The renaissance and evolving design of radical polymerization

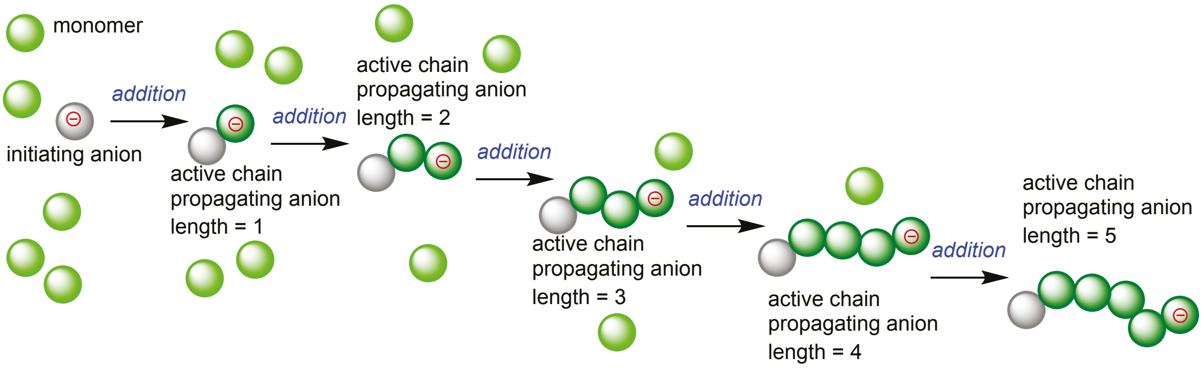
by Graeme Moad

During the 49th World Polymer Congress held 17–21 July 2022 in Winnipeg, Canada, Graeme Moad presented the Stepto Lecture Award [1], describing the mechanism and terminological evolution of reversible deactivation radical polymerization (RDRP) [2-4], including more recent intricate designs through the use of light and electrical propulsion.

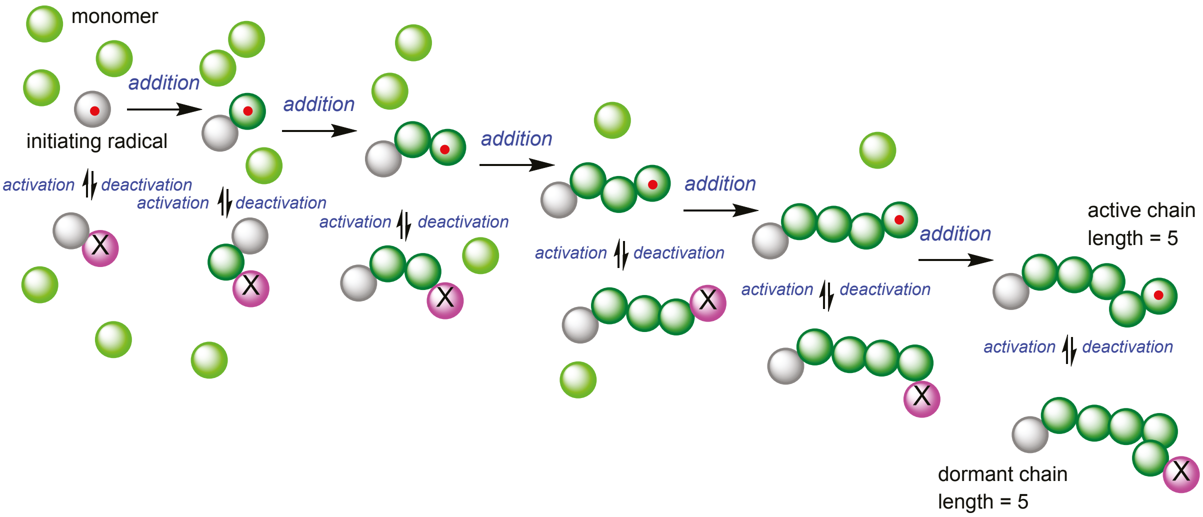
Polymers produced by living chain polymerization (Scheme 1) can have predictable chain length (calculated exactly as the ratio of monomer consumed to number of chains initiated), very low molar mass dispersity and very high end-group integrity. In a living polymerization, chain termination is absent. Despite much argument, this definition is absolute and will not tolerate any compromise.

