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Established and Emerging Strategies for Polymer Chain-End Modification

This manuscript is dedicated to the 75th birthday of Professor Bob Grubbs for his life-long extraordinary achievement in research and education.

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ABSTRACT: The development of "controlled" and "living" polymerization processes with high end-group fidelity has enabled an unprecedented range of polymeric materials with specific chain-end functionality to be prepared. This highlight provides an overview of available strategies and evaluation of recent approaches for the chain-end functionalization of polymers prepared through controlled chain-growth polymerizations. As a tribute to Professor Robert B. Grubbs on the occasion of his 75th birthday, we also take this opportunity to highlight methods for the chain-end modification of polymers prepared by ring-opening metathesis polymerization within the broader context of functional group tolerant, living polymerizations. Finally, we focus attention toward new directions in polymer chain-end modifications, describing existing gaps in current strategies, and detailing recently reported protocols that show significant improvements over traditional methods. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *55*, 2903–2914

KEYWORDS: chain-end modification; controlled polymerization; functional group transformation

INTRODUCTION The development of "controlled" and "living" chain-growth polymerization strategies has revolutionized the design and preparation of functional polymers. These polymerizations have allowed access to materials with low dispersity and high chain-end fidelity. In particular, the potential to control the chain-end functionality has transformed chemists' view of a polymer from ill-defined structures to a versatile building block for the preparation of more complex materials.[1] This has led to a wide range of new applications for polymers, including surface/particle functionalization,[2] self-assembly,[3] molecular labelling,[4] and bioconjugation.[5] Furthermore, the importance and influence of polymer chain-ends on physical properties has emerged as an important consideration in a range of applications.[6–8] For example, chain-ends have been shown to have a significant effect on polymer self-assembly,[9,10] dictating structural ordering, charge transport and overall performance of organic semiconductors.[11–13] As a result, the incorporation of new functionality or removal of unwanted chain-end reactivity is a major theme and essential tool for polymer researchers.

This importance is reflected in the increasing number of studies examining the synthesis of chain-end modified polymers and/or the influence of these groups on overall performance. In this highlight we aim to provide an overview of the common methods available for modification of polymer chain-ends and draw attention to several new and emerging strategies that represent significant improvements over those currently employed. In particular, we focus on the most popular chain-growth processes, including controlled radical [e.g., atom transfer radical polymerization (ATRP), reversible addition fragmentation transfer (RAFT) polymerization, and nitroxide mediated polymerization (NMP)], ring-opening metathesis polymerization (ROMP), as well as highlighting a selection of transition metal-mediated, anionic, and cationic processes. It should be noted that the post-polymerization modification of polymer backbones utilizes many of the same reactions developed for chain-end functionalization, however, backbone derivatization is beyond the scope of this highlight and we direct the reader to a number of comprehensive reviews on the topic.[14,15]

DISCUSSION

Three main strategies exist for the modification of polymer chain-ends (Fig. 1); the use of a functional initiator, use of

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a reactive terminator to end-cap a growing polymer chain, or the post-polymerization modification of pre-existing chain-ends. In all of these cases, the scope of end-groups that can be introduced is dependent on their compatibility with the polymerization process and chemical composition of the polymer. For the majority of polymerizations, the active species is not isolatable and requires termination after polymerization. In the case of controlled radical polymerization (CRP), these terminations are intrinsically coupled to the mechanism (see below) and post-polymerization modification becomes a dominant strategy. For all of these approaches, researchers can draw inspiration from decades of small molecule organic methodology, where conditions have been reported for the transformation of a myriad of functional groups (FG).

This translation from small molecule organic chemistry to polymer modification is not direct. The special requirements

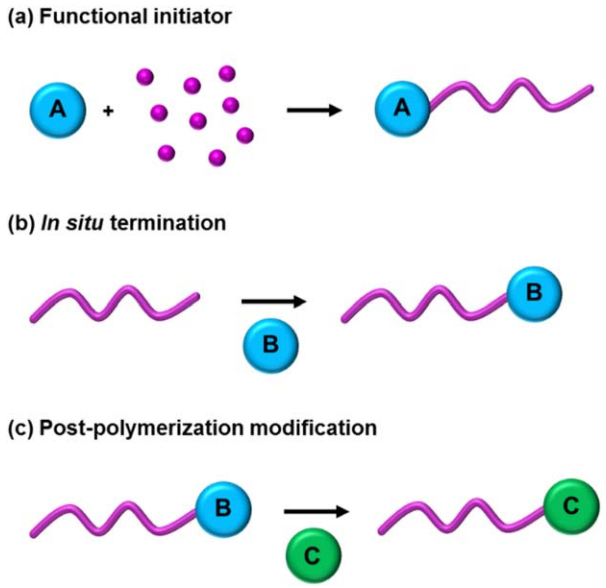

FIGURE 1 Schematic representation of available strategies for the modification of polymer chain-ends; initiation using a functional initiator (a), *in situ* termination using an appropriate quenching reagent (b), and post-polymerization modification of the acquired chain-end functionality (b reacts to afford c). Note that the chain-end moiety to be transformed via strategy C can be located at either polymer terminus.

