Functional end groups for polymers prepared using ring-opening metathesis polymerization

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The precise placement of functional groups on the chain-ends of macromolecules is a major focus of polymer research. Most common living polymerization techniques offer specific methods of end-functionalization governed by the active propagating species and the kinetics of the polymerization reaction. Ring-opening metathesis polymerization has established itself as one of the most functional-group-tolerant living polymerization techniques known, but this tolerance has limited the number of available functionalization reactions. Metathesis chemists have therefore been required to develop a variety of end-functionalizations, adapting each of them to the reactivity scheme of the particular catalysts used and the complexity of the group to be attached. This review presents an overview of the methods developed for different types and generations of metathesis catalysts that are typically used in such polymerizations. We also present a 'field guide' of functionalization methods highlighting the factors to be considered when choosing the most appropriate approach.

Ring-opening metathesis polymerization (ROMP) represents a particularly interesting method among the living polymerization techniques. A unique feature of all metathesis polymerizations is the preservation of carbon double bonds during the polymerization step[1]. Modern metathesis catalysts can polymerize a variety of monomer types ranging from cyclic olefins to bi- and oligocyclic structures. Cyclic olefins such as norbornenes, cyclooctenes, cyclobutadienes and many others can also be substituted with a large range of functional groups, giving rise to highly functional polymers with otherwise inaccessible structures and properties.

The polymerization of such cyclic olefins is catalysed by carbene complexes — that is, transition metal complexes with a metal–carbon double bond. Such complexes have been synthesized with an impressive number of different transition metals. Today, titanium, molybdenum and ruthenium carbenes are the most commonly used in metathesis polymerization, some of which have even become commercially available (see Fig. 1).

Olefin metathesis was discovered as an obscure reaction present in a number of olefin transformations. The rationalization of its unprecedented mechanism by Chauvin[2] gave rise to a chain of new catalyst developments. These featured extremely high metathesis activity and thermal and chemical stability, and led to a better understanding and definition of the catalytic steps involved.

As soon as the development of well-defined catalysts based on titanium had emerged from their heterogeneous predecessors[3,4], first examples of the living ROMP of norbornene were published[5]. The living character of this process was unexpected at first but soon led to groundbreaking developments of well-defined catalysts for the olefin metathesis reaction. Early efforts to synthesize organometallic compounds bearing metal centres of rhenium[6] and tantalum[7] were soon followed by those based on molybdenum and tungsten by Schrock et al. These featured much higher functional-group tolerances as a consequence of being later transition metals[8]. This development eventually culminated in the introduction of late transition metal catalyst systems by Grubbs et al. based on ruthenium[9]. These complexes allow a whole new range of functionalities to be present in the polymers, ranging from ionic to biologically active groups[10,11].

The mechanism of metathesis, which is now generally accepted, was first described by Chauvin and proposes a metalla-cyclobutane

transition state[2]. The metalla-cyclobutane is formed by a [2+2] cycloaddition of the metal–carbene double bond to an olefin. A better understanding of olefin coordination and transition state stability has been the focus of recent catalyst developments and has led to the latest generation of highly reactive catalysts. Kinetic measurements, in particular NMR studies[12], have helped to understand and characterize functionalization reactions, particularly in the case of termination reactions.

Ring-opening metathesis polymerization using new catalyst systems developed in recent decades has become superior to most other living polymerization methods in terms of functional-group tolerance. In general, the functional-group tolerance of each catalyst can be rated by the reactivity of the transition metal centre towards functional groups. Early transition metal complexes based on titanium are highly oxophilic and react readily with functional groups such as ketones and aldehydes in a Wittig-like reaction. Later transition metal complexes, such as those based on ruthenium, even tolerate the presence of molecular oxygen, water or mild carboxylic acids. Table 1 gives a general reactivity scheme of transition metals used in most classical metathesis reactions[1].

Possible reagents that can be used to attach functional groups onto the polymer chain-end by a termination reaction can be found using the very same scheme. Table 1 shows that titanium-based catalysts react readily with ketones and aldehydes. Catalysts based
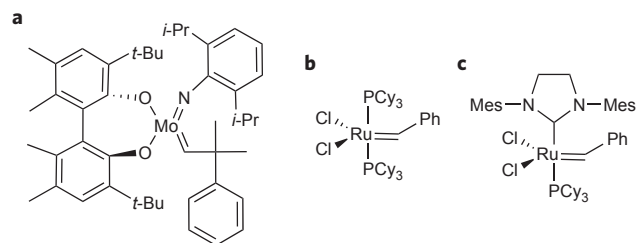

Figure 1 | Examples of commercially available metathesis catalysts based on molybdenum and ruthenium. a, The Schrock–Hoveyda catalyst. **b**, First-generation Grubbs' catalyst. **c**, Second-generation Grubbs' catalyst. Mes = mesityl, Cy = cyclohexyl.

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Titanium	Tungsten	Molybdenum	Ruthenium	
Carboxylic acids	Carboxylic acids	Carboxylic acids	**Olefins**	↑ Increasing reactivity
Alcohols, water	Alcohols, water	Alcohols, water	Carboxylic acids	
Aldehydes	Aldehydes	Aldehydes	Alcohols, water	
Ketones	Ketones	**Olefins**	Aldehydes	
Esters, amides	**Olefins**	Ketones	Ketones	
Olefins	Esters, amides	Esters, amides	Esters, amides	

Catalysts react preferentially with functional groups listed above olefins and tolerate functional groups listed below.

on molybdenum and tungsten still undergo the same termination reaction with aldehydes. However, ruthenium-based metathesis catalysts are only reactive towards olefins. Therefore, polymerizations involving ruthenium-catalysed ROMP have focused mainly on other forms of end-functionalization such as deactivation and chain transfer of olefins.

Chain-end functionalized polymers have attracted interest among scientists across all disciplines. Such materials combine macromolecular properties with defined reactive sites at the chain-end. Polymers of this type can be used for the attachment of other compounds ranging from small tracers, to drugs or biomolecules[13] to other polymers. These conjugates have found manifold applications in medicine for drug immobilization and delivery[14], in solid-state chemistry for the modification of solid surfaces[15], and in polymer science as synthons for complex polymer architectures. In most application-driven studies, there is a need for precisely functionalized polymers bearing a single functional group at the chain-end. Partially and multifunctionalized polymers, or those carrying the wrong functional group, can quickly lead to unpredictable properties of the final conjugate or even to crosslinking during subsequent reaction steps, simply because the structure obtained within those reactions does not match the expected one. It is therefore essential to have reaction protocols at hand that allow the introduction of exactly one functional group with high precision. Living polymerization techniques typically give the best results in terms of end-functionalization precision. The general kinetic criteria attributed to living polymerizations, such as the non-existence of irreversible chain transfer, back-biting or self-termination reactions set the base for precise end-group placement.

