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Living ring-opening metathesis polymerization

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Abstract

Since the discovery of olefin metathesis in the mid-1950s, there has been great interest in using this versatile reaction to synthesize macromolecular materials. More recently, living ring-opening metathesis polymerization (ROMP), a variation of the olefin metathesis reaction, has emerged as a particularly powerful method for synthesizing polymers with tunable sizes, shapes, and functions. The technique has found tremendous utility in preparing materials with interesting biological, electronic, and mechanical properties. This review covers the fundamental aspects of living ROMP and briefly traces its historical development from a catalyst-design perspective. Highlights from the recent literature are used to illustrate the utility of living ROMP in the preparation of macromolecular materials with advanced structures and functions. A discussion on the current status of state-of-the-art catalysts for use in living ROMP reactions as well as opportunities for the future concludes this review.

Keywords: Ring-opening metathesis polymerization (ROMP); Living polymerization; Review; Olefin metathesis; Titanium; Tantalum; Tungsten; Molybdenum; Ruthenium

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1. Overview of ring-opening metathesis polymerization (ROMP)

1.1. Introduction

Although a relatively new player on the field of polymer chemistry, ring-opening metathesis polymerization (ROMP) has emerged as a powerful and broadly applicable method for synthesizing macromolecular materials [1]. The origins of ROMP can be traced to the mid-1950s when various metals and reagents were combined to uncover new transformations and reactivities involving olefins. However, the rapid rise in popularity and utility of this polymerization technique is the result of extensive work on the identification and isolation of key intermediates involved in the general olefin metathesis reaction [2]. This led to the development of well-defined ROMP catalysts and ultimately enabled the synthesis of a wide range of polymers with complex architectures and useful functions. The aim of this review is to provide the reader with a "user's manual" to living ROMP so they may readily begin applying this unique and powerful polymerization method. Following a brief overview of ROMP, a historical account of the polymerization technique will be given. Particular emphasis will be placed on the transition metal catalysts used to mediate the polymerization and their current status in contemporary polymer chemistry. The review will conclude with some current challenges and predictions for the future.

1.2. ROMP essentials: mechanism and thermodynamics

Ring-opening metathesis polymerization (ROMP) is a chain growth polymerization process where a mixture of cyclic olefins is converted to a polymeric material (see Fig. 1 for an illustrative example) [3]. The mechanism of the polymerization is based on olefin metathesis, a unique metal-mediated carbon–carbon double bond exchange process [4]. As a result, any unsaturation associated with the monomer is conserved as it is converted to polymer. This is an important feature that distinguishes ROMP from typical olefin addition polymerizations (e.g. ethylene→polyethylene).

A general mechanism for ROMP, based on Chauvin's original proposal [5], is shown in Fig. 2. Initiation begins with coordination of a transition metal alkylidene complex to a cyclic olefin. Subsequent [2+2]-cycloaddition affords a four-membered metallacyclobutane intermediate which effectively forms the beginning of a growing polymer chain. This intermediate undergoes a cycloreversion reaction to afford a new metal alkylidene. Although the resulting complex has increased in size (due to the incorporated monomer), its reactivity toward cyclic olefins is similar to the initiator. Hence, analogous steps are repeated during the propagation stage until polymerization ceases (i.e. all monomer is consumed, a reaction equilibrium is reached, or the reaction is terminated). Living ROMP reactions are commonly quenched deliberately through the addition of a specialized reagent. The function of this reagent is to (1) selectively remove and deactivate the transition metal from the end of the growing polymer chain and (2) install a known functional group in place of the metal [6].

There are three important features regarding metal-mediated ROMP reactions. First, it is important to note that the propagating metal centers on the growing polymer chains may exist in either

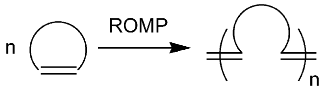

Fig. 1. A generalized example of a ring-opening metathesis polymerization (ROMP) reaction.

