Review article

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Fundamentals of reversible addition–fragmentation chain transfer (RAFT)

Abstract: Radical polymerization is transformed into what is known as reversible addition–fragmentation chain transfer (RAFT) polymerization by the addition of a RAFT agent. RAFT polymerization enables the preparation of polymers with predictable molar mass, narrow chain length distribution, high end-group integrity and provides the ability to construct macromolecules with the intricate architectures and composition demanded by modern applications in medicine, electronics and nanotechnology. This paper provides a background to understanding the mechanism of RAFT polymerization and how this technique has evolved.

Keywords: addition–fragmentation; radical polymerization; RAFT; reversible-deactivation.

Introduction

This paper aims to provide an understanding of the mechanism of reversible addition–fragmentation chain transfer (RAFT) polymerization without going into full detail on the actual chemicals (i.e., monomers, initiators and control agents) used. It is intended for undergraduates who have some understanding of organic or polymer chemistry and already know about reactive intermediates (e.g., carbon-centered radicals, carbanions), reaction types (e.g., addition reaction, fragmentation reaction, substitution reaction) and polymerization.

Radical polymerization is a versatile process that sees widespread use in industry for production of many commodity polymers that include poly(methyl methacrylate) (PMMA, Perspex®), polystyrene, low density polyethylene (LDPE), poly(vinyl chloride) (PVC) and many others. It is compatible with a vast range of monomers, it is tolerant of functionality in the monomers and the polymerization medium, and it can be carried out under a wide range of polymerization conditions (Moad & Solomon, 2006c).

While conventional radical polymerization has advantages, in being relatively low cost, easy to implement and scalable for industrial production, it has limitations in that it produces polymers with a relatively broad chain length distribution (Figure 1), ill-defined end-groups, and there is little scope for the construction of the complex polymer architectures demanded by many modern applications. Applications in medicine, electronics and nanotechnology often call for polymers with a precisely defined structure and composition. Environmental concerns also dictate a need for better controlled methods of polymer synthesis.

Many of these issues might be resolved through the use of what is called living polymerization. A mechanism for living anionic polymerization is shown in Scheme 1. Living polymerization is defined as a chain polymerization from which termination is absent (Penczek & Moad, 2008). This means that the propagating species undergo no irreversible reactions other than addition of monomer, one unit at a time, with regeneration of a new propagating species in each step.

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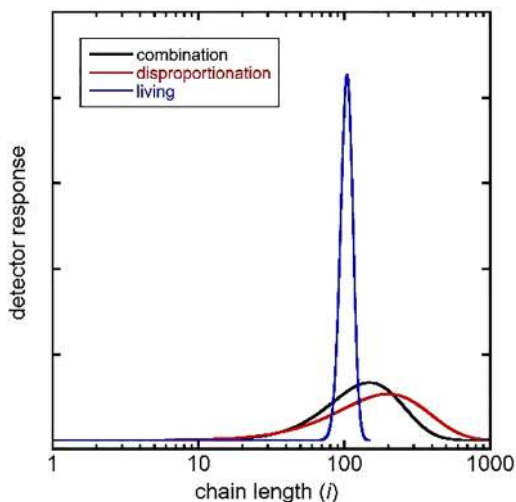
Figure 1: Chain length distributions that might be observed by size exclusion chromatography, for three polymers each with an average chain length (i) of 100, (a) formed by an ideal radical polymerization with termination by combination, (b) by an ideal radical polymerization with termination by disproportionation or chain transfer, and (c) by an ideal living polymerization (this distribution corresponds to a Poisson distribution). Figure adapted from The Chemistry of Radical Polymerization © Elsevier 2006 (Moad & Solomon, 2006d).

living anionic polymerization
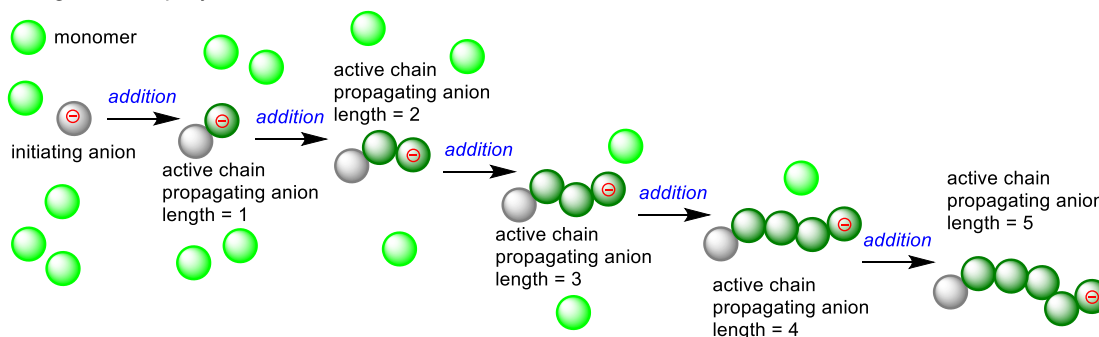
Scheme 1: Mechanism for living anionic polymerization.

Both radical polymerization and living polymerization are referred to as chain polymerizations, not because a polymer chain is produced, rather because the process of polymer synthesis is a chain reaction.