Polymers produced by reversible-deactivation radical polymerization (RDRP, Scheme 2) can have predictable chain length (approximated as the ratio of monomer consumed to number of chains initiated), very low molar mass dispersity and very high end-group integrity. But they typically are not perfect! Even though they might not be always detectable, chain termination and other side reactions occur.

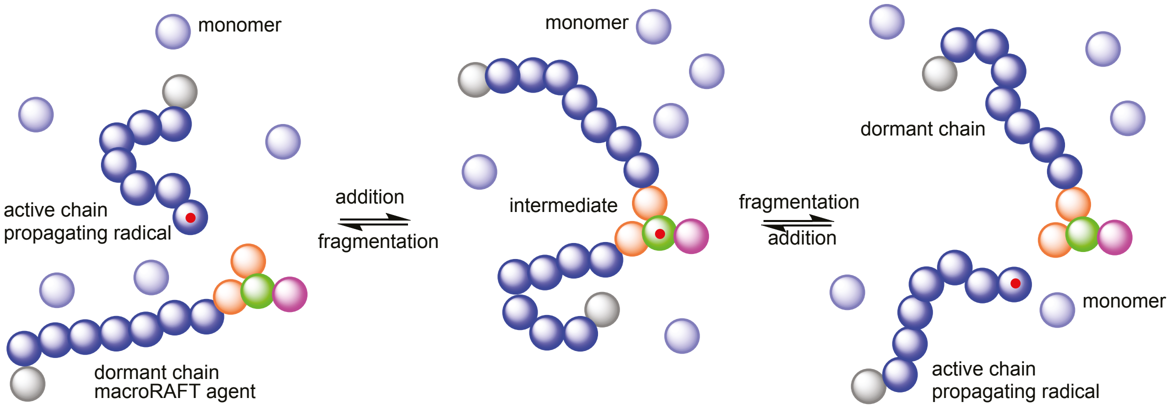
Perfection in chemistry is improbable. Living radical polymerization never was and (probably) never can be. This should not stop people striving for perfection, describing what perfection might look like, and IUPAC retaining the term living radical polymerization. Thus, we strive to achieve living radical polymerization, describe what living radical polymerization might look like, and we retain the term to describe a hypothetical ideal.



Scheme 1. Mechanism for living anionic polymerization. Reproduced from ref [3].



Scheme 2. Mechanism for reversible deactivation radical polymerization (RDRP). Reproduced from ref [3]. Termination reactions, which can occur, are not shown.



Scheme 3. Mechanism for activation–deactivation in reversible addition–fragmentation chain transfer (RAFT). Reproduced from ref [3].

Recent work on reducing incidence of termination during RDRP by manipulating the kinetics of radical polymerization includes taking advantage of:

1. The diffusional characteristics of propagating species.

- Very long chains really don't want to diffuse.
- Ultrahigh pressures slow down diffusion.
-

2. Compartmentalization effects in heterogeneous polymerization.

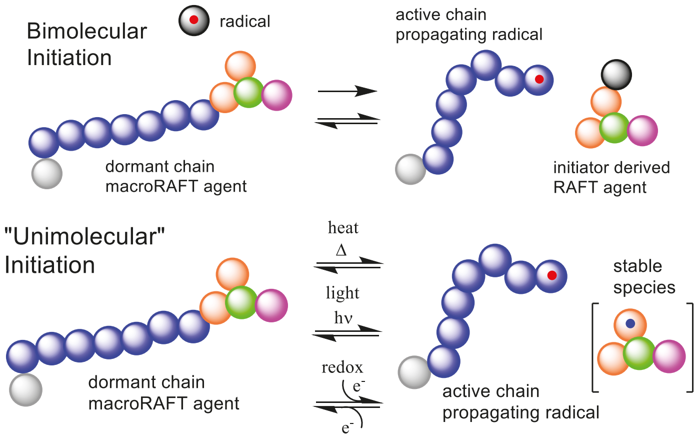
- Single propagating radicals in isolation show a reduced tendency to terminate.