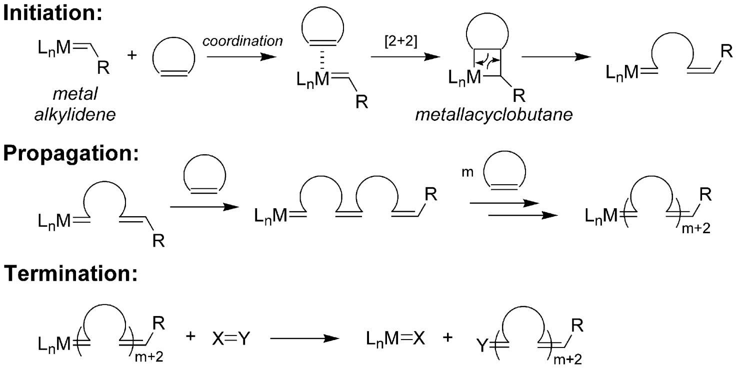

Fig. 2. A general mechanism to a typical ROMP reaction.

the metallacyclobutane or metal alkylidene form. This difference depends on the transition metal and its associated ligands, as well as the reaction conditions. Second, like most olefin metathesis reactions, ROMP reactions are generally reversible. Thus, the basic mechanism illustrated in Fig. 2 can proceed in the opposite direction as shown. Third, although most ROMP reactions are reversible, they are equilibrium-controlled and the position of the equilibrium (monomer vs. polymer) can be predicted by considering the thermodynamics of the polymerization. As with other ring-opening polymerizations, the reaction is driven from monomer to polymer by the release of strain associated with the cyclic olefin (so-called "ring strain") balanced by entropic penalties. The most common monomers used in ROMP are cyclic olefins which possess a considerable degree of strain (>5 kcal/mol) such as cyclobutene, cyclopentene, cis-cyclooctene, and norbornene [7]. One notable exception is cyclohexene. With low ring-strain, this cyclic olefin has very little enthalpic driving force to be polymerized using ROMP.

Accordingly, the temperature and concentration at which the ROMP is conducted has strong influences over the outcome of the reaction. Using the Gibbs free energy equation, one can derive a "ceiling temperature" and a related concentration at which polymerization (for any cyclic olefin) will not occur [8]. Essentially, at this concentration/temperature juncture the entropic penalty is too high to be compensated by the enthalpic contribution associated with the release of ring-strain. These considerations are important when attempting the ROMP of any new cyclic olefin. Generally, the most favorable conditions for a successful ROMP reaction is to use the highest monomer concentration at the lowest temperature possible.

In addition to the general ROMP mechanism illustrated in Fig. 2 (and its related depolymerization mechanism), the equilibria noted above can be established via other metathetical pathways, including intermolecular chain-transfer and intramolecular chain-transfer (so-called "backbiting") reactions. Examples of these types of secondary metathesis reactions are shown in Fig. 3. In an intermolecular chain-transfer reaction, one polymer chain containing an active metal alkylidene on its terminus can react with any olefin along the backbone of a different polymer chain in the same reaction vessel. Although the total number of polymer chains remains the same, the molecular weights of the individual polymers will increase or decrease accordingly. In a backbiting reaction, the active terminus of a polymer chain reacts with itself to release a cyclic species and a polymer chain of reduced molecular weight. Collectively, these chain-transfer reactions effectively broaden molecular weight distribution (or polydispersity) of the system.

Another implication of equilibrium controlled polymerizations such as ROMP is the propensity to form cyclic oligomers. According to the Jacobson–Stockmayer theory of ring–chain equilibria, the formation of cyclic oligomers will always accompany the formation of high molecular weight polymer [9]. The total amount of cyclic species present will depend on factors such as solvent, cis/trans ratio of the polymer backbone, rigidity of the monomer, reaction time, and concentration. Formation of cyclic species is favored at higher temperatures and lower concentrations with a critical value dependent on the factors noted above. While these side reactions challenge the realization of living polymerizations based on ROMP (see below), they can be advantageous. For example,