Functionalization approaches in general
Functional groups can be introduced to the polymer chain in three ways during different stages of the polymerization (see Fig. 2). (1) By initiating the polymerization with a metal complex that bears a functional carbene, it is ensured that all polymer chains carry a defined functional group at one end. (2) Alternatively, a termination reagent added at the end of the polymerization can transfer a functional group onto every polymer chain still containing an active metal carbene site. (3) The third functionalization strategy is carried out by polymerization. A functional group can, for example, be introduced by

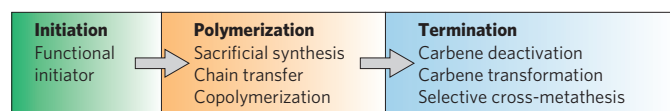| Initiation	Polymerization	Termination
Functional initiator	Sacrificial synthesis / Chain transfer / Copolymerization	Carbene deactivation / Carbene transformation / Selective cross-metathesis

Figure 2 | General approaches for the functionalization of ROMP polymers during the three stages of a polymerization (initiation, polymerization and termination). Reactions during the polymerization include all processes taking place between the initiation and the final termination of the metathesis reaction.

polymerizing a second (cyclic) monomer onto a first polymer block. Decomposition of the second block leaves one functional group at the end of the first polymer chain. Using an acyclic chain-transfer agent, this method allows the synthesis of telechelic polymers; that is, polymers that bear a functional group on both chain-ends[16,17].

All three strategies come with their own challenges. The success of termination reactions strongly depends on the stability and lifetime of the living species and the reactivity of the quenching reagent. Functional initiation, on the other hand, promises to guarantee high degrees of functionalization as every chain that has been initiated will necessarily bear the functional group. This method, however, involves multiple organometallic transformations that require special knowledge and experience with such reactions, thereby limiting the scope of this strategy. The third method, polymerization, seems to be the easiest way of placing end-functional groups onto polymers. Nonetheless, it is limited by lack of control over the molecular weight distribution unless advanced strategies are applied.

Different catalyst systems have been applied to each of these strategies. The challenges that have been faced in developing versatile and efficient reactions for the three different methods outlined above are highlighted, discussed and evaluated in the following sections.

Functional initiators
Among the stages of the polymerization in which a functional group can be introduced, the initiation step seems to be the most reliable. In all polymerizations that do not allow chain-transfer processes, a functionalized initiator guarantees the precise placement of functional groups on one end of every chain. Side reactions such as premature or incomplete termination reactions do not influence the functionalization result. Every initiated chain is ensured to carry the desired functionality. This approach is also a very economical method of functionalization as many modern metathesis initiators have been shown to reach high degrees of initiation. In contrast, termination agents typically have to be added in large excesses rendering them less economical.

Only very few functional initiators based on titanium metal centres have been synthesized. Owing to the extreme reactivity of titanium towards any oxygen-containing groups, all examples reported in the literature bear unreactive alkyl or aryl groups only[18]. Titanium–carbene complexes, which are formed from Tebbe's reagent[19] in most cases, tolerate neither reactive functional groups nor their protected counterparts, rendering them not useful as functionalized metathesis catalysts.

An elegant method for pre-functionalizing a tungsten initiator has been described by Amass *et al.*[20,21], who have formed a tungsten carbene from living polystyrene by addition of WCl_6 (Fig. 3a). The resulting tungsten-alkyl species eliminated HCl to form the metathesis-active polymer–alkylidene complex from which norbornene was polymerized to give a block copolymer using ROMP. This work was the first successful block-copolymer synthesis using a conversion of a polymerization technique that involved ROMP.

The early commercial availability and the enormous chemical versatility of the Grubbs-type ruthenium-based catalysts have facilitated their widespread use in the synthesis of functional initiators. Three strategies have been pursued in the synthesis of pre-functionalized catalyst moieties. A functionalized carbene can be introduced into the complex *a priori* by applying the respective diazoalkane to the precursor complex $RuCl_2(PPh_3)_3$ (ref. 22). This method has been applied mainly by the Grubbs group for the synthesis of a catalyst that can be used both in ROMP and atom transfer radical polymerization (ATRP), as well as for the formation of block copolymers using both methods[23]. A modified strategy uses a cross-metathesis reaction between the commercial ruthenium benzylidene and a functionalized olefin, yielding a new carbene complex and styrene (Fig. 3b, upper pathway) as reported by Slugovc and co-workers who have attached luminescent dyes to Grubbs's first-generation catalyst[24].
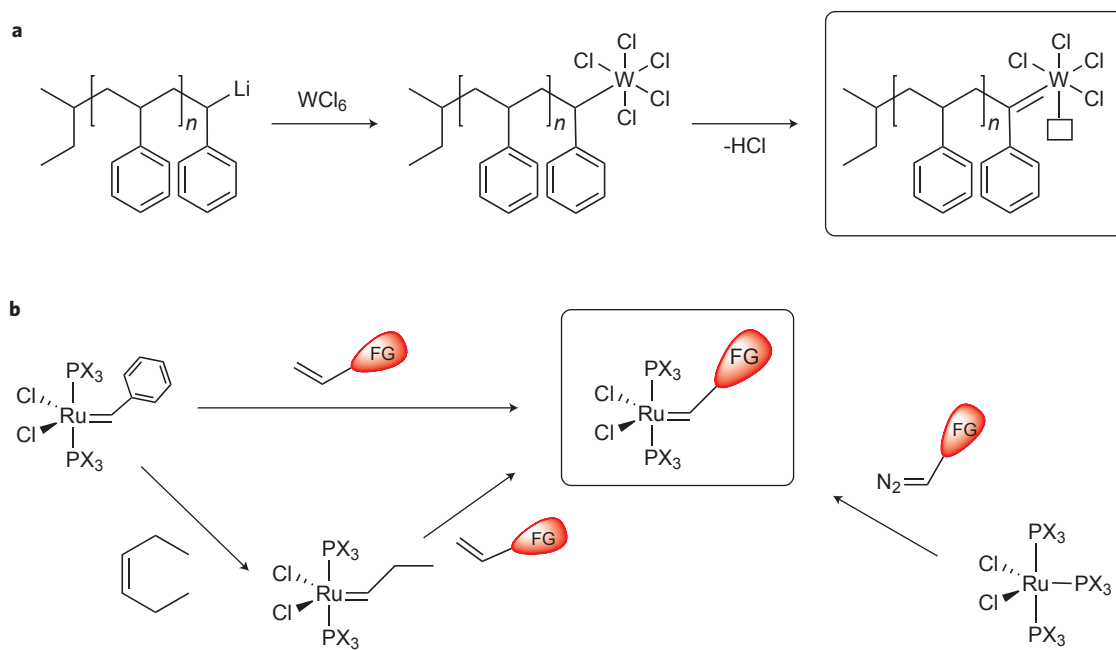
Figure 3 | Examples of the synthesis of pre-functionalized initiators. a, Transformation of a carb-anionic chain-end to a metathesis macroinitiator[20,21]. **b**, Three pathways towards functionalized ruthenium carbenes via cross-metathesis (left) or by direct synthesis of the carbene from a precursor complex and diazoalkane (right). FG: functional group.

