} = k_{\text{act}}/k_{\text{deact}}$) increases with the strength of the X–Cu^{II}/L bond, and decreases with the strength of the C–X bond, i.e. it depends on the halogenophilicity of the Cu^I/L complex.[239] An ATRP equilibrium (cf. **Equation 3**) is maintained in essentially all ATRP systems.[10] Therefore, K_{ATRP} can be easily measured, if relatively high concentrations of [Cu^I/L], [X–Cu^{II}/L] and [RX] are used, which do not change due to the small extent of radical termination.[251] The concentration of radicals ([R[•]]) can be readily determined by following the monomer conversion over time (cf. **Equation 2**), since propagation rate coefficients (k_p) are known from literature.[369-382] The miniscule changes in [X–Cu^{II}/L] due to unavoidable radical termination, as well as monomer conversion can be conveniently simultaneously monitored with a UV-Vis-NIR spectrophotometer.[383] A wide array of K_{ATRP} values obtained in this manner are available in the literature.[154, 383]

K_{ATRP} values can also be determined using the persistent radical effect (PRE), by measuring the amount of accumulated Cu^{II} deactivator species (**Equation 10**), e.g. via UV-Vis spectrophotometry.[25, 384, 385]

$$\begin{cases} Y = (6k_t K_{\text{ATRP}}^2 I_0^2 C_0^2)^{1/3} t^{1/3} \\ R = \left(\frac{K_{\text{ATRP}} I_0 C_0}{6k_t} \right)^{1/3} t^{-1/3} \end{cases}$$

Equation 10. Equations for calculation of ATRP equilibrium constant (K_{ATRP}) from persistent radical effect (PRE). Y = Cu^{II}, R = R[•], C = Cu^I, and I = R–X

The increase of the Cu^{II} deactivator species should be linear with $t^{1/3}$ and the loss of the radicals (R) should be linear with $t^{-1/3}$. This method is particularly appropriate for systems in which values of termination rate coefficients (k_t) are diffusion controlled.[386] However, **Equation 10** precisely describes PRE only up to ≈10% conversion of Cu^I to Cu^{II}, and thus can only be applied for determination of relatively low K_{ATRP} values. Therefore, the equations were

appropriately modified to account for formation of large amounts of Cu^{II} (**Equation 11**).[386, 387]

if $C_0 \neq I_0$:

$$F(Y) = \left(\frac{I_0 C_0}{C_0 - I_0} \right)^2 \left(\frac{1}{C_0^2 (I_0 - Y)} + \frac{2}{I_0 C_0 (C_0 - I_0)} \ln \left(\frac{I_0 - Y}{C_0 - Y} \right) + \frac{1}{I_0^2 (C_0 - Y)} \right)$$

if $C_0 = I_0$:

$$F(Y) = \frac{C_0^2}{3(C_0 - Y)^3} - \frac{C_0}{(C_0 - Y)^2} + \frac{1}{C_0 - Y}$$

Equation 11. Modified equations for calculation of ATRP equilibrium constant (K_{ATRP}) from persistent radical effect (PRE). $Y = \text{Cu}^{\text{II}}$, $C = \text{Cu}^{\text{I}}$, and $I = \text{R-X}$

The plots of $F(Y)$ vs time should be linear, and the value of K_{ATRP} can be obtained from the slope ($K_{\text{ATRP}} = \sqrt{\text{slope} / 2k_t}$).

Finally, K_{ATRP} can be obtained from the ratio of the activation and deactivation rate coefficients ($k_{\text{act}}/k_{\text{deact}}$) obtained via various methods described in **chapters 13.2 and 13.3**.

13.2. Activation (k_{act})

Rate coefficients of activation of alkyl halides by Cu^I/L species (k_{act}) can be measured by a variety of chromatographic and spectroscopic techniques. This can be achieved by following the consumption of alkyl halides or Cu^I/L, or through the increase in concentration of X-Cu^{II}/L (**Scheme 12**). Usually, an excess of a radical trap, such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), is required to prevent the influence of the back reaction, i.e. deactivation of radicals by the X-Cu^{II}/L complex. Since concentrations of Cu^{II}/L and R[•] are typically relatively low, the deactivation reaction, as well as bi-radical termination should be negligible. Therefore, the formed radicals are nearly quantitatively trapped with TEMPO. Furthermore, thermal dissociation of the resulting alkoxyamines (R-TEMPO) is rather slow at the temperatures employed for the measurements and should not contribute to the system.[388]

Scheme 12. Methodology of the activation rate coefficient measurement.

Values of k_{act} were determined using size exclusion chromatography (SEC) by monitoring the consumption of a polymeric macro(alkyl halide) in time.[389] Similarly, ^1H NMR, GC, and HPLC were used to follow the decrease in the concentration of R-X, which was converted to an alkoxyamine (R-TEMPO).[213, 388, 390-395] UV-Vis spectrophotometry was employed to track concentration of X-Cu^{II}/L deactivator.[396] Unfortunately, the limitations associated with these techniques enforce a maximum upper limit on the measurable rate coefficients of about 2 M⁻¹ s⁻¹. [397] Highly reactive alkyl halides and/or highly active Cu^I/L complexes require implementation of other procedures. Owing to fast mixing times and rapid UV-Vis spectrum collection, a stopped-flow method was successfully implemented.[397] Furthermore, electrochemical techniques can be used.[398] Potential step chronoamperometry at a rotating disk electrode allows to follow the consumption of Cu^I. [73, 398, 399] Cyclic voltammetry allows calculation of k_{act} by fitting the simulated voltammograms to the experimental data.[76, 400] Finally, k_{act} can also be estimated using regression analysis.[138, 401]