Both strategies have allowed synthesis of low dispersity, high end-group fidelity, polymers by RDRP that can continue to grow to an average molecular weight M_n greater than 10^6 g mol^{-1}. We will return to this topic.

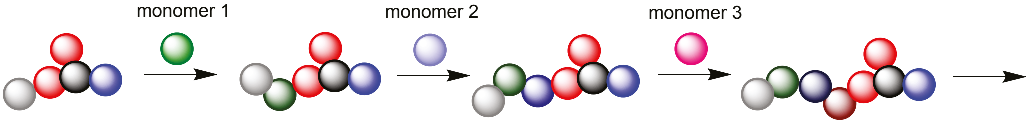
RAFT Polymerization

RAFT (or reversible-addition–fragmentation chain-transfer) polymerization is a RDRP polymerization is a RDRP where activation-deactivation is by reversible-addition-fragmentation chain transfer (Scheme 3). An example is polymerization in presence of an appropriate thiocarbonylthio compound (the RAFT agent), chosen such that chain transfer is very much faster than propagation, and fragmentation and reinitiation are not rate determining. RAFT is then a mechanism for equilibrating polymer chains so that, on average, all chains grow at the same rate and all chains are approximately the same size.

Radicals are neither formed nor destroyed in the RAFT process. Forming polymers by RAFT polymerization requires some form of initiation (Scheme 4). Historically this has, most commonly, involved adding an initiator as a source of radicals (Scheme 4a). However, radicals can also be formed directly from the RAFT agent, thermally, photochemically or in a redox process (Scheme 4b).



Scheme 4. Mechanisms for forming radicals directly from a macroRAFT agent through heating, irradiation, or in a redox process. Scheme 4b is reproduced from ref [3].



Scheme 5. Iterative synthesis of discrete oligomers by RAFT SUMI, by sequential addition, one unit at a time.

Recent Developments in Photoinitiated Reversible Addition Fragmentation Chain Transfer – Single Unit Monomer Insertion (RAFT-SUMI)

These methods are crucial to the success of photoinitiated reversible addition fragmentation chain transfer – single unit monomer insertion (RAFT-SUMI) and the use of iterative photoRAFT SUMI for the synthesis of sequence-defined oligomers [5], wherein the organisation of monomers is precisely defined at the level of the individual units that comprise the polymer chain.

Numerical Simulation of RAFT Polymer Synthesis using a Method of Partial Moments

Numerical simulation of RAFT polymerization is rendered complex by the large number of different polymeric species. In addition to the propagating species and the dead chains formed by their combination, disproportionation, or irreversible side reactions there are the macroRAFT agent and the various intermediates. Expressions were derived to enable rigorous evaluation of the complete molar mass distributions of these, where shorter chains (*e.g.,* N < 200 monomer units) are treated discretely while longer chains (*e.g.,* N ≥ 200 units) are not neglected but are explicitly considered in terms of the partial moments of their molar mass distributions [6]. That for the macroRAFT agent is illustrated in Scheme 6.

This methodology has been applied to compare initiation of RAFT polymerization by conventional methods using an added thermal initiator and direct photoinitiation. It is important to remember that the rate of termination depends on the concentrations of propagating radicals not on how those radicals were generated. Thus, for the same rate of polymerization one has a similar rate of termination.