The most advanced and synthetically challenging approaches have to be applied when the catalytically active species is to be pre-functionalized with a polymer. The difficulties in purification of polymeric materials require special reaction conditions during the organometallic transformations, which promise high catalyst yields and simple removal of side products. Hutchings and Khosravi have found a pathway via a propenylidene intermediate complex (Fig. 3b, lower pathway) and subsequent introduction of the polymer chain in a second cross-metathesis reaction with styrene-end-capped poly(ethylene oxide). In this case, the side product of this cross-metathesis reaction, propene, can easily be removed under vacuum[25].

Termination reactions

The different reactivity and characteristics of the various catalyst types requires a correspondingly high number of matching termination agents. In general, termination agents can be of two types: they can either turn the propagating metal carbene into a different species that shows no metathesis activity; or they can turn it into a deactivated carbene, which can, in principle, still undergo metathesis, albeit at a much lower rate.

Reaction with carbonyl groups. Carbonyls, especially aldehydes, can be used to terminate all metathesis activity of early transition metal complexes. During this reaction, the active site is turned into an oxo-complex, and a functional group attached to the aldehyde is transferred to the respective polymer chain-end in a Wittig-type reaction. Hereby, titanium-based metathesis catalysts follow the same reaction scheme as Tebbe's complex[19]. This complex can transfer its methylene group onto carbonyls in exchange for their oxo-group thus forming an olefin and a titanium oxide. Even amides and esters have been transformed to the respective enamines or vinyl ethers[26,27].

This reaction, involving an oxo-metallacyclobutane intermediate, found its first application in polymer functionalization by the Grubbs group, who were able to place a diphenylethenyl end group on polynorbornene by adding benzophenone to a living titanium-initiated polymerization (Fig. 4g)[28,29]. Also, an early example of a more reactive end group was successfully attached to

polynorbornene by the same group. The addition of an excess of a dialdehyde resulted in selective end-capping, and the obtained terminal aldehyde was subsequently reduced to an alcohol end group (Fig. 4h)[30]. A general overview of the applications of this Wittig-like reaction is given in Fig. 4.

The same publication reports the use of polyaldehyde and aldehyde end-capped polymers as core molecules for block- and graft-copolymer synthesis (Fig. 4f). There, the extremely high reactivity of the titanium–alkylidene species towards aldehydes or ketones is used to scavenge the living chains on a multifunctional quencher, thereby building the new polymer architecture[31].

Molybdenum and tungsten metathesis catalysts are also conveniently quenched by the addition of an aldehyde (Fig. 4e)[32]. The first application of this reaction on tungsten catalysts is reported by Schrock and Grubbs using benzaldehyde as the terminating agent[33]. The resulting styryl end group, however, was not used for subsequent reactions. On molybdenum, the same terminating agent, benzaldehyde, was used with similar success[34]. A broader applicability of this reaction was shown in subsequent publications, where alkyl-substituted aldehydes such as pivalonaldehyde were used[35,36]. By application of pyrenealdehyde, a fluorescence-labelled polynorbornene was synthesized and its fluorescence properties studied in the context of redox-active groups along the polymer chain[37].