of working with high molecular weight polymers require quantitative yields and selectivity due to difficulties associated with purification and removal of side products. While polymer-polymer purification can be challenging, the separation of polymers from small molecules is readily accomplished by leveraging size and solubility differences (e.g., size exclusion chromatography, selective precipitation, and dialysis). In addition, macromolecular reactions are often slower than the comparable small molecule reactions, due primarily to steric considerations. In analogy with solid-phase peptide synthesis, many chain-end functionalization strategies exploit the use of excess small molecule reagents to drive the reactions to full conversion followed by purification.[16]

Controlled Radical Polymerizations

CRPs, referring to any reversible-deactivation radical polymerization,[17] are often considered the method of choice for polymer synthesis due to their monomer scope, comparatively mild reaction conditions and overall versatility.[18–24] CRP relies on the transient formation of a reactive radical species at the polymer chain-end, which is reversibly terminated to a dormant state. This facile termination results in a low concentration of active radicals, reducing side reactions and enabling "control" of the polymerization. The three main CRP techniques, ATRP, RAFT, and NMP, utilize an initiator or chain transfer agent (CTA) that has the appropriate functionality to facilitate this equilibrium. In all cases, the default polymer product is a heterotelechelic macromolecule with the chemical composition of each chain-end terminus determined by the structure of the initiator or CTA (Fig. 2). As such, the predominant strategies for the functionalization of chain-ends often rely on the use of functional initiators or the post-polymerization modification of residual reactive groups.[25,26] Outlined in Figure 3 is an overview of some of the post-polymerization chain-end modifications possible when using polymers prepared by the three main CRP methods. In many of these examples, the first transformation can be considered merely a stepping stone toward more tailored functionality.[26,27]

ATRP is arguably the most versatile CRP for end-group modification as the electrophilic character of the halide that remains after polymerization is ideal for a wide range of post-polymerization transformations (Fig. 3).[18,19,24] By far the majority of these modifications rely on straightforward substitution reactions with a range of nucleophiles, including azides, amines, carboxylic acids, phosphines, and thiols.[18,19] Encompassing many of the pathways available for the modification of terminal bromides, a *user guide* for the chain-end functionalization of poly(acrylates) prepared via ATRP was recently reported.[28] Through the optimization of existing protocols based on simple small molecule transformations, the bromide end-group ofpoly(methyl acrylate) can be quantitatively converted to a range of other functionalities, incorporating nucleophilic, electrophilic, hydrophobic, hydrophilic and charged moieties under mild, non-inert conditions. The inherent reactivity of chain-end moieties introduced by substitution can also be exploited to access polymers with other FG (e.g., terminal thiols from thioesters[29] and primary amines from azides).[18]

The azide functionality is particularly versatile as it can be used for copper-catalyzed or strain promoted azide-alkyne cycloaddition "click" coupling with both reactions being widely exploited in polymer chemistry.[30–32] To expedite azide incorporation at ATRP polymer chain-ends, several one-pot strategies have been developed for the *in situ* azidation of the halide end-group.[33,34] For example, Vermonden and coworkers reported a rapid, non-S_N2 azidation reaction catalyzed by the ATRP copper catalyst that required only a small excess of NaN_3 and enabled the polymerization, functionalization and subsequent "click" conjugation to be performed in one pot.[34] A variety of approaches, including the

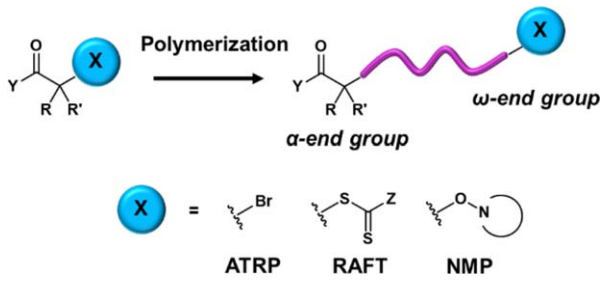

FIGURE 2 Transfer of the chemical functionality of initiators and CTAs into polymers prepared by the three main CRP methods.