A large collection of data measured using the aforementioned methodologies is available in the literature, for a variety of alkyl halides and Cu^I/L complexes.[154, 213, 392] It is worthwhile noting that rate coefficients of alkyl halide activation by Cu^I/L are often expressed as apparent rate coefficients, without consideration of speciation. The effect of solvent,[306, 391, 394, 402, 403] temperature,[396] monomer,[402] counterion,[402-404] Cu^{II}/L concentration,[393] penultimate unit,[405] and [ligand]/[Cu^I] ratio[394, 402, 403] were meticulously evaluated. The values typically range from as low as 10⁻⁵ M⁻¹ s⁻¹ up to 10⁵ M⁻¹ s⁻¹. [154]

13.3. Deactivation (k_{deact})

Determination of deactivation rate coefficients (k_{deact}) is significantly more difficult due to very high values, approaching diffusion controlled limits ($k_{\text{deact}} \approx 10^7 - 10^8$ M⁻¹ s⁻¹).

Furthermore, quantification of the radical concentration, or its isolation is impeded by the rapid rate of self-termination reactions. For this reasons, the vast majority of data currently available from the literature originates not from direct measurement but rather from calculations using activation rate coefficients (k_{act}) and the corresponding ATRP equilibrium constants (K_{ATRP}). Nevertheless, several methods do exist that allow for direct determination of k_{deact} values.

One method utilizes determination of the initial degrees of polymerization.[406] Herein, a reverse ATRP methodology is applied (cf. **chapter 2.1**), in which a conventional radical initiator such as AIBN is thermally decomposed at the onset of the reaction. The generated radicals ($\text{R}^\bullet$) react with the monomer before they are quickly deactivated by $\text{X-Cu}^{\text{II}}/\text{L}$. The generated $\text{Cu}^{\text{I}}/\text{L}$ complexes are rapidly oxidized by O_2 while the amount of radicals trapped by oxygen should be low, since $[\text{R}^\bullet]$ is much lower than $[\text{Cu}^{\text{I}}/\text{L}]$. This allows values for k_{deact} to be extracted by determining the degree of polymerization at low conversion.

Radical clock reactions utilize competitive deactivation of generated $\text{R}^\bullet$ by $\text{X-Cu}^{\text{II}}/\text{L}$ complex and a radical scavenger such as TEMPO.[388] The relative amounts of generated alkyl halide (R-X) and alkoxyamine (R-TEMPO) are quantified and used to calculate k_{deact} , based on the known rate coefficient of deactivation of radicals by TEMPO (k_{TEMPO}). The major setback of this method is the requirement for knowledge of accurate k_{TEMPO} values, which depend on solvent and structure of $\text{R}^\bullet$. Furthermore, reactions with low k_{deact} are difficult to follow due to significantly slower radical trapping by $\text{X-Cu}^{\text{II}}/\text{L}$ than by TEMPO.

A time-resolved single laser pulse-pulsed laser polymerization coupled with electron paramagnetic resonance (SP-PLP-EPR) can also be used.[407] In this procedure decay of the radicals in the presence of $\text{X-Cu}^{\text{II}}/\text{L}$ deactivator is measured. The change in radical concentration arises from termination and deactivation reactions. Reactivation of formed alkyl halides by $\text{Cu}^{\text{I}}/\text{L}$ was negligible under the conditions of the experiment.

Cyclic voltammetry (CV) can be utilized to determine both activation (k_{act}) and deactivation (k_{deact}) rate coefficients, which subsequently can be used to calculate $K_{\text{ATRP}} = k_{\text{act}}/k_{\text{deact}}$. [408] The technique relies on an electrochemical reduction of $\text{Cu}^{\text{II}}/\text{L}$ complex to the $\text{Cu}^{\text{I}}/\text{L}$ activator, which then quickly reacts with the alkyl halide. First, a CV is measured in the presence of a radical scavenger, such as TEMPO, to prevent any contribution from the deactivation reaction. A comparison of the experimental and simulated voltammograms allows determination of k_{act} .

Subsequently, another experiment is performed in the absence of TEMPO. The differences between the catalytic currents recorded in the presence and absence of the radical trapping agent allow for calculation of k_{deact} . Since this method simultaneously provides k_{act} and k_{deact} values it is also a viable route to obtain values of K_{ATRP} .

Deactivation rate coefficients can also be extracted from the kinetic plots of polymerizations and by measuring evolution of dispersity ($\mathcal{D}$) with monomer conversion (cf. **Equation 6** and **Equation 7**).[409-411] The values of k_{deact} vary to a much lower degree than those of k_{act} and are typically in the range of $10^7 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

13.4. Cu^0 activation (k_{a0})

Measurement of the activation rate coefficients of alkyl halides by Cu^0 (k_{a0}) is of the utmost importance for investigation of the RDRP in the presence of Cu^0 . Despite being a heterogeneous reaction, determination of the k_{a0} values is straightforward and can be achieved by following the evolution of the $\text{X-Cu}^{\text{II}}/\text{L}$ species via UV-Vis spectrophotometry.[61, 65, 67] This is because the subsequent activation of alkyl halide by the formed $\text{Cu}^{\text{I}}/\text{L}$ complex is significantly faster, rendering the Cu^0 activation the rate limiting step (**Scheme 13**). It is worthwhile noting that all reactions involving Cu^0 depend on the ratio of the surface area of the metal to the total reaction volume (S/V). Typically, Cu^0 wire is used due to straightforward calculation of surface area, assuming a cylindrical shape. Nevertheless, any other Cu^0 source can be used, provided that the surface area is known.

