Progress in Polymer Science 111 (2020) 101311

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/progpolymsci

# Reversible-deactivation radical polymerization (Controlled/living radical polymerization): From discovery to materials design and applications

Nathaniel Corrigan[a], Kenward Jung[a], Graeme Moad[b,*], Craig J. Hawker[c,*], Krzysztof Matyjaszewski[d,*], Cyrille Boyer[a,*]

[a] Centre for Advanced Macromolecular Design (CAMD), Australian Centre for Nanomedicine (ACN), and School of Chemical Engineering, University of New South Wales (UNSW) Sydney, Sydney, NSW2052, Australia
[b] CSIRO Manufacturing Bag 10, Clayton South, VIC3169, Australia
[c] Materials Research Laboratory and Departments of Materials, Chemistry and Biochemistry, University of California, Santa Barbara, California93106, United States
[d] Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania15213, United States

ARTICLE INFO

*Article history:*
Received 27 August 2020
Revised 8 October 2020
Accepted 12 October 2020
Available online 14 October 2020

*Keywords:*
Reversible-deactivation radical polymerization (RDRP)
Atom transfer radical polymerization
Reversible addition-fragmentation chain transfer polymerization
Polymer architectures
Network
Self-assembly
Bioapplications

ABSTRACT

Reversible-deactivation radical polymerization (RDRP) processes, such as atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization and nitroxide mediated polymerization (NMP) have revolutionized polymer synthesis by providing polymer chemists with powerful tools that enable control over architecture, composition and chain length distributions. The user-friendly nature of these procedures have allowed RDRP-derived polymers to be used in the construction of advanced materials with unique and enhanced properties. This review covers the progress of RDRP from its conception to the current state-of-the-art. A brief introduction to the sources of RDRP, general mechanisms, and methodological progressions are presented, and the suite of advanced and highly tailorable materials possible through these techniques is discussed to illustrate the significant potential for even greater impact across multiple disciplines.

© 2020 Elsevier B.V. All rights reserved.

## 1. Introduction

With the anniversary of Staudinger's pioneering work on macromolecular structures, it is instructive to examine the impact of polymer science in providing solutions to a multitude of societal issues, while also presenting key directions for addressing future challenges. Indeed, the utilization of polymer materials is commonplace in our everyday lives, from commodity polymers used as packaging, paints, or structural materials, to highly engineered polymers used in microelectronics and medicine. Finding new or improved polymer-based solutions to these challenges will require advances in synthetic polymer chemistry, with the ability to tune properties such as biocompatibility, degradability, and mechanical strength through the control of polymer structure being key.

While the future promise of polymer materials is clear, the majority of commercial polymers are produced via conventional step growth or chain growth polymerizations with limited ability to impart fine control over macromolecular structure. Chain growth polymerizations are often characterized by the generation of an active initiating species, propagation by addition of monomer units and the eventual termination of the polymer chains. The occurrence of unavoidable and irreversible chain transfer/termination reactions leads to broad chain length distributions that are inactive with respect to further chain growth; effectively "dead" chains. The properties of polymer materials and the controlled introduction of functional building blocks is therefore limited.

To overcome these challenges, polymerization techniques have been developed which reduce irreversible termination and allow for macromolecular composition, topology, and polymer chain length distributions to be more precisely controlled. A seminal

* Corresponding authors.
*E-mail addresses:* graeme.moad@csiro.au (G. Moad), hawker@mrl.ucsb.edu (C.J. Hawker), matyjaszewski@cmu.edu (K. Matyjaszewski), cboyer@unsw.edu.au (C. Boyer).

https://doi.org/10.1016/j.progpolymsci.2020.101311
0079-6700/© 2020 Elsevier B.V. All rights reserved.

**Abbreviations**

| | |
|---|---|
| 2D | two-dimensional |
| 3D | three-dimensional |
| ARGET | activators regenerated by electron transfer |
| ATRP | atom transfer radical polymerization |
| BIRP | organobismuthine mediated radical polymerization |
| BSA | bovine serum albumin |
| CLRP | controlled/living radical polymerization |
| CSIRO | Commonwealth Scientific and Industrial Research Organization |
| DMAEMA | 2-(dimethylamino)ethyl methacrylate |
| DNA | deoxyribonucleic acid |
| eATRP | electrochemically mediated ATRP |
| eRAFT | electrochemically mediated RAFT |
| GOx | glucose oxidase |
| HRP | horseradish peroxidase |
| ICAR | initiators for continuous activator regeneration |
| iniferter | initiator-transfer agent-terminator |
| ITP | iodine transfer polymerization |
| IUPAC | International Union of Pure and Applied Chemistry |
| L | ligand |
| macro-CTA | macromolecular control agent |
| MADIX | macromolecular design via the interchange of xanthates |
| mechano-ATRP | mechanically mediated ATRP |
| MMA | methyl methacrylate |
| $M_n$ | number average molecular weight |
| $Mt^m$ | transition metal species with an oxidation state of $m$ |
| *n*BA | *n*-butyl acrylate |
| NMP | nitroxide mediated polymerization |
| P | poly (prefix) |
| $P_1$-X | initiator |
| PC | photocatalyst |
| PCR | polymerase chain reaction |
| PEG | poly(ethylene glycol) |
| PET-RAFT | photoinduced electron/energy transfer-RAFT |
| photoATRP | photocontrolled ATRP |
| PISA | polymerization induced self-assembly |
| $P_n$• | carbon centered propagating radical species |
| $P_n$-X | dormant polymer chains |
| $R_1R_2NO$• | stable nitroxide radical |
| $R_1R_2NO$-$P_n$ | dormant alkoxyamine species |
| RAFT | reversible addition-fragmentation chain transfer |
| RDRP | reversible-deactivation radical polymerization |
| SARA | supplemental activator and reducing agent |
| SBRP | organostilbine mediated radical polymerization |
| SCNP | single-chain polymeric nanoparticle |
| SET | single electron transfer |
| SF-RAFT | surfactant-free RAFT |
| SI-RDRP | surface-initiated reversible-deactivation radical polymerization |
| siRNA | small interfering ribonucleic acid |
| St | styrene |
| STEM | structurally tailored and engineered macromolecular |
| TERP | organotellurium mediated radical polymerization |
| UV | ultraviolet |
| VA044 | 2,2′-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride |
| X | control agent |
| X-$Mt^{m+1}$/L | oxidized transition metal complex coordinated to a halide |
| $X_n$ | degree of polymerization |
| $\chi$ | Flory-Huggins interaction parameter |

example is the work of Szwarc describing living ionic polymerizations in which termination of the propagating species is completely avoided through rigorous control over reaction conditions and monomer purity. [1] Following polymerization, further addition of other monomers allows the polymerization to continue, in turn leading to the formation of block copolymers. As the ionic propagating species in these systems are incapable of being terminated by combination or disproportionation, these processes can be considered as living, in the absence of irreversible chain transfer. [2]

In contrast, radical chain growth processes involve unavoidable radical-radical reaction events which does not allow these systems to be living. However, strategies have been developed to effectively minimize radical termination and allow radical polymerization to display most of the characteristics of living polymerization. [2,3] Otsu and Yoshida's introduction of the *ini*tiator-trans*fer* agent-*ter*minator (iniferter) concept in 1982 [4] is widely considered to be one the first examples of "living" radical polymerization, along with Borsig's work using 3,3,4,4-tetraphenyl-hexane as labile initiator, [5] and Tatemoto's work on iodine transfer polymerization (ITP). [6] In Otsu's work, the initial iniferter is a tetraethylthiuram disulfide that can be cleaved at 60 °C or under UV irradiation in the presence of methyl methacrylate (MMA) or styrene (St) to form a telechelic dithiocarbamate capped PMMA or PSt with molecular weights that are dependent on the initial ratio of iniferter to monomer. Critically, the dithiocarbamate functionalized polymers also behaved as iniferters and UV irradiation in the presence of additional monomer led to the formation of diblock copolymers, thus demonstrating reversible termination behavior and reactivation of dormant polymer chains, via a radical mechanism. It should be noted however, that the dithiocarbamate end-groups were degraded during this process and major advances were needed for the development of controlled radical polymerization systems.

Driven by the increased versatility of radical polymerization compared with ionic polymerizations, including wider monomer scope and scalable, user-friendly reaction conditions, there has been an explosion of interest in the development of effective strategies for imparting living characteristics to radical polymerization. [7–14] These systems can be broadly categorized into three distinct chemical mechanisms: stable radical-mediated polymerization, atom transfer radical polymerization, and degenerative-transfer radical polymerization (Fig. 1**a**). While such systems were commonly called living radical polymerization, controlled radical polymerization or controlled/living radical polymerization (CLRP), in 2010 IUPAC recommended the use of the term reversible-deactivation radical polymerization (RDRP) as an encompassing terminology. [2] IUPAC also deprecated all terms that include "living radical" in attempting to describe a radical polymerization that has some living characteristics but in which some amount of irreversible chain termination occurs. These deprecated terms include "living radical", pseudo-living radical, quasi-living radical, and controlled/living radical.

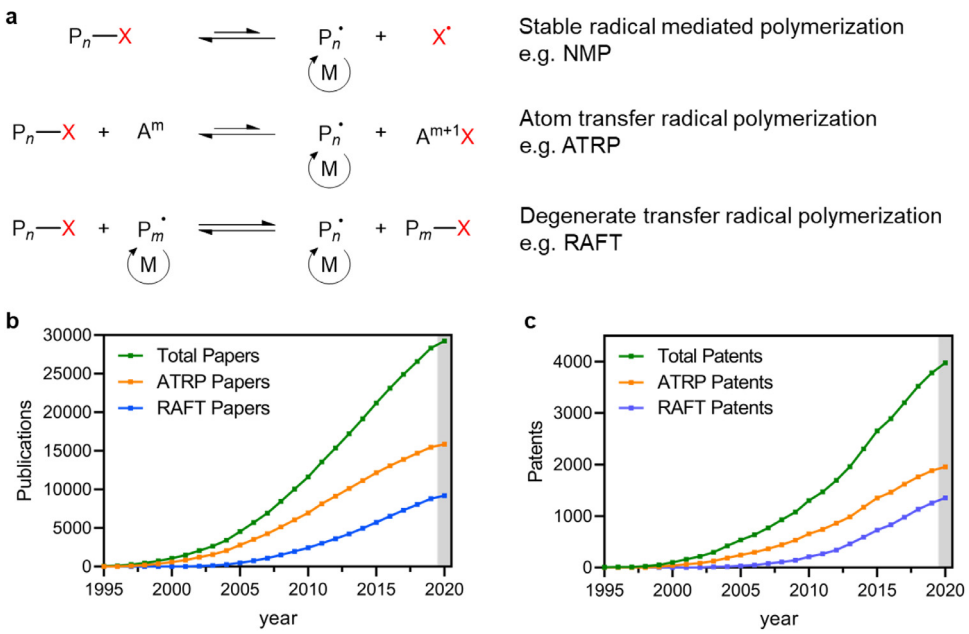


**Fig. 1.** Mechanism and prevalence of RDRP. a) General mechanisms of reversible-deactivation radical polymerization. $P_n$•: propagating radical species, $P_n$-X: dormant capped polymer chains. b) Cumulative Number of papers (articles and reviews) for RDRP from 1995. c) Cumulative Number of patents for RDRP from 1995. Data generated from SciFinder on August 21, 2020 using the search terms for ATRP: "atom transfer radical polymerization", for RAFT: "RAFT polymerization", and for total RDRP: those previously outlined for ATRP and RAFT in addition to "nitroxide mediated polymerization","controlled radical polymerization", "living radical polymerization", or "reversible deactivation radical polymerization".

The successful demonstration of increased versatility, high level of control over the polymerization process, and non-stringent conditions has allowed RDRP to become the preeminent method for polymerization of vinyl monomers. A clear indication of this success is the high number of publications annually, and the broad multidisciplinary fields in which RDRP has been applied. Fig. 1**b** shows the cumulative number of publications (articles and reviews) for RDRP and the two most commonly used RDRP techniques, namely atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization. A similar increase in industrial interest is reflected in the patent literature (Fig. 1**c**).

Since the development of effective RDRP techniques in the 1990's, the growth of the field has been substantial, with more than 30,000 total publications and around 4,000 patents. From early studies focused on method development, RDRP has evolved to encompass an extensive suite of capabilities that facilitate the preparation of polymers for therapeutic applications (nanomedicine), nanotechnology, and materials science. As such, a comprehensive review of RDRP is impractical; instead, the focus of this manuscript is to highlight the major developments and provide an overview of the current capabilities and future potential of RDRP. Herein, the fundamental benefits of RDRP are introduced and compared with those of other polymerization techniques. The unique benefits of RDRP are identified and the evolution of the major variants of RDRP presented. The synthetic methodologies for the preparation of well-defined macromolecules by RDRP and the applications thereby enabled are described. Finally, the authors offer perspectives on the field and trends for future materials, their production and commercialization.

## 2. Benefits of reversible-deactivation radical polymerization

A range of effective strategies for RDRP have been developed which differ in their reaction mechanisms, and reagents and conditions used. However, they are linked by an ability to provide effectively simultaneous growth of all polymer chains. This even chain growth can be achieved when all chains commence growth at the commencement of polymerization, the fraction of chains that undergo termination is small with respect to the total number of living (dormant + active) chains, and the dynamics of dormant-active equilibria is rapid with respect to chain growth and is achieved with the aid of control agents (X). With careful selection of the polymerization conditions, and the initiator ($P_1$-X) and control agent (X), the concentration of dormant polymer chains ($P_n$-X) far exceeds that of the active propagating species during polymerization (typically $[P_n\text{-X}]/[P_n\bullet] > 100{,}000$), [15] and irreversible termination between active propagating radicals can be reduced such that the polymerization shows many of the characteristics normally associated with living polymerization.

One of the main benefits of RDRP stems from the stability and orthogonal nature of the control agent, which allows the polymerization to proceed continuously as in a living process. For the production of linear polymers, successful RDRP displays linearly increasing polymer molecular weights with monomer conversions. As the reagent stoichiometry determines the average number of monomer units per polymer chain (i.e. the predicted degree of polymerization ($X_n$) at full monomer conversion), polymers with predetermined number average molecular weight ($M_n$) can be easily achieved by altering the initial concentrations of control agent and monomer and/or running the reaction to a defined monomer conversion (Fig. 2**b**). In addition, if the initialization process and the rate of active dormant chain equilibration is rapid compared to propagation, the breadth of the polymer chain length distributions is minimized and can approach that of a Poisson distribution (Fig. 2**c-d**). It should be noted that the linear relationship between polymer molecular weight and monomer conversion in RDRP is a direct result of high end-group fidelity; side reactions that result in the loss of control agent can lead to deviations between predicted and experimentally achieved molecular weights.

Retention of the chain-end functionality throughout the polymerization also allows the polymer chains to be extended in the presence of additional monomers (Fig. 2**a**). The ability to perform repeated chain extensions allows the formation of topologically

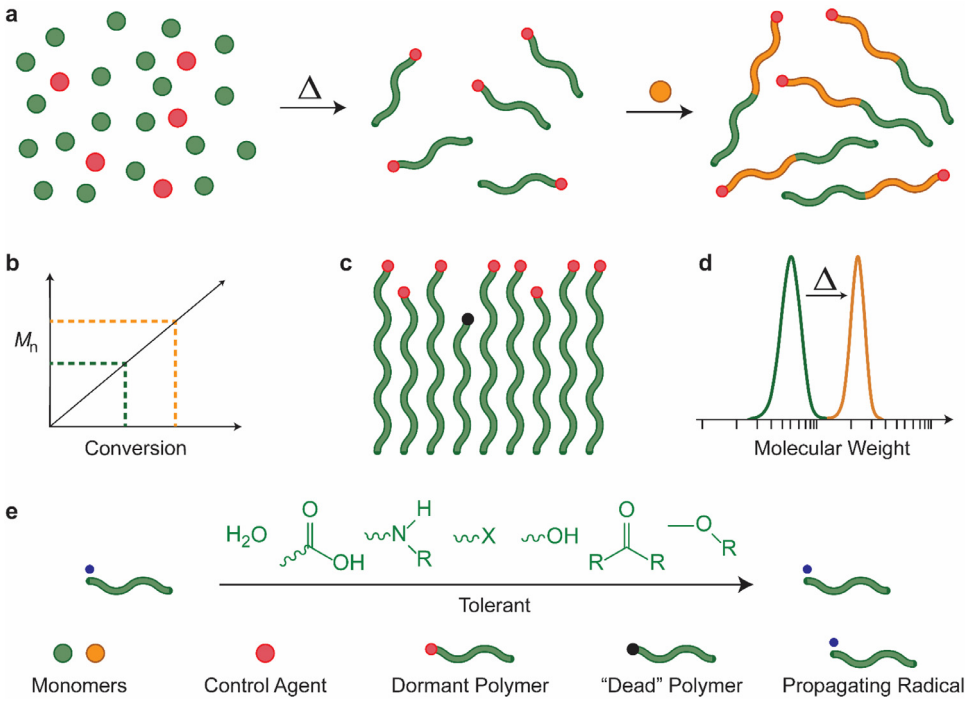


**Fig. 2.** Benefits of successfully mediated RDRP. a) Representative process showing the production of diblock copolymers through RDRP; b) linear relationship between monomer conversion and number average molecular weight; c) even chain length distributions; d) narrow molecular weight distributions approaching a Poisson distribution and the complete shift in molecular weight upon chain extensions; e) high tolerance of typical propagating radical specie to various functional groups.

complex macromolecules, including block, star, and brush copolymers and diverse variants thereof (*vide infra*). In combination with the tightly controlled molecular weights and polymer chain length distributions possible through RDRP, these architecturally diverse polymers have enabled additional opportunities for polymeric materials in high-tech applications owing to their more finely controlled properties.

Another major benefit of RDRP is the orthogonal reactivity of radical polymerization, which provides effective polymerization under more diverse reaction conditions compared with other polymerization techniques. Although the ability to control polymer molecular weights and perform chain extensions are outstanding benefits of RDRP, they are not exclusive to RDRP. Indeed, cationic, anionic, ring opening, and ring opening metathesis polymerization systems can all be used in this regard. However, as RDRP is a radical mediated process, it can be performed under more diverse reaction conditions and in the presence of a greater range of chemical functionalities compared with other polymerization systems (Fig. 2**e**). For instance, cationic and anionic polymerizations must be typically performed under very stringent conditions in the absence of water and air (oxygen and carbon dioxide) due to the sensitivity of the active propagating species to these impurities. Comparatively, RDRP can be performed in a wider range of solvents, including aqueous media. In addition, although the radical propagating species in RDRP are sensitive to oxygen, several strategies have been developed to allow polymerization to proceed fully open to the air (*vide infra*). [16]

In concert with wide tolerance to different reaction conditions, RDRP is compatible with a varied range of chemical functionalities, which has allowed the synthesis of a broader range of functional polymers compared with other polymerization techniques. For example, the polymerization of functional monomers containing carboxylic acids, alcohols, esters, and secondary and tertiary amines can all be successfully controlled through RDRP approaches. Additionally, the dormant chain end functionality in RDRP derived polymers is synthetically accessible and many strategies exist to modify the end-group functionality after polymerization to allow for further transformations. [17,18]

## 3. Mechanistic progression of RDRP

In the interests of brevity, the following section provides only a general overview of the mechanisms for the reversible deactivation of propagating radicals for the most widely utilized RDRP processes. It should be noted, however, that a multitude of mechanistically distinct RDRP variants have been developed to provide control over the propagating radical activation-deactivation equilibrium. In addition, as with any chemical process, kinetic factors underpin the effectiveness of RDRP under different reaction conditions; while reaction kinetics for RDRP are largely outside of the scope of the present review, interested readers are referred to more comprehensive literature on the topic. [15,19]

### 3.1. Mechanisms of RDRP

In the mid-1980s, an RDRP process was developed at the Commonwealth Scientific and Industrial Research Organization (CSIRO) that exploited stable aminoxyl radicals to reversibly deactivate propagating radical species. [20,21] The CSIRO research focused on production of low dispersity, acrylate-based polymers of relatively low molar mass and little was published in the open literature. This aminoxyl-mediated radical polymerization, more commonly referred to as nitroxide-mediated polymerization (NMP), came to prominence in the early 1990s when Georges and colleagues applied NMP to produce low dispersity polystyrene, [8] and was popularized further through the discovery, by Hawker, Benoit and others, of more versatile nitroxides capable of mediating effective RDRP of a wider range of monomer families and extension to alkoxyamine initiating systems. [8,22–25] NMP is performed via a stable radical mediated polymerization mechanism (Fig. 3**a**). At elevated temperatures, the alkoxyamine C-ON bond is cleaved to form a carbon centered radical ($P_n$•) capable of reacting with vinyl

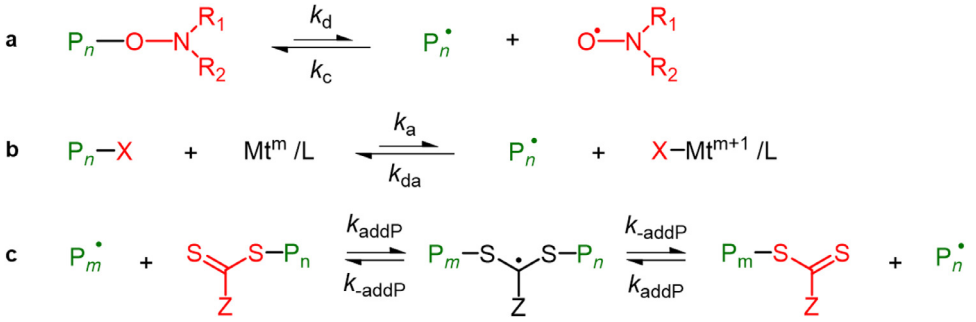


**Fig. 3.** Simplified mechanisms of activation-deactivation equilibria in RDRP. a) Nitroxide mediated polymerization; b) ATRP; c) RAFT polymerization.

monomers and a stable nitroxide radical ($R_1R_2NO•$). Recombination of the propagating radicals and the nitroxide radicals reforms a dormant alkoxyamine species ($R_1R_2NO\text{-}P_n$). Critically, the C-ON bond homolysis is dependent on both the reaction temperature and the alkoxyamine structure, and many variants have been synthesized to successfully regulate RDRP.

In 1994-1995, Matyjaszewski and Wang, [9] and Sawamoto's team, [10] independently presented new metal catalyzed RDRP processes that operated through an atom-transfer radical addition process. [26,27] The system developed by Sawamoto and coworkers employed dichlorotris(triphenylphosphine) ruthenium(II) as a metal catalyst in conjunction with a bulky Lewis acid to mediate the reversible chlorination of MMA propagating radicals. [10] Matyjaszewski and Wang used a ligated copper complex as the metal catalyst in the absence of a Lewis acid to mediate the reversible chlorination of styrenic propagating radical species and provide successful RDRP. Owing to the use of redox-active transition metal catalysts, these processes are often called metal-catalyzed living radical polymerization, [11,28] but are more commonly referred to as atom transfer radical polymerization (ATRP). [29,30] Since these early systems, a large variety of other ATRP systems have been developed that use free radical initiators, [31] reducing agents, [32,33] or zero valent metal species [34–36] to reduce the required catalyst concentrations and reaction temperatures by modulating the activator-deactivator equilibrium. Furthermore, while the majority of systems use copper complexes to mediate RDRP, [37] a variety of other redox active transition metal complexes can also be used effectively [28,38] and all of these successful systems benefit from a wide range of potential ligands that can be used to further modulate catalyst activity.

For ATRP systems, although the starting reagents and catalytic system can vary considerably, the activation-deactivation mechanisms generally follows the same pattern: the activating transition metal complex in its lower oxidation state ($Mt^m$/L, where $Mt^m$ is a transition metal species with an oxidation state of *m*, and L is a ligand) reacts with a dormant alkyl halide ($P_n$-X) to form an oxidized transition metal complex coordinated to a halide (X-$Mt^{m+1}$/L) and a carbon centered propagating radical species ($P_n$•). The deactivating transition metal-halide complex can then react with the propagating radical species to reform the dormant polymer chains and the original transition metal complex (Fig. 3**b**). It should be noted that there has been debate over the mechanism for some variants of Cu(0) mediated ATRP; however, the activation process of dormant species is predominantly based on the reaction with Cu(I)/L complexes and deactivation of growing radicals by the reaction with Br-Cu(II)/L complexes. Cu(0) acts as reducing agent and as a supplemental activator (SARA). [39] Regardless, ATRP has been used extensively to perform successful RDRP as demonstrated by the consistently high number of publications in this area over the past 20 years (Fig. 1**b**).