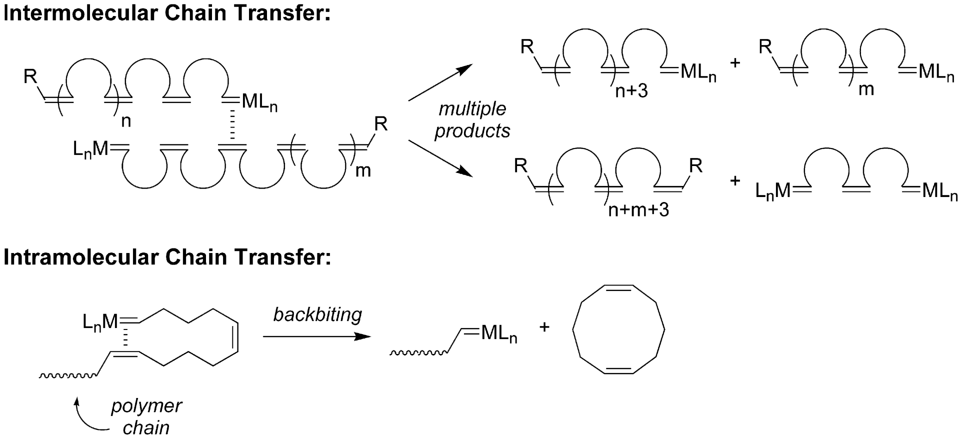

Fig. 3. Examples of secondary metathesis reactions in ROMP reactions. (Top) An example of intermolecular chain transfer producing multiple products with varying molecular weights. Note that the total number of polymer chains and active species remains unchanged. (Bottom) An example of intramolecular chain transfer producing an active polymer chain of reduced molecular weight and a cyclic species.

cyclic oligomers can be synthesized in high yields by simply conducting the ROMP reaction under relatively dilute conditions [10].

1.3. Living ring-opening metathesis polymerization

In 1956, Swarzc defined a "living polymerization" as one that proceeds "without chain transfer or termination" [11,12]. Under certain conditions (defined below), living polymerizations afford polymeric materials that generally have very narrow molecular weight distributions. These distributions are usually quantified through determination of the sample's polydispersity index (PDI), which follows the equation: $\mathrm{PDI} = M_\mathrm{w}/M_\mathrm{n} = 1 + 1/\mathrm{DP}$, where M_w is the weight-averaged molecular weight, M_n is the number-averaged molecular weight, and DP is the degree of polymerization (i.e. the average number of monomer units per polymer chain). Living polymerizations can often be distinguished from condensation or kinetically-controlled (i.e. free radical) polymerizations by analyzing the evolution of the polymer's molecular weight as a function of time and/or monomer conversion. Condensation polymerizations generally provide high molecular weight polymer only at very high conversions while kinetically controlled polymerizations provide high polymer at relatively early stages. In contrast, molecular weight is directly proportional to monomer conversion in living polymerizations since all chain ends are growing at essentially the same rate. As a result, Gold demonstrated that even when the rate of propagation is orders of magnitude greater than the rate of initiation, a living polymerization can lead to polymers with low polydispersities [13]. However, in systems where the rate of initiation is faster or similar to the rate of propagation, control over the polymerization is obtained at an earlier stage. Under these conditions, access to well-defined, monodispersed materials of low molecular weight is possible.

Thus, in addition to Swarzc's original constraint, we will require a ROMP reaction to exhibit the following characteristics in order to be considered "living and controlled": (1) fast and complete initiation, (2) exhibits a linear relationship between the degree of polymerization (typically measured as the number-average molecular weight of the polymer, M_n) and monomer consumption, and (3) PDIs < 1.5 [14]. Assuming complete conversion of monomer to polymer, this enables the synthesis of well-defined polymers with narrow distributions and predictable molecular weights specified by the initial monomer to initiator ratio (M/I). Under a broader context, a ROMP reaction with these features opens the capacity to prepare well-defined block-, graft-, and other types of copolymers, end-functionalized polymers, and various other polymeric materials with complex architectures and useful functions [15].

