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Feature Article

Kinetics of Atom Transfer Radical Polymerization

Pawel Krys, Krzysztof Matyjaszewski*

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA

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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.

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; $Đ$, 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; ISET, 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 Cu^I/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 $X^{-}Cu^{II}$/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_6TREN, 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, *N*,*N*,*N*′,*N*″,*N*″-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)-N,N-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

* Corresponding author.
E-mail address: km3b@andrew.cmu.edu (K. Matyjaszewski).

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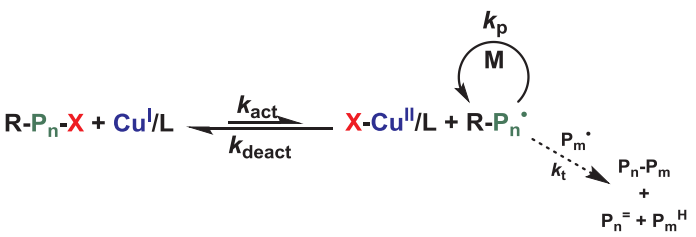
1. Introduction

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 × 1 ms = 1 s, however with 1000 × 1 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 biomaterials. 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 ($P_n^{\cdot}$) (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.