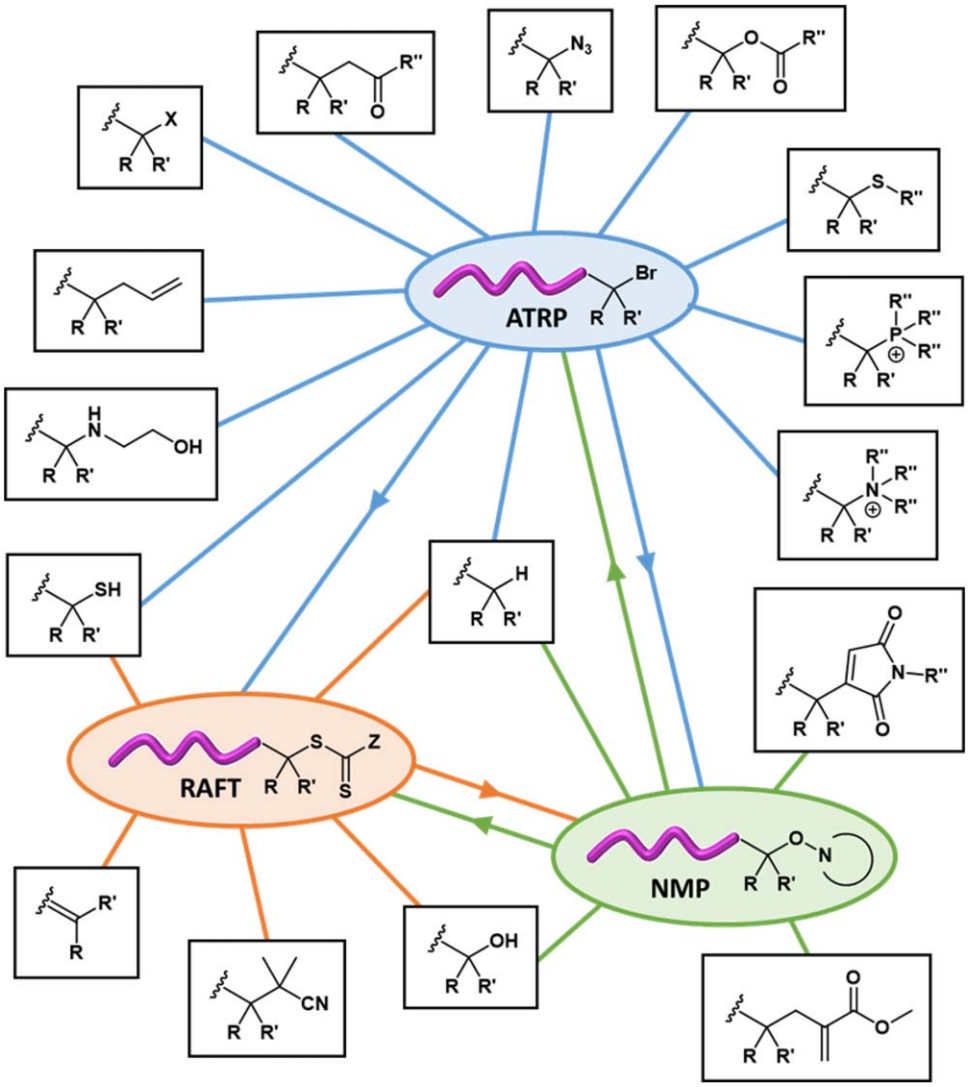

FIGURE 3 Overview of some of the possible ω-end group modifications of polymers prepared by ATRP, RAFT, and NMP. The majority of these transformations can be considered merely a stepping stone toward more bespoke functionality (e.g., amines via azide reduction). End group transformations are often dependent on polymer type. If initiators with appropriate FG are used, α-end group modification is also possible.

use of "click" chemistry,[35] have also been reported for the preparation of macromonomers from ATRP polymers.[36–38] In particular, the chain-end substitution of the terminal bromide of ATRP polymers with acrylic acid or methacrylic acid in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (Fig. 4), affords well-defined macromonomers with high chain-end fidelity under mild conditions.[36,37] Interception of the propagating radical at the polymer chain-end can also be used to terminate ATRP and other CRP procedures, leading to the incorporation of additional functionality. A range of suitable additives have been reported for the trapping of "living" chain-ends using this approach, including nitroxides,[39] silyl enol ethers,[40,41] and "modified" monomers that enable sequential terminal umpolung and alkoxy end-capping of the growing polymer.[42,43] Exploiting the polymerization catalyst itself, Sawamoto and coworkers reported the *in situ* hydrogenation of the terminal halogen obtained via a ruthenium-catalyzed CRP by direct transformation of the polymerization catalyst into a hydrogenation catalyst.[44]

While many substitution reactions have been found to be quantitative, the possibility of intra-chain or inter-chain secondary reactions with backbone repeat units must be considered. To illustrate this point, a recent comprehensive study on the reaction of iodide terminated polymers with functional amines clearly showed intramolecular cyclization of the amine chain-end for poly(butyl acrylate) and poly(methyl methacrylate) derivatives by nuclear magnetic resonance and matrix-assisted laser desorption/ionization.[45] This study also reinforces the need for improved analytical methods. Accurate characterization and quantification of polymer chain-end moieties is critical as minor changes in molecular weight is challenging with both higher molecular weights samples and with polydisperse

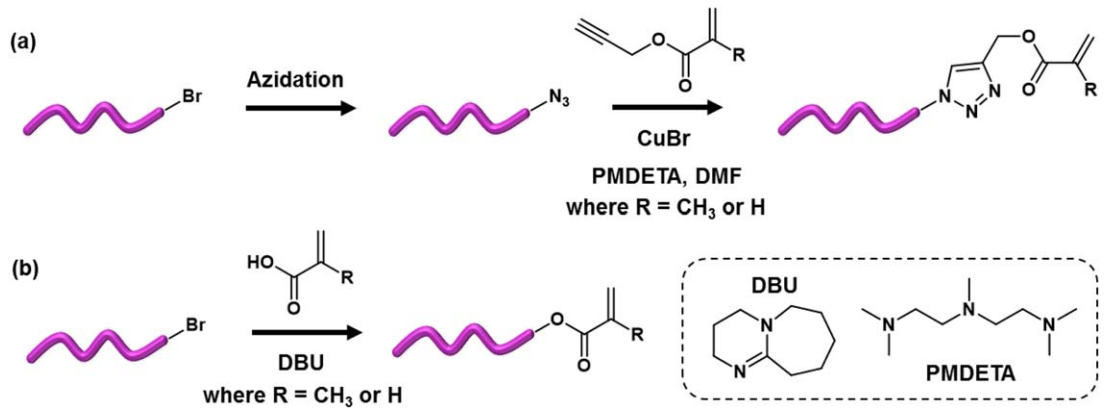

FIGURE 4 Chain-end modification of ATRP polymers to prepare macromonomers via (a) sequential azdiation and "click,"[35] and (b) direct nucleophilic substitution of a bromide chain-end with a carboxylic acid in the presence of DBU.[36,37].