When considering the metal-mediated and equilibrium nature of most ROMP reactions, it quickly becomes apparent that very special metathesis catalysts are needed to satisfy the aforementioned requirements. The catalyst should: (1) convert to growing polymer chains quantitatively and rapidly (i.e. exhibit fast initiation kinetics), (2) mediate a polymerization without an appreciable amount of (intramolecular or intermolecular) chain transfer or premature termination, (3) react with accessible terminating agents to facilitate selective end-functionalization, (4) display good solubilities in common organic solvents (or better: aqueous media), and (5) for practical reasons, show high stability toward moisture, air, and common organic functional groups.

2. Catalysts for living ROMP

2.1. Historical aspects

The advances in ROMP can be attributed to tremendous efforts by a large number of researchers dedicated to the development of well-defined, functional group tolerant catalysts amenable to olefin metathesis. Early catalyst systems were often heterogeneous mixtures that were extremely sensitive toward air and moisture, difficult to characterize, and almost impossible to systematically study and optimize. It was immediately recognized that the development of a catalyst with a well-defined structure was essential for olefin metathesis to reach its full potential. This was especially true for the development of a living ROMP catalyst where knowledge and precise control over polymerization kinetics is critical. It is beyond the scope of this review to give an in-depth analysis of this rich and fascinating history, however, this section includes selected milestones in the historical development of these catalysts suitable for living ROMP. The aim is to provide the reader with an appreciation for the origin and progression of this field which may lead to insight into how challenges in the future may be addressed.

2.2. Ill-defined catalysts

Although the use of olefin metathesis in synthetic organic chemistry (e.g. ring-closing metathesis, cross-metathesis, ring-opening cross metathesis, etc.) has gained in prominence [16], its roots were founded in the field of polymer and petroleum chemistry. In fact, due to their similar beginnings, there were considerable misunderstandings regarding the relationships and respective mechanisms of Ziegler–Natta type olefin addition polymerizations and ROMP.

While studying the oligomerization of ethylene using alkyl aluminum catalysts, Ziegler isolated butenes rather than oligomeric materials [17], a reaction that was ultimately discovered to be catalyzed by Ni salts (contaminants from the reaction vessel). While exploring the utility of other metals, Ziegler and Natta found a series of titanium salts that could polymerize ethylene and propylene to high polymer; work that served as the basis for much of the present polyolefin industry and culminated in the 1963 Nobel Prize in Chemistry [18]. The olefin metathesis reaction was discovered serendipitously by groups searching for new transition metal catalysts and co-catalysts to facilitate the polymerization of other olefins. Interestingly, a majority of these results remained relatively obscure for a number of years. However, this changed dramatically after Phillips Petroleum informed the chemical community that they commercialized this reaction as the "triolefin process" [19] in the 1960s. As a result, massive efforts toward understanding, optimizing, and applying the olefin metathesis reaction were launched. Particular attention was directed toward the isolation and characterization of metal–carbene complexes and metallacyclobutanes, both of which are key intermediates in metathetical reactions (see Fig. 2) [20].

The potential of olefin metathesis in the synthesis of polymeric materials was borne out from reports by Truett and coworkers at Dupont and Natta at almost the same time the reaction was discovered [21]. They independently found that a polymer could be obtained from norbornene using heterogeneous mixtures of various Ti, W, or Mo halides that were often enhanced with strongly Lewis acidic Al co-catalysts. Importantly, the polymer was unsaturated with a repeating unit that was essentially 1,3-dimethylidenecyclopentane (see Fig. 4). This suggested that the norbornene ring had somehow opened during the polymerization. Since the carbon–carbon double bonds along the backbones of the polynorbornenes were mostly of cis geometry, the mechanism of the polymerization was believed to occur through a ring-opening reaction that originated at the bridgehead carbon.