Scheme 13. Reactions relevant to activation of alkyl halides by Cu^0

k_{a0} values are measured from the initial slope of the increase of the $[X-Cu^{II}/L]$. During that time, comproportionation reactions are typically minimized due to a significantly lower $[X-Cu^{II}/L]$ compared to $[RX]$. Disproportionation is negligible due to its square dependence on Cu^I concentration and very low $[Cu^I/L]$ resulting from fast Cu^I activation. Finally, the total concentration of soluble Cu species can typically be approximated by $[X-Cu^{II}/L]$. As the reaction proceeds and RX is depleted, comproportionation surpasses initiation and a decrease in the $X-Cu^{II}/L$ absorbance can be observed, which eventually plateaus when the comproportionation/disproportionation equilibrium is reached (**Figure 14**). Importantly, Cu^0 activation is a relatively slow process, requiring minutes, or hours for completion, while analogous Cu^I activation reactions usually take less than a second to complete.[65]

Figure 14. Time-evolution of $[Cu^{II}]$ and $[MBrP]$ measured by UV-Vis spectroscopy and NMR, respectively. Conditions: 25 °C; $[Me_6TREN]_0:[MBrP]_0 = 15\text{ mM}:10\text{ mM}$ in DMSO; $V = 7\text{ mL}$; Cu^0 wire $l = 4\text{ cm}$, $S = 1.27\text{ cm}^2$, $S/V = 0.18\text{ cm}^{-1}$. Adapted with permission from ref. [65]

Under certain conditions, where comproportionation is significant, the concentration of Cu^{II} species increases exponentially with time at the onset of the reaction. In such a case, the contribution of comproportionation can no longer be neglected. Furthermore, especially in solvents providing low K_{ATRP} values, the total concentration of soluble Cu species might not be accurately approximated by $[X-Cu^{II}/L]$ due to the presence of non-negligible amounts of Cu^I/L . However, activation rate coefficients can still be extracted from the same experiments.[67]

Values of activation rate coefficients were determined for a variety of alkyl halides, ligands, and solvents.[61, 62, 65, 66, 412] Activation was found to be faster in solvents stabilizing Cu^{I} , i.e. $k_{\text{a0}} \text{ MeCN} > \text{DMF} > \text{DMSO}$, which is opposite of what was found for activation by Cu^{I} . [61] Furthermore, ligand choice played a minor role. Interestingly, rates of activation were never faster than those of comproportionation, even when the most active alkyl halides were used. This suggested the presence of a rate limiting step for activation and comproportionation reactions, which could involve desorption of the Cu^{I} formed at the surface of the Cu^0 . When less active alkyl halides were used, atom transfer should still be the rate limiting step. Recently, chain length dependence was also evaluated and found to be highly related to the viscosity of the system.[67, 412] k_{a0} values typically range from $10^{-4} - 10^{-2} \text{ cm s}^{-1}$. This range of ca. 2 orders of magnitude is significantly lower than that of the corresponding Cu^{I} activation rate coefficients (k_{act}), which span ca. 10 orders of magnitude. Due to the heterogeneous nature of the Cu^0 activation, k_{a0} values cannot be directly compared to k_{act} values. However, reaction rates (i.e. the product of rate coefficients and reagent concentrations) can be equated. Such an exercise shows, that in order to match very fast activation rates of 1 mM Cu^{I} /Me₆TREN, an unrealistic 2 km of Cu^0 wire ($d = 0.25 \text{ mm}$) is needed in 10 mL of DMSO/MA solution.[28] Such comparison is even more pronounced in aqueous media, where in order to match 1 μM Cu^{I} /Me₆TREN, 3 km of Cu^0 wire ($d = 0.25 \text{ mm}$) is required in 10 mL of water.[62] It should be stressed that those comparisons relate to corresponding activation rates by Cu^{I} and Cu^0 and not to global polymerization rates in the presence or absence of Cu^0 .

13.5. Disproportionation (k_{disp})

Disproportionation is a redox reaction between two identical species, one of which is oxidized, and other reduced, forming two distinct products. Herein, two Cu^{I} molecules disproportionate to yield Cu^0 and Cu^{II} . It is worthwhile noting that speciation is critically important, as various forms of Cu^{I} (e.g. Cu^{I} , X-Cu^{I} , $\text{Cu}^{\text{I}}/\text{L}$, $\text{X-Cu}^{\text{I}}/\text{L}$, etc.) may have significantly different redox potentials.[69] However, typically stability constants are not known and thus often measured values of disproportionation rate coefficients (k_{disp}) are apparent ones, i.e. not taking speciation into consideration.