materials. To alleviate a number of issues with incomplete chain-end conversion of polymers prepared by ATRP or the occurrence of secondary reactions, the use of functional initiators has been widely employed,[18,19,26] including those with pendant alkynes, alkenes, alcohols, epoxides, acids, azides, and functional units such as azobenzenes.[46]

The monomer scope and versatility of ATRP has enabled its use in a number of industrial applications where low dispersity materials are advantageous. However, the reactivity of the bromide chain-end can lead to stability (thermal and environmental) issues.[47] Inexpensive, scalable and green methods for the removal of reactive polymer chain-ends have, therefore, received significant attention in recent years. Building on small molecule photochemical reactions for the removal of halides at the termini of polymers (Fig. 5),[50,51] a reducing organic photoredox catalyst—10-phenylphenothiazine (PTH)—has been developed for the light-mediated removal of halogen chain-ends from styrenic, acrylic and methacrylic polymers.[48] This quantitative method is

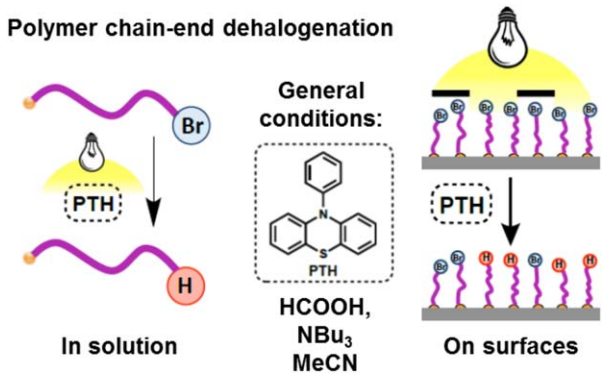

FIGURE 5 Transferal of small molecule organic chemistry for the chain-end modification of polymers. Photochemical dehalogenation of polymers,[48] and polymer brush surfaces[48,49] using PTH. Typical reaction conditions: 5 mol% PTH, HCOOH (5 equiv.) and NBu_3 (5 equiv.) in acetonitrile at room temperature and light irradiation ($\lambda = 380$–405 nm).

readily applicable to thin films, enabling the facile preparation of hierarchical patterned polymer brush films.[48,49]

In analogy with ATRP-based strategies, main advantages of RAFT include monomer scope, tolerance to a variety of polymerization conditions (e.g., aqueous, suspension, and emulsion) and the presence of well-defined chain ends which are directly related to the structure of the original CTA.[22,23] A range of functional CTAs that are tolerant of the radical conditions have been reported leading to a variety of possible α and ω chain-ends (Fig. 2).[25,26] In contrast to ATRP systems, functional CTAs are often more synthetically challenging to prepare due to the inherent reactivity of the carbon-sulfur double bond and for the same reason, chain-end modification of polymers prepared by RAFT need to be considered in detail.[52] There are several comprehensive reviews on the end group removal or modification of RAFT polymers which provide excellent background material[52,53] with the main transformations being summarized in Figure 3. The majority of RAFT polymer chain-end modifications focus on the cleavage of the CTA using an appropriate nucleophile (e.g., a primary or secondary amine, sodium azide,[54] or hydrazine[55]) to afford a thiol-capped polymer suitable for further functionalization.[56,57] Thiols are advantageous in macromolecular design as they can be modified to prepare polymers with a range of different FG or utilized for the preparation of more complex architectures or bioconjugates.[5,58] To illustrate the importance of the secondary reactivity of the thiol chain-end of RAFT derived polymers, Hoogenboom and coworkers reported an elegant *in situ* end-capping approach for the one pot preparation of inert well-defined polymers using residual monomers as Michael acceptors to trap the chain-end thiol [Fig. 6(a)].[59] Other FG can be incorporated, but due to limited methods available for the characterization of polymer chain-ends the efficiency of these strategies is poorly understood.

An additional structural feature to be addressed with RAFT-based materials is their color and odor resulting from the reactive nature of the CTA under even mild conditions.[52] As such, removal of the sulfur-containing end group can be

