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## Overview of RAFT Polymerization

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The first announcement of RAFT (reversible addition–fragmentation chain transfer), polymerization making use of thiocarbonylthio transfer agents as a means of controlling the outcome of radical polymerization was made at the IUPAC World Polymer Congress Macro 98 by Dr Ezio Rizzardo just over 21 years ago in July 1998. The first publication on RAFT polymerization detailing the work at CSIRO was published shortly thereafter [1]. The paper in *Macromolecules* [1] that announced the RAFT process, is currently the most highly cited paper in that journal.

RAFT polymerization had been disclosed in a CSIRO/DuPont patent that was published in January 1998 [2]. 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 [3]. That first RAFT patent [2] 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 a still-increasing number of RAFT-related inventions (Figure 1.1). However, commercial success stories associated with RAFT polymerization and other reversible-deactivation radical polymerization (RDRP) are few [4]. With the first RAFT patents having reached the end of their enforceable life, we might now envisage an upsurge in commercial applications.

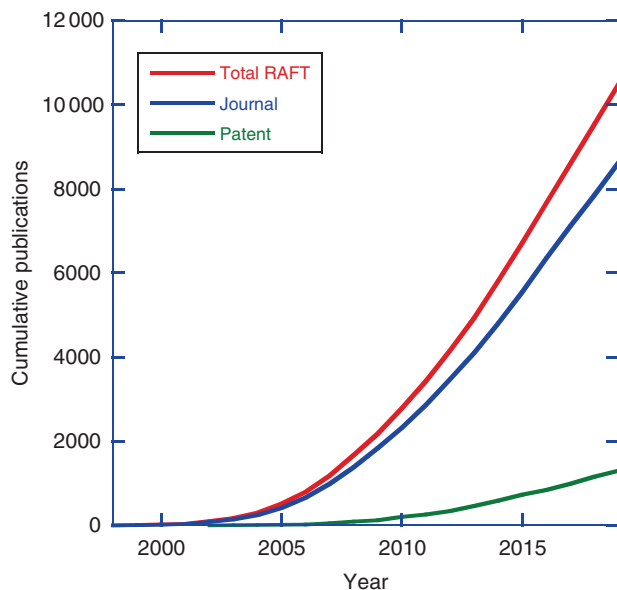
The further development of RAFT was chronicled in a series of reviews that appeared in the *Australian Journal of Chemistry* in 2005 [5], 2006 [6], 2009 [7], and 2012 [8]. Since that time reviews of RAFT polymerization have targeted specific application areas or have been otherwise limited in scope. A number of perspectives have recently appeared to mark the 20th anniversary of the discovery of RAFT polymerization [9–11].

The year 2008 saw the publication of the *Handbook of RAFT Polymerization* that comprised 12 chapters from major players in the field at the time [12]. The 10 years leading up to the handbook had seen a revolution in the field of radical polymerization, which can, in large part, be attributed to the invention of RAFT and other RDRP methods. Many of the same authors who contributed to that handbook have also provided chapters for the present work.

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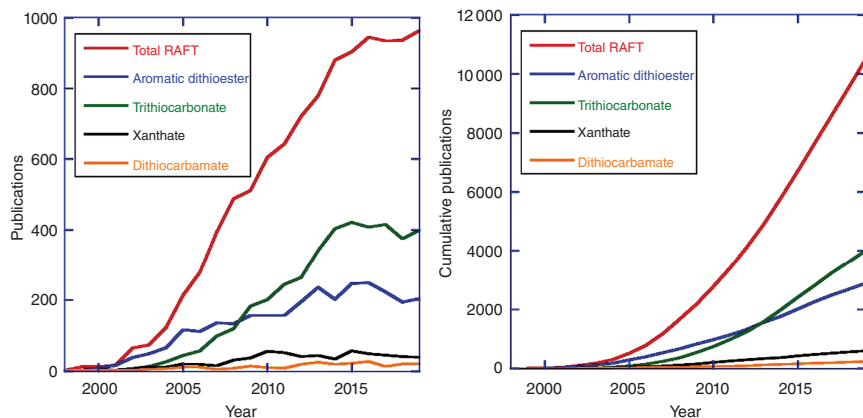
**Figure 1.1** Cumulative publications relating to RAFT polymerization for the period 1998–2019 based on a Scifinder™ substructure search on the major classes of RAFT agent carried out in February 2020 on the RAFT agent structures and the terms ‘RAFT’ and ‘MADIX’ (in the case of xanthates).