Similar to Cu^0 activation rate coefficients, k_{disp} values can be directly measured by UV-Vis spectrophotometry. The method relies on recording rate of evolution of $\text{Cu}^{\text{II}}/\text{L}$ generated by disproportionation of two $\text{Cu}^{\text{I}}/\text{L}$ complexes.[64] One limitation is that if the extent of disproportionation is significant, the measurements can become hampered by the large amount of light scattering from precipitated Cu^0 particles. Alternatively, k_{disp} can be obtained indirectly by measurement of comproportionation rate coefficient (k_{comp}) and disproportionation equilibrium constant $K_{\text{disp}} = k_{\text{disp}}/k_{\text{comp}}$. [61, 64] Disproportionation can also be monitored electrochemically, using a rotating disk electrode to follow the rate of disappearance of Cu^{I} . [69]

Disproportionation can also happen in the presence of existing Cu^0 as a heterogeneous reaction. The rate of disproportionation depends on the ratio of the Cu^0 surface area to the total reaction volume (S/V). [64] K_{disp} is not affected by the Cu^0 surface area, but is highly influenced by the concentration of free ligand (L). Higher [L] shift the equilibrium towards comproportionation. Disproportionation was shown to be a slow reaction in common organic solvents used for an ATRP (DMF, DMSO, MeCN), [61, 64, 66, 69] requiring hours to reach equilibrium position, and overwhelmed by comproportionation. In contrast, disproportionation of many Cu^{I} complexes in pure water is thermodynamically favored and thus fast, with negligible comproportionation. However, the addition of monomer shifts the comproportionation/disproportionation equilibrium towards comproportionation. [62, 71] Furthermore, under polymerization conditions competitive activation of alkyl halides by Cu^{I} renders the instantaneous $[\text{Cu}^{\text{I}}]$ very low (in the order of μM). Since the rate of disproportionation depends on $[\text{Cu}^{\text{I}}]^2$, during polymerization its kinetic contribution to the system is negligible (cf. **chapter 2.2.3**). [62]

13.6. Comproportionation (k_{comp})

Comproportionation is the reverse reaction of disproportionation. Cu^0 reduces Cu^{II} , while simultaneously being oxidized, to yield two Cu^{I} molecules. It is worthwhile noting, that speciation is of particular importance, as comproportionation of $\text{Cu}^{\text{II}}/\text{L}$ vs. $\text{X}-\text{Cu}^{\text{II}}/\text{L}$ was shown to proceed with different rates. [61] However, due to lack of measured stability constants of Cu^{II} complexes, typically only overall apparent comproportionation rate coefficients (k_{comp}) are measured, without consideration of speciation.

Determination of k_{comp} is typically achieved by following the decay of $\text{X-Cu}^{\text{II}}/\text{L}$ concentration in the presence of a Cu^0 source, via the UV-Vis spectrophotometry.[61, 64] Although any form of Cu^0 can be used (powder, mesh, turnings, etc.), typically a wire is employed due to simplicity of determining the surface area, since the wire is assumed to be a perfect cylinder. Similar to disproportionation reactions, comproportionation is typically rather slow, requiring hours or minutes to reach equilibrium. Importantly, when comproportionation (starting from Cu^0 and Cu^{II}) and disproportionation (starting from Cu^{I}) reactions are performed under equivalent conditions, they reach the same equilibrium position, as expected.

Due to the heterogeneity of the reaction the rate of comproportionation is proportional to the ratio of the Cu^0 surface area to the total reaction volume (S/V). [64] Comproportionation studies in the presence of various ligands revealed that the influence of ligand structure on the k_{comp} is moderate. However, significant differences were observed between different solvents, which followed the solubility trend of Cu^{I} , i.e. k_{comp} in $\text{MeCN} > \text{DMF} > \text{DMSO}$. [61, 66] Furthermore, k_{comp} values were always larger than the activation rate coefficients and comparable only to the most active alkyl halides by Cu^0 under analogous conditions. This implied existence of a rate limiting step in both processes, which could comprise desorption of Cu^{I} formed at the Cu^0 surface into the contacting solution.

13.7. Addition of Radical to Monomer (k_{add})

Addition of carbon-centered radicals to alkenes is of particular importance for providing uniform and concurrent chain growth. The choice of the alkyl halide for a particular monomer is often dictated by the similarity in the structure of the initiating alkyl radical and growing polymeric radical. Therefore, 2-bromopropionitrile (BPN) is a common choice for polymerization of acrylonitrile, methyl 2-bromopropionate (MBrP) for methyl acrylate, and 1-phenylethyl bromide (PEBr) for styrene. In principle, ethyl α -bromoisobutyrate (EBiB) could be a good model for methyl methacrylate but it is ca. 10 times less active due to penultimate unit effect in PMMA.[236] Addition of the initially formed radical to the monomer should generally be equally fast or faster than propagation.[413] This allows for rapid conversion of all initiator species into concurrently growing polymer chains. Slow addition, combined with high termination rate coefficients typically observed for low-molar-mass initiators can lead to early

termination. This results in a decrease of the amount of introduced initiator and thus deviation from the targeted degree of polymerization (cf. **chapter 4**). Rate coefficients of addition of radicals to monomer (k_{add}) are typically measured by following the radical concentration via electron paramagnetic resonance (EPR) spectroscopy.[413-415]

13.8. Propagation (k_p)

Propagation rate coefficients (k_p) are measured using the IUPAC-recommended pulsed-laser polymerization coupled with size-exclusion chromatography (PLP-SEC) method. In PLP-SEC, a sequence of laser pulses is applied over regular time intervals to a solution of photoinitiator, monomer, and optionally a solvent.[416, 417] The pulse results in decomposition of the photoinitiator and formation of a generation of radicals. During the time interval between the laser pulses, radicals propagate with the monomer. A subsequent pulse forms a new generation of radicals, some of which terminate with the previous generation. Only a few radicals survive and propagate further until they are eventually terminated by radicals formed by one of the following pulses. This process is repeated multiple times and the resulting polymers are analyzed by SEC (also: gel permeation chromatography, GPC). The molecular weight distributions show several generations of polymers, which are attributed to radical generations that survived different number of laser pulse iterations. Based on the precisely determined molecular weight and known “dark time” between laser pulses, propagation rate coefficients can be evaluated. The technique, introduced by Olaj et al.,[418] was shown to be very reliable and reproducible between various laboratories and experimental setups.