Polymers produced by living polymerization have predictable chain length (the chain length can be calculated exactly as the ratio of monomer consumed to number of chains initiated, Figure 2), low molar mass dispersity (narrow chain length distribution – see Figure 1) and very high end group integrity. One chain end is derived from the initiating species, the other is the active site to which monomer adds. The propagating species possess the capacity to grow for as long as monomer is supplied. The polymerization product comprises only active polymer chains that are deactivated during subsequent work-up and processing. Thus, living polymerization can be used to construct intricate polymer architectures. However, living polymerization has many limitations; it is compatible with very few monomers; it is intolerant of many types of functionality and even trace amounts of impurities must be avoided. Living polymerization requires stringently controlled polymerization conditions.
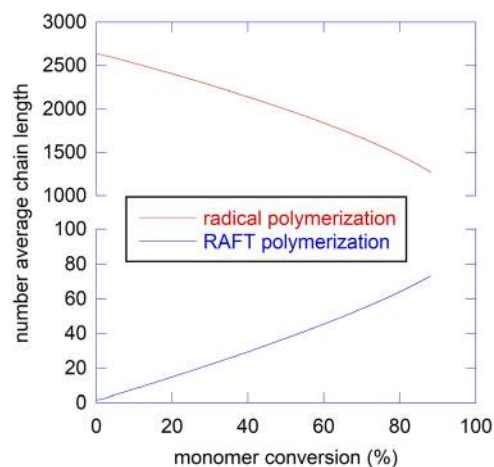
Figure 2: Expected dependence of chain length on monomer conversion in radical polymerization and reversible deactivation radical polymerization (RDRP). Data was generated by numerical simulation using the program Predici[TM] and correspond to situations where, for radical polymerization, the ratio [monomer]:[initiator] is 1000:1 or, for RAFT polymerization, the ratio [monomer]:[RAFT:agent]:[initiator] is 1000:10:1, respectively.

A narrow distribution of chain lengths also requires that all chains are initiated at the commencement of polymerization and that initiation is rapid relative to propagation so that all chains grow at the same rate.

A major benefit of RAFT polymerization is that, with the simple addition of a well-chosen RAFT agent, it is possible to confer the important attributes of living polymerization (e.g., predictable molar mass, narrow chain length distribution and high end-group integrity) on an otherwise conventional radical polymerization. We can retain much of the versatility of conventional radical polymerization, while approaching the precision of living polymerization. RAFT polymerization provides the capacity for continued chain growth while monomer and the conditions for chain growth are supplied, and thus a route to well-defined, yet potentially complex, polymer architectures as demanded by industry.

RAFT polymerization is a form of what is called reversible deactivation radical polymerization (RDRP) (Jenkins, Jones, & Moad, 2010). RDRP is a term that embraces RAFT polymerization along with stable radical-mediated polymerization (SRMP) and atom-transfer radical polymerization (ATRP). This document attempts to describe RAFT polymerization from the viewpoint of the basic mechanism. However, before discussing the RAFT process in detail, it is important to understand radical polymerization.

Radical polymerization

Radical polymerization, like living anionic polymerization, is a form of chain polymerization. The conventional process also comprises initiation and propagation steps but, unlike living anionic polymerization, radical polymerization also comprises termination and potentially irreversible chain transfer steps.

Initiation

Initiation is a process that results in the formation of propagating radicals (Moad & Solomon, 2006b). There are many forms of initiation. Historically, the most common form of initiation involves the thermal decomposition of an initiator such as a dialkyldiazene or a peroxide (Scheme 2). In radical polymerization, new chains must be initiated continuously throughout the polymerization process so as to compensate for chains that are lost
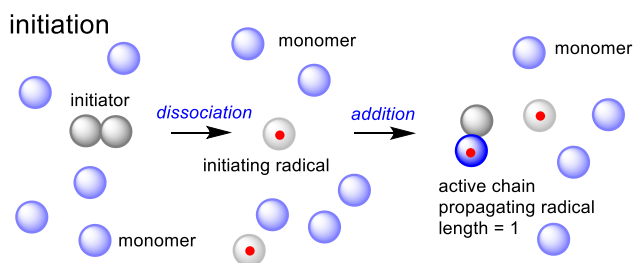
initiation

Scheme 2: Mechanism for initiation in radical polymerization.

through termination and maintain a steady state concentration of propagating radicals. Initiating radicals are those initiator-derived radicals that add a monomer to form a propagating radical.

Propagation

Propagation is the sequential, one-at-a-time, addition of individual monomer units to an active chain, which is called a propagating radical (Scheme 3) (Moad & Solomon, 2006e). Propagation must be selective to the exclusion of other processes. A very wide range of monomers can be used in radical polymerizations. These include methacrylates, acrylates, methacrylamides, acrylamides, acrylonitrile, styrene, vinyl esters, vinyl amides and ethylene. The monomers may contain a wide range of functionalities including carboxylic acid, sulfonic acid, hydroxy, dialkylamino, betaine and many others.

Termination

Active chains, including propagating radicals, undergo termination by self-reaction at a diffusion controlled rate (Moad & Solomon, 2006f). The reaction between two active chains may occur by combination, in which two chains are joined together to form one dead chain (Scheme 4), or by disproportionation, which involves transfer of a hydrogen atom from one chain to the other to form two dead chains (Scheme 5). Termination may also involve reaction between propagating radicals and initiator-derived radicals.
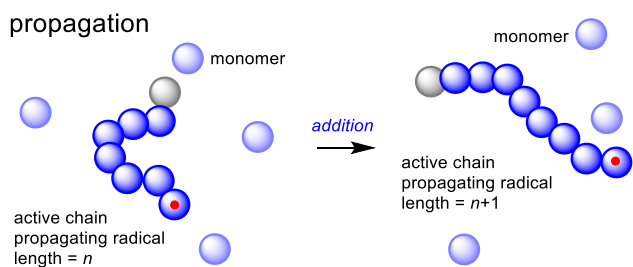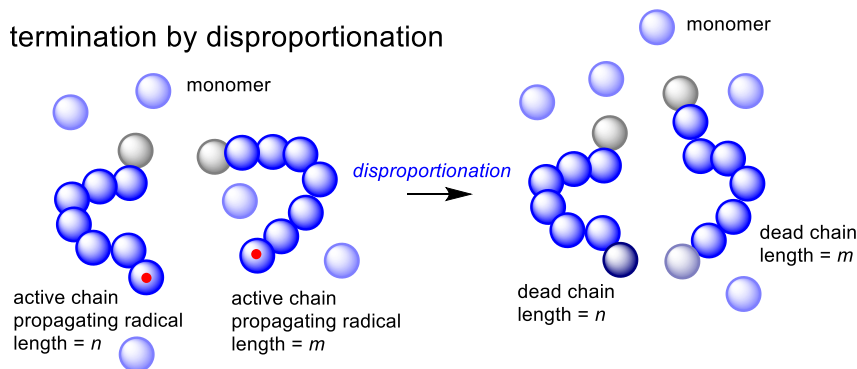
propagation