Publications relating to RAFT polymerization show no signs of abating. The present work is intended as a survey of developments in RAFT polymerization focusing on the last 10 years.

RAFT polymerization is a form of RDRP and can impart living characteristics (low molar mass dispersity, high-end group fidelity, ability to synthesize complex architectures) to radical polymerization. The technique owes its success to the wide range of tolerated functionality and polymerization conditions, and to the vast range of monomers whose (co)polymerization can be successfully controlled.

In 2008, at the time the RAFT Handbook was published, one factor seen as significant in holding back the exploitation of RAFT polymerization was that RAFT agents were not commercially available [13]. This situation has now been redressed [14].

It has often been pointed out that to achieve the highest level of control over polymerization, one needs to select the RAFT agent for the monomer(s) being polymerized. A dizzying array of RAFT agents,  $Z-C(=S)S-R$ , varying in the activating (Z) and reinitiating (R) substituents, are now available commercially or are able to be synthesized [15]. However, with just two RAFT agents, e.g. a trithiocarbonate, for more activated monomers such as styrenes and (meth)acrylates, and a xanthate or a dithiocarbamate, for less activated monomers such as vinyl esters or vinyl amides, one can achieve acceptable control over the full monomer spectrum [16]. Moreover, by using a switchable RAFT agent or a RAFT agent with balanced activity, e.g. a 1*H*-pyrazole-1-carbodithioate [17, 18], one can achieve only slightly compromised control with just one RAFT agent.



**Figure 1.2** Publication rate for RAFT polymerization using different classes of RAFT agent for the period 1998–2019. Includes both patent and open literature publications. Based on a Scifinder™ substructure search carried out in February 2020 on the RAFT agent structures and the terms 'RAFT' and 'MADIX' (in the case of xanthates). The total RAFT number relates to a search on the terms 'RAFT polymerization' or 'reversible addition fragmentation chain transfer'.

In the following text we mention the chapters of this work by topic and refer to chapters of the 2008 Handbook of RAFT Polymerization on similar topics.

We commence with a chapter on terminology in RDRP and RAFT polymerization [19]. Then we go back to the basics and provide a beginner's guide on *How to Do a RAFT polymerization* [14].

There are four chapters concerning the detailed kinetics and mechanism of the RAFT process: *Kinetics and Mechanism of RAFT Polymerizations* [20], *RAFT Polymerization, Mechanistic Considerations* [21], *Mechanisms, Quantum Studies of RAFT Polymerization* [22], and *Mathematical Modelling of RAFT Polymerization* [23]; these concern the detailed kinetics and mechanism of the RAFT process and the ongoing efforts to enhance our understanding of the process (2008 chapters [24, 25]).

The next four chapters provide a critical survey of the four major classes of RAFT agents, namely, dithioesters [26], trithiocarbonates [27], xanthates [28], and dithiocarbamates [29] as regards activity as RAFT agents, polymerization mechanisms, and their application in polymer synthesis (2008 chapters [16, 30, 31]). The year 2008 marked the point in time at which trithiocarbonates became the most popular RAFT agents (Figure 1.2).

There are two chapters concerning the more recent developments in processes for initiating RAFT polymerization. *Overview of Photoregulated Reversible Addition–Fragmentation Chain Transfer (RAFT) Polymerization* [32], *Redox-Initiated RAFT Polymerization, and (Electro)Chemical Activation of RAFT Agents* [33].

Further two chapters relate specifically to RAFT polymerization in aqueous solution or in heterogeneous medium and to polymerization-induced self-assembly: *Considerations for and Applications of Aqueous RAFT Polymerization* [34], *RAFT-Mediated Polymerization-Induced Self-Assembly (PISA)* (2008 chapters [35, 36]) [37].