A large collection of data obtained this way is available in the literature for a variety of monomers such as styrene,[369] acrylates,[377, 419] methacrylates,[370, 372, 376] (meth)acrylic acid,[420-423] acrylonitrile,[379] *N*-vinyl pyrrolidone,[419] and many others. The general trend follows the order of styrene < methacrylates < acrylonitrile < acrylates. The caveat of the method is associated with the necessity to accurately determine the molecular weight of the polymers. Since assortment of available SEC polymer standards is limited, this often requires careful measurement of the Mark–Houwink–Kuhn–Sakurada (MHKS) parameters of the analyzed polymers.[424]

13.9. Termination (k_t)

Termination rate coefficients (k_t) can be measured by a variety of methods.[425] Historically, k_t was determined from the rate of a conventional radical polymerization, assuming steady state concentration of radicals. This method requires accurate knowledge of propagation rate coefficients and properties (decomposition rate coefficient and efficiency) of thermal radical initiators. Some other methods include fitting of molecular weight distributions[425] or following radical concentration by EPR spectroscopy.[426] A recently developed technique utilizes single pulse pulsed laser polymerization coupled with electron paramagnetic resonance spectroscopy (SP-PLP-EPR).[427, 428] In SP-PLP-EPR a single laser pulse generates a burst of radicals and their decay due to termination is followed by a time-resolved EPR apparatus.

Rates of biradical termination reactions are diffusion controlled. Therefore, the degree of monomer conversion, polymer chain length, and viscosity of the system have critical influence on the k_t values.[300] A large collection of data, including chain-length dependent equations, is available in the literature.[429-433] The values typically range between $10^6 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Developing conditions that result in a decrease in termination events is crucial in ATRP for high preservation of chain end functionality (CEF, cf. **chapter 6**). In addition to biradical termination, propagating radicals can also directly react with $\text{Cu}^{\text{I}}/\text{L}$ complexes, yielding $\text{R}-\text{Cu}^{\text{II}}/\text{L}$ species.[33, 163] This organometallic compound can either dissociate back to $\text{R}^\bullet$ and $\text{Cu}^{\text{I}}/\text{L}$ similar to organometallic-mediated radical polymerization (OMRP), or undergo catalytic radical termination (CRT) forming dead chains and regenerating $\text{Cu}^{\text{I}}/\text{L}$. [124] Indeed, a significant retardation in rate of conventional radical polymerization was observed in the presence of $\text{Cu}^{\text{I}}/\text{L}$ complexes.[124, 264] The extent of CRT is dependent on the structure of the chain end and its affinity to $\text{Cu}^{\text{I}}/\text{L}$ to form an organometallic species. The reaction is especially pronounced for acrylates and much slower for polymerization of methacrylates or styrene.[33] It was also found to be highly dependent on the structure of the ligand.[124]

In order to precisely describe CRT process, rate coefficients of addition of radicals to $\text{Cu}^{\text{I}}/\text{L}$, [434] dissociation of $\text{R}-\text{Cu}^{\text{II}}/\text{L}$, and termination of $\text{R}-\text{Cu}^{\text{II}}/\text{L}$ should be known. Since independent determination of all three rate coefficients is challenging, often only overall apparent CRT rate coefficients are measured. This was done e.g. under polymerization

conditions by following monomer consumption along with $\text{Cu}^{\text{II}}/\text{L}$ concentration[33] or molecular weight evolution.[124] The obtained rate coefficients are much lower than the diffusion controlled biradical termination rate coefficients observed in a standard radical polymerization and typically range between $10^1 - 10^4 \text{ M}^{-1} \text{ s}^{-1}$. However, due to much higher $[\text{Cu}^{\text{I}}/\text{L}]$ compared to $[\text{R}^{\bullet}]$, CRT accounts for the majority of terminated chains in an ATRP of acrylates, especially at high catalyst concentration.[124]

13.10. Other: Cu^{II} Reduction (k_{red}), Transfer (k_{tr}), Backbiting (k_{bb}) Constants

Precise description of ATRP systems requires knowledge of contribution of all relevant reactions to the overall process. Among them, reduction of $\text{Cu}^{\text{II}}/\text{L}$ is particularly important for most processes utilizing ppm amounts of catalyst (cf. **chapter 2.2**) due to the dependence of the rate of polymerization on this reaction (cf. **chapter 3.2**). Rate coefficients of reduction (k_{red}) can conveniently be measured by following the $\text{Cu}^{\text{II}}/\text{L}$ concentration over time. This was shown for reduction by Cu^0 (cf. **chapter 13.6**), Ag^0 , [40] or photochemical reduction.[92] In eATRP, k_{red} can be determined by following the change of current with time.[77] k_{red} values depend on the nature of the complex (halide and ligand), solvent, and type of external stimuli (e.g. light wavelength, intensity, distance from the light source). It should be mentioned, that majority of the available values are overall apparent rate coefficients that do not consider speciation of $\text{Cu}^{\text{II}}/\text{L}$ complexes. In ICAR ATRP, rate of polymerization depends on the rate of decomposition of the thermal radical initiator. The decomposition rate coefficients (k_{dc}) for many compounds in various solvents and temperatures are tabulated in the literature.[435]