The aldehyde quenching was established as the standard termination reaction for metathesis polymerizations involving molybdenum or tungsten initiators[38]. Reactive functionalities had to be introduced in a suitably protected form to avoid side reactions and false capping. The compatibility of such protected functional groups bound to benzaldehydes with the reactivity of the initiating complexes was studied by the Schrock group. Quite a remarkable stability towards a number of functional groups such as amines and nitriles was found. Less reactive groups such as halides, ethers and alkylated amines performed accordingly[39]. Also, this strategy has been extended to the termination of polymerizations initiated by catalysts bearing two carbene moieties[40], thus growing polymer chains in two directions. The termination of such polymers gives rise to homobifunctional polymers (telechelics)[41].
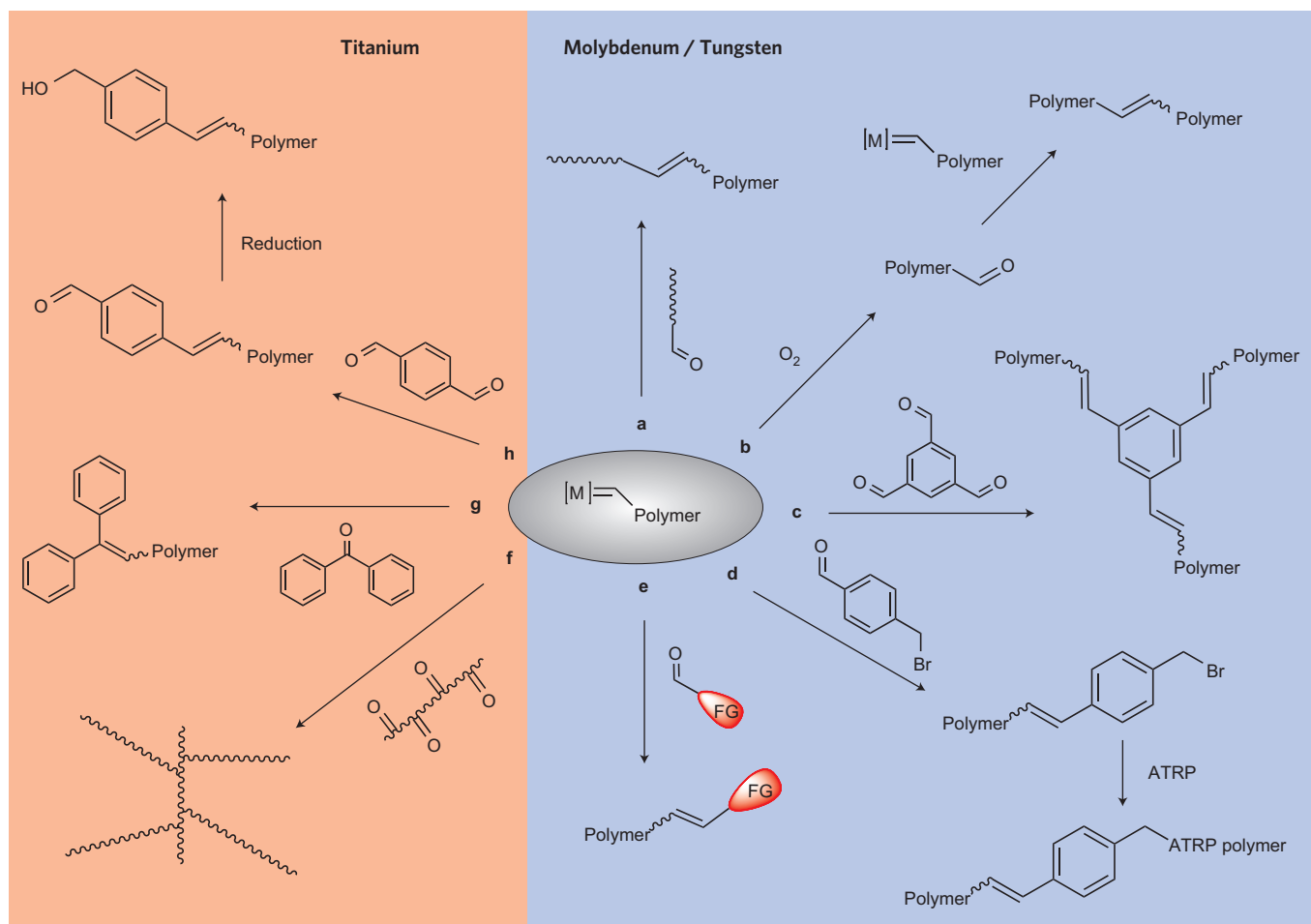
Figure 4 | Addition of functionalized carbonyls to metathesis catalysts based on titanium (red side) or molybdenum and tungsten (blue side). The mechanisms for both types of catalyst are related to the Wittig reaction. The catalyst is transformed into the corresponding metal-oxide during this reaction. FG: functional group.

The versatility of this reaction and the availability of the protected functionalized benzaldehydes have facilitated their use. Nomura *et al.* used this strategy in a number of applications featuring hydroxy-functionalized polynorbornenes and sugar conjugates[42]. This group chose a tetratrimethyl-silyl-protected *p*-hydroxybenzaldehyde as the terminating agent followed by mild removal of the protecting group. After formation of a terminal norbornene ester, a secondary metathesis polymerization of the resulting macromonomers yielded graft-copolymers. The attachment of poly(ethylene glycol) yielded block copolymers[43–45].

Star-shaped polymers were synthesized by Dounis and Feast when a trifunctional aldehyde-quencher, 1,3,5-benzene-tri-carbaldehyde, was added to molybdenum-initiated polynorbornene (Fig. 4c)[46]. More advanced polymer structures, particularly those featuring a change of polymerization method, have been realized by termination of the living polymerization with aldehydes bearing either an initiating or anchoring group for the second polymerization technique. Alternatively, an aldehyde-functionalized polymer was added to form a block copolymer in one step. Similarly, *p*-fluorobenzaldehyde was used to form a terminal fluoride, which could undergo a subsequent polycondensation[47]. Furthermore, *p*-bromomethylbenzaldehyde and *p*-vinylbenzaldehyde were added to synthesize polymers that can function as initiators for ATRP or anionic polymerization (Fig. 4d)[48,49].

The reverse approach was described by Notestein and Register. In their study, an anionic polymerization was terminated in such a manner that an aldehyde end group was obtained. This polymer was then added to the living ROMP polymer to form the conjugate. Block copolymers incorporating polynorbornene and polystyrene or polyisoprene were realized by this termination reaction (Fig. 4a)[50].

The addition of carbonyl groups to living ruthenium-initiated polymers does not terminate the polymerization. In fact, polymerizations can be carried out in solvents such as ethyl acetate, acetone and dimethylformamide[51].

Reaction with molecular oxygen. In the early molybdenum and tungsten functionalization reactions that involved aldehydes, high-molecular-weight shoulders could often be observed in the gel permeation chromatography traces. These were initially considered to be the result of an unwanted side reaction and it was quickly noted that they could be avoided by careful removal of oxygen from all reagents. However, further studies by Feast *et al.*[52] found that the coupling reaction between the active carbene species and an oxygen molecule yielded a terminal aldehyde. This aldehyde group then undergoes bimolecular coupling to another carbene resulting in a polymer chain of twice the length (Fig. 4b). The possibility of rapidly applying large excesses of oxygen to the living polymerization in order to facilitate the aldehyde formation and lower the chance for bimolecular coupling has, however, not been explored so far.

The same primary step was found by Biagini *et al.*[53] with ruthenium carbenes. Differing from the aforementioned early transition metal carbenes, no secondary coupling reaction takes place owing to the tolerance of ruthenium carbenes towards aldehydes. This reaction can therefore be used for the synthesis of aldehyde end-

capped polymers. The reaction is, however, rather slow. Reaction times of 24 hours are expected in most cases, which limits the scope of this reaction and its applicability when oxidizable functionalities are present along the polymer chain.

Reaction with vinyl ethers. As ruthenium carbenes are reactive towards olefins only, deactivation reactions typically involve a metathesis step to form a carbene that does not catalyse further metathesis steps. The most renowned and the first-principal method for the introduction of functional groups at the chain-end of ruthenium-initiated ROMP polymers is carried out by addition of substituted vinyl ethers. The carbene formed in this metathesis reaction represents an electronically deactivated Fischer carbene (structure given on the right-hand side of Fig. 5), which does not re-initiate metathesis reactions on a considerable scale. During this step, the functional group attached to the vinyl ether is transferred to the polymer chain and forms the new end group.