Reversible addition-fragmentation polymerization using macromonomers (the process was not called RAFT polymerization at the time) to form low dispersity methacrylate-based block copolymers was reported by CSIRO in 1995. [40,41] That method (now called sulfur-free RAFT) had limited application, but led to the development at CSIRO of the third major class of RDRP in 1998. [12] The process, now called reversible addition-fragmentation chain transfer (RAFT) polymerization, used thiocarbonylthio compounds to regulate the degenerative exchange of propagating radical species generated via conventional radical initiators. As shown in Fig. 3**c**, the propagating radical species can add to a thiocarbonylthio group to form an intermediate radical species, which further fragments at the weak C-S bond to form a dormant thiocarbonylthio-capped chain and a new propagating radical. [42,43] Successful RDRP can be achieved if the intermediate radical species fragments rapidly which allows all chains in the mixture to grow at approximately the same rate and thus narrow polymer chain length distributions are obtained. Upon completion of the polymerization, most chains are dormant and retain their thiocarbonylthio end-group, which allows isolation and repeated chain extensions to be performed.

RAFT polymerizations have been developed to use a range of thiocarbonylthio compounds, including many variants of dithioesters, [44,45] trithiocarbonates, [46] and dithiocarbamates. [45,47–49] Inspired by Zard's early work, [50] a RAFT variant that utilized xanthates to regulate polymerization was developed at approximately the same time as the pioneering CSIRO work. This process was termed macromolecular design via the interchange of xanthates (MADIX) and patented by Rhodia. [51,52] The MADIX and RAFT processes are essentially identical mechanistically, however, the structure of the thiocarbonylthio compound (i.e. the activating group, Z and the homolytic leaving group, R) determine the effectiveness of RDRP in controlling the polymerization of various monomers (MADIX is more suitable for less-activated monomers, such as vinyl acetate). [42,53]

The processes described above, especially ATRP and RAFT polymerization, are the most utilized for RDRP. It should be noted, however, that several other systems have been developed, some earlier than ATRP or RAFT, to perform effective RDRP. For instance, one of the earliest examples of RDRP utilized iodo-compounds to regulate polymerization via a degenerate transfer radical polymerization mechanism. [54] This process, called iodine transfer polymerization (ITP), relies on an exchange of an iodine capping agent between dormant alkyl iodide polymer chains and propagating radical species. [6,14,55,56] Iodine compounds have also been used as capping agents to reversibly deactivate radical polymerization through the use of germanium, tin, and phosphorus catalysts, [57] and even amines. [58] These systems can be considered to operate via an atom-transfer radical polymerization mechanism, whereby the iodine is reversibly transferred

between the dormant polymer chain and the deactivating species. [2] Several organometallic mediated RDRP systems have also been developed, most notably organocobalt mediated radical polymerization, [13,59,60] but also organotellurium (TERP), organostilbine (SBRP), and organobismuthine-mediated polymerizations (BIRP). [61] These polymerizations generally follow a stable radical mediated polymerization mechanism, however, they can also follow both stable radical mediated and degenerate transfer radical polymerization mechanisms. [59]

### 3.2. Advances in RDRP techniques

While early RDRP systems were primarily activated thermally at elevated temperatures, more modern developments have focused on performing these reactions under more diverse conditions to address a broader scope of applications, particularly temperature sensitive bioapplications. In this regard, a range of different initiating systems have been used to induce RDRP, including those based on electrochemical potentials, [62] mechanical force, [63] enzymatic systems, [64] and light activation. [65,66]

#### 3.2.1. Electrochemical RDRP

In 2011, Matyjaszewski and coworkers proposed the external control of ATRP through the application of electric current, termed eATRP. [62] In this work, a cathodic current was used to reduce the deactivator, a ligated copper complex ($Cu^{II}$-$Br_2$/$Me_6$TREN), to form a $Cu^{I}$-Br/$Me_6$TREN species that could invoke ATRP through the regular halide transfer process from dormant halide capped species (Fig. 4**a**). Critically, the applied potential, current and total charge could be manipulated, which allowed the polymerization rate to be tuned or even completely stopped and restarted by periodic switching of the applied potential. Based on this insight, recent publications have addressed the possibility of performing electrochemically mediated RDRP through RAFT (named eRAFT) [67–69] and NMP. [70]

#### 3.2.2. Light mediated RDRP

Outside of thermal initiation, photochemical activation has been the most frequently used method for activating and controlling RDRP. [71–73] A number of photochemical strategies have been applied for radical generation in RDRP, including conventional type I and type II photoinitiation systems under UV irradiation that have been historically used for radical generation in uncontrolled radical polymerization processes. [74] Following radical generation, RDRP can proceed via the regular mechanisms outlined previously. More recently, strategies have been developed that allow the activation-deactivation equilibrium to be externally controlled through the application of light; such systems are often referred to as photocontrolled. As a result, these processes show spatiotemporal control, allowing the polymerization to be stopped and started on-demand in a spatially resolved manner. [75]

In 2013, Hawker and Fors developed a photocontrolled ATRP process using visible light photoredox catalysis. [65] In this system, irradiation of the Ir-based photoredox catalyst produces an excited state species that has both higher reduction and oxidation potentials in the excited state. [76] The excited state species can reduce an alkyl halide initiator to provide a propagating radical species and an oxidized catalyst-halide complex (Fig. 4**b**). The now highly oxidizing photoredox catalyst complex can reform the dormant polymer chains and the starting catalyst through recombination to close the catalytic cycle. This photoATRP process has been widely used since it was developed, with many reports illustrating and exploiting the high spatiotemporal control imparted through the use of light. [77–79] Moreover, the use of fully organic photoredox catalysts has provided effective RDRP that tailors towards applications that require stringent metal-free conditions. [80–83] PhotoATRP can also be accomplished without photoexcitation of Cu(I)/L activators, but by photoreduction of X-Cu(II)/L species in the presence of electron donors. This process effectively increases the [Cu(I)/L]/[X-Cu(II)/L] ratio and accelerates polymerization which would otherwise halt due to radical termination processes. [84,85]

A powerful extension of photocontrolled RDRP using readily available photocatalysts has been described by Boyer and coworkers. [66] This process, called photoinduced electron/energy transfer-RAFT (PET-RAFT) polymerization, relies on excitation of a photocatalyst (PC) and subsequent interaction with thiocarbonylthio groups to induce either electron or energy transfer from the PC to the thiocarbonyl group. The destabilized RAFT agent then undergoes cleavage of the weak C-S bond to form a propagating radical and a stabilized RAFT agent fragment. Recombination of the propagating radical species with the stabilized RAFT fragment closes the catalytic cycle and regenerates the dormant RAFT agent species (Fig. 4**c**). The propagating radical species can then interact with other dormant RAFT agent capped polymer chains via the regular RAFT degenerative exchange process. Critically, the use of a photocatalytic species in PET-RAFT polymerization eliminates the need for radical initiators in conventional RAFT polymerization, enabling preservation of the $\alpha$-chain-end functionality. Much like photoATRP, a wide range of metal and organic photocatalysts has been used to mediate effective PET-RAFT polymerization. [86–90] An outstanding benefit of the PET-RAFT technique is oxygen tolerance, which allows the polymerization to be performed under less stringent reaction conditions, and even under fully open to air conditions. [89–91]

While photoATRP and PET-RAFT polymerization have been the most widely implemented photocontrolled RDRP systems, many other works have been developed to exploit the benefits of photochemistry. [71] For instance, the early iniferter concept [4] described by Otsu and Yoshida has been performed using UV light, [92,93] and even extended to more mild activation under visible light irradiation. [94] Additionally, photocontrolled NMP systems have been developed by Gigmes, Lalavee and coworkers based on the photoactivation of chromophores tethered to the nitroxide group, and subsequent C-ON bond homolysis. [95] Other notable systems include photoinduced organocobalt mediated polymerization systems developed by Fu and coworkers, [96] and photoinduced reversible complexation mediated polymerization systems developed by Goto and coworkers. [97]

#### 3.2.3. Mechano-initiation in RDRP

The development of mechanochemistry has also inspired polymer chemists to develop systems which can be activated by mechanical stimuli. Mechano-initiation has been successfully implemented in RAFT and ATRP, with an excellent example being the report by Esser-Kahn and coworkers on the use of commercially available barium titanate ($BaTiO_3$) piezoelectric nanoparticles and mechanical force in the way of ultrasonication to induce ATRP. The piezoelectric nanoparticles reduce the ligated $Cu^{II}$ deactivator complexes to the corresponding $Cu^{I}$ activators under ultrasonication, allowing for ATRP in the presence of *n*-butyl acrylate (*n*BA) and an alkyl bromide initiator (Fig. 4**d**). [63] In this case, the generation of the activating species required constant ultrasonic agitation, which provided a route for time dependent polymer growth. Other sonication induced polymerization protocols have been described for ATRP [98] and RAFT. [99] Matyjaszewski, Xia and coworkers have also developed mechano-ATRP through the incorporation of piezoelectric zinc oxide nanoparticles, where an electron transfer from the nanoparticles to ATRP Cu catalysts was activated under ultrasonic agitation to initiate the polymerization. [100] Alternatively, Qiao, Ashokkumar and coworkers proposed ultrasonication of water as a means to generate hydroxyl radicals for polymerization.

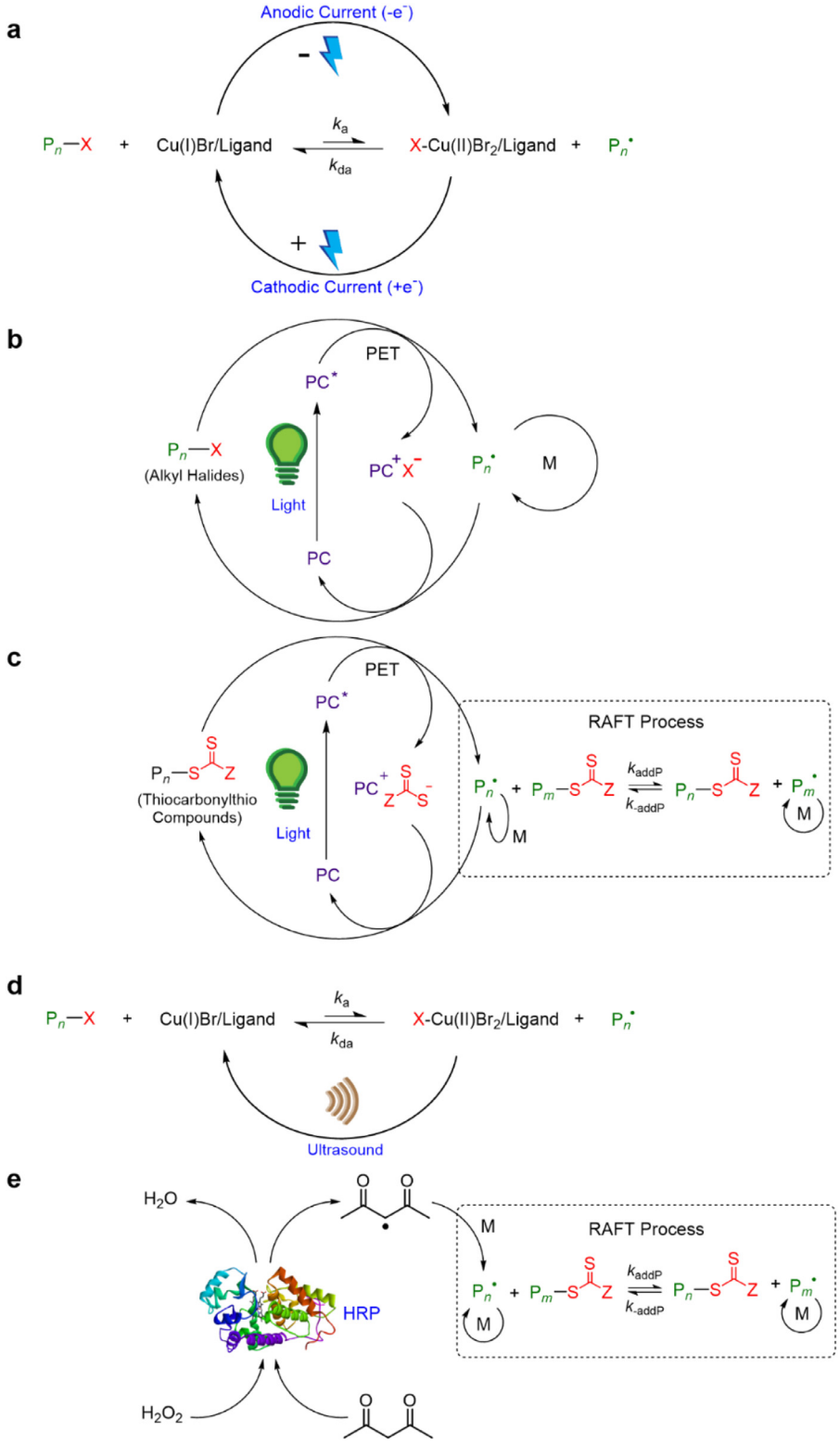


**Fig. 4.** Mechanisms for advanced RDRP techniques mediated by non-thermal stimuli. a) Electrochemically mediated ATRP (eATRP); b) photoATRP; f) PET-RAFT polymerization; d) mechanically controlled ATRP; e) enzyme-initiated RAFT polymerization.

[99] In contrast to previous work which employed low frequency sonication for polymerization, the authors demonstrated that high frequency (~400 kHz) sonication promoted the pyrolytic degradation of water into hydroxyl radicals, which were then used to initiate a RAFT polymerization process.

### 3.2.4. Biologically inspired initiation systems

Enzymes and bioinspired catalysts have also been used as alternatives to activate RDRP at ambient temperatures. For example, Bruns and coworkers have shown that metalloproteins including the hemoprotein horseradish peroxidase (HRP), hemoglobin, and

human erythrocytes are all capable of initiating ATRP in the presence of reducing agents such as ascorbic acid. [101,102] The mechanism for polymerization in these systems is proposed to occur via reduction of the enzyme by the reducing agent, and the subsequent abstraction of the halogen on alkyl halide initiators by the enzyme, typically via an iron heme group. Matyjaszewski and coworkers have similarly demonstrated that hemin and synthetic analogues can be used for ATRP. [103]

For RAFT polymerization, the groups of An and Konkolewicz have demonstrated that HRP catalyzed polymerization can be induced in the presence of acetylacetone and hydrogen peroxide (Fig. 4**e**). [104,105] In these systems, enzymolysis of hydrogen peroxide forms hydroxyl radicals, which can subsequently abstract hydrogen from acetylacetone to provide carbon centered radicals capable of adding across monomer double bonds. Notably, other systems for radical generation using similar bioinspired reactions have been proposed; these radicals can often be used either directly or indirectly to initiate RDRP in the presence of suitable control agents. [106,107] Critically, the use of enzymes provides an environmentally friendly polymerization approach as the catalysts are typically derived from renewable sources. Additionally, polymerization can often be activated under mild conditions including in biological media, which tailors these systems to a wide range of bioapplications and use by non-experts.

## 4. Synthetic scope and methodologies for RDRP

### 4.1. Chemical compatibility of RDRP

The high tolerance to functional groups and reaction conditions in RDRP is evidenced by its extensive synthetic scope. Indeed, RDRP has been widely exploited for the polymerization of an almost endless pool of vinyl monomers and in various solvent environments. For example, functional styrenics, [8,9,12,23,108,109] (meth)acrylates, [12,13,23,58,65,110] (meth)acrylamides, [23,66] vinyl esters, [52,66] and many other monomers, [23,34,36,66,111] have all been successfully polymerized by RDRP. Furthermore, polymerization has been conducted in bulk, [8,9] and in a range of solvents including protic and aprotic solvents with varied polarities, [12,62,66] aqueous media, [99,112] ionic liquids, [113] and supercritical $CO_2$. [110]

In addition to the wide scope of polymerizable monomers and reaction conditions, RDRP is also broadly compatible with other chemistries, which allows additional opportunities for advanced materials syntheses. [114] A wide range of strategies, notably “click” chemistry and other highly efficient covalent linking chemistries, have been developed to post-modify the properties and functionality of polymer chains formed via RDRP. Examples include the covalent linking of polymer chains for block or star copolymer formation, [115–117] modification of the polymer side chain functionality, [118–120] and coupling of functional small molecules [121] or biological substrates [122,123] with polymer chains, among many others. [18,124–126] In addition, the functionality of the dormant polymer end-groups (thiocarbonylthio groups, alkyl halides, etc.) can be chemically altered for secondary modification processes. [127–130] Such polymer post-modification strategies greatly expand the scope of materials possible through RDRP. Indeed, many of the applications of RDRP derived materials rely on polymer-post modification strategies to enhance the functionality of the polymer chains prior to their implementation (*vide infra*).

The majority of polymerization and polymer post-modification protocols have been performed using multistep strategies, however, under carefully considered conditions, both reactions can be performed either simultaneously or sequentially in a single pot. [121,131,132] These approaches rely on the independence (orthogonality) of each reaction pathway to allow more complex multistep syntheses without the requirement of tedious handling and purification steps. [133] The broad chemical scope of RDRP provides many opportunities to perform macromolecular syntheses through such reactions, including for the simultaneous control of multiple independent polymerizations and the selective regulation of a single polymerization process through multiple stimuli, [134] e.g. chemical concentrations, [135,136] temperature, [137,138] pH, [139] electrochemical potential, [140] magnetic fields, [141] or irradiation wavelengths. [142,143] Critically, the ability to impart a fine level of control over polymerization and post-modification strategies through external stimuli provides a high degree of control over the final material properties. [144]

### 4.2. RDRP production methods

Early RDRP processes were typically performed via traditional polymerization procedures; [8,9,12] purified monomer, initiator, solvent, and control agents are added to a flask, deoxygenated via freeze-evacuate-thaw cycles or purging with argon or nitrogen, and subsequently heated in constant temperature baths for the duration of the reaction. These methods provide conditions where radical scavenging by molecular oxygen and retardation of the polymerization via side-reactions with impurities are largely avoided. The development of RDRP has provided more robust production methods (Fig. 5**c**) compared to these early batch systems, including systems which do not require external deoxygenation procedures prior to polymerization. [16,145,146] In traditional radical polymerization systems, molecular oxygen can react with propagating radicals to form alkyl peroxides, in turn retarding the polymerization and often leading to a loss of control over the polymerization process. While external deoxygenation procedures are effective, they significantly limit the ability for RDRP to be performed under less stringent conditions and increases the overall process complexity. In this regard, progress was made by Matyjaszewski and coworkers as early as 1998 through the application of activators regenerated by electron transfer (ARGET) ATRP with zerovalent metals. The intrinsic elimination of oxygen in these systems was proposed to occur through the oxidation of Cu(I)/L species, to form Cu(II) species, which could regenerate the active Cu(I)/L species via reduction or comproportionation with Cu(0) species. This reaction decreased the concentration of molecular oxygen and thus provided a deoxygenated environment in which polymerization could proceed effeciently. [147] Notably, other ATRP variants including initiators for continuous activator regeneration (ICAR)-ATRP, [148] single electron transfer (SET)-LRP/SARA-ATRP, [34,149] photoATRP [150] and eATRP [62] can all display some level of tolerance towards molecular oxygen through similar deoxygenation procedures, i.e., via oxidation and regeneration of catalysts. [16]

For RAFT polymerization, two main strategies have been developed to allow polymerization to proceed without prior deoxygenation. The first strategy uses enzymes for deoxygenation, as described by Yagci and coworkers for radical polymerization. [151] Inspired by this early work, Stevens and coworkers [152] implemented enzymes such as glucose oxidase (GOx) in RAFT polymerization to consume oxygen in the presence of glucose, to form hydrogen peroxide and gluconolactone. [153] The enzyme degassing strategy is attractive due to the high compatibility of GOx in aqueous systems and its relatively low cost. The other main strategy to provide oxygen tolerance in RAFT polymerization is via the use of photocatalysts, as in PET-RAFT polymerization. [66,89–91] In contrast to the enzyme degassing strategy, which is typically limited to aqueous systems, the use of photocatalysts allows implementation in a wider range of solvents and experimental conditions. Following photoexcitation, the catalyst is proposed to either reduce molecular oxygen to spectator superoxide species, [66] or alterna-

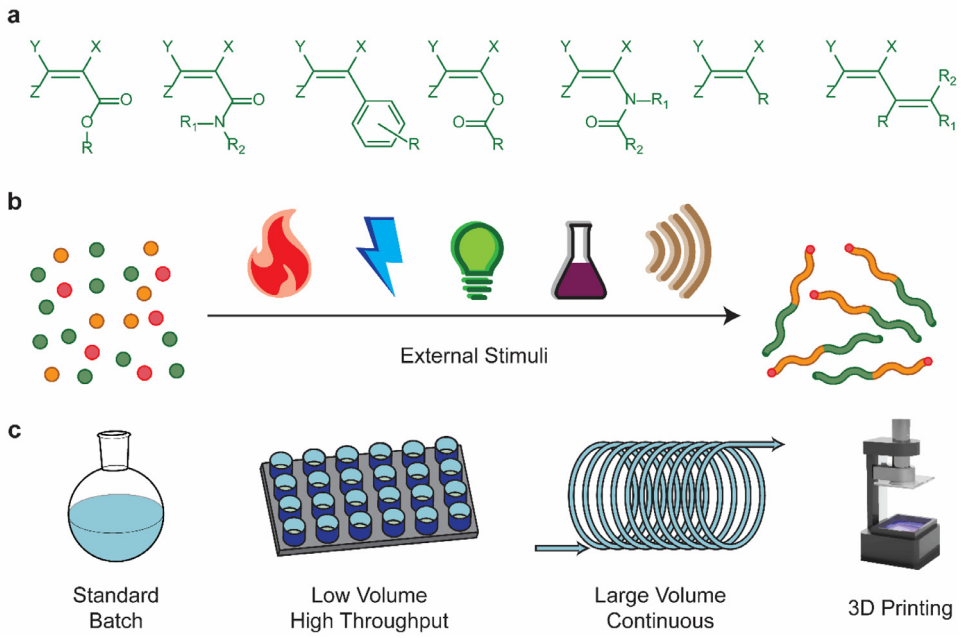


**Fig. 5.** Scope and production methods of RDRP. a) Examples of monomer families polymerizable through RDRP. From left to right: (meth)acrylates, (meth)acrylamides, styrenics, vinyl esters, vinyl amides, general vinyl compounds, general dienes; b) RDRP mediated by external and often independent stimuli including heat, electric potential, light, chemical concentrations, and ultrasound; c) equipment used for RDRP including standard batch setups, microtiter well plates and other small volume reactions, continuous flow chemistry, and 3D printers.

tively, sensitize the formation of singlet oxygen species which can be chemically trapped by solvent, [91] or other species in the reaction mixture. [154] Due to the favorable photophysical properties of photocatalysts used in PET-RAFT polymerization, the deactivation of reactive oxygen species is rapid and RDRP can often be performed under fully open to air conditions. [89,91]

A direct result of more robust polymerization conditions in RDRP is the ability to synthesize functional macromolecules with complex architectures using non-specialized reaction setups under ambient conditions. The oxygen tolerant methods outlined above have been applied for the synthesis of polymer libraries under ambient conditions using standard microtiter well-plate setups, and even free-standing droplets in volumes as low as 20 μL. [155] Examples include the library synthesis of 3- and 4-arm star polymers to examine the binding efficiencies with a model protein, [156] synthesis of self-assembled nano-object libraries, [153] and the synthesis of potentially antimicrobial polymers to combat multidrug resistant bacteria. [157] Notably, the application of RDRP for the generation of other polymer libraries, including functional polymeric biohybrids [150] and stimuli responsive copolymers [158] has been performed using automated synthesizers. The utility of such approaches lies in the ability to rapidly elucidate macromolecular structure-property relationships using low quantities of potentially toxic or expensive reagents, especially biological substrates such as DNA or proteins.