Scheme 3: Mechanism for propagation in radical polymerization.

termination by combination
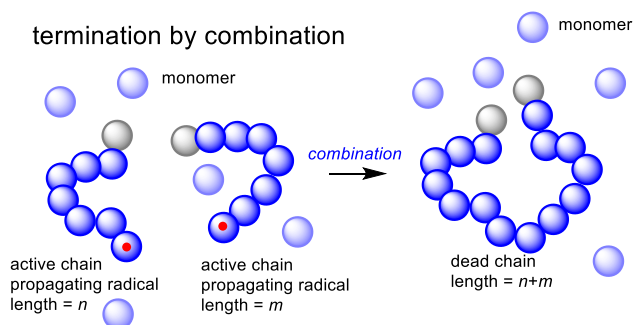
Scheme 4: Mechanism for termination by combination in radical polymerization.

termination by disproportionation

Scheme 5: Mechanism for termination by disproportionation in radical polymerization.

(Irreversible) chain transfer

Chain transfer to initiator, monomer, polymer or an added chain-transfer agent may occur by several mechanisms. The overall process results in termination of one active chain and the generation of an initiating radical to then produce a new propagating radical by addition of monomer (Moad & Solomon, 2006a).

Substitution chain transfer

The most common form of chain transfer involves homolytic substitution in which an atom or group is transferred from a chain-transfer agent to a propagating radical (Scheme 6). Examples of substitution chain-transfer agents are thiols (hydrogen atom transferred), carbon tetrabromide (bromine atom transferred) and dibenzoyl peroxide (benzoate group transferred).
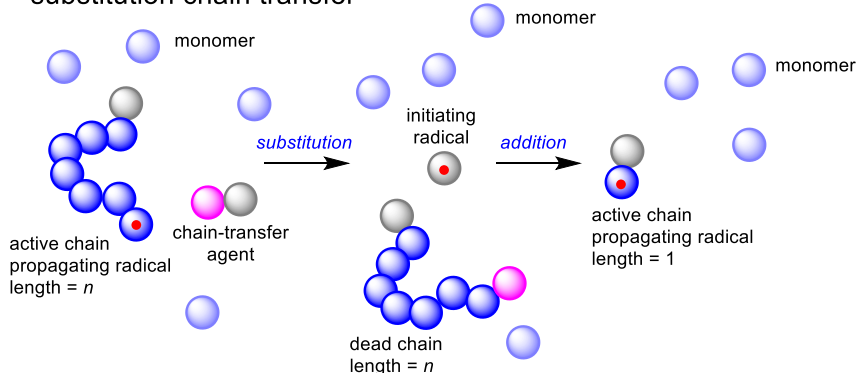
Addition–fragmentation chain transfer

A second mechanism is addition–fragmentation chain transfer (Scheme 7). The propagating radical adds to the reagent to form an intermediate which fragments to form an initiating radical. Examples of (irreversible) addition–fragmentation transfer agents are allyl sulfides and vinyl benzyl ethers.

Chain length distributions in radical polymerization

In a radical polymerization, due to the prevalence of termination, it is not possible to initiate all chains simultaneously at the commencement of the polymerization. Rather, chains are initiated continuously

substitution chain transfer

Scheme 6: Mechanism for substitution chain transfer in radical polymerization.

addition-fragmentation chain transfer
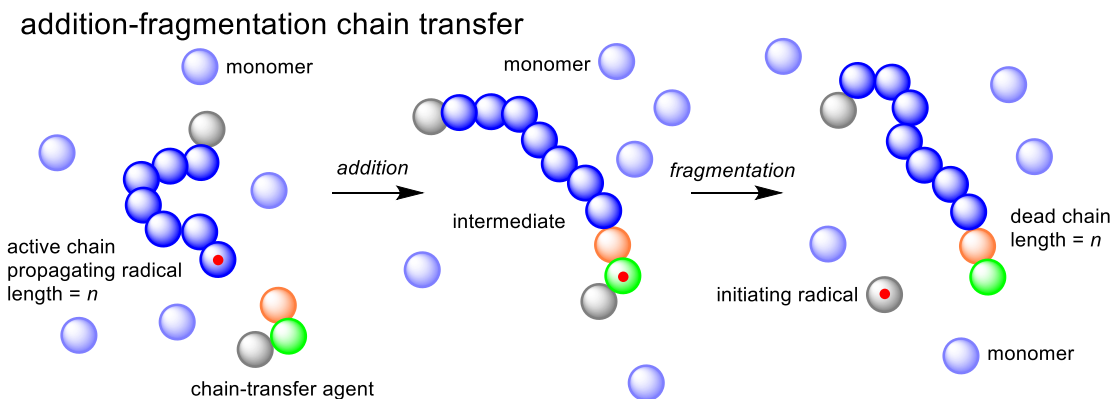
Scheme 7: Mechanism for addition–fragmentation chain transfer in radical polymerization.

throughout the polymerization. A balance between the rate of chain initiation and the rate of chain termination is established such that the concentration of propagating radicals remains approximately constant and very low. The concentration of species in a typical radical polymerization would be, monomer ~10 M, initiator 0.1 M, and propagating radicals 10^{-7} M. Under these conditions, very long chains will be formed from the beginning of the polymerization process and the chain length distribution will be relatively broad (Figure 1).

Reversible-deactivation radical polymerization (RDRP)

The overall process in RDRP is insertion of monomer units sequentially into a dormant chain to form a new dormant chain. The process can be considered as one of polyinsertion (Scheme 8).