During the polymerization of acrylates, a mid-chain radical can be formed via a six-membered ring intramolecular chain transfer to polymer.[381, 436-440] This reaction, commonly referred to as backbiting, transforms a secondary propagating radical into a tertiary mid-chain radical, which leads to creation of branching points. The contribution of backbiting was shown to be more pronounced at elevated temperatures. Since the two distinct radicals have different nature, their propagation and termination rates are dissimilar, effectively influencing propagation kinetics. Electron paramagnetic resonance (EPR) spectroscopy is typically employed for quantification of the backbiting reaction. Tertiary radicals generated by backbiting can subsequently add to the acrylate monomer creating a branch point and reforming a secondary

radical. Interestingly, in ATRP and other RDRP processes, due to the presence of the deactivation step competitive equilibria can suppress branching via deactivation of the tertiary radicals.[139] Indeed, significantly lower branching fractions were observed in polymerizations of butyl acrylate via RAFT, ATRP, or NMP compared to conventional radical polymerization.[441] Tertiary deactivated species were found in NMR spectra of polymers prepared by NMP,[442] but not in those synthesized by ATRP.[443] However, it should be mentioned that the concentration of the tertiary species should be very low (<1%), therefore its determination via NMR spectroscopy might be subject to the instrument error.[326] An alternative explanation for the reduced fraction of branching in RDRP suggested that very short transient radical lifetime minimizes the probability of backbiting.[444]

Finally, since ATRP is a radical-based process, other transfer reactions are also possible, such as transfer to monomer, solvent, ligand, etc. Transfer reactions lead to decrease in molecular weight and can cause a retardation in polymerization rate. Typically, transfer reactions in ATRP are minimized, unless a chain transfer agent is intentionally introduced.[445, 446] This is both due to the relatively low rate coefficients (k_{tr}) for the selected monomers/solvents, and due to the low concentration of radicals and additives such as ligands.

14. Effect of temperature

Temperature affects various reactions involved in the ATRP process to a different degree. Generally, higher temperature leads to a faster polymerization rate due to the increase in propagation rate coefficient (k_p , cf. **chapter 13.8**). Termination reactions have significantly lower activation energies as compared to propagation. Therefore, while higher temperature results in an increase in k_p , only a minor increase of termination rate coefficient (k_t , cf. **chapter 13.9**) is observed.[447, 448] This increases the k_p/k_t ratio which can lead to improved chain end functionality (cf. **chapter 6**). Activation rate coefficients (k_{act} , cf. **chapter 13.2**) as well as ATRP equilibrium constants (K_{ATRP} , cf. **chapter 13.1**) also increase with temperature,[394, 396] while deactivation rate coefficients (k_{deact} , cf. **chapter 13.3**) are fairly constant. Recently, it was shown that a gradual increase of temperature in bulk ICAR ATRP of MMA can lead to high monomer conversion, while maintaining narrow MWD.[449]

Conducting ATRP reactions at high temperatures requires careful consideration of all possible adverse effects. For example, temperature can typically only be increased within a limited range. Since complexation of Cu is an exothermic process, increased temperature leads to a decreased stability of the catalyst in both oxidation states.[450] Furthermore, boiling points of monomer and all involved solvents have to be considered. Additionally, at higher temperatures the contribution of the undesirable side reactions becomes more significant. For example, polymerizations of acrylates suffer from an increased rate of chain transfer reactions (i.e. backbiting, cf. **chapter 13.10**), whereas styrene tends to self-initiate polymerization,[451, 452] and methacrylates can depropagate.[453] One also has to consider thermodynamic limitations of the monomer, i.e., the ceiling temperature (T_c) and equilibrium monomer concentration ($[M]_e$).[195, 208-211] This is of particular importance for polymerization of macromonomers, or monomers with bulky functional substituents. While the solubility of the reaction components is often improved at higher temperatures, certain polymers (e.g. poly(*N*-isopropylacrylamide)) exhibit lower critical solution temperature (LCST) behavior, and such polymerizations often require low temperature conditions for good control.[83, 88, 454, 455]

15. Effect of pressure

Increasing the pressure has a positive influence on ATRP reactions. However, reaching an appropriately high pressure typically requires a dedicated piece of specialized equipment and is more difficult to achieve compared to temperature adjustments.[456] In order to evaluate the effect of pressure on particular component of ATRP, the volume of activation of the reaction ($\Delta V^\ddagger$) has to be considered. A negative value of $\Delta V^\ddagger$ indicates that the volume of the transition state is lower than that of the reactants. In such a case, an increase of pressure accelerates the reaction. Propagation has a negative $\Delta V^\ddagger$, while termination has a positive $\Delta V^\ddagger$ (attributed to the increased solution viscosity under high pressure). Therefore, conducting the polymerization at elevated pressure results in a desirable increase in k_p/k_t ratio, resulting in better preservation of chain end functionality (cf. **chapter 6**) and improved synthesis of high molecular weight polymers.[117, 457, 458] Furthermore, since termination reactions are minimized, ATRP under high pressure can be conducted with low catalyst concentration, avoiding the persistent radical effect (PRE)[25, 26] and the need for reducing agents.[459] It is worth mentioning that

application of excessively high pressure might result in vitrification of the reaction mixture, effectively halting the polymerization.