Another alternative to the traditional batch based RDRP methods is the implementation of flow methodologies. [159] Since the early use of packed column flow reactors for the continuous production of ATRP derived polymers, [160] many flow mediated RDRP procedures have been developed to exploit the inherent advantages of flow mediated processes. Specifically, flow processing allows continuous production of well-defined and architecturally diverse macromolecules, [153,161] simplification of multistep polymerization and post-modification procedures through reactor telescoping, [162–164] with automated control systems also increasing reproducibility and structural precision. [165,166] Furthermore, for photoinduced RDRP systems performed in flow reactors, strong light intensity gradients and corresponding rate heterogeneity that occurs due to the Beer-Lambert law in batch systems can be mitigated by using short path length narrow bore tubing. [91,167,168] Notably, many of the diverse polymerization and polymer post-modification reactions that have been developed in batch systems have been successfully applied to flow-based production methods. [169–171]

While the previously mentioned methods cover the syntheses of polymers via homogeneous RDRP, the fabrication methodologies for heterogeneous systems, surface functionalization, and composite materials production often differs. Heterogeneous media comprising an immiscible monomer phase dispersed within a continuous solvent offer interesting and unique capabilities not available in homogeneous (bulk and solution) polymerization systems. [172–174] By moving the locus of polymerization to a dispersed phase, a low-viscosity medium can be maintained throughout the polymerization process. Often, the desired continuous phase is water; the excellent heat dissipation of water, in conjunction with its obvious environmentally friendliness, combine to provide an effective means of upscaling reactions to industrial levels. As a consequence, methods such as emulsion polymerization have remained the predominant method of producing a wide range of adhesives, paints, binders, and commodity polymers.

For surface functionalization via RDRP, the main approach relies on the fixation of initiating species or a transfer agent to the surface and subsequent chain growth from these initiating sites. [175–177] Generally, following initiator attachment, the polymerization proceeds under very similar conditions to standard batch protocols. Alternatively, polymers can be grown externally and attached to surfaces after synthesis (named as “grafting onto”), often via similar chemistries to those discussed earlier, i.e. click chemistry and other efficient covalent chemistries. Recently, some innovative approaches to surface functionalization have been developed through the combination of flow chemistry and photocontrolled surface-initiated polymerization. [78] These processes can streamline surface functionalization with increased spatial control over the polymer chain growth, opening new opportunities for intricate and highly resolved surface functionalization.

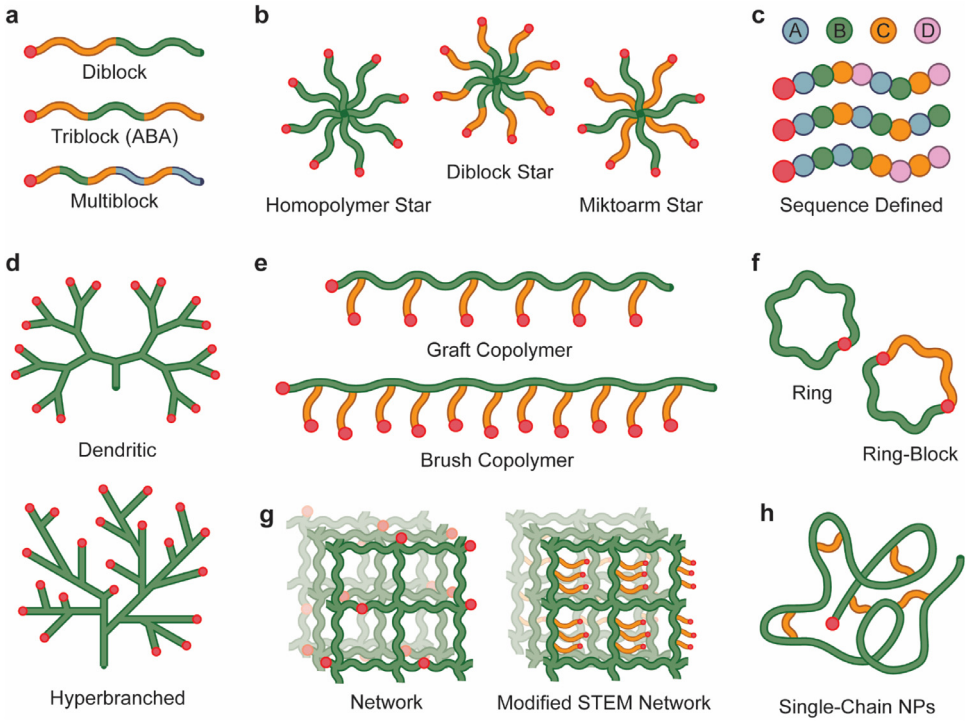


**Fig. 6.** Polymer topologies achievable through RDRP. a) block copolymers; b) star copolymers; c) sequence defined copolymers; d) branched copolymers; e) graft and brush copolymers; f) ring copolymers; g) network copolymers; h) single chain nanoparticles.

Finally, the synthesis of bulk polymer networks has also been achieved via RDRP. [178] These methods are generally performed by polymerizing mixtures of multifunctional monomers to cause branched polymer formation and eventually gelation. [179] As an alternative, the prefabrication of well-defined linear or branched polymers and subsequent coupling or further grafting from the existing networks using secondary chemistries can also be used. [180,181] Notably, the possibility of three-dimensional (3D) printing network polymers via RDRP was recently presented [182] and while typical RDRP procedures are too slow to be effectively applied to 3D printing, the use of rapid PET-RAFT polymerization allowed the formation of 3D printed networks under ambient conditions. Such 3D printing systems present a more accessible method for producing geometrically complex bulk polymeric materials. [183]

## 5. Materials and applications of RDRP

Arguably the most significant advantage of RDRP is the ability to synthesize diverse materials for an ever-expanding scope of potential applications. The following sections highlight a range of important material classes that can be fabricated through RDRP.

### *5.1. Advanced polymer topologies and compositions*

The reactivatable nature of RDRP provides pathways for the synthesis of topologically complex macromolecules and architecturally diverse nano-objects. Even for a simple copolymerization of two monomers, linear polymers with virtually any desired composition can be produced, including statistical, periodic, block, and gradient copolymers with diverse chemical functionalities. [184] Notably, RDRP has been applied for the synthesis of sequence controlled linear copolymers, [185,186] that is, polymers that have a precise placement of individual monomer units along the polymer chain (Fig. 6**c**). [187–189] While these methods are only emerging, they show the intriguing possibility for synthetic polymer materials to approach the precision seen only in natural biopolymers, such as proteins and DNA. In addition, the fine control over polymer chain lengths in RDRP can be exploited to synthesize polymer mixtures with tailored molecular weight distributions. [162,190–193] As polymer properties are derived from the overall molecular weight distribution and polymer composition, these approaches may be useful for tightly controlling the properties of polymeric materials, for example, by changing concentration of X-Cu(II)/L deactivator, block copolymers with tunable dispersity were prepared which self-assembled into materials with different morphologies, including hexagonally perforated lamellae. [194,195]

Individual linear chains may also serve as precursors to more advanced architectures under highly dilute conditions favorable for intramolecular interactions or via reactions between precisely placed chemical moieties. [196] Ring closure of RDRP derived polymers into cyclic architectures has been achieved through the interaction of defined $\alpha$- and $\omega$-chain-end functionalities, which lead to cyclic polymers without chain-ends (Fig. 6**f**). [197–199] Considering that many interactions of linear chains arise from the participation of chain-ends, cyclic polymers exhibit intriguing differences when compared to their linear counterparts of identical molecular weight that include, but are not limited to, reduced hydrodynamic diameters, [200] increased cloud points and circulation times. [201,202] Intramolecular reactions or interactions of pendant functionalities can also afford collapsed structures referred to as single-chain polymeric nanoparticles (SCNPs, Fig. 6**h**). [203–206] These unimolecular 3D macromolecular architectures are formed via intramolecular crosslinking, or alternatively, Nature-inspired folding via non-covalent interactions to afford ultra-small globular entities that are attractive for implementation as enzyme-like nanoreactors or catalysts. [207–211]

One of the most well studied and useful classes of macromolecules synthesized through repeated chain extensions are linear (multi)block copolymers. These polymers are constituted by covalently bound segments of chemically distinct polymers

(Fig. 6**a**). [48,212–217] (Multi)block copolymers have been synthesized with various block orders (e.g. A-*block*-B-*block*-A, A-*block*-B-*block*-C, A-*stat*-B-*block*-C, etc.), where each block can be hydrophobic, hydrophilic, fluorinated, [218] charged, [219] or stereospecific, [220] among others. The synthesis of these polymers is typically performed through repeated chain extensions in the presence of secondary monomers, however, synthesis and coupling strategies have also been widely employed. [115] Importantly, block-copolymers can be assembled on surfaces to form patterned thin films, [221] or in solution to produce higher order supramolecular assemblies with various morphologies. [222,223] Indeed, the self-assembly of block copolymers derived by RDRP has been a major research focus due to the utility of the assembled structures in advanced applications including drug-delivery and other biomedical applications. [224,225]

Well-defined non-linear polymer architectures are also possible through RDRP. For instance, star polymers that are composed of multiple linear arms originating from a central branching point have been synthesized by many research groups (Fig. 6**b**). [105,178,226] Such star polymers can be synthesized via both arm-first approaches, where the arms are synthesized and subsequently coupled, [117,227] or core-first approaches where the arms are grown from a central branching point *in-situ*. [228,229] The central branching point can be a functional small molecule or macromolecule, or a more densely crosslinked network structure, while the arms can take on a variety of forms such as homopolymers, statistical copolymers, (multi)block copolymers, or mixtures thereof. [105,230] The formation of branched and hyperbranched [231] copolymers, and dendrimer [232] like branched or star structures can also be achieved by RDRP via self-condensing vinyl polymerization or sequential polymerization and grafting procedures (Fig. 6**d**). [230,232–234] Similar to block copolymers, star and branched copolymers can self-assemble to form higher order structures. [235,236]

Graft and brush (co)polymers are some of the most interesting macromolecules that can be formed by RDRP (Fig. 6**e**). [131,237] These polymers generally contain a linear polymer backbone with secondary polymer chains (arms) extending from it, and can be produced by attaching pre-formed arms to the backbone (grafting-to), [238] growing arms from the backbone (grafting-from), [239] or via a macromonomer (grafting-through) approach. [240] While graft and brush copolymers have similar topologies, brush copolymers generally have higher arm grafting densities which causes the main polymer backbone to adopt a more elongated conformation. The properties of these polymers are highly unusual due to the strong steric repulsion of the densely grafted arms. For instance, brush copolymers with supersoft and superelastic properties have been developed by Sheiko and coworkers. [241,242]

### 5.2. Network polymers

Crosslinked polymer networks developed through RDRP can be considered as an extension of the topologically diverse polymers mentioned previously. Indeed, the progression from linear, to branched, to crosslinked polymer networks can occur upon increasing multivinyl monomer conversion in a single reaction mixture. [178] Interestingly, for polymer networks made by polymerizing multivinyl monomers, RDRP provides a more homogeneous network structure compared to networks made via uncontrolled polymerization techniques. This effect occurs due to the formation of more uniformly branched polymer structures during the early stages of the polymerization in RDRP processes, which causes the final network to exhibit a more even crosslink density throughout. [178,179] Furthermore, the mechanical properties of these networks are often dependent on the concentration of control agent, which provides a straightforward tool to tune bulk material properties. [182] Polymerization-induced phase separation was also employed for the synthesis of nanostructured crosslinked networks by addition of crosslinker during bulk polymerizations. [243] If the two block polymers are carefully selected to be incompatible, the copolymer will phase separate during the polymerization, resulting in the formation of structured materials with length scales that are restricted by the macromolecular dimensions of the block polymers formed. [244] This process has been employed for the preparation of high-modulus, high-conductivity nanostructured polymer electrolyte membranes and other materials. [245] Aside from the multivinyl monomer approach, polymer networks can also be synthesized by coupling free polymers using secondary post-polymerization reactions, such as click chemistry. [180] These networks have the advantage of more tightly controlled topologies, including crosslink density and polymer strand length between network junctions while also minimizing dangling chains.

An added advantage of polymer networks synthesized through RDRP is the intrinsic inclusion of functional groups within the network, which allows facile modification of the network structure after polymerization. Several recent reports have demonstrated the post-modification of structurally tailored and engineered macromolecular (STEM) networks to alter the properties of the network after the initial synthesis. [182,246,247] Living functional groups embedded within the polymer network strands allow repeated chain extensions to be performed, in turn changing the chemical structure and physical properties of the resulting materials. [248] Critically, such transformations are not possible in conventional polymer networks made via uncontrolled polymerization methods due to the irreversible termination of the active chain carrier. Furthermore, the embedded functional groups in networks made via RDRP can provide access to self-healing materials, [249] or on demand network dissociation. [180,250] Notably, ultra-high capacity, water absorbing polymer networks (hydrogels) can be synthesized via RDRP [250,251] with these crosslinked systems showing potential applications in drug delivery systems, biosensing and tissue engineering.

### 5.3. Self-assembly of block copolymers in bulk

Fine control over the polymer architecture on the nanoscale can be further exploited in the fabrication of advanced polymeric materials with controlled micro- and macroscopic properties. For instance, based on RDRP and living ionic polymerization, the self-assembly of block copolymers with non-compatible blocks has been extensively studied. [252,253] If block segments are incompatible, they can self-assemble into domains with different physical and chemical properties due to unfavorable mixing enthalpies. A range of morphologies have been observed, including body-centered cubic phases, hexagonal packed cylinders, bicontinuous gyroids, and lamellae. The morphology depends on several parameters, including the composition, number of repeating units, and the Flory-Huggins interaction parameter ($\chi$) as well as conformational asymmetry. [253,254] More recently, polymerization-induced phase separation was proposed as alternative method to prepare nanostructured polymers in the solid state. [243,244] In contrast to the conventional assembly method, which uses pre-synthesized block copolymers, the assembly occurs during the polymerization process and allows the production of structured materials containing domains with different physical and chemical properties. This process is similar to the polymerization induced self-assembly (PISA) process, [255–258] which is performed in solution (*vide infra*). In the polymerization-induced solid phase separation, a macromolecular control agent (macro-CTA) is chain extended via RDRP in bulk monomer, which results in the *in-situ* for-

mation of diblock copolymers and the formation of nanostructured polymeric materials. The use of RDRP allows simultaneous growth of block copolymers which can reach the point of becoming incompatible in the polymerizing monomer medium, leading to microphase separation over a small-time interval and thus providing homogeneous nanostructured materials.

### 5.4. Heterogeneous RDRP systems

Polymerizations conducted in dispersed phases allows facile access to polymeric colloids, which find use in a wide range of research activities. Although free radical polymerization processes in heterogeneous media are well established, the addition of control agents in RDRP systems complicated early implementations; the bimolecular nature of reversible deactivation processes in RDRP impact both kinetics and control during the polymerization process. A notable feature of RDRP performed in dispersed systems is the compartmentalization effect, which describes the inability of two species segregated into separate particles to react with each other (segregation effect), while two species confined to the same particle react at a faster rate as the size of the particle decreases (confined space effect). [259] Additionally, considering the reversible attachment of control agents to chain ends, the design of a dispersed phase polymerization must take into consideration the exit and (re)entry tendencies influenced by the physicochemical properties of the reaction components. [260] The unique aspects of heterogeneous RDRP has been addressed in recent studies with many challenges overcome through a detailed understanding of the process. Indeed, early reports of poor control and outright destabilization have been replaced by efforts describing the preparation of well-defined multiblock copolymers at multigram scales. [213,214,261–263]

Polymerizations in dispersed phases may be conducted by a variety of different approaches, which differ in terms of components, nucleation mechanisms and kinetics. More importantly, from an applications perspective, RDRP in dispersed phases enables the direct preparation of functional polymer colloids. The most common approaches reported in the literature include emulsion, miniemulsion, and dispersion polymerization; each of these methods provide access to polymeric particles of distinct morphologies and can be further elaborated by conducting the procedure under inverse or seeded conditions, or in the case of miniemulsions, encapsulation of immiscible solvents to afford hollow nanocapsules (Fig. 7). [264,265] It should also be noted that composite or hybrid (nano)particles may be accessed in dispersed media by utilizing polymer or control agent modified substrates, which may be encapsulated through miniemulsion polymerization or polymerized *in-situ* (*vide infra*) under dispersion or emulsion conditions, respectively.

Stemming from the expertise found in traditional free radical polymerization, early reports of heterogeneous RDRP utilized conventional stabilizers. The transition away from conventional stabilizers may be attributed to the work of Gilbert and coworkers, wherein the authors not only reported seminal *ab initio* RAFT emulsion polymerization, they did so by utilizing an amphipathic macroRAFT agent as the stabilizer. [266,267] Now widely referred to as the surfactant-free approach, solvophilic or amphiphilic polymers possessing the relevant end-group functionality for the desired RDRP process are used in place of conventional stabilizers. These polymers are essentially chain-extended in the dispersed environment with their covalent attachment providing colloidal stabilization during and long after the synthesis has ended. The inherent tailorability of these chains and their potential for introducing diverse functionalities into the particle corona has led to a range of advantages for surfactant-free approaches and these strategies are

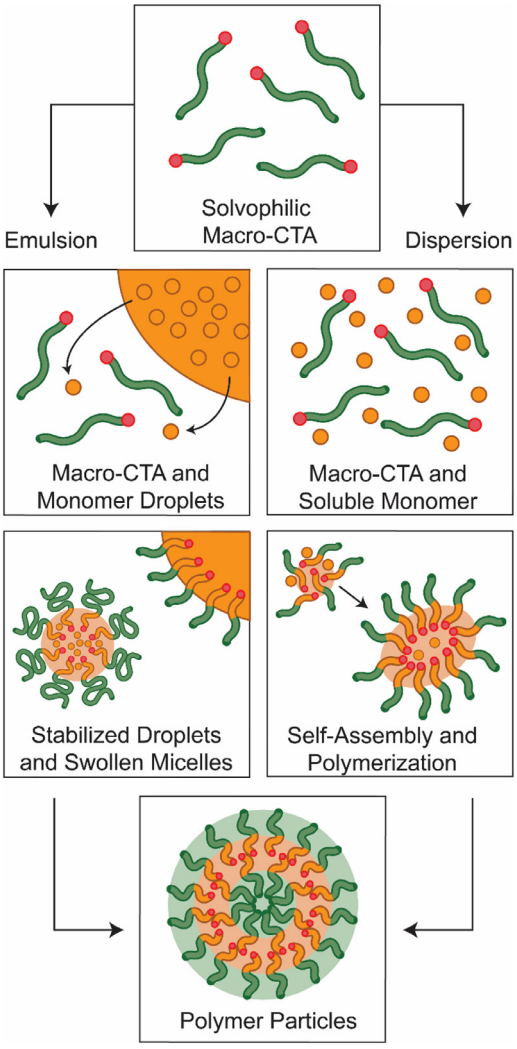


**Fig. 7.** Polymerization-induced self-assembly (PISA) for the synthesis of polymer particles. Left path represents emulsion polymerization: macro-CTA is solubilized in the continuous phase while monomer is the discontinuous phase; transport of monomer to the continuous phase leads to the formation of swollen micelles and stabilized droplets. Right path represents dispersion polymerization: monomer and macro-CTA are both soluble; self-assembly and subsequent polymerization lead to the formation of stabilized nano-objects of various morphologies.

now widely used and for the most part, have supplanted conventional stabilizers.

In heterogenous ATRP systems, the catalyst (both activator and deactivator) should be located in the particle phase and therefore ligands with long hydrophobic alkyl substituents (such as octadecyl) are typically used. However, interestingly, the “intelligent” ion pair consisting of hydrophilic Cu/tris(pyridylmethyl)amine cation and dodecyl sulfate anion was extremely efficient in both miniemulsion and true emulsion polymerization. [268,269] Approximately 1% of the catalyst were located inside the droplets, 4% in the aqueous phase and 95% at the surface, providing very efficient interfacial catalysis with 50 ppm Cu catalyst and with only 0.3 ppm residual Cu in the precipitated polymers. Moreover, polymers with complex architectures such as brushes and stars were efficiently prepared. ATRP has been also employed for inverse miniemulsion processes to prepare well-defined water soluble crosslinked degradable polymeric particles. [270]

From these heterogeneous RDRP studies has evolved polymerization induced self-assembly (PISA), a predominantly RAFT-mediated process, wherein a solvophilic macro-CTA is chain

extended in the presence of a monomer capable of forming a solvophobic block, leading to the *in-situ* generation of amphiphilic species. [255–258] As these chains increase in solvophobicity, they assemble into self-stabilized aggregates which continue to grow into particles. The distinguishing feature of PISA is the variety of higher-order morphologies that may be formed. Contrary to previous RDRP in dispersed systems that were restricted to spherical morphologies in the absence of post-polymerization processing, PISA processes enable the *in-situ* transition of the initial spherical micellar aggregates into cylindrical, lamellar, and vesicular entities. Crucially, PISA delivers these nano-objects, which had been restricted to post-polymerization processing in dilute solution, at higher concentrations and in fewer steps, opening the door to cost-effective scale up of these sought-after nanomaterials. As PISA continues to attract increasing attention, research at the cutting edge is focused on both fundamental aspects, such as the preparation of inverse bicontinuous morphologies and more application-focused endeavors exploiting recently developed benign initiation methods for *in-situ* encapsulation of therapeutic enzymes. [271–273]

### 5.5. Hybrid materials

The preparation of hybrid materials composed of organic, inorganic or biological components has been a major focal point of RDRP development, driven in part by the availability of well-defined and stable functionalized initiators. [274–287]The diverse methods facilitating their preparation may be categorized into two general strategies: i) grafting-to, wherein premade polymers are attached via covalent reactions or non-covalent interactions to the desired inorganic component, or ii) grafting-from, which involves the attachment of an RDRP control agent from which polymer chains may be grown directly. Of the two, polymerizing *in-situ* (i.e. grafting-from) plays to the inherent strengths of RDRP processes and affords a robust and versatile approach to the generation of hybrid materials. Perhaps the simplest form of hybrid materials are copolymers composed of an RDRP derived polymer segment in combination with a natural or synthetically derived (macro)molecular substrate. Examples of naturally derived substrates include proteins, peptides and DNA for bioapplications (*vide infra*), or alternatively, inexpensive polysaccharides and cellulosic materials as green alternatives to those derived from fossil fuels. [288–290] Conversely, synthetic components may range from poly(ethylene glycol) derived from anionic polymerization, to two- and three-dimensional materials such as graphene and metal organic frameworks for more advanced applications. [291–293]

The covalent attachment of polymers onto solid substrates provides a facile means to modulate and tailor interfacial properties such as wettability, biocompatibility, corrosion resistance, tribology, and many others. The application of the grafting-from strategy to colloids and bulk surfaces is collectively termed surface-initiated reversible-deactivation radical polymerization (SI-RDRP) and is one of the most versatile and robust methods for hybrid material fabrication, enabling precise control over the polymer architecture, functionality location, composition and film thicknesses (Fig. 8**a**). [176,294–296] Critically, compared to grafting-to strategies that are limited by steric hindrance, the grafting-from strategy affords the capability to prepare highly dense monolayers of control agents and consequently a high density of attached chains. The steric crowding arising from the high density forces these chains to adopt an extended conformation normal to the surface, forming an architecture known as polymer brushes, and garners unique properties in comparison to other forms of thin films (Fig. 8**b**). High grafting density of polymeric brushes provides high lubrication and unusually low friction coefficients of modified surfaces. [297]

Control agent or initiator attachment to a variety of surfaces has been demonstrated in a wide variety of systems with initial reports utilizing conventional substrates such as silicon, silica, and gold. These fundamental studies allowed extension to more exotic substrates, including poly(dimethylsiloxane), [298] indium tin oxide, [299] montmorillonite, [300] steel, [301] gallium arsenide, [302] and even liquid metals such as eutectic gallium/indium alloy. [303] In the latter case a dramatic decrease of crystallization temperature from +15 °C to -80 °C was observed by decreasing the size of alloy nanodroplets below 100 nm via grafting polymethacrylate chains. As an alternative to these substrate-specific methods, universal dopamine based initiators that draw inspiration from mussel adhesive proteins have also been developed, enabling SI-RDRP to be conducted from virtually any surface. [275,277,287] By virtue of growing polymers from a variety of substrates, SI-RDRP processes enable the compatibilization of bulk surfaces and improves the dispersion of inorganic colloids in a variety of bulk and solution mediums. This provides a powerful means to prepare (nano)composite materials and assemblies for a vast array of explored and yet to be explored applications. [274,279,285] At this juncture, it must be noted that the polymers formed via RDRP may themselves be used as macromolecular templates for the preparation of inorganic polymer hybrids. Self-assembled micelles, or macromolecular structures such as star polymers and cylindrical brush polymers have been converted into inorganic-polymer nanoparticles via reaction of metal ions coordinating to precisely placed functional groups within the polymeric architecture. [282,304–307] Similar strategies have been applied to polymer brushes synthesized from flat substrates, leading to examples such as micropatterned silica, [308] calcite, [309] gold [310] and silver thin films. [311] This strategy can even be extended to polymer functionalized colloids by the preparation of nanoporous carbon films via pyrolysis of a precursor film composed of poly(acrylonitrile)-silica hybrid nanoparticles. [312,313] Polymer brushes have been extensively investigated in their capacity as antifouling thin films that can be prepared on a variety of substrates, including membranes, [314] to prevent the non-specific adhesion of species ranging from proteins to marine micro- and macro- organisms. [276,281,315,316] As is the case with all RDRP-derived chains, polymer brushes may be imbued with antibacterial and/or stimuli-responsive capabilities through the judicious selection of monomers functionalities. [284,286,317,318] Critically, these features may be introduced onto a variety of diverse substrates and geometries that range from micro- and macroscopic gels, [319,320] 3D printed materials [321] to microfluidic channels [322] and prosthetics. [323] Indeed, the (nano)composite materials formed via SI-RDRP are increasingly investigated for more advanced applications in the biomedical and energy sectors. [278,280,282,283] While the variety of substrates has remained largely unchanged, a progressive sophistication of the functions programmed into the brush layer is clearly apparent (Fig. 8**c**). [324–328] SI-ATRP is a very robust process and under appropriate conditions does not require deoxygenation, and in many systems, SI-ATRP is biocompatible (cytocompatible). [329,330]