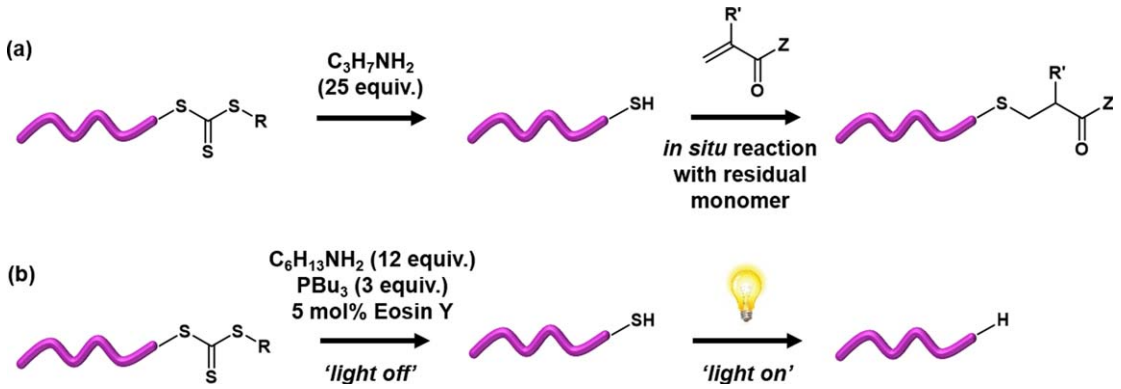

FIGURE 6 Recently reported metal-free strategies for the preparation of RAFT polymers with inert chain-ends. (a) Aminolysis and *in situ* capping of the resulting thiol chain-end with residual monomer.[59] (b) Chain-end reduction of RAFT polymers utilizing visible light. By turning the light source on or off, the reaction pathway in one pot can be switched between complete desulfurization (hydrogen chain-end) and traditional aminolysis (thiol chain-end), respectively.[60]

advantageous. Several methods for complete removal of CTA groups have been reported. However, these often require harsh reaction conditions, excess of reagents or afford product mixtures.[52,61,62] As an alternative approach, mild and metal-free strategies for the conversion of trithiocarbonates into inert hydrogen chain-ends have recently been reported.[48,60] For example, expanding on small molecule transformations developed for the desulfurization of cysteine residues, aminolysis in the presence of an organic photocatalyst and visible light has been shown to quantitatively remove the reactive end groups from RAFT polymers.[60] Significantly, this method allows a dual-pathway approach, affording polymers with hydrogen or thiol chain-ends, dependent on the presence or absence of visible light, respectively [Fig. 6(b)].

As with ATRP and RAFT, a range of alkoxyamine initiators have been used to introduce desired chain-end functionality with NMP.[20,63] However, a key difference between NMP and either RAFT or ATRP is no requirement for additional catalysts or initiators.[20,21] This inherent thermal reactivity has been exploited for the chain-end modification of NMP-derived polymers. For example, using excess maleic anhydride and maleimide derivatives under elevated temperatures enables the facile chain-end transformation of NMP-derived polymers.[64] This strategy takes advantage of the high reactivity of the radical chain-end species and the inability for maleic anhydride and maleimides to undergo homopolymerization, enabling selective functionalization where a single maleic anhydride or maleimide unit quantitatively replaces the alkoxyamine chain-end. In addition to providing a versatile functional handle, replacement of the nitroxide end group with a maleimide derivative significantly improved the thermal stability of polystyrene prepared by NMP. The utility of this transformation has also been demonstrated with a variety of polymer families, including poly(*n*-butyl acrylate) and polyisoprene.[64]

This facile chain-end transformation has also been expanded to include heating a nitroxide-terminated polymer in the presence of an excess of methyl methacrylate monomer to generate an alkene-terminated polymer along with the corresponding small molecule hydroxylamine.[65] Alternatively, a combination of zinc and acetic acid has been reported to reduce the N–O bond in the alkoxyamine end-group to a terminal hydroxyl functionality, which offers a versatile handle for secondary chemical modification. Guillaneuf et al. more recently developed radical chain-end modification strategies for the direct transformation of the terminal alkoxyamine to azide, halide, or hydroxyl functionalities.[66] While the aforementioned methods offer facile conversion of nitroxide end groups to other reactive functionalities, the ability to achieve a chemically inert chain-end can also be accomplished. Rizzardo and coworkers developed an elegant solution for the transformation of nitroxide chain-ends to hydrogen, using excess thiol as a hydrogen atom donor at elevated temperatures.[65]

A hallmark of CRP processes is the ability to switch polymerization type by chain end modification (Fig. 3). The bromide end-group of an ATRP polymer can, therefore, be converted into a chain-end suitable for NMP (halide to alkoxyamine)[21,39] or RAFT (halide to thiocarbonate),[67] and conversely, the alkoxyamine chain-ends that remains after NMP can be converted to ATRP[68] and RAFT[69,70] macroinitiators. Interestingly, while it is possible to prepare a NMP macroinitiator from a RAFT polymer chain-end,[21,70] the conversion of a RAFT polymer chain-end to a bromide, suitable for ATRP or direct nucleophilic substitution, to the best of our knowledge has not been shown. This is particularly surprising as RAFT is a versatile CRP techniques in terms of monomer scope and reaction conditions, and the bromide chain-end installed in an ATRP reaction is the most amenable FG for further modification. Overall, post-polymerization functionalization appears to be the most widely used method for the chain-end modification of polymers prepared by CRP, due in part to ease of purification and the potential for divergent functionalization from a common polymer precursor. However, the use of functional initiators or additives for *in situ* termination has its advantages. Depending on the polymerization process, compatible functional initiators