High pressure additionally increases the ceiling temperature of the monomer, and decreases the equilibrium monomer concentration, rendering it a particularly attractive technique for polymerization of macromonomers.[195] Furthermore, ATRP equilibrium constants (K_{ATRP}) were increased with pressure in Cu-mediated ATRP.[460-462] While using Fe-based catalysts, the pressure dependence was governed by the nature of the catalyst. Iron halide catalysts without external ligands showed a decrease of K_{ATRP} with pressure.[463, 464] However, in the presence of certain ligands, such as chloro-substituted amine-bis(phenolate) K_{ATRP} increased with pressure.[465]

16. Industrial processes and applications

Availability of the reaction components, possibility to tailor the polymer structure, and a straightforward reaction setup led to successful commercialization of the process. ATRP has been subject of 16 industrial licenses, and is being used for large scale production of block, graft, telechelic, and other architecture (co)polymers, with various compositions.[466] For example, Kaneka Corporation operates a full-scale plant to produce telechelic polyacrylates for the use as high-performance heat, oil, and UV-resistant sealants and adhesives. ATRP Solutions successfully prepared well-defined polymers with star architecture. The entire process was conducted at a 750-gallon scale in standard Pfaudler glass lined reactors and took less than 12 hours, including charging and rinse out time. Excellent reproducibility was demonstrated over 20 consecutive runs.

Nevertheless, upscaling of ATRP meets some challenges. Lack of removal of inhibitors from monomers may lead to lower quality of the products. Efficient heat dissipation is critical, especially when thermal radical initiators are used (cf. ICAR ATRP, **chapter 2.2.1**). Finally, depending on the targeted application, removal of the catalyst might be of importance, although recently developed methods allowed for significant decrease in the catalyst loadings. Some of the challenges were addressed by ATRP Solutions in a technique named Ultimate ATRPSM. [36] In this method, the system operates under the same principle as ICAR ATRP, however the process is ran at much higher temperature (e.g. 100°C). Under these conditions, the half-lifetime of

thermal radical initiators is typically low (e.g. AIBN ~5 min at 100°C vs. ~10 h at 65°C). Therefore, they are slowly fed into the reactor, decompose promptly, and regenerate the catalyst. Since instantaneous concentration of thermal radical initiator is very low, Ultimate ATRPSM provides better control over the process and some degree of safety. This is because upon the interruption of the feeding, the polymerization shortly ceases.

ATRP was successfully conducted in a variety of reactor systems. Batch reactors are often studied due to their simplicity. However, they offer limited control over the polymerization due to all reagents being supplied to the reactor at once.[467] Semibatch reactors offer increased control over the copolymer composition, as well as better reaction rate and temperature control.[133, 468] Use of continuous reactors (e.g. tubular) permits facile synthesis of polymers with controlled microstructure.[469, 470] This is achieved by carefully distributing the feed streams along the reactor and adjusting the flow rate. Furthermore, tubular reactors offer efficient control over the reaction temperature, and if required can relatively easily be operated under pressure. Finally, a continuous stirred tank reactor (CSTR) system can be used. Due to lower degree of fouling, these reactors are sometimes preferred in industrial settings over tubular reactors.[469]

In addition to normal ATRP, activator regeneration methods were also successfully used. SARA ATRP and ARGET ATRP were employed in both CSTR[471, 472] and tubular reactors,[473, 474] including ones made of Cu⁰ tubing.[475] Finally, microflow reactors were also studied and gained attention due to ease in scale up.[476] They are particularly interesting for upscaling of photoATRP, due to otherwise limited depth of light penetration in batch processes.[477]

17. Outlook

An in-depth mechanistic understanding of ATRP was acquired over the past two decades. This was achieved through a systematic evaluation of structure-property relationships of initiators, catalysts, ligands, additives, and monomers. Furthermore, detailed investigation of the effect of temperature, solvent, and pressure on the system was conducted. Multiple methodologies were applied to reduce the transition metal concentration by employing various reducing agents, external stimuli, or using photoredox catalysts. All the accumulated information

allows for rational design of more active systems, which should allow for a further decrease in the catalyst loading. Simultaneously, many adverse side reactions were identified, analyzed, and quantified. However, many challenges, such as an efficient ATRP of vinyl acetate, still remain unresolved.

Detailed mechanistic studies led to improved understanding of the fundamentals of the ATRP process which allows to synthesize materials with higher degrees of chain end functionality (CEF). In order to suppress termination events and retain high CEF, appropriate reaction conditions should be selected. Universal conditions applicable for a variety of monomers are attractive due to simplicity in performing a reaction. However, they should be treated with caution, as optimization of reaction conditions for particular monomer should lead to a better defined product with narrow MWD and high CEF. Proper reaction conditions depend on the nature of the monomer, particularly the propagation and termination rate coefficients (k_p and k_t , respectively), but also on the targeted degree of polymerization, monomer conversion, and initial monomer concentration. Furthermore, both catalyst and initiator should be appropriately paired with the monomer. Initiators providing efficient and rapid initiation allow for simultaneous growth of all polymer chains and in turn narrow molecular weight distributions. The latter also requires the presence of a sufficient amount of deactivator species. In normal ATRP the deactivator can be formed *in situ via* termination reactions (i.e. the persistent radical effect, PRE) or can be initially added to the reaction mixture. The ratio of $\text{Cu}^{\text{I}}/\text{L}$ activator to $\text{X}-\text{Cu}^{\text{II}}/\text{L}$ deactivator, together with K_{ATRP} value dictate the radical concentration and thus the rate of polymerization. In ATRP conducted with ppm levels of catalyst (i.e. ATRP with activator regeneration), polymerization rate depends on the flux of radicals or electrons externally supplied to the system. This can be done e.g. *via* thermal radical initiators, chemical reducing agents, zerovalent metals, light, or electric current. In such processes, the ratio of $[\text{Cu}^{\text{I}}/\text{L}]$ to $[\text{X}-\text{Cu}^{\text{II}}/\text{L}]$ adjusts to fit the steady state concentration of radicals, based on the K_{ATRP} value. Therefore, in order to maintain sufficiently fast deactivation, more active ligands should be used to provide adequately high concentration of the deactivator complex.