Considering the increasing levels of sophistication, two facets of SI-RDRP that are of rising importance for many applications are the ability to easily access brush polymer architectures and the patterning of such brushes to confer spatially defined properties. While a wide variety of homo-, block, statistical, branched and mixed brush architectures have been translated onto substrates, more complex gradients with spatially varied brush heights and layered grafting densities are especially challenging and serve as future research targets. [177,331–335] On the other hand, patterning in SI-RDRP has been traditionally restricted to selective initiator attachment (bottom-up) or removal of attached polymers (top-down) to obtain the desired patterns. [336] Although effective, binary and more elaborate brush architectures may require repetition of this process, leading to complex (error-prone) and

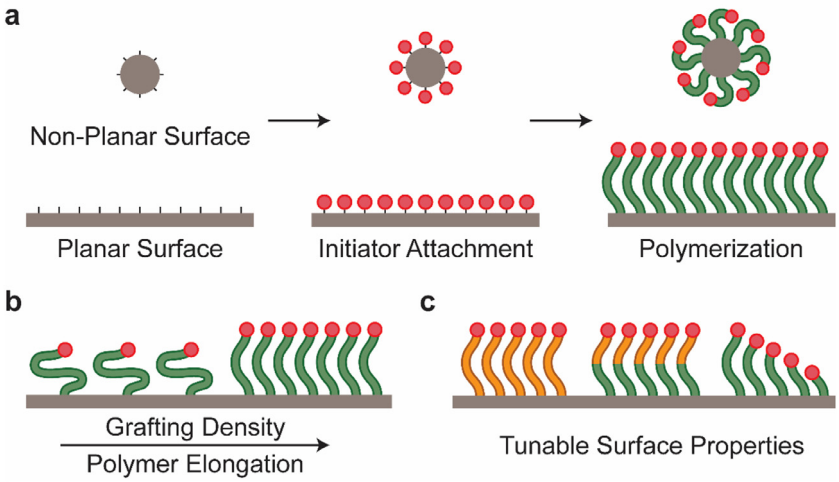


**Fig. 8.** Surface-initiated RDRP (SI-RDRP). a) general process for hybrid material fabrication including initiator attachment to substrates and subsequent polymerization from initiator or control agent bound to the substrate surface; b)increase in brush height due to increase in polymer chain density; c) representation of tunable surface properties: diblock copolymers, varied brush compositions and gradient brush heights.

time-consuming (costly) workflows. The application of an external field to spatially control the locality of polymerization holds great promise to fulfil this emerging need. Although, electrochemically mediated ATRP using sacrificial anodes has shown promise for spatiotemporal control, particularly in regard to gradient brush heights, additional studies are needed for widespread adoption by the community. [333,337]

Owing to its roots in photolithography, photochemical mediation of SI-RDRP has become a powerful strategy which enables more finely controlled patterning capabilities that are also more easily accessible. [338] This has been demonstrated in the work of Hawker and coworkers, wherein binary and grayscale masks were used to produce defined and gradient patterns respectively, leaving unexposed areas available for secondary reactions. [79,339] Notably, photographs could be replicated using grayscale masks, demonstrating the potential to create non-linear gradients. [78] Implementation of this process within stop-flow cells allows for the streamlined preparation of highly complex patterns including the challenging layered architectures; facile material exchanges in combination with externally swappable masks and light sources enable spatially defined brush growth, chain-end deactivation and side chain post modifications without the need for costly processing and realignment steps. [77,78]

### 5.6. Bioapplications

In the last 20 years, RDRP has been widely explored for the systematic design and synthesis of biomaterials, [340–342] largely due to the enhanced control over polymer structure and mild, orthogonal reaction conditions. In particular, polymers synthesized through RDRP have been applied in three main areas to provide biomaterials with specific and enhanced properties, namely, i) the conjugation of synthetic polymers to biomacromolecules such as peptides, proteins and siRNA, ii) the development of functional polymeric nanoparticles for the transport of therapeutic and imaging agents, and iii) the development of bioactive polymers that can trigger biological responses. These three areas all take advantage of RDRP to precisely control the polymer architectures and molecular weights.

#### 5.6.1. Hybrid synthetic polymer-biomacromolecule conjugates

Natural biomacromolecules, such as proteins, siRNA, DNA, etc., play a critical role in the regulation of living organisms. Indeed, a deficiency of specific proteins can cause chronic diseases, with the direct administration of proteins or peptides being the standard of care. However, these biomacromolecules typically have a very low therapeutic efficiency due to their rapid degradation when administered. If synthetic polymers are carefully selected, their conjugation to biomacromolecules can slow this degradation by providing steric stabilization and enhance the stability of biomolecules. [343–345] The groups of Maynard, [122,346,347] Matyjaszewski [123,348,349] and Haddleton [350–352] pioneered the use of RDRP for the synthesis of functional polymers for protein and DNA conjugation. Early strategies employed a grafting-to approach, which allowed facile control over the synthetic polymer end-groups and molecular weights. Subsequent efficient and selective conjugation reactions between proteins and synthetic polymers resulted in the preparation of a wide variety of hybrid biomacromolecule-synthetic polymers. Notably, different conjugation strategies have been used in the grafting-to approach. For instance, non-selective conjugation reactions have been used, where polymers terminated by aldehyde or activated ester groups react with primary amine functionalities present on the proteins to yield conjugates. Although these reactions are efficient, the non-specific attachment of polymers to these proteins may result in the loss of bioactivity. To overcome this limitation, conjugations using specific functional groups, such as thiols, have been exploited to modulate the impact of polymer attachment to the protein. [122] One limitation of this grafting-to approach is the separation of unconjugated polymers from the bioconjugates, as a large excess of polymers is typically required to achieve high yields.

Several groups have implemented grafting-from approaches, [123,350,353–356] where polymers can be grown from a protein (Fig. 9**a**). In contrast to grafting-to, these approaches present numerous advantages, including high retention of bioactivity and simplified purification/automation. [357,358] As only residual monomers and control agents need to be removed from the mixture, pure hybrid biomacromolecule-synthetic polymers can be typically obtained through dialysis. The attachment site on a protein is tunable and ATRP initiators can be incorporated via genetic modification of green fluorescent protein. [348] Also, attachment sites were tuned by stoichiometric addition of ATRP initiators and selective blocking of more active sites by “dummy” initiation sites. [357] RAFT polymerization offers simple methods for preparing protein-polymer conjugates prepared via the grafting-from approach. For instance, RAFT agents containing pyridyl disulfide functionalities have been prepared and covalently bound to thiols present on proteins such as bovine serum albumin (BSA).

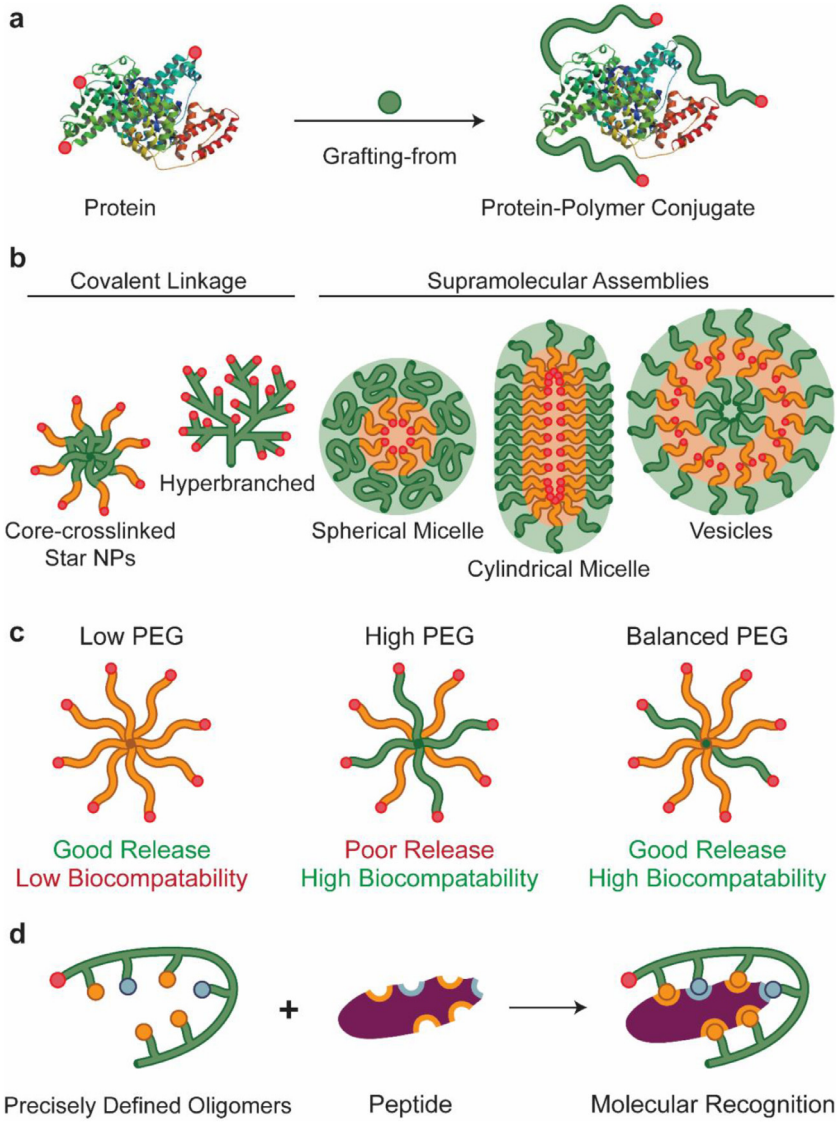


**Fig. 9.** Biomaterials through RDRP. a) Protein polymer conjugation; b) drug delivery and theranostic vehicles; c) representative example of tunable properties (biocompatibility and cargo release) of delivery vehicles synthesized through RDRP; d) molecular recognition between proteins and precisely defined oligomers synthesized through RDRP.

[354,355] Subsequent RAFT polymerization using water soluble and room temperature initiators, such as the azo-initiator VA044, allows retention of the protein bioactivity. Alternatively, photoinduced approaches can be used to also ensure high activity. Using RDRP, different functional groups can also be introduced and the structure of the bioconjugates can be easily tuned. For example, Sumerlin and coworkers have prepared BSA-diblock polymers which can self-assemble into polymeric nanoparticles to facilitate transport of therapeutic agents. [359]

*5.6.2. Polymeric nanoparticles for the transport of therapeutic and imaging agents*

As discussed above, RDRP has been successfully employed to prepare a broad range of amphiphilic copolymers with various functionality that undergo self-assembly to form supramolecular structures with morphologies ranging from spheres to vesicles and higher ordered structures (Fig. 9**b**). [222] Critically, these polymeric nanoparticles can provide a vehicle for the delivery of therapeutic agents and can be decorated with targeting moieties. [360,361] Indeed, a large variety of hydrophobic therapeutic agents have been loaded into the core of these supramolecular assemblies using hydrophobic interactions or conjugated to their core via secondary functional groups. Due to the tolerance to various functional groups in RDRP, diverse monomers can be used to form nanoparticles containing functional groups, including aldehydes, primary amines, ketones, etc. [362] The loaded therapeutic compounds can be subsequently released from the nanoparticles upon a change in their surrounding environment, such as changes to pH, temperature, or ionic strength. In addition, the polymeric shells or cores of these nanoparticles can be crosslinked to manipulate the release profiles of the therapeutic agents and maintain their stability at low concentration. [120,363,364] Due to the versatility and robustness of RDRP, a plethora of systems have been designed and tested *in vitro* and *in vivo*, showing promising results for the treatment of cancers, heart diseases, and infectious diseases. [365] In addition to the encapsulation of therapeutic compounds, the introduction of imaging modalities has also been proposed to afford theranostic nanoparticles, which transport therapeutic compounds as well as provide imaging capabilities to monitor the biodistribution of these nanoparticles. [366] For example, nanoparticles prepared using comb-copolymers containing $^{64}$Cu radiolabeling and targeting peptide were successfully employed for the detection of

atherosclerosis in rabbits by targeting the natriuretic peptide clearance receptor (NPRC). [367,368] As demonstrated by the vast number of publications in this area, the use of RDRP has allowed scientists to precisely design nanoparticle size and shape, and accurately control the release of payloads.

RDRP has also been exploited for the synthesis of complex unimolecular macromolecules, such as star polymers (or core-crosslinked nanoparticles) [363,369–371] and hyperbranched polymers [372] that can be used to deliver cargo in a similar manner to the supramolecular assemblies mentioned above. In contrast, however, star and hyperbranched polymers are typically smaller in size compared to polymeric nanoparticles prepared by the assembly of diblock copolymers. These structures have shown promising results for the delivery of siRNA or DNA *in vitro* or *in vivo*. [373–377] For instance, efficient encapsulation of siRNA was achieved using PEG/poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) star copolymers for the treatment of pancreatic cancer. [377] The reversible electrostatic interactions between cationic groups of PDMAEMA and phosphoric acid of siRNA preserved the stability of siRNA in biological environment, and after cell uptake, the siRNA was released. In this system, the addition of PEG into the star polymers was critical as the nanoparticle cytotoxicity was reduced and the *in vivo* circulation time and accumulation in the tumor was increased (Fig. 9**c**). [377] Furthermore, if the PEG content was too low the nanoparticles were rapidly captured by the immune system, whereas a high content of PEG prevented the release of siRNA, resulting in poor therapeutic efficacy. Clearly, the ability to tune the polymer architecture via RDRP offers a convenient approach to optimize long *in vivo* circulation and therapeutic efficacy. [367,368]

#### 5.6.3. Design of bioactive polymers

The precision seen in natural polymers such as DNA, proteins, and peptides allow specific biological responses which sustain life. While researchers have proposed the use of synthetic polymers to mimic the functions of natural polymers, this goal has only recently become realistic due to advances in polymer science. [185,378] RDRP has provided new opportunities for the design of synthetic polymers with characteristics of natural polymers due to the ability to perform multiple chain extensions and control the precise placement of functional groups within a polymer. [213,379,380] As an illustration, exploiting the precision and high functional group tolerance of RDRP, combinations of hydrophobic, cationic and hydrophilic monomers have been polymerized for the synthesis of antimicrobial polymers, i.e., polymers capable of killing or restricting the growth of bacteria. [381,382] The structures of these synthetic polymers draw inspiration from antimicrobial peptides, which are short chain length natural polymers that can selectively kill bacteria. Recent studies have illustrated the importance of controlling the polymer architecture to confer antimicrobial activity as well as bioactivity. Boyer and coworkers, [383] have demonstrated that the sequence of short blocks (hydrophilic, hydrophobic and cationic) within linear high-order quasi-block copolymers affect their bioactivity and selectivity to kill specific strains of bacteria. For instance, short blocks of cationic segments coupled with an amphiphilic hydrophilic-*stat*-hydrophobic segment showed specific activity against *Pseudomonas aeruginosa* (Gram negative bacteria). It was also found that the localized ratio of hydrophobic to hydrophilic functional groups within amphiphilic sections appears to be a critical factor to influence biocompatibility as well as antimicrobial activity.

RDRP has also been successfully employed for the design and synthesis of polymers capable of biological recognition and binding with peptides, cell surfaces, etc. (Fig. 8**d**). Hoshino and coworkers designed and synthesized oligomeric ligands through RAFT polymerization for the recognition of epitope sequences on a target peptide and neutralization of its toxicity. [384] Inspired by Hawker and coworkers [385] recent purification techniques for the preparation of discrete oligomers using automated flash chromatography systems, RDRP was used to prepare block copolymers which were subsequently purified to provide a polymer library with precise control of each block within the polymers. Using a hemolytic study, the authors demonstrated that the structure of block copolymers (number of monomers for each block) is a critical parameter for determination of binding affinity with Melittin. The high binding affinity of these synthetic block copolymers neutralized the hemolytic activity of the peptide. The distribution of glycol-monomers within synthetic polymer chains can also significantly affect the binding with different virus glycan proteins, therefore demonstrating that specific copolymers can have selective biological recognition. [386–388]

## 6. Current challenges and future prospects

Recent improvements in RDRP, including the ability to perform polymerization without the need for deoxygenation and the versatility inherent with external stimuli, such as light, electricity, ultrasound, etc., has removed entry barriers to non-polymer chemists. This has created new opportunities for the design of complex macromolecules and materials, greatly increasing the impact of RDRP in areas beyond traditional polymer science. Nevertheless, to reach its full potential in fields such as nanomedicine, energy, and advanced materials, more research on RDRP is required. [389] The following section outlines important areas that need to be addressed to further enhance the capabilities of RDRP and allow adoption by industry and the broader materials community.

### 6.1. Fundamental progress in RDRP

While RDRP has been extensively explored to generate solutions to a wide range of global issues in the laboratory, the slower uptake of such solutions in industry suggests more development is necessary. Current RDRP chemistries often include mediators and catalysts that can be a drawback from both biological and industrial perspectives. In the case of RAFT, the presence of sulfur is a source of color, odor, and potential degradation, [390] whereas the use of metallic catalysts is a constraint for ATRP. As such, there is a need to develop improved methods for sulfur-free RAFT polymerization [41,213] and non-metallic (organo)catalysts for ATRP. [82] Recently, major progress has been made to tackle these challenges, but additional work is needed to increase the robustness and versatility of these processes. The reaction rate of RDRP can also be a limiting factor for some applications; increasing the reaction rate often reduces the degree of control over the resulting polymer properties. Recent innovations and improvements focusing on the initiation of RDRP processes have highlighted that reactions can be performed faster while maintaining good control over the process. [391] Additionally, the application of external stimuli to regulate these processes has revealed new ways to improve energy efficiency and atom economy. The innate compatibility of radicals with aqueous environments also garners inherent advantages with respect to reaction conditions; further improvement of RDRP with respect to speed, energy efficiency, and atom economy, while maintaining good control, will continue to make RDRP techniques more attractive for the production of advanced polymeric materials irrespective of the reaction environment.

### 6.2. Interconversion and orthogonal chemistry

While the broad versatility of RDRP processes may allow it to be viewed as a panacea to some, the reality is that it exists as

just a (small) part of the larger knowledge base of polymer chemistry. In this respect, promising avenues of research exists at the interface between RDRP and other areas of polymer chemistry. The production of hybrid copolymers comprising segments prepared by different polymerization techniques has the potential to combine distinct but cooperative properties and characteristics, giving rise to new materials and applications. While these materials are currently formed through ligation and post-polymerization reactions, an alternative interconversion strategy may facilitate more streamlined access to these systems.

In line with this goal, researchers have demonstrated the potential of utilizing species possessing the RAFT termini to mediate both cationic and anionic polymerizations in tandem with RAFT-mediated RDRP. [136,138,140,392] These recent advances have also highlighted an emerging interest in the implementation of orthogonal polymerization processes. The temporal control demonstrated in many externally regulated RDRP processes holds potential for significant material sophistication through the intermittent introduction of orthogonal polymerizations and organic transformations. Various block copolymers were prepared by using dual ATRP and anionic/cationic/ring-opening and condensation polymerizations. [29,393] In addition to compressing complicated workflows into one-pot procedures, the use of orthogonal processes may enable the realization of novel design paradigms. For instance, the formation of hybrid chains composed of conjugated organic and organometallic segments through tandem polymerization procedures may create unprecedented and exciting opportunities. While the discovery and development of further orthogonal chemistries is a great challenge, this untapped potential will continue to attract significant attention from the broader research community.

### 6.3. Sequence and tacticity control

Polymer architectures can be “relatively” well-controlled via RDRP. Perhaps one of the most remarkable examples is the synthesis of multiblock copolymers of up to 21 blocks without the need of intermediate purification. [380] However, RDRP does not allow control over the precise placement of monomers within polymer chains. The use of single unit monomer insertion or atom transfer radical addition procedures in RAFT and ATRP, respectively, provides a potential scalable solution for the precise introduction of functionality within synthetic polymer chains. [188,394,395] However, these techniques have only been used thus far to produce oligomers (typically $X_n < 5$). Therefore, there is a need to further expand the scope of RDRP for the precise control of monomer sequence within polymer chains. [396]

Another parameter that RDRP does not readily provide control over is the polymer tacticity. Although tacticity is a critical parameter that affects the properties of polymers and materials, only limited examples of influencing tacticity in RDRP have been reported, e.g., through the use of Lewis acids. [220,397] Moreover, these methods allow enhanced stereospecificity (i.e., a more isotactic or syndiotactic polymer) but do not provide stereocontrol (choice of tacticity and control over the stereosequence distribution). The realization of both tacticity and sequence control could afford synthetic polymers possessing unprecedented capabilities, for instance, self-folding into precisely programmed structures to afford catalytic activity, thus mimicking the properties of natural polymers. Such synthetic polymers could be used to catalyze selective chemical reactions like enzymes, selectively recognize and interact with biomolecules, or store information like DNA does for living organisms. Developments in this area would lead to a convergence of synthetic polymer chemistry and biology.

### 6.4. Materials design

The use of RDRP will further improve the fabrication of advanced materials with superior performance. Indeed, recent progress in RDRP has improved the retention of the propagating end-group, enabling the preparation of multiblock copolymers without intermediate purification, as well as the synthesis of ultrahigh molecular weight polymers. [93,398,399] While past research has focused on decreasing the dispersity, capabilities exist in RDRP to exert control over synthetic parameters to shape molecular weight distributions. [191,194] For instance, manipulating the molecular weight distribution to generate both short chains, which can act as plasticizers, and longer chains, that can provide strength, allows for increases in processability while maintaining mechanical properties. Moreover, the ability to tune molecular weight distributions can have a significant impact on the self-assembly of polymer chains in solution or in the solid state, resulting in the emergence of new morphologies and material properties. [194] While a significant amount of research has been conducted on self-assembly of block copolymers with low dispersity, block copolymers containing various molecular weight distributions have rarely been explored. [162]

The current ability to graft functional polymers onto the surfaces of organic and bio-derived materials via RDRP provides countless opportunities for the fabrication of advanced plastic composites. Indeed, polymeric nanocomposites can provide exceptional properties if their structures are controlled. Further development will allow enhancement of interfacial properties between inorganic materials and polymers and dispersion of these materials within a polymer matrix may result in further performance enhancement. Composite materials made using RDRP also provides additional opportunities for responsive and self-healing materials. While synthetic materials slowly degrade due to environmental conditions or mechanical stresses, natural materials are capable of reorganization and repair. The ability to integrate RDRP into composite materials will allow researchers to expand the scope of self-healing polymers for applications in repairable and reshapeable materials. Significant progress has been made over the last decade in this regard as exemplified by polar thermoplastic elastomers and vitrimers, but the full potential is yet to be realized.

The persistence of many synthetic polymers in our environment is a significant and growing global issue. [400] As the large majority of vinyl monomers polymerized through RDRP processes afford backbones that do not readily degrade, the development of new chemistries and processes are required. The polymerization of cyclic monomers, such as cyclic ketene acetals, can afford (bio)degradable backbone esters and are a potential solution to this challenge. [401–404] However, polymerization of such monomers is complicated by propagation of ring-closed units and low incorporation when copolymerized with more activated monomers; the latter can be addressed by pairing the electron-rich cyclic ketene acetal with electron-deficient maleic anhydride or *N*-substituted maleimides, or copolymerizing with less activated vinyl acetate or vinyl ether monomers. [401,402] More recently, thionolactones have been introduced as monomers capable of radical ring-opening polymerization to afford degradable thioesters into the backbone. [405] Such advances are not only exciting for increasing the range of (bio)degradable polymers, they offer avenues to new backbone functionalities that may provide new properties and capabilities to RDRP-derived materials.