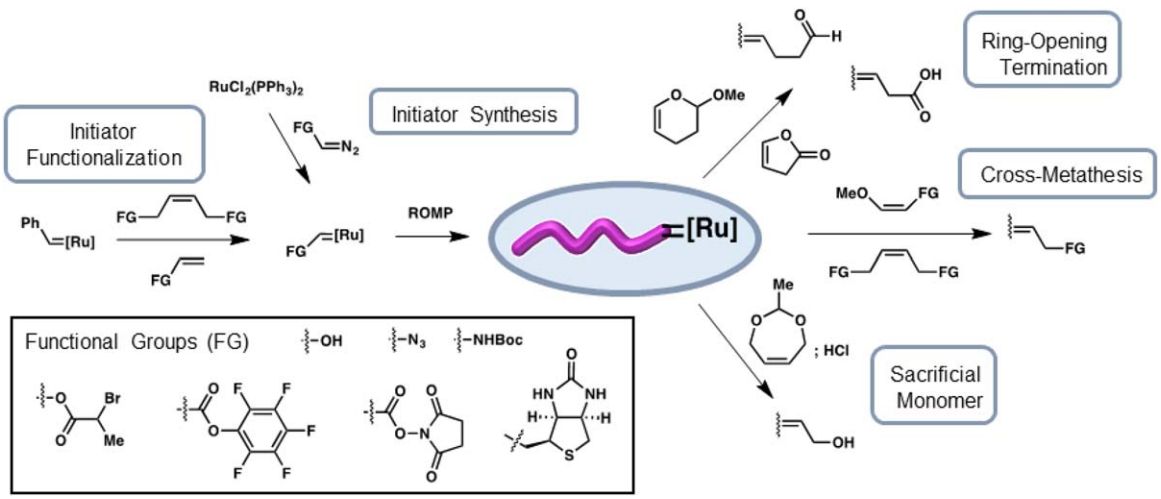

FIGURE 7 Strategies for chain-end functionalization of ROMP polymers through modification of the initiator structure and selective terminations. A noncomprehensive sampling of FG introduced in these approaches is shown.

can be used to achieve complete transfer of a chemical moiety to the terminus of a polymer, even at low monomer conversion. Concurrently, new methods for the *in situ* termination of CRPs have enabled the development of a variety of one pot routes to well-defined and functional materials.

Ring-Opening Metathesis Polymerization

ROMP operates through the exchange of strained double bonds in cycloalkene monomers and is traditionally catalyzed by an organometallic initiator.[71] These polymerizations were pioneered using early transition metal complexes such as tungsten, molybdenum and titanium, but their synthetic utility was limited due to the high oxophilicity of the catalyst, reacting rapidly with air, moisture and many heteroatom-containing FG. A renaissance in both the small molecule organic and synthetic polymer communities occurred with the introduction of ruthenium alkylidene complexes by Grubbs and coworkers in the 1990's.[72] These systems were found to be highly chemoselective for olefins and were much more tolerant of oxygen and a multitude of common FG, including esters, alcohols, amides, and ketones. These discoveries, along with further advances in ligand design, have allowed ROMP to be used without the need for a glove box or rigorously purified materials, greatly enhancing potential applications.[73–75] While more FG tolerant catalysts are being developed for ROMP using early-transition metals, ruthenium-based catalysts are still the most widely used and are the focus of this section.[76] We direct the reader to more comprehensive reviews on chain-end functionalization for metathesis-derived polymers using other systems.[77–79]

The exquisite chemoselectivity of ruthenium alkylidenes also creates challenges for developing selective chain-end functionalizations that occur rapidly and quantitatively since many potential coupling groups are simply unreactive. As a result, ω-chain-end functionalization of ROMP polymers has been more extensively investigated than α-functionalization methods since the active ruthenium chain-ends require termination before isolation of the polymer. Standard practice is to terminate the polymerization with an excess of ethyl vinyl ether to transfer a non-functional methylene to the polymer chain-end, along with a metathesis-inert Fischer-type carbene. Expanding on this approach, carboxylate functionalized vinyl ethers were developed by Kiessling and coworkers to introduce a fluorescein label to the polymer chain-end for imaging neoglycopolymer binding to cell surfaces (Fig. 7).[80] This strategy has since been used by numerous groups to introduce a wide range of FG, including azides,[81] biotin,[82] ketones,[83] hydrogen bond pairs.[84] Due to regioselectivity issues during cross metathesis, acyclic vinyl ethers do not always result in high (>90%) chain-end functionalization.[85] Given the higher reactivity of the *cis*-isomers in metathesis, though, Kilbinger innovatively developed cyclic vinyl carbonate, lactone, and acetal small molecules that give useful carboxylic acid or aldehyde end-groups after ring opening. High functionalization efficiencies and deactivation of the ruthenium species are observed.[86,87] As an alternative to vinyl ethers, Li explored the possibility of cross metathesis reactions with a symmetrical Z-olefin to introduce ω-chain-end functionality.[88] This approach was further studied by Matson and Grubbs where it was found to be superior to the vinyl ether approach, frequently giving near quantitative chain-end conversions.[89] Importantly, the hindered backbone olefins in the poly(oxa)norbornenes studied resist secondary metathesis from the ruthenium alkylidene after cross metathesis, as demonstrated by the low dispersities of the isolated chain-end functionalized polymers. A significant advantage of this strategy is the wide range of FG that can be introduced to ROMP polymers, including alcohols,[89] Boc-amine,[90] ATRP initiators,[85] and NHS/pentafluorophenyl esters.[91] A different approach for ω-end functionalization is to use "sacrificial monomers," such as dioxepines, that can be polymerized as a second block and then subsequently degraded to a single function group after post-polymerization hydrolysis.[92] In addition to alcohols,