Electrochemically-initiated RAFT polymerization - eRAFT

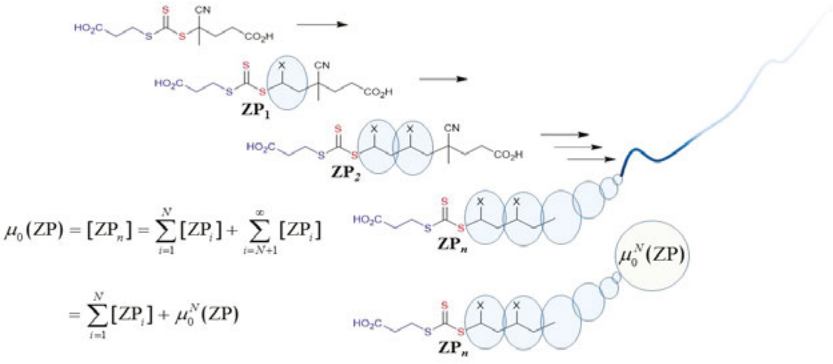
Three methods examined for electrochemically initiated RAFT polymerization (eRAFT) involve:

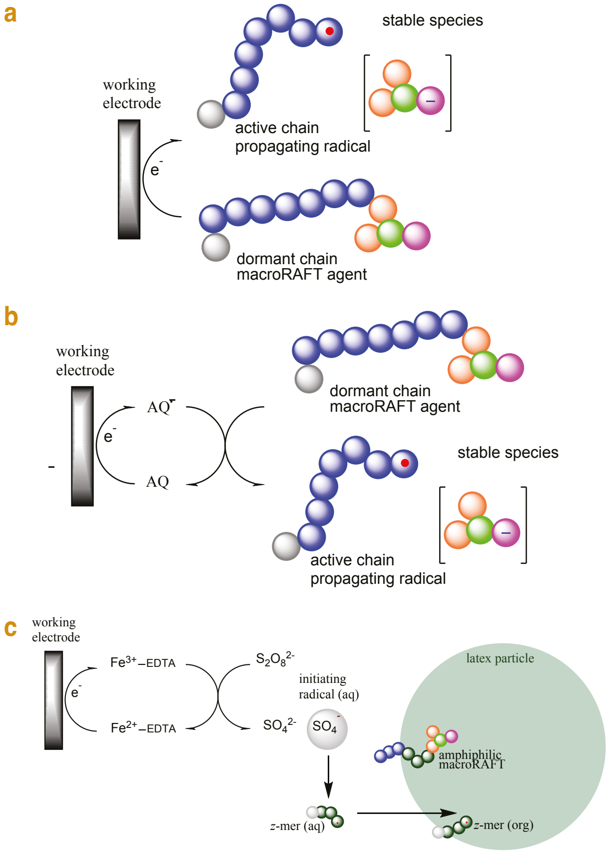
- Direct electrochemical reduction of the (macro) RAFT agent [7]. Low-energy negative ion mass spectrometry and theoretical calculations show that the radical anion formed by electron attachment should give the desired chemistry [8]. However, side reactions at the electrode prevent the being a from becoming method for initiating eRAFT. (see Scheme 7a)
- Mediated electrochemical reduction of RAFT agent [9]. The use of a mediator means that reduction of the (macro)RAFT agent and radical formation occur away from the electrode and mitigate the possibility of secondary reactions. A slow rate of fragmentation of the radical anion intermediate limits the scope of the process. (Scheme 7b)
- Electrochemical generation of initiating radicals (in emulsion polymerization) [10,11]. Our initial experiments on *ab initio* eRAFT in emulsion worked in providing rapid synthesis to a product with low molar mass dispersity but were compromised by poor latex rheology. (Scheme Fig 7c)

Efficient Synthesis of Multiblock Copolymers via MacroRAFT-Mediated Emulsion Polymerization

The last five years have seen major advances in multiblock copolymer synthesis by thermally initiated seeded RAFT emulsion polymerization, which are summarized in a recent review [12]. These developments take advantage of "nanoreactor concept" and the inherent compartmentalization effects to provide optimized conditions for multiblock copolymer

Scheme 6. In the method of partial moments, the macroRAFT agent species (ZP_n) are treated discretely when chain length is smaller than *N* but only in terms of the partial moment [$\mu_x^N(ZP)$] when chain length is longer or equal to *N*. Other polymeric species are treated similarly. Illustration reproduced from ref [6].