In a living polymerization, processes for chain termination (i.e., combination, disproportionation and irreversible chain transfer) are absent. A living radical polymerization is not considered possible because of the very high probability that radicals, specifically, propagating radicals, will undergo termination by self-reaction. RDRP provides a way of rendering termination processes insignificant and thereby conferring many of the important characteristics of living polymerization on radical polymerization. These characteristics

reversible deactivation radical polymerization (RDRP)
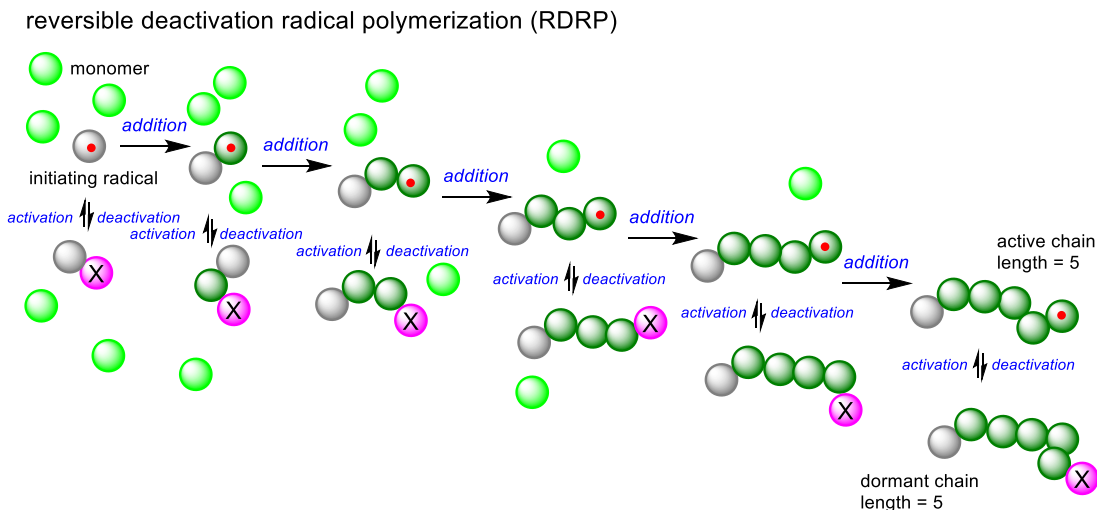
Scheme 8: Mechanism for reversible deactivation polymerization (RDRP).

include predictable molar mass, low molar mass dispersity, high end group fidelity, and chains that possess the capacity to grow while monomer and the conditions for polymerization are supplied.

Reversible deactivation

There are three main mechanisms for reversible deactivation.

(a) Stable radical-mediated radical polymerization (SRMP) involves unimolecular activation by dissociation of the bond to the incipient propagating radical and the group X in a dormant species (Scheme 9). An example of SRMP is aminoxyl-mediated radical polymerization (commonly called nitroxide-mediated polymerization, NMP), where X is an aminoxyl radical, also known as a nitroxide.

(b) Atom-transfer radical polymerization (ATRP) involves bimolecular activation by transfer of the group X (typically, a halogen atom such as bromine) to an activator with formation of a propagating radical (Scheme 10). An example of ATRP has the activator as a copper(I) complex, the group transferred as a bromine atom, and the deactivator as a copper(II) complex.

(c) Radical polymerization with degenerate chain transfer (DTRP) involves reversible transfer of a group X between a dormant species and a propagating radical to form a new dormant species and a new propagating radical (Scheme 11). An example of DTRP where transfer involves substitution chain transfer is iodine-transfer polymerization where the group transferred group is an iodine atom.
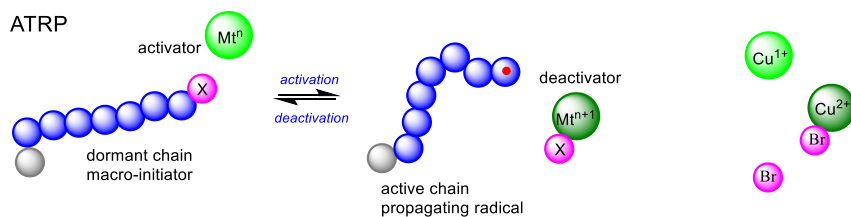
RAFT polymerization is another form of DTRP where the chain transfer occurs by reversible addition fragmentation (Scheme 12).
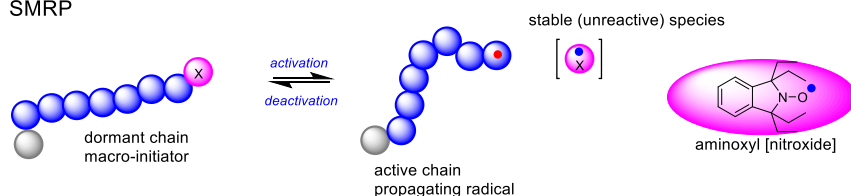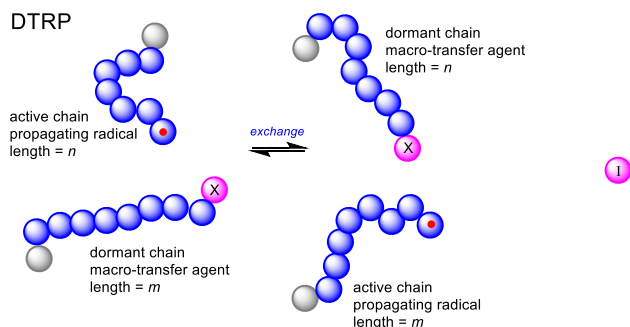

Scheme 9: Mechanism for activation-deactivation in stable radical-mediated radical polymerization (SRMP) and example of a stable or unreactive species; an aminoxyl radical.

Scheme 10: Mechanism for activation-deactivation in atom-transfer radical polymerization (ATRP) and examples of a transferred group, an activator and a deactivator.