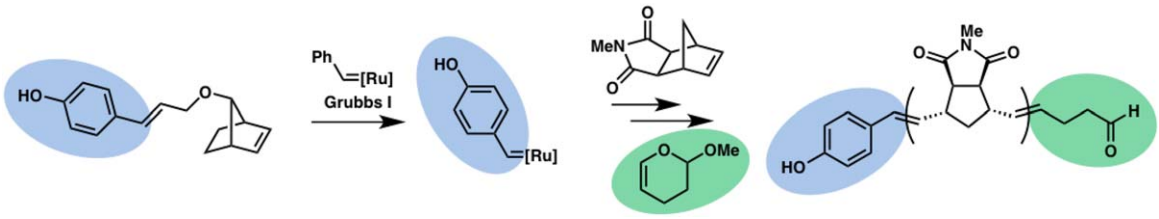

FIGURE 8 A ring-opening-ring-closing strategy for initiator functionalization developed by Kilbinger and coworkers combined with selective termination to give an α, ω-heterotelechelic polymer.

analogous heterocyclic monomers for the introduction of thiols and amines through sacrificial coupling have been developed.[93,94]

In contrast to ω-end functionalization via termination, methods for α-end functionalization of ROMP polymers are less developed. While discrete synthesis of new initiators is a viable pathway (Fig. 7), multistep synthesis of organometallic complexes is neither straightforward or high-yielding.[95] Direct modification of commercial Grubbs catalysts have generally involved implementing a cross-metathesis reaction prior to polymerization using either functionalized styrenes[96] or symmetrical olefins.[90] However, this method is limited as these groups can also act as reactive terminators, affording homotelechelic polymers.[97] Kilbinger has also demonstrated the effectiveness of the sacrificial monomer approach toward α-end functionalization by growing the sacrificial block first,[98] and very recently has described a ring-opening-ring-closing strategy with norbornene derivatives (Fig. 8).[99] In this system, the strained norbornene reacts with the Grubbs initiator, followed by a rapid intramolecular ring closure to give a less reactive 6-membered ring and a functionalized ruthenium initiator. In combination with the cyclic vinyl acetal terminator, this has been used to create α, ω-heterotelechelic polymers with phenol and aldehyde end-groups.

The promise of these useful methods for chain-end functionalization of ROMP polymers, coupled with the utility of these materials for a variety of applications, suggest many more opportunities for development and improvement, particularly with regards to initiator functionalization. Many of these techniques employ a moderate to large excess of terminating agent (usually 3–10 equiv) and require long reaction times to reach completion. The development of rapid and stoichiometric terminating agents would, therefore, pave the way toward direct functionalization with more complex FG where an excess would be undesirable or even toward direct coupling with chain-end functionalized homopolymers to afford novel, ROMP-based block copolymers.

Emerging Chain-End Functionalized Materials

While many polymerization strategies are amenable to chain-end modification, the cationic polymerization of 2-oxazolines[100,101] and the ring-opening polymerization of strained metallocenophanes[102,103] are of increasing interest for the preparation of biocompatible and semi-crystalline block copolymers, respectively. Although not a focus of this highlight, it is important to briefly discuss ionic polymerizations as a means to prepare chain-end functionalized polymers. Ionic polymerizations were the first chain-growth process reported to have "living" characteristics.[104] As such, there has been considerable focus on the chain-end modification of materials prepared by living anionic or cationic polymerization.[105] While synthetically challenging, a large variety of polymer families can be polymerized under anionic conditions and their chain-ends modified through *in situ* termination and subsequent post-polymerization modification.[105,106] Although less widely studied, functional initiators can also be used for anionic or cationic polymerizations provided they are tolerant of the reaction conditions and they do not reduce the nucleophilicity of the initiating anion, two factors which would lead to a loss of control of the polymerization. There are several comprehensive reviews on the design and

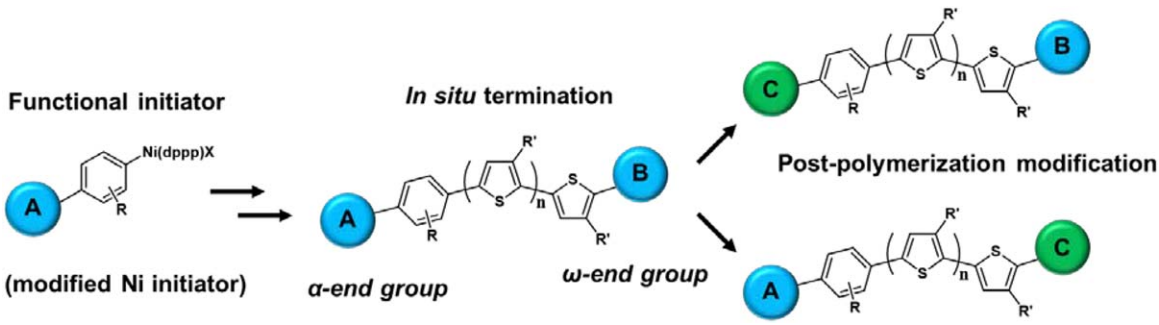

FIGURE 9 Schematic representation of the three strategies for the chain-end modification of poly(3-alkylthiophene), enabling the heterobifunctional incorporation of a variety of chemical moieties.[110]