In addition, further fundamental knowledge in RDRP and application to materials science should allow the rational design of precisely structured materials. As RDRP allows precise control over primary polymer structures, there exists an opportunity to control secondary polymer structuration, i.e., the interaction and assembly of polymers into ordered domains. By achieving fine structural

**Table 1**
Examples of commercially available RDRP-derived polymer products as of June 2020.

| Company | Product range | Type | RDRP | Ref. |
|---|---|---|---|---|
| 3M | Dyneon | Fluoroelastomer | ITP | [407] |
| AGC | Aflas | Fluoroelastomer | ITP | [408] |
| Daikin Industries | Dai-El | Fluoroelastomer | ITP | [409] |
| Chemours | Viton | Fluoroelastomer | ITP | [410] |
| Solvay | Tecnoflon | Fluoroelastomer | ITP | [411] |
| | Rhodibloc RS | Nonionic amphiphilic block copolymer stabilizer | MADIX/RAFT | [411] |
| | Rhodibloc FL | Cement additive | RAFT | [412] |
| | Rhodibloc GC | Gas migration control agent | RAFT | [413] |
| BYK-Chemie | DISPERBYK-2xxx | Wetting agents, pigment dispersants | non-disclosed | [414] |
| Lubrizol | Asteric | Viscosity modifier | RAFT | |
| Arkema | BlocBuilder DB | RAFT agent | RAFT | |
| Boron Molecular | BM RAFT agents | RAFT agents | RAFT | |
| Axalta | Performance Coatings | Pigment dispersants | SF-RAFT | |
| Kaneka | XMAP | Sealant, adhesive | ATRP | [415] |
| Pilot Polymer Technologies™ | fractASSIST<br>Crystalein<br>Surfaclear<br>Advantomer | Oilfield chemicals and personal care & cosmetics | ATRP | [416] |
| ThermoFisher Scientific | ProPac IMAC-10 | GPC and HPLC columns | ATRP | [417] |
| PPG | Andaro® | Pigments | ATRP | [418] |
| BASF | EFKA PX | Solvent-based dispersant | NMP | [419] |
| | Dispex Ultra PX | Waterborne dispersant | NMP | [419] |
| Arkema | Nanostrength (MAM) | Adhesives, Thermoplastic elastomer | NMP | [420] |
| Bostik | SAF | Adhesive | NMP | [421] |
| Altuglass | ShieldUp | Chemical and impact resistance acrylic sheet | NMP | [422] |
| Otsuka | Terplus D | Pigment dispersant | TERP | [423] |

control, polymer materials derived through RDRP will mimic the intricate and complex structures of natural materials, such as wood and silk, and thus exhibit unique properties. While RDRP is on the cusp of more extensive investigation for the fabrication of 3D materials, [182] future work focusing on the construction of precise polymer networks containing well-defined macromolecular architectures will result in the preparation of materials with enhanced and tunable mechanical properties. For example, the preparation of 3D materials can be envisioned where control over the polymer network structure via RDRP can allow multidomain materials containing soft and hard domains. These materials may show the ability to absorb shock or respond to external stimuli in the same way as natural polymeric materials.

### 6.5. Automation

The automated synthesis of DNA and proteins has been transformative for the life sciences. Critically, mundane and repetitive tasks are performed by machines, which frees up time for researchers, while providing more reliable results. Such advantages, if translated to the field of polymer chemistry, could increase the rates of discovery for novel materials and eliminate batch to batch discrepancies. Recent works have demonstrated the potential to use DNA synthesizers and polymerase chain reaction (PCR) for the production of complex macromolecules. [150,406] Furthermore, with the integration of machine learning, time consuming tasks such as incremental optimizations may be handled without the constant attention of polymer chemists, freeing their minds to focus on application specific design and development. However, compared to the limited number of building blocks used in DNA and proteins, there exists a dizzying array of monomers polymerizable through RDRP, each with their own optimum polymerization conditions. Additionally, the potential for diverse architectures and post-synthetic procedures further complicates work-up and characterization processes.

Perhaps, the greatest challenge for automation in RDRP is the selection of a universal synthetic platform on which to base such an automatic synthesizer. With the continued progression of RDRP techniques, the state-of-the-art with respect to their distinct advantages and disadvantages are constantly changing, making investment in a specific process a risky affair. Regardless, more user-friendly and economical automatic synthesizers capable of producing high purity block copolymers, would be an enabling tool that could greatly improve many existing workflows; perhaps the first product to market will determine which of the various RDRP processes becomes the *de facto* choice.

### 6.6. Translation into commercial products

A frequent criticism directed towards RDRP is the slow translation into commercial products. However, one of the first RDRP techniques, ITP, was paradoxically introduced by Daikin Industries under the guidance of Tatemoto 40 years ago. [6,54] The intense exploration of RDRP methods in academia and the wealth of patents awarded to or in conjunction with large commercial entities indicate the value and potential of controlled radical polymerizations and their products. While the versatility and robustness of RDRP methods are undeniable, the introduction of new products made using such techniques is complicated by the existence of established products and their respective synthetic methods, which have been refined and optimized for their specific use cases. Such economic considerations necessitate RDRP-derived products to provide substantially improved performance or new capabilities to offset the increased cost of manufacture.

Table 1 provides a snapshot of RDRP-derived product available in 2020. It must be noted that this table is far from comprehensive due to the scantiness of information regarding commercial products. Additionally, the table includes only those product ranges whose existence is supported online. As such, products in the pipeline that have yet to be realized, or those that have previously existed but whose current status is unclear have not been included. The level of elaboration with regards to process chemistry varies from company to company; whereas the Otsuka Chemical Co. clearly states their use of TERP, with clear explanation of their

technology, companies such as Kaneka, BASF and Arkema utilize the broader term of “living” or “controlled” radical technologies, which are clarified by secondary sources. [424–427] On the other hand, BYK-Chemie is an example where the production method of their Disperbyk range of products is made using an undisclosed RDRP method. Considering the overall lack of declaration, as it is there right to do so, in combination with unknown production and sales figures, it is impossible to provide a clear picture of current industrial products utilizing RDRP technologies. Despite this, insight into the current status of RDRP in industry can still be gained from the information shown in Table 1.

ITP and its capability to control the polymerization of fluoromonomers [428] has been effectively translated into fluoroelastomer products by several companies. [426,429] In a similar fashion, NMP has been adopted by BASF (through Ciba) and Arkema for dispersants, adhesives and other specialty products. ITP and NMP were indeed developed earlier in comparison to other RDRP processes. Relatively cheap control agents and simple chemistry that could be implemented in existing infrastructure have increased the attractiveness of these techniques for rapid adoption. It must be noted that in all cases the adoption of RDRP methods has been used to produce specialty products; the more demanding use cases obviously necessitate more rigorous testing and therefore a longer development period.

From an academic perspective, there is significant potential for exciting new commercialization opportunities based on current RDRP targets. The large-scale surface modifications of various substrates via an economical surface-initiated ARGET process were recently demonstrated. [430,431] Indeed, the oxygen tolerance of ARGET polymerizations has been an enabling capability that has warranted its widespread adoption. [432] Such technology paves the way for commercial development of new product segments with controlled physicochemical properties at solid interfaces. More recently developed photocatalyzed RDRP processes also offer spatiotemporal control in addition to oxygen tolerance and room temperature reaction conditions. This further enhances possible industrial application of RDRP compared with conventional free radical processes. In addition to improved atom and energy efficiency, these externally regulated processes provide means for more effective scalability through microfluidic chips and the production of higher value products through nano- and microscale 2D and 3D implementations. Considering the specificity of these advancements, it is likely that many of these newer technologies will be realized as components within more complex devices as opposed to standalone products as is the case today.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgment

CJH acknowledges continued support by the National Science Foundation (NSF) through the Materials Research Science and Engineering Center at University of California Santa Barbara, DMR-1720256 (IRG-3). KM acknowledges support form the National Science Foundation, CHE- 2000391. We acknowledge Professor Mitsuo Sawamoto for insightful discussions.

## References

[1] Szwarc M. ‘Living’ Polymers. Nature 1956;178:1168–9.
[2] Aubrey DJ, Richard GJ, Graeme M. Terminology for reversible-deactivation radical polymerization previously called "controlled" radical or "living" radical polymerization (IUPAC Recommendations 2010). Pure Appl Chem 2009;82:483–91.
[3] Otsu T, Yoshida M, Tazaki T. A model for living radical polymerization. Makromol Chem Rapid Commun 1982;3:133–40.
[4] Otsu T, Yoshida M. Role of initiator-transfer agent-terminator (iniferter) in radical polymerizations: Polymer design by organic disulfides as iniferters. Makromol Chem Rapid Commun 1982;3:127–32.
[5] Borsig E, Lazár M, Čapla M, Florián Š. Reinitiation reactions of poly(methyl methacrylate) with labile bound fragments of initiator. Angew Makromolek Chem 1969;9:89–95.
[6] Tatemoto M, Suzuki T, Tomoda M, Furukawa Y, Ueta Y. Fluorine-containing polymer easily curable and its curable composition. JP S53-125491A, 1978.
[7] Matyjaszewski K, Gaynor S, Greszta D, Mardare D, Shigemoto T. ‘Living’ and controlled radical polymerization. J Phys Org Chem 1995;8:306–15.
[8] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. Narrow molecular weight resins by a free-radical polymerization process. Macromolecules 1993;26:2987–8.
[9] Wang JS, Matyjaszewski K. Controlled/"living" radical polymerization. Atom transfer radical polymerization in the presence of transition-metal complexes. J Am Chem Soc 1995;117:5614–15.
[10] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris- (triphenylphosphine)ruthenium(ii)/methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization. Macromolecules 1995;28:1721–3.
[11] Percec V, Barboiu B. "Living" radical polymerization of styrene initiated by arenesulfonyl chlorides and CuI(bpy)nCl. Macromolecules 1995;28:7970–2.
[12] Chiefari J, Chong YK, Ercole F, Krstina J, Jeffery J, Le TPT, et al. Living free-radical polymerization by reversible addition−fragmentation chain transfer: the RAFT process. Macromolecules 1998;31:5559–62.
[13] Wayland BB, Poszmik G, Mukerjee SL, Fryd M. Living radical polymerization of acrylates by organocobalt porphyrin complexes. J Am Chem Soc 1994;116:7943–4.
[14] Gaynor SG, Wang JS, Matyjaszewski K. Controlled radical polymerization by degenerative transfer: effect of the structure of the transfer agent. Macromolecules 1995;28:8051–6.
[15] Goto A, Fukuda T. Kinetics of living radical polymerization. Prog Polym Sci 2004;29:329–85.
[16] Yeow J, Chapman R, Gormley AJ, Boyer C. Up in the air: oxygen tolerance in controlled/living radical polymerisation. Chem Soc Rev 2018;47:4357–87.
[17] Coessens V, Pintauer T, Matyjaszewski K. Functional polymers by atom transfer radical polymerization. Prog Polym Sci 2001;26:337–77.
[18] Iha RK, Wooley KL, Nyström AM, Burke DJ, Kade MJ, Hawker CJ. Applications of orthogonal “click” chemistries in the synthesis of functional soft materials. Chem Rev 2009;109:5620–86.
[19] Moad G. A critical assessment of the kinetics and mechanism of initiation of radical polymerization with commercially available dialkyldiazene initiators. Prog Polym Sci 2019;88:130–88.
[20] Solomon DH, Rizzardo E, Cacioli P. Free radical polymerization and the produced polymers. EP 135280A2, 1985.
[21] Moad G, Rizzardo E. Chapter 1 The history of nitroxide-mediated polymerization. In: Gigmes D, editor. Nitroxide Mediated Polymerization: From Fundamentals to Applications in Materials Science. London: The Royal Society of Chemistry; 2016. p. 1–44.
[22] Hawker CJ, Bosman AW, Harth E. New polymer synthesis by nitroxide mediated living radical polymerizations. Chem Rev 2001;101:3661–88.
[23] Benoit D, Chaplinski V, Braslau R, Hawker CJ. Development of a universal alkoxyamine for “living” free radical polymerizations. J Am Chem Soc 1999;121:3904–20.
[24] Hawker CJ. Molecular weight control by a "living" free-radical polymerization process. J Am Chem Soc 1994;116:11185–6.
[25] Nicolas J, Guillaneuf Y, Lefay C, Bertin D, Gigmes D, Charleux B. Nitroxide–mediated polymerization. Prog Polym Sci 2013;38:63–235.
[26] Bamford CH, Eastmond GC, Hargreaves K. Free radical sources based on zero-valent metal derivatives. Nature 1965;205:385–6.
[27] Jasperse CP, Curran DP, Fevig TL. Radical reactions in natural product synthesis. Chem Rev 1991;91:1237–86.
[28] Kamigaito M, Ando T, Sawamoto M. Metal-catalyzed living radical polymerization. Chem Rev 2001;101:3689–746.
[29] Matyjaszewski K. Atom transfer radical polymerization (ATRP): current status and future perspectives. Macromolecules 2012;45:4015–39.
[30] Patten TE, Xia J, Abernathy T, Matyjaszewski K. Polymers with very low polydispersities from atom transfer radical polymerization. Science 1996;272:866–8.
[31] Gromada J, Matyjaszewski K. Simultaneous reverse and normal initiation in atom transfer radical polymerization. Macromolecules 2001;34:7664–71.
[32] Min K, Gao H, Matyjaszewski K. Use of ascorbic acid as reducing agent for synthesis of well-defined polymers by ARGET ATRP. Macromolecules 2007;40:1789–91.
[33] Jakubowski W, Min K, Matyjaszewski K. Activators regenerated by electron transfer for atom transfer radical polymerization of styrene. Macromolecules 2006;39:39–45.
[34] Percec V, Guliashvili T, Ladislaw JS, Wistrand A, Stjerndahl A, Sienkowska MJ, et al. Ultrafast synthesis of ultrahigh molar mass polymers by metal-catalyzed living radical polymerization of acrylates, methacrylates, and vinyl chloride mediated by SET at 25°C. J Am Chem Soc 2006;128:14156–65.

[35] Matyjaszewski K, Coca S, Gaynor SG, Wei M, Woodworth BE. Zerovalent metals in controlled/"living" radical polymerization. Macromolecules 1997;30:7348–50.
[36] Percec V, Popov AV, Ramirez-Castillo E, Monteiro M, Barboiu B, Weichold O, et al. Aqueous room temperature metal-catalyzed living radical polymerization of vinyl chloride. J Am Chem Soc 2002;124:4940–1.
[37] Boyer C, Corrigan NA, Jung K, Nguyen D, Nguyen TK, Adnan NNM, et al. Copper-mediated living radical polymerization (atom transfer radical polymerization and copper(0) mediated polymerization): from fundamentals to bioapplications. Chem Rev 2016;116:1803–949.
[38] di Lena F, Matyjaszewski K. Transition metal catalysts for controlled radical polymerization. Prog Polym Sci 2010;35:959–1021.
[39] Konkolewicz D, Wang Y, Krys P, Zhong M, Isse AA, Gennaro A, et al. SARA ATRP or SET-LRP. End of controversy? Polym Chem 2014;5:4396–417.
[40] Moad CL, Moad G, Rizzardo E, Thang SH. Chain transfer activity of $\omega$-unsaturated methyl methacrylate oligomers. Macromolecules 1996;29:7717–26.
[41] Krstina J, Moad G, Rizzardo E, Winzor CL, Berge CT, Fryd M. Narrow polydispersity block copolymers by free-radical polymerization in the presence of macromonomers. Macromolecules 1995;28:5381–5.
[42] Moad G, Rizzardo E, Thang SH. Living radical polymerization by the RAFT process – a third update. Aust J Chem 2012;65:985–1076.
[43] Perrier S. 50th anniversary perspective: RAFT polymerization—a user guide. Macromolecules 2017;50:7433–47.
[44] Barner-Kowollik C, Buback M, Charleux B, Coote ML, Drache M, Fukuda T, et al. Mechanism and kinetics of dithiobenzoate-mediated RAFT polymerization. I. The current situation. J Polym Sci Part A Polym Chem 2006;44:5809–31.
[45] Mayadunne RTA, Rizzardo E, Chiefari J, Chong YK, Moad G, Thang SH. Living radical polymerization with reversible addition−fragmentation chain transfer (RAFT polymerization) using dithiocarbamates as chain transfer agents. Macromolecules 1999;32:6977–80.
[46] Mayadunne RTA, Rizzardo E, Chiefari J, Krstina J, Moad G, Postma A, et al. Living polymers by the use of trithiocarbonates as reversible addition−fragmentation chain transfer (RAFT) agents: ABA triblock copolymers by radical polymerization in two steps. Macromolecules 2000;33:243–5.
[47] Destarac M, Charmot D, Franck X, Zard SZ. Dithiocarbamates as universal reversible addition-fragmentation chain transfer agents. Macromol Rapid Commun 2000;21:1035–9.
[48] Benaglia M, Chiefari J, Chong YK, Moad G, Rizzardo E, Thang SH. Universal (Switchable) RAFT agents. J Am Chem Soc 2009;131:6914–15.
[49] Moad G. A critical survey of dithiocarbamate reversible addition-fragmentation chain transfer (RAFT) agents in radical polymerization. J Polym Sci Part A Polym Chem 2019;57:216–27.
[50] Zard SZ. On the trail of xanthates: some new chemistry from an old functional group. Angew Chem Int Ed 1997;36:672–85.
[51] Perrier S, Takolpuckdee P. Macromolecular design via reversible addition–fragmentation chain transfer (RAFT)/xanthates (MADIX) polymerization. J Polym Sci Part A Polym Chem 2005;43:5347–93.
[52] Charmot D, Corpart P, Adam H, Zard SZ, Biadatti T, Bouhadir G. Controlled radical polymerization in dispersed media. Macromol Symp 2000;150:23–32.
[53] Keddie DJ, Moad G, Rizzardo E, Thang SH. RAFT agent design and synthesis. Macromolecules 2012;45:5321–42.
[54] Tatemoto M, Nakagawa T. Segmented polymers containing fluorine and iodine and their production. US 4158678A, 1979.
[55] David G, Boyer C, Tonnar J, Ameduri B, Lacroix-Desmazes P, Boutevin B. Use of iodocompounds in radical polymerization. Chem Rev 2006;106:3936–62.
[56] Tatemoto M. Development of “iodine transfer polymerization” and its applications to telechelically reactive polymers. Kobunshi Ronbunshu 1992;49:765–83.
[57] Goto A, Zushi H, Hirai N, Wakada T, Tsujii Y, Fukuda T. Living radical polymerizations with germanium, tin, and phosphorus catalysts – reversible chain transfer catalyzed polymerizations (RTCPs). J Am Chem Soc 2007;129:13347–54.
[58] Goto A, Suzuki T, Ohfuji H, Tanishima M, Fukuda T, Tsujii Y, et al. Reversible complexation mediated living radical polymerization (RCMP) using organic catalysts. Macromolecules 2011;44:8709–15.
[59] Debuigne A, Poli R, Jérôme C, Jérôme R, Detrembleur C. Overview of cobalt–mediated radical polymerization: Roots, state of the art and future prospects. Prog Polym Sci 2009;34:211–39.
[60] Poli R. Organometallic mediated radical polymerization. In: Reference Module in Materials Science and Materials Engineering. London: Elsevier Ltd; 2012. p. 351–75.
[61] Yamago S. Precision polymer synthesis by degenerative transfer controlled/living radical polymerization using organotellurium, organostibine, and organobismuthine chain-transfer agents. Chem Rev 2009;109:5051–68.
[62] Magenau AJD, Strandwitz NC, Gennaro A, Matyjaszewski K. Electrochemically mediated atom transfer radical polymerization. Science 2011;332:81–4.
[63] Mohapatra H, Kleiman M, Esser-Kahn AP. Mechanically controlled radical polymerization initiated by ultrasound. Nat Chem 2017;9:135–9.
[64] Enciso AE, Fu L, Russell AJ, Matyjaszewski K. A breathing atom-transfer radical polymerization: fully oxygen-tolerant polymerization inspired by aerobic respiration of cells. Angew Chem Int Ed 2018;57:933–6.
[65] Fors BP, Hawker CJ. Control of a living radical polymerization of methacrylates by light. Angew Chem Int Ed 2012;51:8850–3.
[66] Xu J, Jung K, Atme A, Shanmugam S, Boyer C. A robust and versatile photoinduced living polymerization of conjugated and unconjugated monomers and its oxygen tolerance. J Am Chem Soc 2014;136:5508–19.
[67] Strover LT, Cantalice A, Lam JYL, Postma A, Hutt OE, Horne MD, et al. Electrochemical behavior of thiocarbonylthio chain transfer agents for RAFT polymerization. ACS Macro Lett 2019;8:1316–22.
[68] Lorandi F, Fantin M, Shanmugam S, Wang Y, Isse AA, Gennaro A, et al. Toward electrochemically mediated reversible addition–fragmentation chain-transfer (eRAFT) polymerization: can propagating radicals be efficiently electrogenerated from RAFT agents? Macromolecules 2019;52:1479–88.
[69] Bray C, Li G, Postma A, Strover LT, Wang J, Moad G. Initiation of RAFT polymerization: electrochemically initiated RAFT polymerization in emulsion (Emulsion eRAFT), and direct PhotoRAFT polymerization of liquid crystalline monomers. Aust J Chem 2020:9. doi:10.1071/CH20260.
[70] Zhang L, Laborda E, Darwish N, Noble BB, Tyrell JH, Pluczyk S, et al. Electrochemical and electrostatic cleavage of alkoxyamines. J Am Chem Soc 2018;140:766–74.
[71] Corrigan N, Yeow J, Judzewitsch P, Xu J, Boyer C. Seeing the light: advancing materials chemistry through photopolymerization. Angew Chem Int Ed 2019;58:5170–89.
[72] Chen M, Zhong M, Johnson JA. Light-controlled radical polymerization: mechanisms, methods, and applications. Chem Rev 2016;116:10167–211.
[73] Pan X, Tasdelen MA, Laun J, Junkers T, Yagci Y, Matyjaszewski K. Photomediated controlled radical polymerization. Prog Polym Sci 2016;62:73–125.
[74] Yagci Y, Jockusch S, Turro NJ. Photoinitiated polymerization: advances, challenges, and opportunities. Macromolecules 2010;43:6245–60.
[75] Konkolewicz D, Schröder K, Buback J, Bernhard S, Matyjaszewski K. Visible light and sunlight photoinduced ATRP with ppm of Cu catalyst. ACS Macro Lett 2012;1:1219–23.
[76] Corrigan N, Shanmugam S, Xu J, Boyer C. Photocatalysis in organic and polymer synthesis. Chem Soc Rev 2016;45:6165–212.
[77] Carbonell C, Valles D, Wong AM, Carlini AS, Touve MA, Korpanty J, et al. Polymer brush hypersurface photolithography. Nat Commun 2020;11 1244/1-8.
[78] Pester CW, Narupai B, Mattson KM, Bothman DP, Klinger D, Lee KW, et al. Engineering surfaces through sequential stop-flow photopatterning. Adv Mater 2016;28:9292–300.
[79] Fors BP, Poelma JE, Menyo MS, Robb MJ, Spokoyny DM, Kramer JW, et al. Fabrication of unique chemical patterns and concentration gradients with visible light. J Am Chem Soc 2013;135:14106–9.
[80] Singh VK, Yu C, Badgujar S, Kim Y, Kwon Y, Kim D, et al. Highly efficient organic photocatalysts discovered via a computer-aided-design strategy for visible-light-driven atom transfer radical polymerization. Nat Catal 2018;1:794–804.
[81] Lim CH, Ryan MD, McCarthy BG, Theriot JC, Sartor SM, Damrauer NH, et al. Intramolecular charge transfer and ion pairing in N,N-diaryl dihydrophenazine photoredox catalysts for efficient organocatalyzed atom transfer radical polymerization. J Am Chem Soc 2017;139:348–55.
[82] Theriot JC, Lim CH, Yang H, Ryan MD, Musgrave CB, Miyake GM. Organocatalyzed atom transfer radical polymerization driven by visible light. Science 2016;352 1082/1-6.
[83] Treat NJ, Sprafke H, Kramer JW, Clark PG, Barton BE, Read de Alaniz J, et al. Metal-free atom transfer radical polymerization. J Am Chem Soc 2014;136:16096–101.
[84] Ribelli TG, Konkolewicz D, Bernhard S, Matyjaszewski K. How are radicals (re)generated in photochemical ATRP? J Am Chem Soc 2014;136:13303–12.
[85] Dolinski ND, Page ZA, Discekici EH, Meis D, Lee IH, Jones GR, et al. What happens in the dark? Assessing the temporal control of photo-mediated controlled radical polymerizations. J Polym Sci Part A Polym Chem 2019;57:268–73.
[86] McClelland KP, Clemons TD, Stupp SI, Weiss EA. Semiconductor quantum dots are efficient and recyclable photocatalysts for aqueous PET-RAFT polymerization. ACS Macro Lett 2020;9:7–13.
[87] Wu C, Corrigan N, Lim CH, Jung K, Zhu J, Miyake G, et al. Guiding the design of organic photocatalyst for PET-RAFT polymerization: halogenated xanthene dyes. Macromolecules 2019;52:236–48.
[88] Hakobyan K, Gegenhuber T, McErlean CSP, Müllner M. Visible-light-driven MADIX polymerisation via a reusable, low-cost, and non-toxic bismuth oxide photocatalyst. Angew Chem Int Ed 2019;58:1828–32.
[89] Shanmugam S, Xu J, Boyer C. Exploiting metalloporphyrins for selective living radical polymerization tunable over visible wavelengths. J Am Chem Soc 2015;137:9174–85.
[90] Xu J, Jung K, Boyer C. Oxygen tolerance study of photoinduced electron transfer–reversible addition–fragmentation chain transfer (PET-RAFT) polymerization mediated by Ru(bpy)3Cl2. Macromolecules 2014;47:4217–29.
[91] Corrigan N, Rosli D, Jones JWJ, Xu J, Boyer C. Oxygen tolerance in living radical polymerization: investigation of mechanism and implementation in continuous flow polymerization. Macromolecules 2016;49:6779–89.
[92] Quinn JF, Barner L, Barner-Kowollik C, Rizzardo E, Davis TP. Reversible addition−fragmentation chain transfer polymerization initiated with ultraviolet radiation. Macromolecules 2002;35:7620–7.
[93] Carmean RN, Becker TE, Sims MB, Sumerlin BS. Ultra-high molecular weights via aqueous reversible-deactivation radical polymerization. Chem 2017;2:93–101.
[94] Xu J, Shanmugam S, Corrigan NA, Boyer C. Catalyst-free visible light-induced RAFT photopolymerization. ACS Symp Ser 2015;1187:247–67.