The first description of this process involved the reaction of neat catalyst with ethyl vinyl ether and 2,3-dihydrofurane, which resulted in stoichiometric formation of the polymer-bound Fischer carbene[54]. Soon after, the addition of ethyl vinyl ether was considered as a standard termination reaction for ROMP polymerizations involving Grubbs-type ruthenium catalysts[55] because it is commercially available and the ruthenium complex is cleanly removed from the polymer chain. Therefore, both the stability and purity of the resulting polymer are enhanced as no secondary metathesis reaction within the polymer chains can take place and the catalyst is washed away during workup of the polymer. One advantage of vinyl ethers as quenching reagents is their straightforward functionalization starting from the respective functional aldehydes in a Wittig reaction, using a phosphorus ylide based on, for example, chloromethyl ethyl ether[56].

Vinyl ether termination has established itself as a versatile strategy for the introduction of complex functional end groups. The Kiessling group in particular has put forth this method featuring biocompatible labels on bioactive polymers and interesting binding motives bound to highly functional ROMP polymers. In their first publication, they managed to attach a fluorescein to a polymer that is capable of inhibiting L-selectins (a type of cell adhesion molecule). By applying this polymer to living cells, the distribution of L-selectin moieties within the cell could be traced[57]. An even more advanced approach features an end group that can be bound to a surface, carrying functionalities along the polymer chain, which act as multivalent ligands highly selective for several selectins. A sensor chip for such selectins was built and shown to detect them more sensitively than regular detecting surfaces[58]. Also, binding of those functionalized polymers to a solid support has been developed by the same group in an effort to enable a functionalization of the polymer chain similar to solid-supported peptide synthesis[59]. As depicted in Fig. 5, biotin molecules were also bound to a vinyl ether in order to transfer them onto a polymer chain-end. Monofunctional amphiphilic block copolymers capped with this reagent were then micellized and exposed to streptavidine, which caused non-covalent aggregation of these structures[60].

A broad spectrum of vinyl ethers bearing protected reactive functional groups has been studied for capping efficiency and reaction conditions[61]. Also, an azide-functionalized vinyl ether was used to introduce a universal group for the Huisgen 1,3-dipolar cycloaddition, commonly known as the alkyne–azide 'click' reaction[62].

The addition of vinyl ethers to ruthenium carbenes does not terminate ROMP activity completely. Some studies have shown that the Fischer carbenes formed in this reaction exhibit a residual capability to initiate a metathesis polymerization, albeit with a
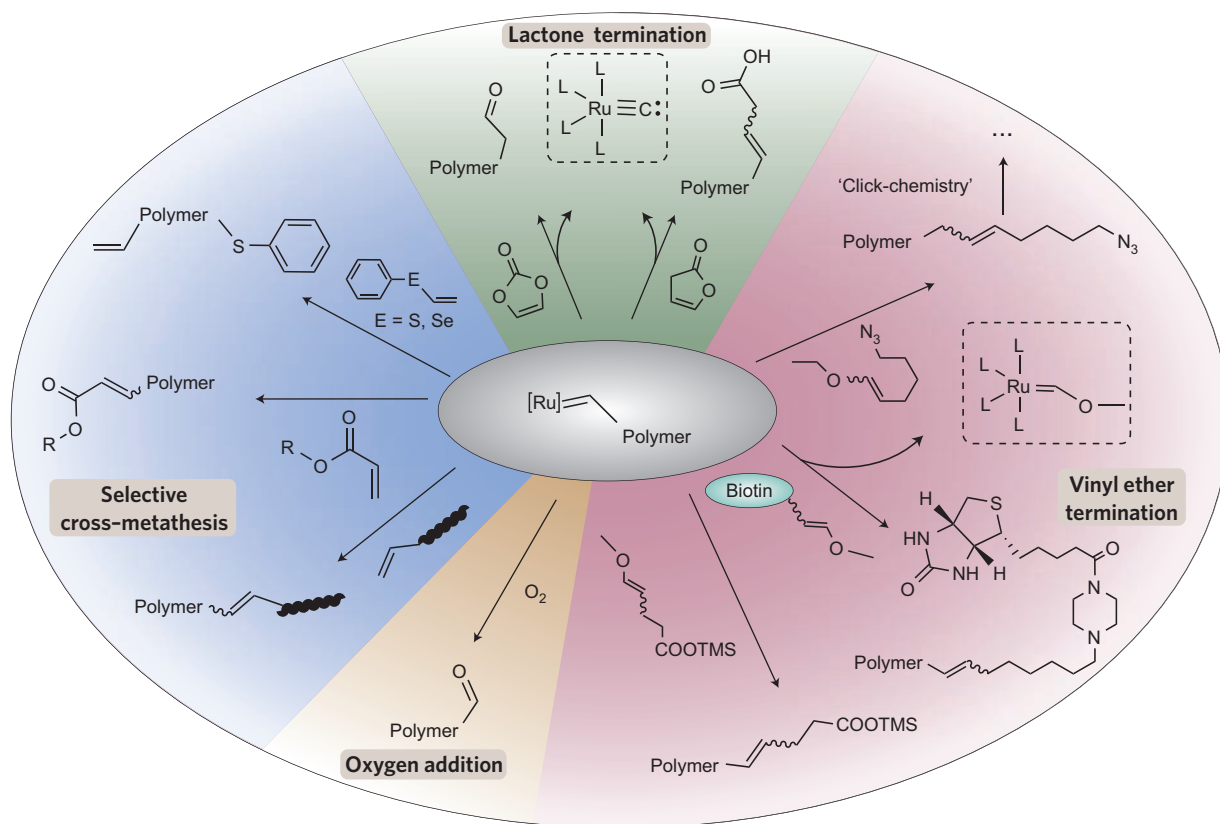

Figure 5 | Termination strategies for ruthenium-catalysed ROMP. Vinyl ether termination, in which the catalyst is deactivated, provides the most general approach to various functional groups, especially when azide functionalities are involved, which can be transformed to almost any group by click-chemistry in subsequent reactions. Lactone termination gives rise to aldehyde and carboxylic acid functionalized polymers without the need for protecting groups. The selective cross-metathesis relies on the regioselectivity of the metathesis step and is therefore limited in the degree of functionalization.

rather low rate of initiation[63]. In this case, the vinyl ether acts as an acyclic chain-transfer agent that reacts regioselectively to give a telechelic polymer bearing an ether group on one end and the functional group formerly bound to the vinyl ether on the other in fairly good definition. This selectivity is caused during the polymerization deactivation step by the vinyl ether in which the energetically favourable Fischer carbene is formed.