Three chapters concern the synthesis of functional polymers, sequence-defined polymers, and RAFT end-group transformation. *RAFT Functional End Groups: Installation and Transformation* [38], *Sequence-Encoded RAFT Oligomers and Polymers* [39], *Synthesis and Application of Reactive Polymers via RAFT Polymerization* (2008 chapter [40]) [41].

We then go into detail on the other aspects of polymer architecture with chapters on *RAFT Crosslinking Polymerization* [42], *Complex Polymeric Architectures Synthesized Through RAFT Polymerization* [43], *Star Polymers by RAFT Polymerization* [44], *Surface and Particle Modification via RAFT Polymerization: An update* (2008 chapters [45–47]).

Two chapters relate to application areas. *An Industrial History of RAFT Polymerization* [48] describes the development of RAFT by reference to the patent literature and points to where RAFT is being applied in industry (2008 chapters [49, 50]). The application of high throughput robotic platforms to RAFT polymerization as an aid to shortcut the process of selecting reaction conditions and to create polymer libraries for screening purposes is discussed in *High Throughput/High Output Experimentation in RAFT Polymer Synthesis* [51].

A final chapter demonstrates that the RAFT process is not applicable only to radical polymerization and details the recent work on *Cationic RAFT Polymerization* [52].

It is our hope that by compiling and highlighting recent achievements in RAFT chemistry, we will inspire further research and further drive the ever-increasing range of applications.

It should be stated that there is no lack of recent review material relating to RAFT polymerization and its application. At least 30 reviews have been published since 2017 specifically on RAFT polymerization (non-English language reviews are not included in this list). These include overviews and perspectives [9–11, 53, 54], polymerization-induced self-assembly (PISA) [55\*, 56–58], monomers from renewable resources [59], polymer brushes [60], therapeutics and bioapplications [61–63], star polymers for bioapplications [64], hydrogels for drug delivery [65], organic/inorganic nanohybrids for bioapplications [66], gold nanoparticles [67], 3D-printing [68], stimuli-responsive polymers [69], conjugated diene monomers [70], single-unit monomer insertion (RAFT-SUMI) [71], redox initiation [72], hydroxyl radical initiation [73], photoRAFT [74], externally regulated polymerization [75], initiation with ionizing radiation [76], dithiocarbamate RAFT agents [77]\*, optoelectronic applications [78], and graft copolymers by transfer-to [79]. An asterisk (\*) indicates that an update to the review appears in this volume. Earlier reviews on RAFT polymerization have been summarized previously [5–8, 69].

There are additionally many reviews on radical or RDRP methods more generally that contain substantial content on RAFT polymerization or RAFT applications. The more than 50 reviews published since 2017 include reviews on ultrahigh molar mass polymers [80, 81], self-condensing vinyl polymerization [82], complex architectures by copolymerization of multi-vinyl monomers [83], nanoparticles by surface-initiated polymerization [84], synthesis of multi-block copolymers

[85], PISA [86–89], biosensors [90, 91], hydrogels [92], biopolymer conjugates [93–95], glycopolymers for bioapplications [96, 97], phosphonium polymers for bioapplications [98], stimuli-responsive polymers in bioapplications [99–101], oligonucleotide-based nanomaterials [102], star polymers for bioapplications [103, 104], biocatalytic initiation [105, 106], alkylborane initiators [107], the use of Fenton chemistry for initiation [108], dialkyldiazene initiation [109], influence of external fields on radical polymerization [110], polymerization of alkyl 2-cyanoacrylates [111], semi-fluorinated (meth)acrylates [112], terpenes [113], rosin-derived monomers [114], polymers with pedant fatty acid chains [115], lignin-derived polymers [116], chitosan-derived polymers [117], graphene-derived polymers [118], functionalization of carbon nanotubes [119], cyclopolymerization for sequence-defined polymers [120], PhotoRDRP [121–124], thermoresponsive polymer ionic liquids [125], polyhedral oligomeric silsesquioxane (POSS)-hybrids [126], 3D-printing [127], porous polymers [128], combination or RAFT or atom-transfer-radical polymerization (ATRP) with ring-opening polymerization [129], metal-free RDRP [130], cyclic polymers [131], end-group modification [132], and metallopolymers [133].

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