[95] Guillaneuf Y, Bertin D, Gigmes D, Versace DL, Lalevée J, Fouassier JP. Toward nitroxide-mediated photopolymerization. Macromolecules 2010;43:2204–12.
[96] Zhao Y, Yu M, Fu X. Photo-cleavage of the cobalt–carbon bond: visible light-induced living radical polymerization mediated by organo-cobalt porphyrins. Chem Commun 2013;49:5186–8.
[97] Ohtsuki A, Lei L, Tanishima M, Goto A, Kaji H. Photocontrolled organocatalyzed living radical polymerization feasible over a wide range of wavelengths. J Am Chem Soc 2015;137:5610–17.
[98] Wang Z, Pan X, Yan J, Dadashi-Silab S, Xie G, Zhang J, et al. Temporal control in mechanically controlled atom transfer radical polymerization using low ppm of Cu catalyst. ACS Macro Lett 2017;6:546–9.
[99] McKenzie TG, Colombo E, Fu Q, Ashokkumar M, Qiao GG. Sono-RAFT polymerization in aqueous medium. Angew Chem Int Ed 2017;56:12302–6.
[100] Wang Z, Pan X, Li L, Fantin M, Yan J, Wang Z, et al. Enhancing mechanically induced ATRP by promoting interfacial electron transfer from piezoelectric nanoparticles to Cu catalysts. Macromolecules 2017;50:7940–8.
[101] Sigg SJ, Seidi F, Renggli K, Silva TB, Kali G, Bruns N. Horseradish peroxidase as a catalyst for atom transfer radical polymerization. Macromol Rapid Commun 2011;32:1710–15.
[102] Silva TB, Spulber M, Kocik MK, Seidi F, Charan H, Rother M, et al. Hemoglobin and red blood cells catalyze atom transfer radical polymerization. Biomacromolecules 2013;14:2703–12.
[103] Simakova A, Mackenzie M, Averick SE, Park S, Matyjaszewski K. Bioinspired iron-based catalyst for atom transfer radical polymerization. Angew Chem Int Ed 2013;52:12148–51.
[104] Zhang B, Wang X, Zhu A, Ma K, Lv Y, Wang X, et al. Enzyme-initiated reversible addition–fragmentation chain transfer polymerization. Macromolecules 2015;48:7792–802.
[105] Danielson AP, Van Kuren DB, Lucius ME, Makaroff K, Williams C, Page RC, et al. Well-defined macromolecules using horseradish peroxidase as a RAFT initiase. Macromol Rapid Commun 2016;37:362–7.
[106] Reyhani A, McKenzie TG, Fu Q, Qiao GG. Fenton-chemistry-mediated radical polymerization. Macromol Rapid Commun 2019;40 1900220/1-16.
[107] Zhou F, Li R, Wang X, Du S, An Z. Non-natural photoenzymatic controlled radical polymerization inspired by DNA photolyase. Angew Chem Int Ed 2019;58:9479–84.
[108] Percec V, Barboiu B, Kim HJ. Arenesulfonyl halides: a universal class of functional initiators for metal-catalyzed “living” radical polymerization of styrene(s), methacrylates, and acrylates. J Am Chem Soc 1998;120:305–16.
[109] Qiu J, Matyjaszewski K. Polymerization of substituted styrenes by atom transfer radical polymerization. Macromolecules 1997;30:5643–8.
[110] Xia J, Johnson T, Gaynor SG, Matyjaszewski K, DeSimone J. Atom transfer radical polymerization in supercritical carbon dioxide. Macromolecules 1999;32:4802–5.
[111] Pan X, Lamson M, Yan J, Matyjaszewski K. Photoinduced metal-free atom transfer radical polymerization of acrylonitrile. ACS Macro Lett 2015;4:192–6.
[112] Xu J, Jung K, Corrigan NA, Boyer C. Aqueous photoinduced living/controlled polymerization: tailoring for bioconjugation. Chem Sci 2014;5:3568–75.
[113] Sarbu T, Matyjaszewski K. ATRP of methyl methacrylate in the presence of ionic liquids with ferrous and cuprous anions. Macromol Chem Phys 2001;202:3379–91.
[114] Hawker CJ, Wooley KL. The convergence of synthetic organic and polymer chemistries. Science 2005;309:1200–5.
[115] Quémener D, Davis TP, Barner-Kowollik C, Stenzel MH. RAFT and click chemistry: A versatile approach to well-defined block copolymers. Chem Commun 2006:5051–3.
[116] Iovu MC, Craley CR, Jeffries-El M, Krankowski AB, Zhang R, Kowalewski T, et al. Conducting regioregular polythiophene block copolymer nanofibrils synthesized by reversible addition fragmentation chain transfer polymerization (RAFT) and nitroxide mediated polymerization (NMP). Macromolecules 2007;40:4733–5.
[117] Chan JW, Yu B, Hoyle CE, Lowe AB. Convergent synthesis of 3-arm star polymers from RAFT-prepared poly(N,N-diethylacrylamide) via a thiol–ene click reaction. Chem Commun 2008:4959–61.
[118] Gacal B, Durmaz H, Tasdelen MA, Hizal G, Tunca U, Yagci Y, et al. Anthracene−maleimide-based diels−alder “click chemistry” as a novel route to graft copolymers. Macromolecules 2006;39:5330–6.
[119] Sumerlin BS, Tsarevsky NV, Louche G, Lee RY, Matyjaszewski K. Highly efficient “click” functionalization of poly(3-azidopropyl methacrylate) prepared by ATRP. Macromolecules 2005;38:7540–5.
[120] Zhang Q, Remsen EE, Wooley KL. Shell cross-linked nanoparticles containing hydrolytically degradable. Crystalline Core Domains. J Am Chem Soc 2000;122:3642–51.
[121] Mantovani G, Ladmiral V, Tao L, Haddleton DM. One-pot tandem living radical polymerisation–Huisgens cycloaddition process (“click”) catalysed by N-alkyl-2-pyridylmethanimine/Cu(i)Br complexes. Chem Commun 2005:2089–91.
[122] Bontempo D, Heredia KL, Fish BA, Maynard HD. Cysteine-reactive polymers synthesized by atom transfer radical polymerization for conjugation to proteins. J Am Chem Soc 2004;126:15372–3.
[123] Lele BS, Murata H, Matyjaszewski K, Russell AJ. Synthesis of uniform protein−polymer conjugates. Biomacromolecules 2005;6:3380–7.
[124] Tasdelen MA, Yagci Y. Light-induced click reactions. Angew Chem Int Ed 2013;52:5930–8.
[125] Theato P. Synthesis of well-defined polymeric activated esters. J Polym Sci Part A Polym Chem 2008;46:6677–87.
[126] Schmidt BVKJ, Fechler N, Falkenhagen J, Lutz JF. Controlled folding of synthetic polymer chains through the formation of positionable covalent bridges. Nat Chem 2011;3:234–8.
[127] Willcock H, O'Reilly RK. End group removal and modification of RAFT polymers. Polym Chem 2010;1:149–57.
[128] Lutz JF, Börner HG, Weichenhan K. Combining atom transfer radical polymerization and click chemistry: a versatile method for the preparation of end–functional polymers. Macromol Rapid Commun 2005;26:514–18.
[129] Lowe AB, Sumerlin BS, Donovan MS, McCormick CL. Facile preparation of transition metal nanoparticles stabilized by well-defined (co)polymers synthesized via aqueous reversible addition-fragmentation chain transfer polymerization. J Am Chem Soc 2002;124:11562–3.
[130] Boyer C, Granville A, Davis TP, Bulmus V. Modification of RAFT-polymers via thiol-ene reactions: A general route to functional polymers and new architectures. J Polym Sci Part A Polym Chem 2009;47:3773–94.
[131] Xu B, Feng C, Huang X. A versatile platform for precise synthesis of asymmetric molecular brush in one shot. Nat Commun 2017;8 333/1-8.
[132] Sun Z, Choi B, Feng A, Moad G, Thang SH. Nonmigratory poly(vinyl chloride)-block-polycaprolactone plasticizers and compatibilizers prepared by sequential RAFT and ring-opening polymerization (RAFT-T-ROP). Macromolecules 2019;52:1746–56.
[133] Corrigan N, Ciftci M, Jung K, Boyer CAJM. Mediating reaction orthogonality in polymer and materials science. Angew Chem Int Ed 2019:35. doi:10.1002/anie.201912001.
[134] Pan X, Fantin M, Yuan F, Matyjaszewski K. Externally controlled atom transfer radical polymerization. Chem Soc Rev 2018;47:5457–90.
[135] Peterson BM, Kottisch V, Supej MJ, Fors BP. On demand switching of polymerization mechanism and monomer selectivity with orthogonal stimuli. ACS Cent Sci 2018;4:1228–34.
[136] Satoh K, Sun Z, Uchiyama M, Kamigaito M, Xu J, Boyer C. Interconvertible and switchable cationic/PET-RAFT copolymerization triggered by visible light. Polym J 2020;52:65–73.
[137] Chen M, Deng S, Gu Y, Lin J, MacLeod MJ, Johnson JA. Logic-controlled radical polymerization with heat and light: multiple-stimuli switching of polymer chain growth via a recyclable, thermally responsive gel photoredox catalyst. J Am Chem Soc 2017;139:2257–66.
[138] Zhang Z, Zeng TY, Xia L, Hong CY, Wu DC, You YZ. Synthesis of polymers with on-demand sequence structures via dually switchable and interconvertible polymerizations. Nat Commun 2018;9 2577/1-9.
[139] Wu C, Chen H, Corrigan N, Jung K, Kan X, Li Z, et al. Computer-guided discovery of a pH-responsive organic photocatalyst and application for pH and light dual-gated polymerization. J Am Chem Soc 2019;141:8207–20.
[140] Supej MJ, Peterson BM, Fors BP. Dual stimuli switching: interconverting cationic and radical polymerizations with electricity and light. Chem 2020;6:1794–803.
[141] Li X, Ye S, Zhang YC, Zhao HP, Huang Y, Zhang B, et al. Magnetic Janus nanocomposites with iridium(iii) complexes for heterogeneous catalysis of logic controlled RAFT polymerization using multiplexed external switching. Nanoscale 2020;12:7595–603.
[142] Fu C, Xu J, Boyer C. Photoacid-mediated ring opening polymerization driven by visible light. Chem Commun 2016;52:7126–9.
[143] Kottisch V, Michaudel Q, Fors BP. Photocontrolled interconversion of cationic and radical polymerizations. J Am Chem Soc 2017;139:10665–8.
[144] Leibfarth FA, Mattson KM, Fors BP, Collins HA, Hawker CJ. External regulation of controlled polymerizations. Angew Chem Int Ed 2013;52:199–210.
[145] Zhang L, Wu C, Jung K, Ng YH, Boyer C. An oxygen paradox: catalytic use of oxygen in radical photopolymerization. Angew Chem Int Ed 2019;58:16811–14.
[146] Szczepaniak G, Łagodzińska M, Dadashi-Silab S, Gorczyński A, Matyjaszewski K. Fully oxygen-tolerant atom transfer radical polymerization triggered by sodium pyruvate. Chem Sci 2020;11:8809–16.
[147] Matyjaszewski K, Coca S, Gaynor SG, Wei M, Woodworth BE. Controlled radical polymerization in the presence of oxygen. Macromolecules 1998;31:5967–9.
[148] Matyjaszewski K, Jakubowski W, Min K, Tang W, Huang J, Braunecker WA, et al. Diminishing catalyst concentration in atom transfer radical polymerization with reducing agents. Proc Natl Acad Sci USA 2006;103 15309/1-6.
[149] Fleischmann S, Rosen BM, Percec V. SET-LRP of acrylates in air. J Polym Sci Part A Polym Chem 2010;48:1190–6.
[150] Pan X, Lathwal S, Mack S, Yan J, Das SR, Matyjaszewski K. Automated synthesis of well-defined polymers and biohybrids by atom transfer radical polymerization using a DNA synthesizer. Angew Chem Int Ed 2017;56:2740–3.
[151] Oytun F, Kahveci MU, Yagci Y. Sugar overcomes oxygen inhibition in photoinitiated free radical polymerization. J Polym Sci Part A Polym Chem 2013;51:1685–9.
[152] Chapman R, Gormley AJ, Herpoldt KL, Stevens MM. Highly controlled open vessel RAFT polymerizations by enzyme degassing. Macromolecules 2014;47:8541–7.
[153] Baeten E, Haven JJ, Junkers T. RAFT multiblock reactor telescoping: from monomers to tetrablock copolymers in a continuous multistage reactor cascade. Polym Chem 2017;8:3815–24.
[154] Xu S, Ng G, Xu J, Kuchel RP, Yeow J, Boyer C. 2-(Methylthio)ethyl methacrylate: a versatile monomer for stimuli responsiveness and polymerization-induced self-assembly in the presence of air. ACS Macro Lett 2017;6:1237–44.
[155] Yeow J, Chapman R, Xu J, Boyer C. Oxygen tolerant photopolymerization for ultralow volumes. Polym Chem 2017;8:5012–22.

[156] Gormley AJ, Yeow J, Ng G, Conway Ó, Boyer C, Chapman R. An oxygen-tolerant PET-RAFT polymerization for screening structure–activity relationships. Angew Chem Int Ed 2018;57:1557–62.
[157] Judzewitsch PR, Zhao L, Wong EHH, Boyer C. High-throughput synthesis of antimicrobial copolymers and rapid evaluation of their bioactivity. Macromolecules 2019;52:3975–86.
[158] Fournier D, Hoogenboom R, Thijs HML, Paulus RM, Schubert US. Tunable pH- and temperature-sensitive copolymer libraries by reversible addition−fragmentation chain transfer copolymerizations of methacrylates. Macromolecules 2007;40:915–20.
[159] Zaquen N, Rubens M, Corrigan N, Xu J, Zetterlund PB, Boyer C, et al. Polymer synthesis in continuous flow reactors. Prog Polym Sci 2020;107 101256/1-40.
[160] Shen Y, Zhu S, Pelton R. Packed column reactor for continuous atom transfer radical polymerization: Methyl methacrylate polymerization using silica gel supported catalyst. Macromol Rapid Commun 2000;21:956–9.
[161] Wenn B, Martens AC, Chuang YM, Gruber J, Junkers T. Efficient multiblock star polymer synthesis from photo-induced copper-mediated polymerization with up to 21 arms. Polym Chem 2016;7:2720–7.
[162] Corrigan N, Manahan R, Lew ZT, Yeow J, Xu J, Boyer C. Copolymers with controlled molecular weight distributions and compositional gradients through flow polymerization. Macromolecules 2018;51:4553–63.
[163] Hornung CH, Nguyen X, Dumsday G, Saubern S. Integrated continuous processing and flow characterization of RAFT polymerization in tubular flow reactors. Macromol React Eng 2012;6:458–66.
[164] Hornung CH, von Känel K, Martinez-Botella I, Espiritu M, Nguyen X, Postma A, et al. Continuous flow aminolysis of RAFT polymers using multistep processing and inline analysis. Macromolecules 2014;47:8203–13.
[165] Haven JJ, Vandenbergh J, Junkers T. Watching polymers grow: real time monitoring of polymerizations via an on-line ESI-MS/microreactor coupling. Chem Commun 2015;51:4611–14.
[166] Rubens M, Vrijsen JH, Laun J, Junkers T. Precise polymer synthesis by autonomous self-optimizing flow reactors. Angew Chem Int Ed 2019;58:3183–7.
[167] Ramsey BL, Pearson RM, Beck LR, Miyake GM. Photoinduced organocatalyzed atom transfer radical polymerization using continuous flow. Macromolecules 2017;50:2668–74.
[168] Melker A, Fors BP, Hawker CJ, Poelma JE. Continuous flow synthesis of poly(methyl methacrylate) via a light-mediated controlled radical polymerization. J Polym Sci Part A Polym Chem 2015;53:2693–8.
[169] Zaquen N, Yeow J, Junkers T, Boyer C, Zetterlund PB. Visible light-mediated polymerization-induced self-assembly using continuous flow reactors. Macromolecules 2018;51:5165–72.
[170] Huang Z, Corrigan N, Lin S, Boyer C, Xu J. Upscaling single unit monomer insertion to synthesize discrete oligomers. J Polym Sci Part A Polym Chem 2019;57:1947–55.
[171] Parkinson S, Hondow NS, Conteh JS, Bourne RA, Warren NJ. All-aqueous continuous-flow RAFT dispersion polymerisation for efficient preparation of diblock copolymer spheres, worms and vesicles. React Chem Eng 2019;4:852–61.
[172] Cunningham MF. Controlled/living radical polymerization in aqueous dispersed systems. Prog Polym Sci 2008;33:365–98.
[173] Qiu J, Charleux B, Matyjaszewski K. Controlled/living radical polymerization in aqueous media: homogeneous and heterogeneous systems. Prog Polym Sci 2001;26:2083–134.
[174] Zetterlund PB, Thickett SC, Perrier S, Bourgeat-Lami E, Lansalot M. Controlled/living radical polymerization in dispersed systems: an update. Chem Rev 2015;115:9745–800.
[175] Barbey R, Lavanant L, Paripovic D, Schüwer N, Sugnaux C, Tugulu S, et al. Polymer brushes via surface-initiated controlled radical polymerization: synthesis, characterization, properties, and applications. Chem Rev 2009;109:5437–527.
[176] Zoppe JO, Ataman NC, Mocny P, Wang J, Moraes J, Klok HA. Surface-initiated controlled radical polymerization: state-of-the-art, opportunities, and challenges in surface and interface engineering with polymer brushes. Chem Rev 2017;117:1105–318.
[177] Yan J, Bockstaller MR, Matyjaszewski K. Brush-modified materials: Control of molecular architecture, assembly behavior, properties and applications. Prog Polym Sci 2020;100 101180/1-51.
[178] Gao H, Matyjaszewski K. Synthesis of functional polymers with controlled architecture by CRP of monomers in the presence of cross-linkers: From stars to gels. Prog Polym Sci 2009;34:317–50.
[179] Moad G. RAFT (Reversible addition–fragmentation chain transfer) crosslinking (co)polymerization of multi-olefinic monomers to form polymer networks. Polym Int 2015;64:15–24.
[180] Johnson JA, Lewis DR, Díaz DD, Finn MG, Koberstein JT, Turro NJ. Synthesis of degradable model networks via ATRP and click chemistry. J Am Chem Soc 2006;128:6564–5.
[181] Cuthbert J, Balazs AC, Kowalewski T, Matyjaszewski K. STEM gels by controlled radical polymerization. Trends Chem 2020;2:341–53.
[182] Zhang Z, Corrigan N, Bagheri A, Jin J, Boyer C. A versatile 3D and 4D printing system through photocontrolled RAFT polymerization. Angew Chem Int Ed 2019;58:17954–63.
[183] Jung K, Corrigan N, Ciftci M, Xu J, Seo SE, Hawker CJ, et al. Designing with light: advanced 2D, 3D, and 4D materials. Adv Mater 2020;32 1903850/1-21.
[184] Matyjaszewski K. Advanced materials by atom transfer radical polymerization. Adv Mater 2018;30 1706441/1-22.
[185] Lutz JF, Ouchi M, Liu DR, Sawamoto M. Sequence-controlled polymers. Science 2013;341 1238149/1-8.
[186] Zhou Y, Zhang Z, Reese CM, Patton DL, Xu J, Boyer C, et al. Selective and rapid light-induced RAFT single unit monomer insertion in aqueous solution. Macromol Rapid Commun 2020;41 1900478/1-6.
[187] Alsubaie F, Anastasaki A, Wilson P, Haddleton DM. Sequence-controlled multi-block copolymerization of acrylamides via aqueous SET-LRP at 0°C. Polym Chem 2015;6:406–17.
[188] Xu J, Fu C, Shanmugam S, Hawker CJ, Moad G, Boyer C. Synthesis of discrete oligomers by sequential PET-RAFT single-unit monomer insertion. Angew Chem Int Ed 2017;56:8376–83.
[189] Huang Z, Noble BB, Corrigan N, Chu Y, Satoh K, Thomas DS, et al. Discrete and stereospecific oligomers prepared by sequential and alternating single unit monomer insertion. J Am Chem Soc 2018;140:13392–406.
[190] Corrigan N, Almasri A, Taillades W, Xu J, Boyer C. Controlling molecular weight distributions through photoinduced flow polymerization. Macromolecules 2017;50:8438–48.
[191] Whitfield R, Parkatzidis K, Rolland M, Truong NP, Anastasaki A. Tuning dispersity by photoinduced atom transfer radical polymerisation: monomodal distributions with ppm copper concentration. Angew Chem Int Ed 2019;58:13323–8.
[192] Whitfield R, Parkatzidis K, Truong NP, Junkers T, Anastasaki A. Tailoring polymer dispersity by RAFT polymerization: a versatile approach. Chem 2020;6:1340–52.
[193] Liu K, Corrigan N, Postma A, Moad G, Boyer C. A comprehensive platform for the design and synthesis of polymer molecular weight distributions. Macromolecules 2020;53:8867–82.
[194] Gentekos DT, Sifri RJ, Fors BP. Controlling polymer properties through the shape of the molecular-weight distribution. Nat Rev Mater 2019;4:761–74.
[195] Listak J, Jakubowski W, Mueller L, Plichta A, Matyjaszewski K, Bockstaller MR. Effect of symmetry of molecular weight distribution in block copolymers on formation of “metastable” morphologies. Macromolecules 2008;41:5919–27.
[196] Ouchi M, Badi N, Lutz JF, Sawamoto M. Single-chain technology using discrete synthetic macromolecules. Nat Chem 2011;3:917–24.
[197] Altintas O, Gerstel P, Dingenouts N, Barner-Kowollik C. Single chain self--assembly: preparation of $\alpha,\omega$-donor–acceptor chains via living radical polymerization and orthogonal conjugation. Chem Commun 2010;46:6291–3.
[198] Jia Z, Monteiro MJ. Cyclic polymers: Methods and strategies. J Polym Sci Part A Polym Chem 2012;50:2085–97.
[199] Laurent BA, Grayson SM. An efficient route to well-defined macrocyclic polymers via “click” cyclization. J Am Chem Soc 2006;128:4238–9.
[200] Poelma JE, Ono K, Miyajima D, Aida T, Satoh K, Hawker CJ. Cyclic block copolymers for controlling feature sizes in block copolymer lithography. ACS Nano 2012;6:10845–54.
[201] Chen B, Jerger K, Fréchet JMJ, Szoka FC. The influence of polymer topology on pharmacokinetics: Differences between cyclic and linear PEGylated poly(acrylic acid) comb polymers. J Controlled Release 2009;140:203–9.
[202] Qiu XP, Tanaka F, Winnik FM. Temperature-induced phase transition of well-defined cyclic poly(n-isopropylacrylamide)s in aqueous solution. Macromolecules 2007;40:7069–71.
[203] Altintas O, Barner-Kowollik C. Single-chain folding of synthetic polymers: a critical update. Macromol Rapid Commun 2016;37:29–46.
[204] Gonzalez-Burgos M, Latorre-Sanchez A, Pomposo JA. Advances in single chain technology. Chem Soc Rev 2015;44:6122–42.
[205] Mavila S, Eivgi O, Berkovich I, Lemcoff NG. Intramolecular cross-linking methodologies for the synthesis of polymer nanoparticles. Chem Rev 2016;116:878–961.
[206] Stals PJM, Li Y, Burdyńska J, Nicolaÿ R, Nese A, Palmans ARA, et al. How far can we push polymer architectures? J Am Chem Soc 2013;135:11421–4.
[207] Azuma Y, Terashima T, Sawamoto M. Self-folding polymer iron catalysts for living radical polymerization. ACS Macro Lett 2017;6:830–5.
[208] Knöfel ND, Rothfuss H, Willenbacher J, Barner-Kowollik C, Roesky PW. Platinum(II)-crosslinked single-chain nanoparticles: an approach towards recyclable homogeneous catalysts. Angew Chem Int Ed 2017;56:4950–4.
[209] Perez-Baena I, Barroso-Bujans F, Gasser U, Arbe A, Moreno AJ, Colmenero J, et al. Endowing single-chain polymer nanoparticles with enzyme-mimetic activity. ACS Macro Lett 2013;2:775–9.
[210] Rothfuss H, Knöfel ND, Roesky PW, Barner-Kowollik C. Single-chain nanoparticles as catalytic nanoreactors. J Am Chem Soc 2018;140:5875–81.
[211] Sanchez-Sanchez A, Arbe A, Colmenero J, Pomposo JA. Metallo-folded single-chain nanoparticles with catalytic selectivity. ACS Macro Lett 2014;3:439–43.
[212] Chong YK, Le TPT, Moad G, Rizzardo E, Thang SH. A more versatile route to block copolymers and other polymers of complex architecture by living radical polymerization: the RAFT process. Macromolecules 1999;32:2071–4.
[213] Engelis NG, Anastasaki A, Nurumbetov G, Truong NP, Nikolaou V, Shegiwal A, et al. Sequence-controlled methacrylic multiblock copolymers via sulfur-free RAFT emulsion polymerization. Nat Chem 2017;9:171–8.
[214] Clothier GKK, Guimarães TR, Khan M, Moad G, Perrier S, Zetterlund PB. Exploitation of the nanoreactor concept for efficient synthesis of multiblock copolymers via macroRAFT-mediated emulsion polymerization. ACS Macro Lett 2019;8:989–95.
[215] Soeriyadi AH, Boyer C, Nyström F, Zetterlund PB, Whittaker MR. High-order multiblock copolymers via iterative Cu(0)-mediated radical polymerizations (SET-LRP): toward biological precision. J Am Chem Soc 2011;133:11128–31.