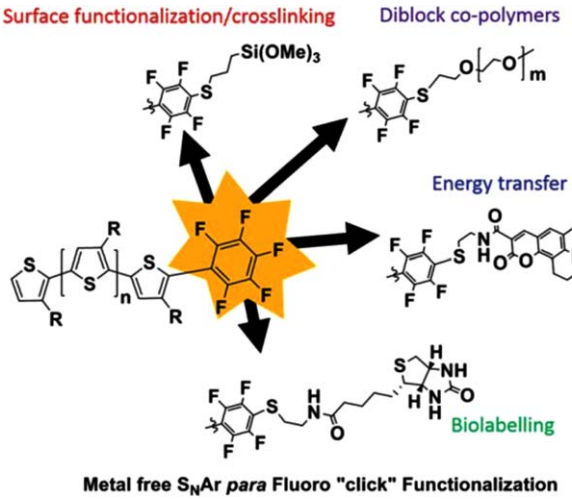

FIGURE 10 *In situ* termination of P3AT with a terminal pentafluorophenyl group, and post-polymerization modification of the resulting "click" handle, enabling the divergent synthesis of a range of chain-end functionalized materials. Reproduced with permission from Ref. 133 - published by The Royal Society of Chemistry.

synthesis of macromolecular architectures via ionic polymerization strategies.[107,108]

In a similar fashion, a number of transition metal-catalyzed routes to polymers bearing chain-end FG have been recently developed. In particular, Nickel-catalyzed Kumada catalyst-transfer polycondensation (KCTP), also known as Grignard metathesis polymerization, is a chain-growth process that has been widely exploited for the preparation of π-conjugated materials.[109] This method is commonly used for the preparation of regioregular poly(3-alkylthiophenes), affording polymers with molecular weight control, low polydispersity, and well-defined chain-ends. Significant effort has focused on the modification of the termini of polythiophene derivatives because of their potential use in optoelectronic devices (Fig. 9).[11–13,110–112] In particular, as KCTP is limited to bifunctional aromatic small molecules, chain-end modification is almost the exclusive route to prepare rod-coil block copolymers for potential applications in nanoelectronics.[113–115] The Nickel catalyst can also be used as an initiator to deliver a functionalized aryl group to the α-chain-end[116,117] and this has been exploited for the chain-end incorporation of a range of FG,[118–120] including protected alkynes,[118,121,122] siloxanes,[119] and alcohols.[118,120]

As the catalyst is actively associated with the growing chain-end,[123] *in situ* termination is also a popular route to introduce end-group functionality.[124,125] McCullough and coworkers reported that the addition of excess Grignard reagent after the polymerization could be used to introduce a variety of FG via reductive elimination.[126,127] Depending on the electronics of the organometallic reagents, mono- or di-capped polymers could be prepared that could be further functionalized via post-polymerization modification.[128–131] Building on the benefits of incorporating chain-end thiols for macromolecular design described earlier, Okamoto and Luscombe reported the use of *in situ* quenching of the polymerization with sulfur powder or triisopropylsilanethiol to selectively install thiol end groups at the ω-chain-end or at both the α and ω-chain-ends, respectively.[132]

The introduction of "click" handles during a direct functionalization step is often used to enable the divergent modification of a parent material leading to a library of materials with the same backbone structure. For example, Heeney and coworkers recently reported that a pentafluorophenyl group can be incorporated as a versatile "click" handle, enabling a range of nucleophilic aromatic substituions.[133] Specifically, this method achieved up to 70% monofunctionalization, and enabled the incorporation of sensitive moieties, including biotin and a trialkylsiloxane unit (Fig. 10). Direct post-polymerization modification of chain-ends has also been widely reported. By exploiting the hydrogen or bromine chain-ends that remain after a classical KCTP polymerization, pendant alcohols,[134,135] amines,[136] or carboxylic acids,[137,138] can be introduced. This opens up a wealth of possibilities for their potential application.[139] An important consideration when comparing these two approaches is the percentage incorporation of the desired chain-ends. Although a wide range of chain-end functionalized polythiophene derivatives have been prepared, due in part to the product distribution of KTCP (Br/H chain-end mixtures) there are still significant opportunities for additional quantitative and selective functionalization strategies for conjugated polymer chain-ends.

CONCLUSIONS

One of the defining features of polymer synthesis is the close connection between functional and applied research. In both avenues, the ultimate commercial success or failure of a material can be driven by the molecular structure, with well-defined and functional polymer chain-ends being of central importance. In this highlight we have provided a brief overview of the substantial field of polymer chain-end modification, focusing on the most popular chain-growth processes, with the key aim of illustrating key areas for future focus. While a range of new and improved synthetic strategies for polymer chain-end modification has been recently reported, a major limitation is the lack of facile and reliable techniques for the quantification of their success, or indeed, the starting chain-end fidelity afforded by "controlled" or "living" chain-growth polymerizations. Assuming high chain-end fidelity, the quantitative conversion of chemical moieties is essential to avoid product distributions which necessitate costly separations. While one pot and *in situ* transformations exist and greatly simplify the preparation of functional polymeric materials, these transformations have limited efficacy for all polymer families. In particular, there exists a significant opportunity to apply reliable small molecule transformations for the quantitative functionalization of polymer chain-ends, with a focus on those methods that are rapid, chemoselective, green, biocompatible, or are simply more user friendly

than existing techniques. Advances in all areas of chain-end modification will lead to more diverse applications and a greater understanding of the importance of chain-ends in determining physical and mechanical properties.

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