ATRP has become an everyday, rather than a specialty polymerization method as a result of the breadth of available techniques, and their robustness conjoined with the simplicity of reaction set up. Polymers with a variety of complex architectures including block and gradient

copolymers, stars, brushes, inorganic-organic hybrid materials, bioconjugates, and many others were successfully prepared via ATRP. The present deep understanding of the underlying mechanism paves the way for further process optimization leading to commercialization of the products.

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19. List of Abbreviations

AGET	activators generated by electron transfer
AIBN	azobisisobutyronitrile
ARGET	activators regenerated by electron transfer
ATRP	atom transfer radical polymerization
BDE	bond dissociation energy
BPMODA	bis(2-pyridylmethyl)octadecylamine
BPN	2-bromopropionitrile
bpy	2,2'-bipyridine
CEF	chain end functionality
CRT	catalytic radical termination
CSTR	continuous stirred tank reactor
CV	cyclic voltammetry
$\bar{D}$	dispersity
DCF	dead chain fraction
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dNbpy	4,4'-dinonyl-2,2'-dipyridine
DP	degree of polymerization
DT	degenerative transfer
e ATRP	electrochemically mediated ATRP
EBiB	ethyl α -bromoisobutyrate
EBPA	ethyl bromophenylacetate
EPR	electron paramagnetic resonance
f	thermal radical initiator efficiency
GC	gas chromatography
GPC	gel permeation chromatography (also: SEC)
HPLC	high performance liquid chromatography
ICAR	initiators for continuous activator regeneration
IPA	isopropyl alcohol
ISSET	inner sphere electron transfer
k_{a0}	rate coefficient of activation of alkyl halides by Cu^0
k_{act}	rate coefficient of activation of alkyl halides by $\text{Cu}^{\text{I}}/\text{L}$
k_{add}	rate coefficient of addition of radical to monomer
K_{ATRP}	ATRP equilibrium constant
k_{bb}	rate coefficient of backbiting
k_{comp}	rate coefficient of comproportionation
k_{dc}	rate coefficient of thermal radical initiator decomposition
k_{deact}	rate coefficient of deactivation of radicals by $\text{X}-\text{Cu}^{\text{II}}/\text{L}$
k_{disp}	rate coefficient of disproportionation
K_{X}^{II}	halidophilicity equilibrium constant
k_{p}	rate coefficient of propagation
k_{red}	rate coefficient of reduction of Cu^{II} complex
k_{t}	rate coefficient of termination
k_{tr}	rate coefficient of transfer
L	ligand

LCST	lower critical solution temperature
$[M]_e$	equilibrium monomer concentration
MA	methyl acrylate
MBrP	methyl 2-bromopropionate
MBPA	methyl bromophenylacetate
Me ₆ TREN	tris[2-(dimethylamino)ethyl]amine
MeCN	acetonitrile
MHKS	Mark-Houwink-Kuhn-Sakurada parameters
MMA	methyl methacrylate
MW	molecular weight
MWD	molecular weight distribution
NMP	nitroxide mediated polymerization
NMR	nuclear magnetic resonance spectroscopy
OMRP	organometallic mediated radical polymerization
OSET	outer sphere electron transfer
PEBr	1-phenylethyl bromide
PHC	principle of halogen conservation
photoATRP	photochemically mediated ATRP
PLP-SEC	pulsed laser polymerization-size exclusion chromatography
PMDETA	<i>N,N,N',N'',N'''</i> -Pentamethyldiethylenetriamine
P _n -X	macro alkyl halide
ppm	parts-per-million
PRE	persistent radical effect
PTZ	10-phenylphenothiazine
R_{a0}	rate of activation of alkyl halides by Cu ⁰
R_{a1}	rate of activation of alkyl halides by Cu ^I /L
RAFT	reversible addition-fragmentation chain transfer polymerization
RCMP	reversible complexation mediated polymerization
R_{d1}	rate of deactivation of radicals by X-Cu ^{II} /L
RDRP	reversible deactivation radical polymerization
RP	conventional radical polymerization
R_p	rate of propagation
R_t	rate of termination
RX or R-X	alkyl halide
S/V	ratio of surface area of Cu ₀ to the total reaction volume
SARA	supplemental activator and reducing agent
SEC	size exclusion chromatography (also: GPC)
SET-LRP	single electron transfer living radical polymerization
SI-ATRP	surface-initiated ATRP
SP-PLP-EPR	single pulse-pulsed laser polymerization-electron paramagnetic resonance
SR&NI	simultaneous reverse and normal initiation
T_c	ceiling temperature
TEABr	tetraethylammonium bromide
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
TPMA	tris(2-pyridylmethyl)amine
TPMA ^{*3}	tris((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)amine

TPMA ^{*N}	2-((bis((4-(dimethylamino)pyridin-2-yl)methyl)amino)methyl)- <i>N,N</i> -dimethylpyridin-4-amine
β^I	Cu ^I /L complex stability constant
β^{II}	Cu ^{II} /L complex stability constant
$\Delta V^\ddagger$	volume of activation

Notes

The authors declare no competing financial interest.

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Kinetics of Atom Transfer Radical Polymerization

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