[216] Bates CM, Bates FS. 50th anniversary perspective: block polymers—pure potential. Macromolecules 2017;50:3–22.
[217] Pfeifer S, Lutz JF. A facile procedure for controlling monomer sequence distribution in radical chain polymerizations. J Am Chem Soc 2007;129:9542–3.
[218] Hansen NML, Jankova K, Hvilsted S. Fluoropolymer materials and architectures prepared by controlled radical polymerizations. Eur Polym J 2007;43:255–93.
[219] Mori H, Yahagi M, Endo T. RAFT polymerization of N-vinylimidazolium salts and synthesis of thermoresponsive ionic liquid block copolymers. Macromolecules 2009;42:8082–92.
[220] Lutz JF, Neugebauer D, Matyjaszewski K. Stereoblock copolymers and tacticity control in controlled/living radical polymerization. J Am Chem Soc 2003;125:6986–93.
[221] Bang J, Kim SH, Drockenmuller E, Misner MJ, Russell TP, Hawker CJ. Defect-free nanoporous thin films from ABC triblock copolymers. J Am Chem Soc 2006;128:7622–9.
[222] Mai Y, Eisenberg A. Self-assembly of block copolymers. Chem Soc Rev 2012;41:5969–85.
[223] Yeow J, Boyer C. Photoinitiated polymerization-induced self-assembly (Photo-PISA): new insights and opportunities. Adv Sci 2017;4 1700137/1-14.
[224] Yin X, Hoffman AS, Stayton PS. Poly(N-isopropylacrylamide-co-propylacrylic acid) copolymers that respond sharply to temperature and pH. Biomacromolecules 2006;7:1381–5.
[225] Gregory A, Stenzel MH. Complex polymer architectures via RAFT polymerization: From fundamental process to extending the scope using click chemistry and nature's building blocks. Prog Polym Sci 2012;37:38–105.
[226] Sun Z, Wang M, Li Z, Choi B, Mulder RJ, Feng A, et al. Versatile approach for preparing PVC-based mikto-arm star additives based on RAFT polymerization. Macromolecules 2020;53:4465–79.
[227] Xia J, Zhang X, Matyjaszewski K. Synthesis of star-shaped polystyrene by atom transfer radical polymerization using an "arm first" approach. Macromolecules 1999;32:4482–4.
[228] Matyjaszewski K, Miller PJ, Pyun J, Kickelbick G, Diamanti S. Synthesis and characterization of star polymers with varying arm number, length, and composition from organic and hybrid inorganic/organic multifunctional initiators. Macromolecules 1999;32:6526–35.
[229] Stenzel MH, Davis TP. Star polymer synthesis using trithiocarbonate functional $\beta$-cyclodextrin cores (reversible addition–fragmentation chain-transfer polymerization). J Polym Sci Part A Polym Chem 2002;40:4498–512.
[230] Hedrick JL, Trollsås M, Hawker CJ, Atthoff B, Claesson H, Heise A, et al. Dendrimer-like star block and amphiphilic copolymers by combination of ring opening and atom transfer radical polymerization. Macromolecules 1998;31:8691–705.
[231] Voit BI, Lederer A. Hyperbranched and highly branched polymer architectures—synthetic strategies and major characterization aspects. Chem Rev 2009;109:5924–73.
[232] Hawker CJ, Frechet JMJ, Grubbs RB, Dao J. Preparation of hyperbranched and star polymers by a "living", self-condensing free radical polymerization. J Am Chem Soc 1995;117:10763–4.
[233] Gaynor SG, Edelman S, Matyjaszewski K. Synthesis of branched and hyperbranched polystyrenes. Macromolecules 1996;29:1079–81.
[234] Matyjaszewski K, Gaynor SG, Kulfan A, Podwika M. Preparation of hyperbranched polyacrylates by atom transfer radical polymerization. 1. acrylic AB* monomers in "living" radical polymerizations. Macromolecules 1997;30:5192–4.
[235] Stenzel-Rosenbaum MH, Davis TP, Fane AG, Chen V. Porous polymer films and honeycomb structures made by the self-organization of well-defined macromolecular structures created by living radical polymerization techniques. Angew Chem Int Ed 2001;40:3428–32.
[236] Bosman AW, Vestberg R, Heumann A, Fréchet JMJ, Hawker CJ. A modular approach toward functionalized three-dimensional macromolecules: from synthetic concepts to practical applications. J Am Chem Soc 2003;125:715–28.
[237] Sheiko SS, Sumerlin BS, Matyjaszewski K. Cylindrical molecular brushes: Synthesis, characterization, and properties. Prog Polym Sci 2008;33:759–85.
[238] Gao H, Matyjaszewski K. Synthesis of molecular brushes by "grafting onto" method: combination of ATRP and click reactions. J Am Chem Soc 2007;129:6633–9.
[239] Beers KL, Gaynor SG, Matyjaszewski K, Sheiko SS, Möller M. The synthesis of densely grafted copolymers by atom transfer radical polymerization. Macromolecules 1998;31:9413–15.
[240] Cho HY, Krys P, Szcześniak K, Schroeder H, Park S, Jurga S, et al. Synthesis of poly(OEOMA) using macromonomers via "grafting-through" ATRP. Macromolecules 2015;48:6385–95.
[241] Daniel WFM, Burdyńska J, Vatankhah-Varnoosfaderani M, Matyjaszewski K, Paturej J, Rubinstein M, et al. Solvent-free, supersoft and superelastic bottlebrush melts and networks. Nat Mater 2016;15:183–9.
[242] Vatankhah-Varnosfaderani M, Daniel WFM, Everhart MH, Pandya AA, Liang H, Matyjaszewski K, et al. Mimicking biological stress–strain behaviour with synthetic elastomers. Nature 2017;549:497–501.
[243] Seo M, Hillmyer MA. Reticulated nanoporous polymers by controlled polymerization-induced microphase separation. Science 2012;336:1422–5.
[244] Motokawa R, Iida Y, Zhao Y, Hashimoto T, Koizumi S. Living polymerization induced macro- and microdomain investigated by focusing ultra-small-angle neutron scattering. Polym J 2007;39:1312–18.
[245] Schulze MW, McIntosh LD, Hillmyer MA, Lodge TP. High-modulus, high–conductivity nanostructured polymer electrolyte membranes via polymerization-induced phase separation. Nano Lett 2014;14:122–6.
[246] Chen M, Gu Y, Singh A, Zhong M, Jordan AM, Biswas S, et al. Living additive manufacturing: transformation of parent gels into diversely functionalized daughter gels made possible by visible light photoredox catalysis. ACS Cent Sci 2017;3:124–34.
[247] Cuthbert J, Beziau A, Gottlieb E, Fu L, Yuan R, Balazs AC, et al. Transformable materials: structurally tailored and engineered macromolecular (STEM) gels by controlled radical polymerization. Macromolecules 2018;51:3808–17.
[248] Shanmugam S, Cuthbert J, Flum J, Fantin M, Boyer C, Kowalewski T, et al. Transformation of gels via catalyst-free selective RAFT photoactivation. Polym Chem 2019;10:2477–83.
[249] Amamoto Y, Otsuka H, Takahara A, Matyjaszewski K. Self-healing of covalently cross-linked polymers by reshuffling thiuram disulfide moieties in air under visible light. Adv Mater 2012;24:3975–80.
[250] Ercole F, Thissen H, Tsang K, Evans RA, Forsythe JS. Photodegradable hydrogels made via RAFT. Macromolecules 2012;45:8387–400.
[251] Liu Q, Zhang P, Qing A, Lan Y, Lu M. Poly(N-isopropylacrylamide) hydrogels with improved shrinking kinetics by RAFT polymerization. Polymer 2006;47:2330–6.
[252] Guo Z, Zhang G, Qiu F, Zhang H, Yang Y, Shi AC. Discovering ordered phases of block copolymers: new results from a generic Fourier-space approach. Phys Rev Lett 2008;101 028301/1-4.
[253] Orilall MC, Wiesner U. Block copolymer based composition and morphology control in nanostructured hybrid materials for energy conversion and storage: solar cells, batteries, and fuel cells. Chem Soc Rev 2011;40:520–35.
[254] Bates MW, Lequieu J, Barbon SM, Lewis RM, Delaney KT, Anastasaki A, et al. Stability of the A15 phase in diblock copolymer melts. Proc Natl Acad Sci USA 2019;116:13194–9.
[255] Canning SL, Smith GN, Armes SP. A critical appraisal of RAFT-mediated polymerization-induced self-assembly. Macromolecules 2016;49:1985–2001.
[256] Charleux B, Delaittre G, Rieger J, D'Agosto F. Polymerization-induced self--assembly: from soluble macromolecules to block copolymer nano-objects in one step. Macromolecules 2012;45:6753–65.
[257] D'Agosto F, Rieger J, Lansalot M. RAFT-mediated polymerization-induced self--assembly. Angew Chem Int Ed 2020;59:8368–92.
[258] Derry MJ, Fielding LA, Armes SP. Polymerization-induced self-assembly of block copolymer nanoparticles via RAFT non-aqueous dispersion polymerization. Prog Polym Sci 2016;52:1–18.
[259] Zetterlund PB, D'hooge DR. The nanoreactor concept: kinetic features of compartmentalization in dispersed phase polymerization. Macromolecules 2019;52:7963–76.
[260] Stace SJ, Vanderspikken J, Howard SC, Li G, Muir BW, Fellows CM, et al. Ab initio RAFT emulsion polymerization mediated by small cationic RAFT agents to form polymers with low molar mass dispersity. Polym Chem 2019;10:5044–51.
[261] Khan M, Guimarães TR, Zhou D, Moad G, Perrier S, Zetterlund PB. Exploitation of compartmentalization in RAFT miniemulsion polymerization to increase the degree of livingness. J Polym Sci Part A Polym Chem 2019;57:1938–46.
[262] Guimarães TR, Khan M, Kuchel RP, Morrow IC, Minami H, Moad G, et al. Nano-engineered multiblock copolymer nanoparticles via reversible addition–fragmentation chain transfer emulsion polymerization. Macromolecules 2019;52:2965–74.
[263] Richardson RAE, Guimarães TR, Khan M, Moad G, Zetterlund PB, Perrier S. Low-dispersity polymers in ab initio emulsion polymerization: improved macroRAFT agent performance in heterogeneous media. Macromolecules 2020;53:7672–83.
[264] Li W, Matyjaszewski K, Albrecht K, Möller M. Reactive surfactants for polymeric nanocapsules via interfacially confined miniemulsion ATRP. Macromolecules 2009;42:8228–33.
[265] Utama RH, Stenzel MH, Zetterlund PB. Inverse miniemulsion periphery RAFT polymerization: a convenient route to hollow polymeric nanoparticles with an aqueous core. Macromolecules 2013;46:2118–27.
[266] Ferguson CJ, Hughes RJ, Nguyen D, Pham BTT, Gilbert RG, Serelis AK, et al. Ab initio emulsion polymerization by RAFT-controlled self-assembly. Macromolecules 2005;38:2191–204.
[267] Ferguson CJ, Hughes RJ, Pham BTT, Hawkett BS, Gilbert RG, Serelis AK, et al. Effective ab initio emulsion polymerization under RAFT control. Macromolecules 2002;35:9243–5.
[268] Lorandi F, Wang Y, Fantin M, Matyjaszewski K. Ab initio emulsion atom–transfer radical polymerization. Angew Chem Int Ed 2018;57:8270–4.
[269] Wang Y, Lorandi F, Fantin M, Chmielarz P, Isse AA, Gennaro A, et al. Miniemulsion ARGET ATRP via interfacial and ion-pair catalysis: from ppm to ppb of residual copper. Macromolecules 2017;50:8417–25.
[270] Oh JK, Tang C, Gao H, Tsarevsky NV, Matyjaszewski K. Inverse miniemulsion ATRP: a new method for synthesis and functionalization of well-defined water-soluble/cross-linked polymeric particles. J Am Chem Soc 2006;128:5578–84.
[271] Lv F, An Z, Wu P. Scalable preparation of alternating block copolymer particles with inverse bicontinuous mesophases. Nat Commun 2019;10 1397/1-7.
[272] Penfold NJW, Yeow J, Boyer C, Armes SP. Emerging trends in polymerization-induced self-assembly. ACS Macro Lett 2019;8:1029–54.

[273] Blackman LD, Varlas S, Arno MC, Houston ZH, Fletcher NL, Thurecht KJ, et al. Confinement of therapeutic enzymes in selectively permeable polymer vesicles by polymerization-induced self-assembly (PISA) reduces antibody binding and proteolytic susceptibility. ACS Cent Sci 2018;4:718–23.
[274] Pyun J, Matyjaszewski K. Synthesis of nanocomposite organic/inorganic hybrid materials using controlled/"living" radical polymerization. Chem Mater 2001;13:3436–48.
[275] Advincula RC. Surface initiated polymerization from nanoparticle surfaces. J Dispersion Sci Technol 2003;24:343–61.
[276] Baskaran D, Mays JW, Bratcher MS. Polymer-grafted multiwalled carbon nanotubes through surface-initiated polymerization. Angew Chem Int Ed 2004;43:2138–42.
[277] Fan X, Lin L, Dalsin JL, Messersmith PB. Biomimetic anchor for surface-initiated polymerization from metal substrates. J Am Chem Soc 2005;127:15843–7.
[278] Giussi JM, Cortez ML, Marmisollé WA, Azzaroni O. Practical use of polymer brushes in sustainable energy applications: interfacial nanoarchitectonics for high-efficiency devices. Chem Soc Rev 2019;48:814–49.
[279] Kango S, Kalia S, Celli A, Njuguna J, Habibi Y, Kumar R. Surface modification of inorganic nanoparticles for development of organic–inorganic nanocomposites—A review. Prog Polym Sci 2013;38:1232–61.
[280] Krishnamoorthy M, Hakobyan S, Ramstedt M, Gautrot JE. Surface-initiated polymer brushes in the biomedical field: applications in membrane science, biosensing, cell culture, regenerative medicine and antibacterial coatings. Chem Rev 2014;114:10976–1026.
[281] Krishnan S, Weinman CJ, Ober CK. Advances in polymers for anti-biofouling surfaces. J Mater Chem 2008;18:3405–13.
[282] Luo H, Zhou X, Ellingford C, Zhang Y, Chen S, Zhou K, et al. Interface design for high energy density polymer nanocomposites. Chem Soc Rev 2019;48:4424–65.
[283] Senaratne W, Andruzzi L, Ober CK. Self-assembled monolayers and polymer brushes in biotechnology: current applications and future perspectives. Biomacromolecules 2005;6:2427–48.
[284] Stuart MAC, Huck WTS, Genzer J, Müller M, Ober C, Stamm M, et al. Emerging applications of stimuli-responsive polymer materials. Nat Mater 2010;9:101–13.
[285] Zhao N, Yan L, Zhao X, Chen X, Li A, Zheng D, et al. Versatile types of organic/inorganic nanohybrids: from strategic design to biomedical applications. Chem Rev 2019;119:1666–762.
[286] Zhou F, Huck WTS. Surface grafted polymer brushes as ideal building blocks for "smart" surfaces. Phys Chem Chem Phys 2006;8:3815–23.
[287] Zhu B, Edmondson S. Polydopamine-melanin initiators for surface-initiated ATRP. Polymer 2011;52:2141–9.
[288] Glasing J, Champagne P, Cunningham MF. Graft modification of chitosan, cellulose and alginate using reversible deactivation radical polymerization (RDRP). Curr Opin Green Sustain Chem 2016;2:15–21.
[289] Tizzotti M, Charlot A, Fleury E, Stenzel M, Bernard J. Modification of polysaccharides through controlled/living radical polymerization grafting—towards the generation of high performance hybrids. Macromol Rapid Commun 2010;31:1751–72.
[290] Wohlhauser S, Delepierre G, Labet M, Morandi G, Thielemans W, Weder C, et al. Grafting polymers from cellulose nanocrystals: synthesis, properties, and applications. Macromolecules 2018;51:6157–89.
[291] Lee SH, Dreyer DR, An J, Velamakanni A, Piner RD, Park S, et al. Polymer brushes via controlled, surface-initiated atom transfer radical polymerization (ATRP) from graphene oxide. Macromol Rapid Commun 2010;31:281–8.
[292] Georgakilas V, Otyepka M, Bourlinos AB, Chandra V, Kim N, Kemp KC, et al. Functionalization of graphene: covalent and non-covalent approaches, derivatives and applications. Chem Rev 2012;112:6156–214.
[293] McDonald KA, Feldblyum JI, Koh K, Wong-Foy AG, Matzger AJ. Polymer@MOF@MOF: "grafting from" atom transfer radical polymerization for the synthesis of hybrid porous solids. Chem Commun 2015;51:11994–6.
[294] Azzaroni O. Polymer brushes here, there, and everywhere: Recent advances in their practical applications and emerging opportunities in multiple research fields. J Polym Sci Part A Polym Chem 2012;50:3225–58.
[295] Chen WL, Cordero R, Tran H, Ober CK. 50th anniversary perspective: polymer brushes: novel surfaces for future materials. Macromolecules 2017;50:4089–113.
[296] Hui CM, Pietrasik J, Schmitt M, Mahoney C, Choi J, Bockstaller MR, et al. Surface-initiated polymerization as an enabling tool for multifunctional (nano-)engineered hybrid materials. Chem Mater 2014;26:745–62.
[297] Banquy X, Burdyńska J, Lee DW, Matyjaszewski K, Israelachvili J. Bioinspired bottle-brush polymer exhibits low friction and amontons-like behavior. J Am Chem Soc 2014;136:6199–202.
[298] Azzaroni O, Moya SE, Brown AA, Zheng Z, Donath E, Huck WTS. Polyelectrolyte brushes as ink nanoreservoirs for microcontact printing of ionic species with poly(dimethyl siloxane) stamps. Adv Funct Mater 2006;16:1037–42.
[299] Tomofumi S, Hideo O, Masataka O, Shinzaburo I, Yoshinobu T, Takeshi F. Fabrication and electrochemical properties of high-density graft films with ferrocene moieties on ITO substrates. Chem Lett 2005;34:1366–7.
[300] Behling RE, Williams BA, Staade BL, Wolf LM, Cochran EW. Influence of graft density on kinetics of surface-initiated ATRP of polystyrene from montmorillonite. Macromolecules 2009;42:1867–72.
[301] Yang WJ, Cai T, Neoh KG, Kang ET, Dickinson GH, Teo SLM, et al. Biomimetic anchors for antifouling and antibacterial polymer brushes on stainless steel. Langmuir 2011;27:7065–76.
[302] Cai QJ, Fu GD, Zhu FR, Kang ET, Neoh KG. GaAs–polymer hybrids formed by surface-initiated atom-transfer radical polymerization of methyl methacrylate. Angew Chem Int Ed 2005;44:1104–7.
[303] Yan J, Malakooti MH, Lu Z, Wang Z, Kazem N, Pan C, et al. Solution processable liquid metal nanodroplets by surface-initiated atom transfer radical polymerization. Nat Nanotechnol 2019;14:684–90.
[304] Khanal A, Inoue Y, Yada M, Nakashima K. Synthesis of silica hollow nanoparticles templated by polymeric micelle with core−shell−corona structure. J Am Chem Soc 2007;129:1534–5.
[305] Pang X, He Y, Jung J, Lin Z. 1D nanocrystals with precisely controlled dimensions, compositions, and architectures. Science 2016;353:1268–72.
[306] Pang X, Zhao L, Han W, Xin X, Lin Z. A general and robust strategy for the synthesis of nearly monodisperse colloidal nanocrystals. Nat Nanotechnol 2013;8:426–31.
[307] Yuan J, Xu Y, Walther A, Bolisetty S, Schumacher M, Schmalz H, et al. Water–soluble organo-silica hybrid nanowires. Nat Mater 2008;7:718–22.
[308] Kim DJ, Lee KB, Lee TG, Shon HK, Kim WJ, Hj Paik, et al. Biomimetic micropatterning of silica by surface-initiated polymerization and microcontact printing. Small 2005;1:992–6.
[309] Tugulu S, Harms M, Fricke M, Volkmer D, Klok HA. Polymer brushes as ionotropic matrices for the directed fabrication of microstructured calcite thin films. Angew Chem Int Ed 2006;45:7458–61.
[310] Paripovic D, Klok HA. Polymer brush guided formation of thin gold and palladium/gold bimetallic films. ACS Appl Mater Interfaces 2011;3:910–17.
[311] Sugnaux C, Mallorquí AD, Herriman J, Klok HA, AFi Morral. Polymer brush guided formation of conformal, plasmonic nanoparticle-based electrodes for microwire solar cells. Adv Funct Mater 2015;25:3958–65.
[312] Kopeć M, Lamson M, Yuan R, Tang C, Kruk M, Zhong M, et al. Polyacrylonitrile-derived nanostructured carbon materials. Prog Polym Sci 2019;92:89–134.
[313] Tang C, Bombalski L, Kruk M, Jaroniec M, Matyjaszewski K, Kowalewski T. Nanoporous carbon films from "hairy" polyacrylonitrile-grafted colloidal silica nanoparticles. Adv Mater 2008;20:1516–22.
[314] Singh N, Chen Z, Tomer N, Wickramasinghe SR, Soice N, Husson SM. Modification of regenerated cellulose ultrafiltration membranes by surface-initiated atom transfer radical polymerization. J Membr Sci 2008;311:225–34.
[315] Ma H, Wells M, Beebe TP Jr, Chilkoti A. Surface-initiated atom transfer radical polymerization of oligo(ethylene glycol) methyl methacrylate from a mixed self-assembled monolayer on gold. Adv Funct Mater 2006;16:640–8.
[316] Yang WJ, Neoh KG, Kang ET, Teo SLM, Rittschof D. Polymer brush coatings for combating marine biofouling. Prog Polym Sci 2014;39:1017–42.
[317] Huang J, Murata H, Koepsel RR, Russell AJ, Matyjaszewski K. Antibacterial polypropylene via surface-initiated atom transfer radical polymerization. Biomacromolecules 2007;8:1396–9.
[318] Chen T, Ferris R, Zhang J, Ducker R, Zauscher S. Stimulus-responsive polymer brushes on surfaces: Transduction mechanisms and applications. Prog Polym Sci 2010;35:94–112.
[319] Liu G, Liu Z, Li N, Wang X, Zhou F, Liu W. Hairy polyelectrolyte brushes–grafted thermosensitive microgels as artificial synovial fluid for simultaneous biomimetic lubrication and arthritis treatment. ACS Appl Mater Interfaces 2014;6:20452–63.
[320] Zhang K, Yan W, Simic R, Benetti EM, Spencer ND. Versatile surface modification of hydrogels by surface-initiated, cu0-mediated controlled radical polymerization. ACS Appl Mater Interfaces 2020;12:6761–7.
[321] Wang X, Cai X, Guo Q, Zhang T, Kobe B, Yang J. i3DP, a robust 3D printing approach enabling genetic post-printing surface modification. Chem Commun 2013;49:10064–6.
[322] Ionov L, Houbenov N, Sidorenko A, Stamm M, Minko S. Smart microfluidic channels. Adv Funct Mater 2006;16:1153–60.
[323] Moro T, Takatori Y, Ishihara K, Konno T, Takigawa Y, Matsushita T, et al. Surface grafting of artificial joints with a biocompatible polymer for preventing periprosthetic osteolysis. Nat Mater 2004;3:829–36.
[324] Masuda T, Akimoto AM, Nagase K, Okano T, Yoshida R. Artificial cilia as autonomous nanoactuators: Design of a gradient self-oscillating polymer brush with controlled unidirectional motion. Sci Adv 2016;2 e1600902/1-8.
[325] Page ZA, Narupai B, Pester CW, Bou Zerdan R, Sokolov A, Laitar DS, et al. Novel strategy for photopatterning emissive polymer brushes for organic light emitting diode applications. ACS Cent Sci 2017;3:654–61.
[326] Ma S, Zhang X, Yu B, Zhou F. Brushing up functional materials. NPG Asia Mater 2019;11 24/1-39.
[327] Yi C, Yang Y, Liu B, He J, Nie Z. Polymer-guided assembly of inorganic nanoparticles. Chem Soc Rev 2020;49:465–508.
[328] Gonzato C, Courty M, Pasetto P, Haupt K. Magnetic molecularly imprinted polymer nanocomposites via surface-initiated RAFT polymerization. Adv Funct Mater 2011;21:3947–53.
[329] Layadi A, Kessel B, Yan W, Romio M, Spencer ND, Zenobi-Wong M, et al. Oxygen tolerant and cytocompatible iron(0)-mediated atrp enables the controlled growth of polymer brushes from mammalian cell cultures. J Am Chem Soc 2020;142:3158–64.
[330] Navarro LA, Enciso AE, Matyjaszewski K, Zauscher S. Enzymatically degassed surface-initiated atom transfer radical polymerization with real-time monitoring. J Am Chem Soc 2019;141:3100–9.