When sulfur or seleno-derivatives of vinyl ethers are applied, the deactivation is less pronounced, resulting in more vivid chain-transferring activity. Whereas vinyl ether chain-transferred polymerizations required one to three days to be complete, the reaction involving vinyl sulfides was finished after a few hours at ambient temperatures[64]. Higher vinyl chalcogenides performed accordingly, but steric influences need to be considered. The selectivity also remains high when higher analogues of vinyl ethers are applied. The study of Katayama *et al.*[65] implies a very selective mechanism for the chain transfer directed by the resulting Fischer carbenes produced in the cross-metathesis step. Titanium, molybdenum and tungsten catalysts are not terminated when vinyl ethers are added.

In contrast to vinyl ethers, acyl carbenes form inactive and unstable Fischer carbenes. They decompose to the respective carboxylic acid and another ruthenium complex containing a carbido ligand, that is, a ruthenium–carbon triple bond[66]. This complex can not undergo further metathesis reactions unless reactivated by addition of a strong acid or an oxidant[67,68]. Furthermore, cyclic terminating agents can be applied in the case of vinyl esters, as the consecutive decomposition reaction will also cleave the catalyst off the chain. Another advantage of cyclic terminating agents is the fact that olefins in small cycles are purely *cis*-substituted. This enhances the reactivity of metathesis catalysts towards them owing to lower steric hindrance at the double bond.

Two unsaturated lactones have been applied for the functionalization of metathesis polymers[69]. Vinylene carbonate, which is also commercially available, can be used for the attachment of aldehydes at the chain-end. In this case decomposition of the acyl carbene gives a carbonic acid semi-ester leaving the terminal aldehyde on the polymer chain-end. Addition of 3*H*-furanone, readily synthesized from furfural in a Baeyer–Villiger oxidation, resulted in termination and the formation of a terminal polymeric carboxylic acid.

This strategy represents a particularly useful method for the end-functionalization of polymers with aldehydes or carboxylic acids as no work-up such as deprotection is needed. Therefore, this approach not only yields two of the most interesting and reactive functional groups, but can also be applied when rather sensitive groups are present along the polymer chain. Owing to its unique decomposition reaction to a non-carbene complex, this method is one of the very few real deactivation reactions involving olefins for the ruthenium-catalysed metathesis known to date.

Reaction with neutral olefins. When sterically hindered polymers are used, for example those of norbornene derivatives, a simple olefin can be applied to induce a functionalization at the chain-end. In this case, the living characteristics of the polymerization are used to ensure the exact placement of one functional end group onto the polymer. Because sterically demanding structures virtually forbid the event of intra- and intermolecular cross-metathesis with the olefin groups along the polymer chain or within other polymer chains, the addition of a functionalized acyclic olefin leads to a functionalizing cross-metathesis with the active polymer chain-end. In the absence of a monomer, the latter cannot initiate a new polymer chain.

The addition of acrylates (see Fig. 5, left) represents a particularly simple end-functionalization method, as these are readily available. However, they give only moderate degrees of functionalization as the regiospecific direction of the metathesis step by the acrylate group is low[70]. The addition of symmetrically functionalized olefins, however, leads to quite appreciable functionalization results. Initiator groups for the ATRP[71,72] and building blocks for click-reactions[73] have been attached to polynorbornenes by this method.

Polymerization functionalization

By chain-transfer agents. The addition of chain-transfer agents (CTAs) in order to control the molecular weight of a polymer and to attach functional groups to the polymer chain-ends was a very common method in other polymerization techniques long before the metathesis polymerization had been established. The method is based on the addition of an acyclic olefin, which undergoes cross-metathesis with the active chain-end (mechanism given in Fig. 6), whereby the polymer chain is cleaved off the metal centre and a new polymer chain is initiated by the newly formed carbene. In addition, the cross-metathesis of double bonds along the polymer chain with the CTA leads to an equilibration in which the average molecular weight is determined solely by the stoichiometry of the initial reagents, that is, monomer and CTAs. As far as the equilibration reaction is concerned, the structure of the polymer has to be taken into account.

CTAs were first used in the synthesis of telechelic polymers using molybdenum and tungsten catalysts. In an early approach, Schrock *et al.* chose an unprecedented way to activate chain transfer by using olefin-substituted cyclopentene derivatives. Here, a strained cyclopentene double bond is used to trigger incorporation into the polymer chain. The second olefin is attached in such a manner that a cross-metathesis with this double bond forms a favourable six-membered ring and a free carbene, which can initiate a new chain[74]. The chain-transferring activity of these agents, however, proved to be rather poor.

Later, it was shown that activated double bonds increased cross-metathesis activity, and consequently their incorporation into polyenes was improved. Styrene and 1,3-butadiene, in particular, were used as CTAs for the polymerization of norbornene. In this case,
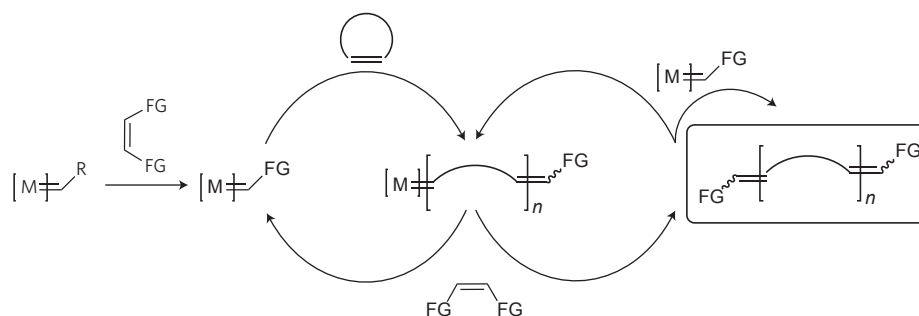

Figure 6 | Mechanism for the formation of telechelic polymers by application of chain-transfer agents (CTAs). The incorporation of the CTA, and therefore the molecular weight determination, relies on both the polymerization kinetics and the equilibration of the CTA into the polymer by cross-metathesis. Polymers with low polydispersity index can be obtained by pulsed addition of monomer to a highly reactive catalyst in the presence of a CTA. FG: functional group.

where highly reactive monomers are used and the polymerization is fast, impressively narrow molecular weight distributions can be obtained by pulsing the polymerization mixture with fresh monomer[75]. Reactive functional groups have not yet been introduced to polymer chains by this method.

The use of CTAs as functionalizing agents for the ruthenium-catalysed ROMP was studied largely during the early development of chain-end functionalized polymers owing to the high functional-group tolerance of the ruthenium carbenes. The theoretical basis and a proposed mechanism of the chain transfer and the subsequent equilibration reaction have been studied in the Grubbs group[76]. Further studies involving the kinetics of the reaction and the influence of the monomer structure on the equilibration reaction followed[77], which also set the foundation for the synthesis of monofunctional polymers (see below).