Scheme 7. Illustration of eRAFT in Emulsion. Reproduced from ref [10].

synthesis by sequential monomer addition. (Scheme 8) Compartmentalization results in a reduced rates of termination and consequently higher polymerization rates. Higher (near complete) monomer conversions with improved end group integrity obviate the need for purification of intermediate blocks. Thus, we have been able to prepare multiblocks with higher molecular weights, lower molar mass dispersities, unconventional block orders, and defined particle architectures. Colloidal stability of the seed is typically maintained without the use of a surfactant through the use of an amphiphilic macroRAFT, which also provides the basis for the formation of the nanoreactors [13-23].

The marriage of the nanoreactor concept for well-defined multiblock polymer synthesis with eRAFT initiation has produced a further significant breakthrough [11]. (Scheme 9)

Electrochemically-initiated RAFT polymerization – eRAFT in Emulsion

Success is attributed to the compartmentalization effects that act to reduce the impact of bimolecular termination and provide high rates of polymerization even of monomers with a low propagation rate coefficient (k_p), also reduce the irreversible consumption of RAFT agent and passivation of the working electrode. The eRAFT polymerization process was performed at ambient temperature; lower temperatures may be possible. This offers clear advantages when low boiling monomers (*e.g.,* butadiene), temperature-sensitive monomers (*e.g.,* epoxy functional), or systems comprising biomolecules susceptible to denaturation are used. A further advantage of the eRAFT process relates is that initiation can be turned off or on at the flick of a switch or precisely controlled by adjusting current. This temporal control enhances multiblock synthesis by enabling the process to be halted at a chosen conversion (*e.g.,* to remove samples for analysis) or at complete conversion to be restarted for subsequent monomer additions. The process is demonstrated with the one pot synthesis of a triblock, poly(butyl methacrylate)-*block*-polystyrene-*block*-poly(4-methylstyrene) [PBMA-*b*-PSt-*b*-PMS], and a tetrablock, poly(butyl methacrylate)-*block*-polystyrene-*block*-poly(styrene-*stat*-butyl acrylate)-*block*-polystyrene [PBMA-*b*-PSt-*b*-P(BA-*stat*-St)-*b*-PSt], each block with high monomer conversion (> 95%), low molar mass dispersity ($Đ < 1.115$) as free-flowing, colloidally stable latexes [11].

Outlook

RDRP and RAFT polymerization were invented 30 years ago bringing new life to radical polymerization, then considered a mature technology with few prospects for further development. The renaissance continues, as the methodology continues to evolve, enabling current and future technologies.

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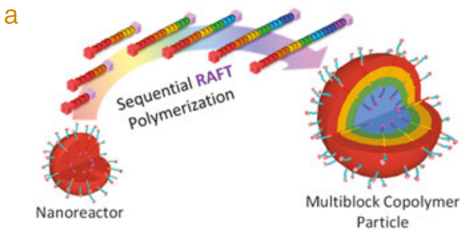