Scheme 11: Mechanism for activation-deactivation in degenerate chain transfer radical polymerization (DTRP) and an example of a transferred group, I, an iodine atom.

In all cases, the deactivation process is the reverse of the activation process.

The inclusion of a process for reversible deactivation does not suppress termination reactions. For high end-group integrity, the fraction of dormant chains must far exceed the likely formation of dead chains by termination (Scheme 12). The number of chains formed in radical polymerization, and the chain length of those chains, relates directly to the amount of initiator used and the number of initiating radicals generated. The number of chains formed in RAFT polymerization is the number of RAFT agent molecules used plus those formed by initiation (Figure 2).

To achieve a low molar mass dispersity or narrow molar mass distribution, it is important that the rate of the activation–deactivation process is rapid with respect to the rate of propagation. In well-controlled processes, the number of monomer units inserted per activation cycle (i.e., the period that the polymer chain is active) will often be <1.

The mechanisms that are available and the species X that are most effective depend strongly on the monomers being polymerized and the conditions of polymerization. Much research effort has been devoted to determining those that are most effective (Corrigan et al., 2020).

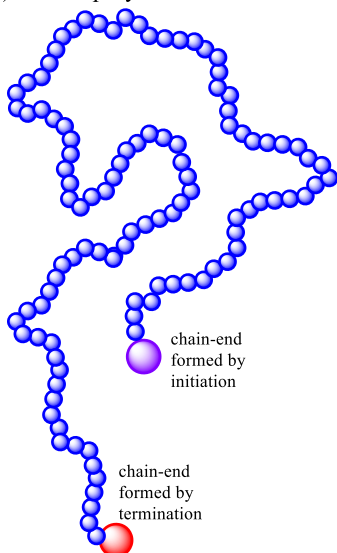## Stable radical-mediated radical polymerization (SRMP)

The stable species in SRMP need not be thermodynamically stable but must display kinetic stability under the polymerization conditions (i.e., not undergo side reactions).

Examples of SRMP include the iniferter process (Otsu, 2000) and aminoxyl-mediated radical polymerization (Moad & Rizzardo, 2016). SRMP can also be used to initiate DTRP including RAFT polymerization.
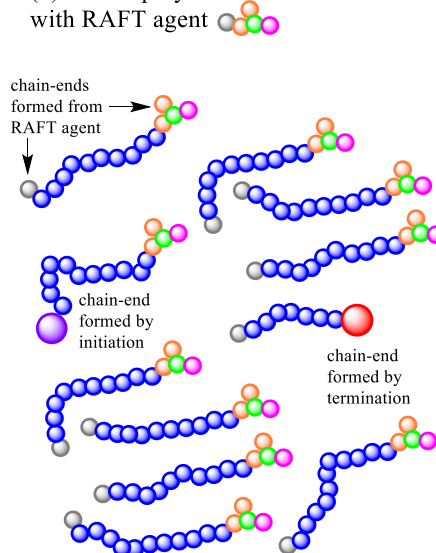
Atom-transfer radical polymerization (ATRP)

Atom (or group) transfer polymerization (ATRP) differs from SRMP in that initiation is bimolecular (Scheme 10). ATRP might, in principle, occur by direct transfer of ligand from the macroinitiator to the metal complex or by a multistep process involving initial electron transfer. In either case, the overall process can be represented by Scheme 10. Common forms of ATRP make use of copper or ruthenium-based activators (Anastasaki et al., 2016; Boyer et al., 2016; Matyjaszewski & Tsarevsky, 2014; Ouchi, Terashima, & Sawamoto, 2009). Mechanistically analogous processes not involving metals are also known.

(a) radical polymerization

(b) radical polymerization
with RAFT agent

chain-ends
formed from
RAFT agent

chain-end
formed by
initiation

chain-end
formed by
initiation

chain-end
formed by
termination

chain-end
formed by
termination

Scheme 12: (a) Polymer chain formed by conventional radical polymerization with degree of polymerization (number of monomer units in chain) of 110. (b) Eleven polymer chains, with average degree of polymerization of 10, formed by reversible addition–fragmentation chain transfer (RAFT) polymerization with conventional initiation. Initiation and termination are rendered insignificant as mechanisms for chain-end formation as most chains have end-groups derived from the RAFT agent.

An often-stated drawback of ATRP is that the polymer product is contaminated with activator, which is typically a transition metal complex. However, in well-designed experiments, the amount of activator is often very small with respect to the number of dormant chains.
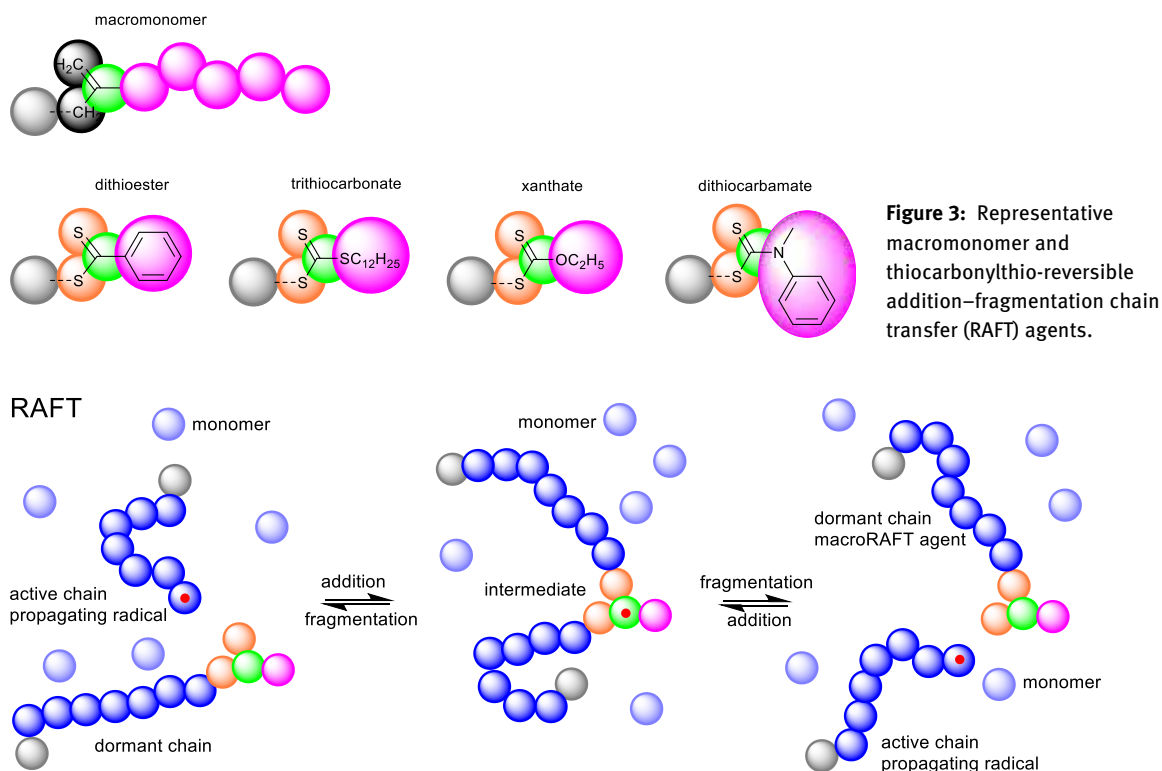
Radical polymerization with degenerate chain transfer (DTRP)