The use of CTAs in ruthenium-catalysed ROMP has by far become the most applied method for the attachment of reactive termini on polymer chain-ends. First applications involved protected reactive functional groups such as alcohols[78], amines and carboxylic acid[79]. Also, less reactive functional groups were introduced without protection. In particular, groups such as halides, pseudo-halides[80], methacrylates and epoxides[81], which can function as initiating sites for different polymerization techniques including ATRP, free radical or ionic polymerization, were introduced this way. Furthermore, complex CTAs bearing polymers[82] or groups that possess liquid crystalline properties[83] have been synthesized and applied.

The latest generation of extremely reactive ruthenium carbenes featuring pyridyl ligands has recently also been applied in a pulsed-addition ROMP, where fresh monomer is added to a catalyst–CTA solution[84]. This approach could drastically increase the number of well-defined polymer chains per catalyst molecule and has shown the impressive reactivity and selectivity of the latest catalyst developments. As such, this report also demonstrates how well these catalysts can compete with their molybdenum and tungsten cousins in those terms.

A related method has been reported by Fraser et al.[85], who have used cleavable cyclic monomers in a statistical copolymerization with classical ROMP monomers. Here, the functional chain-ends are set free by subsequent hydrolysis of the cleaving sites. Acetal monomers were found to be suitable for the synthesis of hydroxy-telechelic polymers. As far as molecular weight control and the definition of the molecular weight distribution are concerned, this method is controlled not by the chemist, but by the kinetic characteristics of the reaction. The stable monomer has great influence on the equilibration reaction, which gives the molecular weight control. Sterically demanding monomers would require an azeotropic copolymerization to give polymers of the molecular weight that is predetermined by the stoichiometry of the reaction. The molecular weight distributions are generally expected to be rather broad as a statistical copolymerization process takes place.

Sacrificial synthesis. In contrast to the majority of the aforementioned methods of mono-functionalization, sacrificial synthesis is not based on a catalyst deactivation step. Rather, it represents an advanced strategy of polymerization of cleavable cyclic monomers, thereby circumventing the negative kinetic aspects of a copolymerization. In this approach, an additional block of a cleavable monomer is polymerized onto the desired polymer[86]. This block can then be destroyed in a subsequent deprotection reaction, thereby liberating the functional group as illustrated in Fig. 7. This approach has shown potential, particularly in the placement of highly reactive functional groups, which can be protected in such a way that cyclic monomers are formed.

The first report on this strategy, which received significant attention[87], focused on the formation of terminal alcohols. In this case, 1,3-dioxepines similar to the cyclic acetals used in the copolymerization technique (see above) were used to form the sacrificial block. After
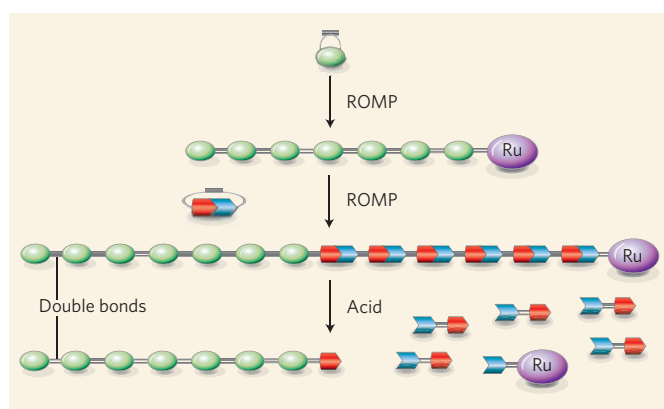

Figure 7 | Synthetic concept of sacrificial synthesis. The green monomer forms the later functionalized polymer. The second monomer (blue and red) can be cleaved in a subsequent reaction. The block copolymerization of these monomers gives rise to a well-defined precisely monofunctionalized polymer with alcohol or thiol end groups. Telechelic polymers have also been accessed via this approach. Figure reprinted from ref. 87, © 2007 NPG.

removal by acidic hydrolysis or hydrogenation, 'half a dioxepine' — that is, an alcohol group — was left on the polymer chain-end. The degree of functionalization is primarily given by the degree of initiation of the sacrificial block. Any reaction of an additional sacrificial monomer unit does not contribute to the degree of functionalization as it is removed later on. Therefore, excesses of the cleavable monomer have to be added to ensure high degrees of functionalization.

The resulting precisely and reactively end-functionalized polymers have been applied in the construction of more complex polymeric architectures. By derivatization with a norbornene acid, macromonomers were formed and polymerized to the respective graft-copolymers using the same catalyst that had been used for the synthesis of the side chains[88]. Using the Huisgen-type azide–alkyne click reaction, block copolymers were formed with different polymers after esterification of the terminal alcohol with propargylic acid[89].

An efficiency study[90] has focused on the kinetic characteristics of the reaction and the block transfer to optimize the process and minimize the amounts of sacrificial monomer needed. By using kinetic equations for the living anionic polymerization, this key initiation step could be understood in detail. Thiol end groups have also been accessed in the same fashion polymerizing a dithiepine, which can be removed by hydrogenation with Raney nickel. The resulting thiol end group was used to coat the surface of gold nanoparticles with the ROMP polymer[91]. In summary, precise placement of exactly one alcohol or thiol group on the ROMP polymer chain-end has been accomplished by sacrificial synthesis.

Because the process of introducing the functional group by sacrificial synthesis is non-deactivating, the method can also be used to place a functional group at the beginning of the polymer chain. Hydroxy-telechelic polymers, or polymers bearing an alcohol group at both ends, have been realized in this manner from sacrificial triblock copolymers where the outer blocks consisted of polyacetals. Using this method, the first well-defined telechelic materials showing narrow molecular weight distribution have been synthesized by ruthenium-catalysed ROMP[92].

The number of telechelic chains produced per molecule of catalyst could be increased by increasing the number of alternating blocks to five or seven. This means that two or three non-hydrolysable blocks are enclosed and separated by the respective number of sacrificial blocks. However, partial loss of molecular weight definition due to increasingly poor block transfers was observed. Nonetheless, this method is especially suitable for short telechelic polymers with

Table 2 | A field guide of functionalization methods for the living ROMP.