[331] Dehghani ES, Du Y, Zhang T, Ramakrishna SN, Spencer ND, Jordan R, et al. Fabrication and interfacial properties of polymer brush gradients by surface-initiated Cu(0)-mediated controlled radical polymerization. Macromolecules 2017;50:2436–46.
[332] Fantin M, Ramakrishna SN, Yan J, Yan W, Divandari M, Spencer ND, et al. The role of Cu0 in surface-initiated atom transfer radical polymerization: tuning catalyst dissolution for tailoring polymer interfaces. Macromolecules 2018;51:6825–35.
[333] Yan J, Li B, Yu B, Huck WTS, Liu W, Zhou F. Controlled polymer-brush growth from microliter volumes using sacrificial-anode atom-transfer radical polymerization. Angew Chem Int Ed 2013;52:9125–9.
[334] Orski SV, Fries KH, Sontag SK, Locklin J. Fabrication of nanostructures using polymer brushes. J Mater Chem 2011;21:14135–49.
[335] Romio M, Trachsel L, Morgese G, Ramakrishna SN, Spencer ND, Benetti EM. Topological polymer chemistry enters materials science: expanding the applicability of cyclic polymers. ACS Macro Lett 2020;9:1024–33.
[336] Chen T, Amin I, Jordan R. Patterned polymer brushes. Chem Soc Rev 2012;41:3280–96.
[337] Park S, Chmielarz P, Gennaro A, Matyjaszewski K. Simplified electrochemically mediated atom transfer radical polymerization using a sacrificial anode. Angew Chem Int Ed 2015;54:2388–92.
[338] Corrigan N, Boyer C. In the limelight: 2D and 3D materials via photo-controlled radical polymerization. Trends Chem 2020;2:689–706.
[339] Poelma JE, Fors BP, Meyers GF, Kramer JW, Hawker CJ. Fabrication of complex three-dimensional polymer brush nanostructures through light-mediated living radical polymerization. Angew Chem Int Ed 2013;52:6844–8.
[340] Boyer C, Bulmus V, Davis TP, Ladmiral V, Liu J, Perrier S. Bioapplications of RAFT polymerization. Chem Rev 2009;109:5402–36.
[341] Hu Q, Gan S, Bao Y, Zhang Y, Han D, Niu L. Controlled/"living" radical polymerization-based signal amplification strategies for biosensing. J Mater Chem B 2020;8:3327–40.
[342] Siegwart DJ, Oh JK, Matyjaszewski K. ATRP in the design of functional materials for biomedical applications. Prog Polym Sci 2012;37:18–37.
[343] Pelegri-O'Day EM, Bhattacharya A, Theopold N, Ko JH, Maynard HD. Synthesis of zwitterionic and trehalose polymers with variable degradation rates and stabilization of insulin. Biomacromolecules 2020;21:2147–54.
[344] Mansfield KM, Maynard HD. Site-specific insulin-trehalose glycopolymer conjugate by grafting from strategy improves bioactivity. ACS Macro Lett 2018;7:324–9.
[345] Nguyen TH, Kim SH, Decker CG, Wong DY, Loo JA, Maynard HD. A heparin-mimicking polymer conjugate stabilizes basic fibroblast growth factor. Nat Chem 2013;5:221–7.
[346] Messina MS, Messina KMM, Bhattacharya A, Montgomery HR, Maynard HD. Preparation of biomolecule-polymer conjugates by grafting-from using ATRP, RAFT, or ROMP. Prog Polym Sci 2020;100 101186/1-25.
[347] Pelegri-O'Day EM, Lin EW, Maynard HD. Therapeutic protein–polymer conjugates: advancing beyond PEgylation. J Am Chem Soc 2014;136:14323–32.
[348] Peeler JC, Woodman BF, Averick S, Miyake-Stoner SJ, Stokes AL, Hess KR, et al. Genetically encoded initiator for polymer growth from proteins. J Am Chem Soc 2010;132:13575–7.
[349] Averick SE, Dey SK, Grahacharya D, Matyjaszewski K, Das SR. Solid-phase incorporation of an ATRP initiator for polymer–DNA biohybrids. Angew Chem Int Ed 2014;53:2739–44.
[350] Nicolas J, Miguel VS, Mantovani G, Haddleton DM. Fluorescently tagged polymer bioconjugates from protein derived macroinitiators. Chem Commun 2006:4697–9.
[351] Tao L, Mantovani G, Lecolley F, Haddleton DM. $\alpha$-aldehyde terminally functional methacrylic polymers from living radical polymerization: application in protein conjugation "pegylation". J Am Chem Soc 2004;126:13220–1.
[352] Mantovani G, Lecolley F, Tao L, Haddleton DM, Clerx J, Cornelissen JJLM, et al. Design and synthesis of N-maleimido-functionalized hydrophilic polymers via copper-mediated living radical polymerization: a suitable alternative to PEgylation chemistry. J Am Chem Soc 2005;127:2966–73.
[353] Sumerlin BS. Proteins as initiators of controlled radical polymerization: grafting-from via ATRP and RAFT. ACS Macro Lett 2012;1:141–5.
[354] De P, Li M, Gondi SR, Sumerlin BS. Temperature-regulated activity of responsive polymer–protein conjugates prepared by grafting-from via RAFT polymerization. J Am Chem Soc 2008;130:11288–9.
[355] Boyer C, Bulmus V, Liu J, Davis TP, Stenzel MH, Barner-Kowollik C. Well-defined protein–polymer conjugates via in situ RAFT polymerization. J Am Chem Soc 2007;129:7145–54.
[356] Theodorou A, Liarou E, Haddleton DM, Stavrakaki IG, Skordalidis P, Whitfield R, et al. Protein-polymer bioconjugates via a versatile oxygen tolerant photoinduced controlled radical polymerization approach. Nat Commun 2020;11 1486/1-11.
[357] Carmali S, Murata H, Matyjaszewski K, Russell AJ. Tailoring site specificity of bioconjugation using step-wise atom-transfer radical polymerization on proteins. Biomacromolecules 2018;19:4044–51.
[358] Murata H, Carmali S, Baker SL, Matyjaszewski K, Russell AJ. Solid-phase synthesis of protein-polymers on reversible immobilization supports. Nat Commun 2018;9 845/1-10.
[359] Li M, Li H, De P, Sumerlin BS. Thermoresponsive block copolymer–protein conjugates prepared by grafting-from via RAFT polymerization. Macromol Rapid Commun 2011;32:354–9.
[360] Farokhzad OC, Langer R. Nanomedicine: Developing smarter therapeutic and diagnostic modalities. Adv Drug Delivery Rev 2006;58:1456–9.
[361] Ferrari M. Cancer nanotechnology: opportunities and challenges. Nat Rev Cancer 2005;5:161–71.
[362] Cheng R, Meng F, Deng C, Klok HA, Zhong Z. Dual and multi-stimuli responsive polymeric nanoparticles for programmed site-specific drug delivery. Biomaterials 2013;34:3647–57.
[363] O'Reilly RK, Hawker CJ, Wooley KL. Cross-linked block copolymer micelles: functional nanostructures of great potential and versatility. Chem Soc Rev 2006;35:1068–83.
[364] Elsabahy M, Wooley KL. Design of polymeric nanoparticles for biomedical delivery applications. Chem Soc Rev 2012;41:2545–61.
[365] Mura S, Couvreur P. Nanotheranostics for personalized medicine. Adv Drug Delivery Rev 2012;64:1394–416.
[366] Li Y, Duong HTT, Laurent S, MacMillan A, Whan RM, Elst LV, et al. Nanoparticles based on star polymers as theranostic vectors: endosomal-triggered drug release combined with MRI sensitivity. Adv Healthcare Mater 2015;4:148–56.
[367] Liu Y, Luehmann HP, Detering L, Pressly ED, McGrath AJ, Sultan D, et al. Assessment of targeted nanoparticle assemblies for atherosclerosis imaging with positron emission tomography and potential for clinical translation. ACS Appl Mater Interfaces 2019;11:15316–21.
[368] Shokeen M, Pressly ED, Hagooly A, Zheleznyak A, Ramos N, Fiamengo AL, et al. Evaluation of multivalent, functional polymeric nanoparticles for imaging applications. ACS Nano 2011;5:738–47.
[369] Ren JM, McKenzie TG, Fu Q, Wong EHH, Xu J, An Z, et al. Star polymers. Chem Rev 2016;116:6743–836.
[370] Yang DP, Oo MNNL, Deen GR, Li Z, Loh XJ. Nano-star-shaped polymers for drug delivery applications. Macromol Rapid Commun 2017;38 1700410/1-25.
[371] O'Reilly RK, Joralemon MJ, Hawker CJ, Wooley KL. Preparation of orthogonally-functionalized core Click cross-linked nanoparticles. New J Chem 2007;31:718–24.
[372] Chen S, Zhang XZ, Cheng SX, Zhuo RX, Gu ZW. Functionalized amphiphilic hyperbranched polymers for targeted drug delivery. Biomacromolecules 2008;9:2578–85.
[373] Cho HY, Srinivasan A, Hong J, Hsu E, Liu S, Shrivats A, et al. Synthesis of biocompatible PEG-based star polymers with cationic and degradable core for siRNA delivery. Biomacromolecules 2011;12:3478–86.
[374] Li S, Omi M, Cartieri F, Konkolewicz D, Mao G, Gao H, et al. Cationic hyperbranched polymers with biocompatible shells for siRNA delivery. Biomacromolecules 2018;19:3754–65.
[375] Cho HY, Averick SE, Paredes E, Wegner K, Averick A, Jurga S, et al. Star polymers with a cationic core prepared by ATRP for cellular nucleic acids delivery. Biomacromolecules 2013;14:1262–7.
[376] Nakayama Y. Hyperbranched polymeric "star vectors" for effective DNA or siRNA delivery. Acc Chem Res 2012;45:994–1004.
[377] Teo J, McCarroll JA, Boyer C, Youkhana J, Sagnella SM, Duong HTT, et al. A rationally optimized nanoparticle system for the delivery of RNA interference therapeutics into pancreatic tumors in vivo. Biomacromolecules 2016;17:2337–51.
[378] Lutz JF, Lehn JM, Meijer EW, Matyjaszewski K. From precision polymers to complex materials and systems. Nat Rev Mater 2016;1 16024/1-14.
[379] Boyer C, Soeriyadi AH, Zetterlund PB, Whittaker MR. Synthesis of complex multiblock copolymers via a simple iterative Cu(0)-mediated radical polymerization approach. Macromolecules 2011;44:8028–33.
[380] Gody G, Maschmeyer T, Zetterlund PB, Perrier S. Rapid and quantitative one-pot synthesis of sequence-controlled polymers by radical polymerization. Nat Commun 2013;4 2505/1-9.
[381] Ergene C, Yasuhara K, Palermo EF. Biomimetic antimicrobial polymers: recent advances in molecular design. Polym Chem 2018;9:2407–27.
[382] Mizutani M, Palermo EF, Thoma LM, Satoh K, Kamigaito M, Kuroda K. Design and synthesis of self-degradable antibacterial polymers by simultaneous chain- and step-growth radical copolymerization. Biomacromolecules 2012;13:1554–63.
[383] Judzewitsch PR, Nguyen TK, Shanmugam S, Wong EHH, Boyer C. Towards sequence-controlled antimicrobial polymers: effect of polymer block order on antimicrobial activity. Angew Chem Int Ed 2018;57:4559–64.
[384] Hoshino Y, Taniguchi S, Takimoto H, Akashi S, Katakami S, Yonamine Y, et al. Homogeneous oligomeric ligands prepared via radical polymerization that recognize and neutralize a target peptide. Angew Chem Int Ed 2020;59:679–83.
[385] Lawrence J, Lee SH, Abdilla A, Nothling MD, Ren JM, Knight AS, et al. A versatile and scalable strategy to discrete oligomers. J Am Chem Soc 2016;138:6306–10.
[386] Mitchell DA, Zhang Q, Voorhaar L, Haddleton DM, Herath S, Gleinich AS, et al. Manipulation of cytokine secretion in human dendritic cells using glycopolymers with picomolar affinity for DC-SIGN. Chem Sci 2017;8:6974–80.
[387] Yilmaz G, Uzunova V, Napier R, Becer CR. Single-chain glycopolymer folding via host–guest interactions and its unprecedented effect on DC-SIGN binding. Biomacromolecules 2018;19:3040–7.
[388] Zhang Q, Collins J, Anastasaki A, Wallis R, Mitchell DA, Becer CR, et al. Sequence-controlled multi-block glycopolymers to inhibit DC-SIGN-gp120 binding. Angew Chem Int Ed 2013;52:4435–9.
[389] Parkatzidis K, Wang HS, Truong NP, Anastasaki A. Recent developments and future challenges in controlled radical polymerization: a2020 update. Chem 2020;6:1575–88.
[390] Moad G. An industrial history of RAFT polymerization. RAFT Polymerization: Materials, Synthesis and Applications. Moad G, Rizzardo, editors, Weinheim: Wiley-VCH; 2021. TBA. ISBN 9783527344956.

[391] Ribelli TG, Lorandi F, Fantin M, Matyjaszewski K. Atom transfer radical polymerization: billion times more active catalysts and new initiation systems. Macromol Rapid Commun 2019;40 1800616/1-44.
[392] Aoshima H, Uchiyama M, Satoh K, Kamigaito M. Interconvertible living radical and cationic polymerization through reversible activation of dormant species with dual activity. Angew Chem Int Ed 2014;53:10932–6.
[393] Reinicke S, Schmalz H. Combination of living anionic polymerization and ATRP via "click" chemistry as a versatile route to multiple responsive triblock terpolymers and corresponding hydrogels. Colloid Polym Sci 2011;289:497–512.
[394] Satoh K, Ozawa S, Mizutani M, Nagai K, Kamigaito M. Sequence-regulated vinyl copolymers by metal-catalysed step-growth radical polymerization. Nat Commun 2010;1 6/1-6.
[395] Houshyar S, Keddie DJ, Moad G, Mulder RJ, Saubern S, Tsanaktsidis J. The scope for synthesis of macro-RAFT agents by sequential insertion of single monomer units. Polym Chem 2012;3:1879–89.
[396] Ouchi M, Sawamoto M. Sequence-controlled polymers via reversible-deactivation radical polymerization. Polym J 2018;50:83–94.
[397] Shanmugam S, Boyer C. Stereo-, temporal and chemical control through photoactivation of living radical polymerization: synthesis of block and gradient copolymers. J Am Chem Soc 2015;137:9988–99.
[398] An Z. 100th anniversary of macromolecular science viewpoint: achieving ultrahigh molecular weights with reversible deactivation radical polymerization. ACS Macro Lett 2020;9:350–7.
[399] Gong H, Gu Y, Zhao Y, Quan Q, Han S, Chen M. Precise synthesis of ultra-high-molecular-weight fluoropolymers enabled by chain-transfer--agent differentiation under visible-light irradiation. Angew Chem Int Ed 2020;59:919–27.
[400] Rochman CM, Browne MA, Halpern BS, Hentschel BT, Hoh E, Karapanagioti HK, et al. Classify plastic waste as hazardous. Nature 2013;494:169–71.
[401] Jackson AW. Reversible-deactivation radical polymerization of cyclic ketene acetals. Polym Chem 2020;11:3525–45.
[402] Hedir GG, Arno MC, Langlais M, Husband JT, O'Reilly RK, Dove AP. Poly(oligo(ethylene glycol) vinyl acetate)s: a versatile class of thermoresponsive and biocompatible polymers. Angew Chem Int Ed 2017;56:9178–82.
[403] Hill MR, Guégain E, Tran J, Figg CA, Turner AC, Nicolas J, et al. Radical ring-opening copolymerization of cyclic ketene acetals and maleimides affords homogeneous incorporation of degradable units. ACS Macro Lett 2017;6:1071–7.
[404] Tardy A, Nicolas J, Gigmes D, Lefay C, Guillaneuf Y. Radical ring-opening polymerization: scope, limitations, and application to (bio)degradable materials. Chem Rev 2017;117:1319–406.
[405] Smith RA, Fu G, McAteer O, Xu M, Gutekunst WR. Radical approach to thioester-containing polymers. J Am Chem Soc 2019;141:1446–51.
[406] Gurnani P, Floyd T, Tanaka J, Stubbs C, Lester D, Sanchez-Cano C, et al. PCR-RAFT: rapid high throughput oxygen tolerant RAFT polymer synthesis in a biology laboratory. Polym Chem 2020;11:1230–6.
[407] 3M. flexible resistance with 3M(TM) dyneon(TM) fluoroelastomers products (FKM & FFKM). https://www.3m.com/3M/en_US/company-us/all-3m-products/?N=5002385±8745513±8711017±8721867±8733376±3294857497&rt=r3/ 2020; accessed June 2020.
[408] AmericasAC. AFLAS(R) fluoroelastomers. https://www.agcchem.com/products/fluoropolymer-resins/fluoroelastomers/ 2020; accessed June 2020.
[409] Daikin America I. DAI-EL: applications. https://daikin-america.com/dai-el-applications/ 2020; accessed June 2020.
[410] CompanyTC. Viton(TM) fluoroelastomer: the imagination component. https://www.viton.com/en/ 2020; accessed June 2020.
[411] Solvay. Tecnoflon(R) FKM & PFR FFKM. https://www.solvay.com/en/brands/tecnoflon-fkm-pfr-ffkm/ 2020; accessed June 2020.
[412] Solvay. RHODIBLOC RS. https://www.solvay.com/en/product/rhodibloc-rs/ 2020; accessed June 2020.
[413] Solvay. RHODIBLOC FL-A. https://www.solvay.com/en/product/rhodibloc-fl/ 2020; accessed June 2020.
[414] BYK. Additives by name. https://www.byk.com/en/product/additives-by-name/disperbyk/ 2020; accessed June 2020.
[415] NV KB. Kaneka XMAP(TM) novel reactive liquid acrylic polymer. http://www.kaneka.be/products/liquid-polymers/kaneka-xmap/ 2020; accessed June 2020.
[416] Technologies PP. Personal care & cosmetics. https://www.pilotpolymertech.com/personal_care.html 2020; accessed June 2020.
[417] Scientific TF. ProPac(TM) IMAC-10 HPLC columns. https://www.thermofisher.com/order/catalog/product/063272#/063272/ 2020; accessed June 2020.
[418] Industries P. Andaro(R) special effect pigments. http://www.ppgaerospace.com/getdoc/fa7a870e-3e4d-4e39-9b2e-cbdc14b69969/Andaro.aspx 2020; accessed June 2020.
[419] BASF. EFKA(R) formulation additives for non-aqueous systems. https://www.basf.com/us/en/products/General-Business-Topics/dispersions/Products/Efka.html 2020; accessed June 2020.
[420] Arkema. Nanostrength(R): self-assembling block copolymers. https://www.arkema.com/en/products/product-finder/range-viewer/Nanostrength-self-assembling-block-copolymers/ 2020; accessed June 2020.
[421] Bostik. SAF(R), MMA adhesive technology. https://www.bostik.com/aecpolymers/our-products/ 2020; accessed June 2020.
[422] Altuglas. Chemical and impact resistance acrylic sheet: Altuglas(R) shieldup. https://www.altuglas.com/en/sheet/specialty-cast-sheet/impact-the-world/altuglas-shieldup/ 2020; accessed June 2020.
[423] Otsuka Chemical Co L. TERPLUS D Series. https://www.otsukac.co.jp/en/products/chemical/terplus-d/ 2020; accessed June 2020.
[424] Matyjaszewski K, Spanswick J. Controlled/living radical polymerization. Mater Today 2005;8:26–33.
[425] Destarac M. Controlled radical polymerization: industrial stakes, obstacles and achievements. Macromol React Eng 2010;4:165–79.
[426] Ameduri B. Fluoropolymers: the right material for the right applications. Chem Eur J 2018;24:18830–41.
[427] Destarac M. Industrial development of reversible-deactivation radical polymerization: is the induction period over? Polym Chem 2018;9:4947–67.
[428] Boyer C, Valade D, Lacroix-Desmazes P, Ameduri B, Boutevin B. Kinetics of the iodine transfer polymerization of vinylidene fluoride. J Polym Sci Part A Polym Chem 2006;44:5763–77.
[429] Améduri B. The promising future of fluoropolymers. Macromol Chem Phys 2020;221 1900573/1-14.
[430] Dunderdale GJ, Urata C, Miranda DF, Hozumi A. Large-scale and environmentally friendly synthesis of pH-responsive oil-repellent polymer brush surfaces under ambient conditions. ACS Appl Mater Interfaces 2014;6:11864–8.
[431] Sato T, Dunderdale GJ, Urata C, Hozumi A. Sol–gel preparation of initiator layers for surface-initiated ATRP: large-scale formation of polymer brushes is not a dream. Macromolecules 2018;51:10065–73.
[432] Matyjaszewski K, Dong H, Jakubowski W, Pietrasik J, Kusumo A. Grafting from surfaces for "everyone": ARGET ATRP in the presence of air. Langmuir 2007;23:4528–31.