### Radical polymerization with reversible addition–fragmentation chain transfer (RAFT polymerization)

In its simplest form, RAFT polymerization is a conventional radical polymerization conducted in the presence of a RAFT agent (Figure 3). The product of RAFT polymerization is also a RAFT agent; a higher molar mass RAFT agent, which is called a macroRAFT agent. The processes and kinetics of conventional radical polymerization are not substantially changed in RAFT polymerization.

The RAFT activation–deactivation equilibria involve a propagating species adding to a macroRAFT agent to form an intermediate (Scheme 13). The intermediate is transient and fragments rapidly to form a new propagating species and a new macroRAFT agent. The overall process is one of degenerate chain transfer. In this context, degenerate means the products and the starting materials are similar, differing only in the chain length of the attached chain.

In SRMP and ATRP, the activation process produces the radicals which initiate polymerization. In DTRP, including RAFT, activation of one chain is always accompanied by deactivation of another. There is no net change in the radical concentration. RAFT polymerization can be initiated in the same way as conventional radical polymerization. It is also possible to generate radicals directly from the RAFT agent thermally, photochemically or in a redox process in ways that are formally analogous to activation in SRMP or ATRP (Scheme 14). This means that there are no initiator-derived by-products formed.

Figure 3: Representative macromonomer and thiocarbonylthio-reversible addition–fragmentation chain transfer (RAFT) agents.

Scheme 13: Mechanism for activation–deactivation in reversible addition–fragmentation chain transfer (RAFT).

Initiation
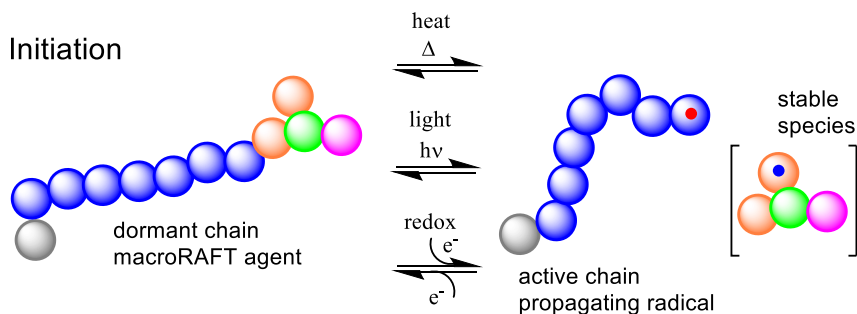
Scheme 14: Mechanisms for forming radicals directly from a macroRAFT agent though heating, irradiation, or in a redox process.

Benefits of RAFT polymerization

RAFT polymerization is used to prepare polymers with a narrow distribution of chain lengths, with a defined molar mass, and to prepare polymers with precisely known chain-ends. Another benefit of RAFT polymerization is that it can be used to prepare gradient and block copolymers and polymers of more complex architecture.

One advantage of RAFT polymerization, over SRMP and ATRP, is its high tolerance of functionality that may be present in the monomer and the reaction medium. This means that RAFT polymerization is applicable to most monomers polymerizable by radical polymerization and can be conducted under homogeneous conditions in bulk monomer, in aqueous or organic solution, or under heterogeneous conditions in emulsion, suspension or dispersion. RAFT polymerization can also be successfully conducted over wide range of temperatures (typically within the range −20 to 150 °C).

Guidelines for selecting RAFT agents for the application and polymerization conditions have been published (Moad, 2017b).

Block copolymers comprise segments that differ in terms of composition or sequence (i.e., what the monomer units are and how they are arranged in the polymer chain). Block copolymers can be prepared by the sequential addition of different monomers as illustrated in Scheme 15.

Different monomers typically have different reactivities in radical polymerization meaning that some will be consumed faster than others which causes the composition of the monomer feed to drift as monomer is converted to polymer. This means that, in conventional radical polymerization, polymer formed at the beginning of the polymerization will have a different composition to that formed at the end of the polymerization as shown in Scheme 16. The product is a blend of polymers that differ in composition according to when they were formed. In a living polymerization or an RDRP, such as RAFT polymerization, at any given instant during polymerization all polymer chains have essentially the same composition. The compositional drift is captured within each polymer chain and the product is called a gradient copolymer as shown in Scheme 17. In some cases, it is possible to purposely add monomers during polymerization to introduce functionality and control the sequence of monomer within the polymer chains.