Functionality	Catalyst	No. of FG*	Methods†	% FG‡	PDI§	Comment	References
–OH	Ti	1	(CHO)$_2$	Medium	Broad	Reduction of aldehyde to OH, also coupling	30
	Mo/W	1	CHO	High	Narrow		42,43
	Ru	1	Sacrificial synthesis	High	Narrow		86–90
		2	CTA	High	Statistical		77,78,82
		2	Copolymerization with acetals	High	Statistical		85
		2	Sacrificial synthesis	High	Narrow–broad	Dependent on number of blocks	92
–COOH	Mo/W	1	CHO	High	Narrow	As methyl ester	39
	Ru	1	VE	Med	Narrow		61
		1	3HF	High	Narrow	No deprotection required	69
		2	CTA	High	Statistical		79
–NH$_2$	Mo/W	1	CHO	High	Narrow		39
	Ru	1	VE	Medium	Narrow		61
		2	CTA	High	Statistical		79
–SH	Ru	1	Sacrificial synthesis	High	Narrow		91
–CHO	Ti	1	(CHO)$_2$	Medium	Broad	Also coupling	30
	Mo/W	1	(CHO)$_2$	High	Broad	Also coupling	39
	Ru	1	O$_2$ addition	Medium	Narrow	Long reaction time	53
		1	VC	High	Narrow		69
Polymerizable or initator groups	Mo/W	1	CHO	High	Narrow	ATRP, ionic polymerization, poly-condensation	42–45,48,49
	Ru	1	CTA	High	Narrow	Bulky monomers, ATRP, 'click'	71,72,73
		2	CTA	High	Statistical	For example, ATRP, radical polymerization	81
Polymers	Ti	1	Polymer-C=O	Medium	Broad	Block and star copolymers	31
	Mo/W	1	Polymer-CHO	High	Broad	Block and star copolymers	46,50
	W	1	FI	High	Narrow	Living styrene + WCl$_6$	20,21
	Ru	1	FI	High	Narrow	Challenging procedure	25
		1–2	CTA	Medium	Broad		82
Bio-related groups	Ru	1	VE	Medium	Narrow	For example, biotin	58,60
Label groups	Ti	1	CHO/C=O	Medium	Narrow	For example, pyrene-CHO	18
	Mo/W	1	CHO	High	Narrow	For example, pivalonaldehyde	32,34–39
		1–2	CTA	Low	Statistical	For example, styrene	75
		2	Aldehyde	High	Narrow	Bifunctional initiator	40,41
	Ru	1	FI	High	Narrow		22,24
		1	Acrylate	Low	Narrow		70
		1	VE	Medium	Narrow	For example, ethyl vinyl ether	57,59,61,62
		2	CTA	High	Narrow	Pulsed addition of monomer	84
		1–2	CTA	High	Narrow		80,83,84

*Number of functional groups (1=monofunctional, 2=telechelic).
†CHO: addition of an aldehyde; (CHO)$_2$: addition of a dialdehyde; VE: addition of a vinyl ether; CTA: addition of a chain-transfer agent; 3HF: addition of 3H-furanone; VC: addition of vinylene carbonate; C=O: addition of a ketone; FI: use of a prefunctionalized initiator complex.
‡Degree of functionalization achieved in % of polymer chains. High: >95%; low: <75%.
§Molecular weight definition (polydispersity index). Narrow: according to the catalyst, typically <1.2; broad: typically >1.2; statistical: typically ~2

narrow molecular weight distribution, which would otherwise require stoichiometric amounts of catalyst per polymer chain.

A general functionalization guide

A number of factors have to be considered in order to choose the most appropriate method of end-functionalization. First, the chosen monomer has a great influence on the choice of catalyst, owing to both potential functional group incompatibilities and the general reactivity of the catalyst. Second, the method of functionalization has to be chosen with respect to the number of functional end groups that have to be attached, that is, monofunctional or telechelic polymers. Moreover, the desired molecular weight definition has

an important role in many application-oriented syntheses. Table 2 summarizes the methods available and classifies them according to functional group classes, catalyst generations, polymer types and other factors to give a general navigation map through the wide field of methods.

Conclusions and outlook

An overwhelming number of functionalization reactions have been developed for the ROMP. Whereas most functionalization strategies focus on the termination of the polymerization reaction for the introduction of a functional group, others have used a functional initiation step. A third group of methods has deployed specialized

polymerization techniques for the introduction of the desired functionalities. Owing to the fundamental differences of the different catalyst types and generations in terms of functional group tolerance, polymerization activity and general reactivity towards substrates, every catalyst type requires its specific functionalization techniques.

Catalysts based on molybdenum, ruthenium and tungsten have the most dominant role in recent ROMP research. In the case of molybdenum, catalysed metathesis polymerization functionalization is affected in most cases by the addition of an aldehyde bearing the desired functional group. Although this reaction is quick and efficient, only a limited variety of well-protected functional groups can be generated owing to the relatively high reactivity of molybdenum towards such groups. Ruthenium carbenes, with some exceptions, are reactive towards olefins only. As a consequence, olefins were used, which deactivate the catalyst after the metathesis step, thereby terminating the metathesis reaction. Electron-deficient olefins, which can be found in vinyl ethers and vinyl lactones, are used for these purposes today.

The most modern ruthenium catalysts, which combine both functional group tolerance and high metathesis activity, will certainly have a key role in future metathesis development. The large variety of functionalization methods for these complexes will also set the tone for future approaches to place functional sites on or along the polymer chain. Among the variety of methods, three have emerged as generally applicable strategies for the most useful functional groups. The termination with vinyl lactones and the sacrificial synthesis give rise to very reactive end groups and can be conducted conveniently. They can therefore be termed useful for broad application as the resulting highly functionalized polymers can be reacted and derivatized easily, even by non-specialists. Vinyl lactone termination, in particular, promises an extremely broad applicability as the functional groups produced by this method are liberated during the termination reaction and need no further reaction steps. This allows even labile groups to be present in the monomer structure as the functional end group is released under very mild conditions.

Vinyl ether termination is a much broader functionalization technique with many more possible types of functional group available. Yet it is also a strategy that requires more knowledge and experience with the ROMP process and higher demands in the synthesis of the respective terminating agents. The method will, however, remain a driving force in the field of bio-related functional polymers, where complex molecular motifs have to be mildly reacted onto the polymer chain-end to conserve their function and specificity. Furthermore, this method will certainly remain the reference method for the evaluation of other functionalization techniques and a reliable work horse for all functional groups that can not be incorporated in cyclized monomers for sacrificial synthesis or lactone termination (such as azides or halides).

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