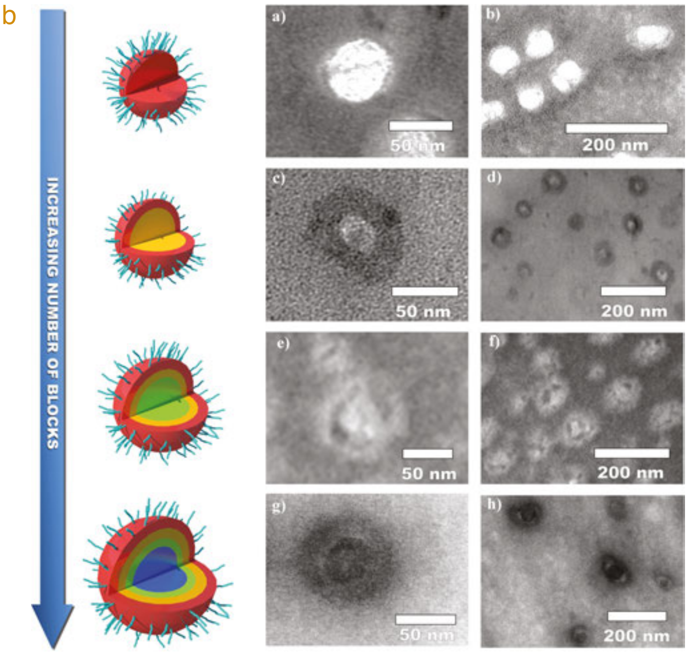

Scheme 8 (a) Illustration of the nanoreactor concept for seeded RAFT emulsion polymerization. (b) Development of particle morphology. Reproduced from ref [24] © American Chemical Society, and ref [16] © Wiley, respectively

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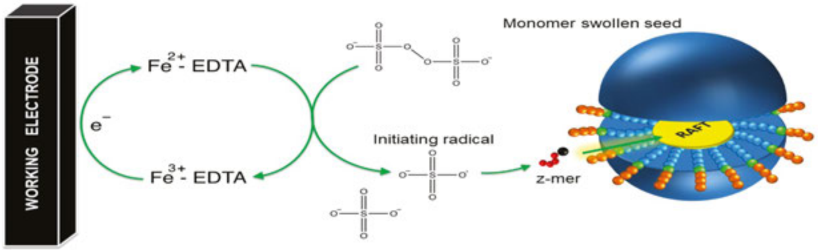

Scheme 9. Illustration of electrochemically initiated seeded RAFT emulsion polymerization. Reproduced from ref [11].

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The Stepto Lecture Award

The Stepto Lecture Award was established in 2016 to honour Bob Stepto, who was a substantial contributor to the IUPAC Polymer Division over several decades, including as Chair of the Commission on Macromolecular Nomenclature (now the Subcommittee on Polymer Terminology) for the period 1991–2000 and then as Chair of the Polymer Division over 2002–05 [1]. Bob was also an outstanding polymer scientist, with over 300 publications to his name, and a friend and mentor to many, both within and outside of IUPAC.

The award comprises a special plenary lecture at Macro meetings. The winner should not only be an exceptional polymer scientist recognized as a true world leader in his or her research field, but—in the true spirit of Bob—should also have made an indelible contribution to the polymer science community beyond the research domain, whether through IUPAC and/or by other means. The inaugural winner of the Stepto Lecture Award at Macro2016 in Istanbul was Michael Buback. Following this, Chris Ober received the Award at Macro2018 in Cairns and Tony Ryan at Macro2020+.

The next Stepto Lecture will be presented in July 2024 during the 50th World Polymer Congress that will take place at the University of Warwick, in Coventry, UK. (www.macro2024.org)

Graeme Moad's first connection with IUPAC was as an observer at an polymer meeting in Berlin in September 1982. However, his IUPAC career began with the Santa Margaretha Ligure meetings on Radical Polymerization in 1987 and 1996, which saw the birth of what is now the IUPAC Polymer Division Subcommittee for Modeling of Polymerization Kinetics and Processes. In 2001, he was coerced by Bob Gilbert to join the Polymer Division Subcommittee for Polymer Terminology. He has played an active role in both subcommittees since that time. He was a titular member of the Polymer Division 2012-2015, an associate member 2016-2021, a leader or member of various projects, and remains an active member of the Division.