By combining multiple RAFT agent functionalities into a single precursor, it is possible to make complex architectures. For example, 3-arm star polymers can be constructed by either of the two methods shown in Scheme 18.
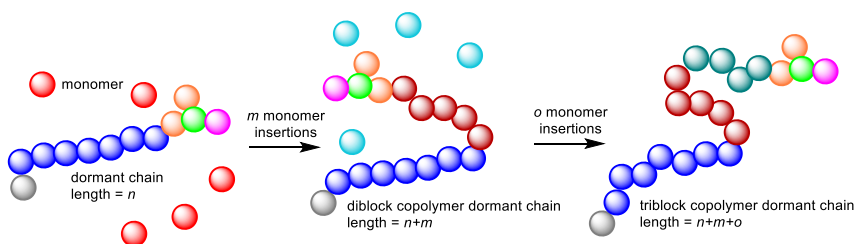

Scheme 15: Overall process for block copolymer synthesis by reversible addition–fragmentation chain transfer (RAFT) polymerization and sequential monomer addition.
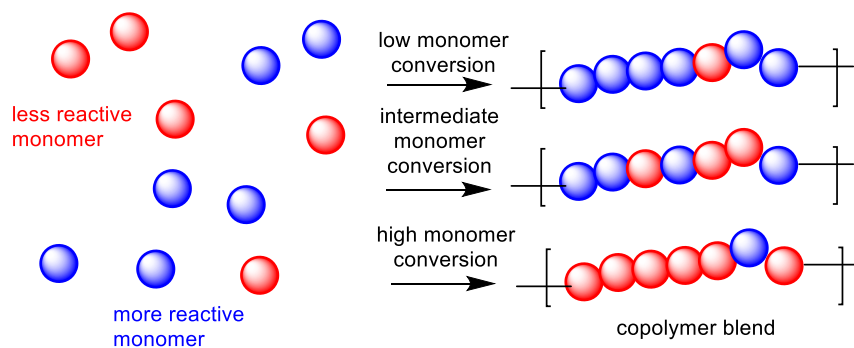
Scheme 16: The outcome for copolymer synthesis by a traditional radical polymerization is a polymer blend. Segments of the copolymer formed at low, intermediate and high momomer conversion are shown, and they become progressively richer in the less reactive monomer. The composition of the copolymer being formed at any particular time will reflect the instantaneous composition of the monomer feed.
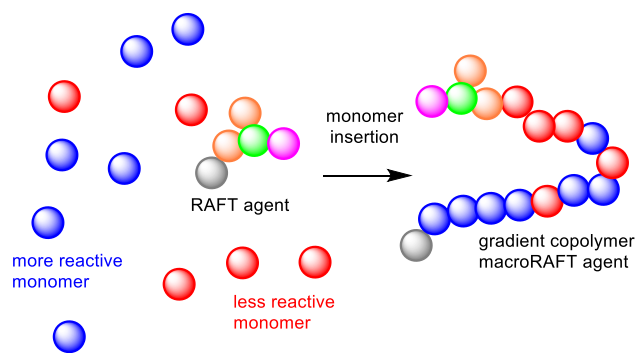
Scheme 17: The outcome of copolymer synthesis by reversible addition–fragmentation chain transfer (RAFT) polymerization is a gradient copolymer. Any change in the monomer feed compsition with time or monomer conversion is captured within each copolymer chain. Essentially all of the copolymer chains formed will have a similar composition.
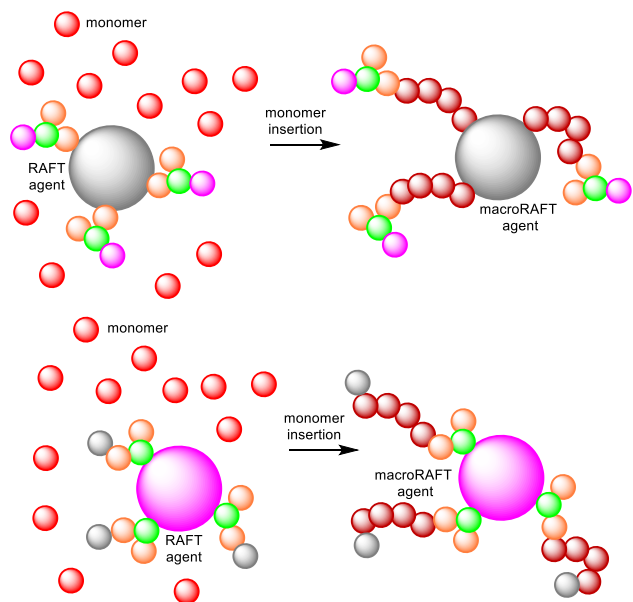
Scheme 18: Overall process for the synthesis of complex architectues by reversible addition–fragmentation chain transfer (RAFT) polymerization. The examples shown are 3-arm stars. The structures formed depend on how the RAFT agent functionality is connected to the core of the star in the initial multi-RAFT agent. In one case, the functionality is at the ends of the arms; in the other, it remains at the core of the star. A wide variety of architectures can be designed.

History and application of RAFT polymerization

The first examples of RAFT polymerization, reported in 1995, made use of so-called macromonomer chain transfer agents (Figure 3) (Krstina et al., 1995). It was not called RAFT polymerization at the time. With appropriate choice of reaction conditions, the macromonomer RAFT agents could be used to impart most of the characteristics associated with living polymerization to a radical polymerization.

Much of the initial impetus for the development of RAFT polymerization related to achieving improved environmental outcomes in the preparation of polymers used in automotive coatings. RAFT polymerization was used for the preparation of low VOC (volatile organic content, e.g., solvents) acrylic coatings. The polymers produced were low dispersity gradient copolymers with guaranteed functionality. Subsequent work targeted water-borne coatings and pigment dispersants by what is now called surfactant-free emulsion polymerization. However, macromonomer RAFT polymerization was only applicable to a narrow range of monomers and thus had a limited range of applications.

RAFT polymerization with thiocarbonylthio compounds (dithioesters, trithiocarbonates, xanthates and dithiocarbamates – Figure 3) as RAFT agents, first reported in 1998 (Chiefari et al., 1998), was more broadly applicable to most monomers polymerizable by radical polymerization. The paper that described the RAFT process is currently the most highly cited paper in the journal *Macromolecules* with more than 4000 citations (Web of Science).

This form of RAFT polymerization was initially disclosed in a CSIRO/DuPont patent that was published in January 1998 (Le, Moad, Rizzardo, & Thang, 1998). A patent describing the parallel development of MADIX (MAcromolecule Design by Interchange of Xanthates – RAFT with xanthate transfer agents) at Rhodia was published in December 1998 (Corpart, Charmot, Biadatti, Zard, & Michelet, 1998). The first RAFT patent (Le et al., 1998) was, by 2005, one of the most highly cited patents in the field of chemistry and related science, and the patent literature now abounds with an ever-increasing number of RAFT-related inventions (Figure 4).

The development of RAFT polymerization through 2012 can be traced through a series of reviews (Moad, Rizzardo, & Thang, 2005, 2006, 2009, 2012). Since that time, the very large number of publications has meant that comprehensive coverage of the field is no longer practicable, and more recent reviews have had to focus on specific aspects or applications of RAFT polymerization. At least 30 such reviews on RAFT polymerization have been published within the last 3 years (Moad & Rizzardo, 2021a). A larger number have appeared on RDRP
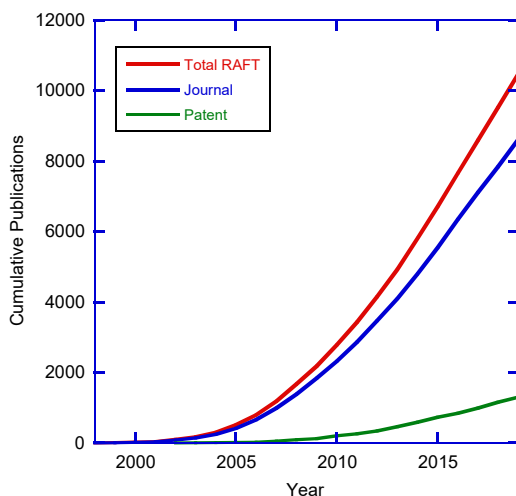
Figure 4: Cumulative publications relating to reversible addition–fragmentation chain transfer (RAFT) polymerization 1998–2019 based on a Scifinder™ substructure search on the major classes of RAFT agent carried out in February 2020 on the RAFT agent structures and the terms "RAFT" (and "MADIX" in the case of xanthates).
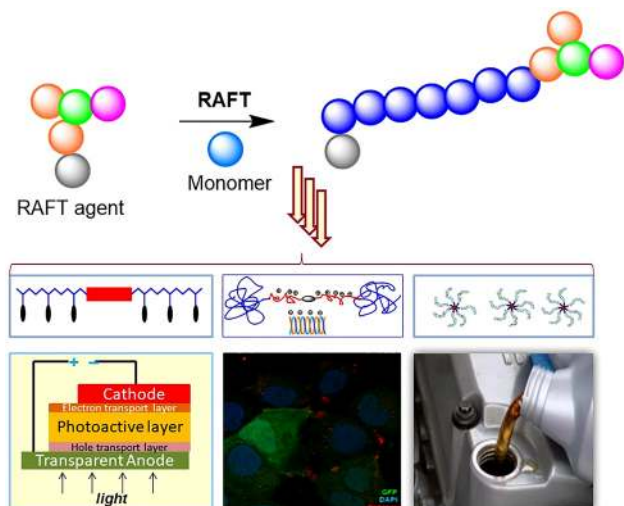
Figure 5: Some reversible addition–fragmentation chain transfer (RAFT) applications. From left to right optoelectronics, polymer therapeutics, rheology control agents. Figure adapted from (Moad, Rizzardo, & Thang, 2013) © Wiley-VCH.

including RAFT. Some applications that we have worked on at CSIRO include bioapplications (Boyer et al., 2009; Fairbanks, Gunatillake, & Meagher, 2015), optoelectronic polymers (Moad et al., 2011), cross-linked polymers (Moad, 2015), conjugated diene polymers (Moad, 2017a) and stimuli-responsive polymers (Moad, 2017b). A current awareness search on RAFT polymerization in Scifinder™ results in an average ~80 citations per week. Recently, several perspectives on RAFT polymerization have been published to mark the 20th anniversary of the invention of RAFT polymerization (Matyjaszewski, 2020; Moad & Rizzardo, 2020; Perrier, 2017). A two volume book specifically on RAFT polymerization is due for publication in 2021 (Moad & Rizzardo, 2021b). While, commercial success stories associated with RAFT polymerization and other RDRP are currently few (Destarac, 2018), we might anticipate a new upsurge in commercial activity with the enforceable life of the first RAFT patents having come to an end.

There are a multitude of applications described in the patent literature (Moad, 2021). These include bioapplications (polymer therapeutics, polymers for drug delivery and targeting, biosensors, cosmetics), electronics (plastic solar cells, organic semiconductors, light emitting diodes, resists), industrial applications (desalination membranes, lubricants, surfactants, paints, inks and adhesives (Figure 5). These applications also feature in publications in the open literature (Moad et al., 2013).

Many applications of RAFT polymerization can be seen to have positive environmental outcomes (Semsarilar & Perrier, 2010). An example is Lubrizol's Asteric rheology control agents for automotive applications. These are star polymers prepared by RAFT polymerization that impart long term, temperature independent, viscosity to fluids such as oils (Brzytwa & Johnson, 2011). A further example is the preparation of novel RAFT synthesized additives that enable production of flexible PVC that is free of migratory additives and plasticizers (Sun, Choi, Feng, Moad, & Thang, 2019; Sun et al., 2020).

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