Soon after, similar reports on the conversion of norbornene and other cyclic olefins into unsaturated polymers began to emerge. Calderon and coworkers at Goodyear reported a new catalyst system that

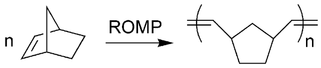

Fig. 4. The ring-opening metathesis polymerization of norbornene.

was prepared from a mixture of WCl_6, $AlEt_2Cl$, and ethanol [22]. Importantly, this mixture provided a homogeneous catalyst that showed reproducible activities which created opportunities for commercial applications. The catalyst also helped in demonstrating the potential of ROMP in synthesizing new macromolecular materials. For example, in the late 1960s, Calderon and coworkers reported that polymerization of 1-methyl-1,5-cyclooctadiene afforded a material that was essentially a perfectly alternating copolymer of 1,4-butadiene and isoprene (see Fig. 5) [23].

A large number of other catalyst systems based on a wide range of transition metals were also discovered by Natta, Michelotti, Dall'Asta, Banks, Rinehart, and other researchers from around the world [24]. Detailed studies on the performance of many of these catalysts in ROMP can be found in reports by Osborn, Rooney, Ivin, Feast, and others [25]. Although ROMP reactions using these catalyst mixtures (heterogeneous or homogeneous) were not living and many required extremely dry and air-free conditions, they collectively provided insight into the mechanism of olefin metathesis and built a solid foundation for the development of well-defined catalysts.

One of the first reports of a well-defined catalyst that was capable of mediating ROMP was from Katz in 1976. He reported a series of tungsten complexes $(CO)_5W=CPhR$ (**1**, R = Ph or OCH_3), which were previously prepared by Casey and Fischer [26], that were found to catalyze the polymerization of a variety of cyclic olefins, including cyclobutene, cycloheptene, cyclooctene, and norbornene, without the need for any cocatalyst (see Fig. 6). Although there was little molecular weight control over these polymerizations and the polydispersities of the resultant polymers were relatively broad (PDI > 1.85), the disubstituted methylidene moiety on the catalyst was found on the ends of the polymer chains [27]. Thus, the catalyst appeared to suffer from either poor initiation characteristics and/or extensive secondary metathesis reactions (or both). Regardless, the contribution provided tremendous credence to the feasibility of a catalyst capable of mediating a living ROMP.

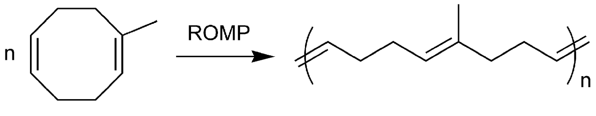

Fig. 5. The ring-opening metathesis polymerization of 1-methyl-1,5-cyclooctadiene afforded a material with a structure consistent with a perfectly alternating polymer of butadiene and isoprene.

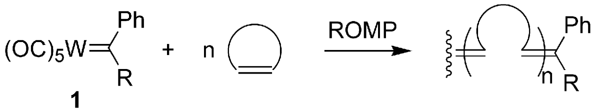

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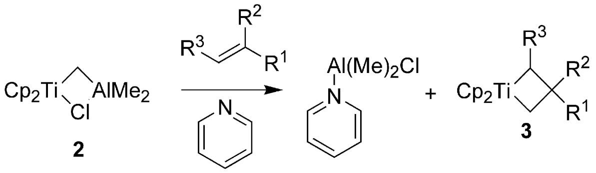
Fig. 6. Polymerization of various cyclic olefins (cyclobutene, cycloheptene, cyclooctene, and norbornene) with well-defined tungsten–akylidene complexes.

2.3. Titanium

The first examples of single component, well-defined catalysts capable of mediating living ROMP reactions were based on Ti. As shown in Fig. 7, by reacting the Tebbe reagent (**2**) [28] with various olefins in the presence of pyridines (to sequester the aluminum), a variety of well-defined, metathesis active bis(cyclopentadienyl) titanacyclobutanes (**3**) were obtained [29]. Although these complexes were not extremely active, they did mediate the ROMP of norbornene without any evidence of chain transfer reactions [30].

Subsequent attention focused on the synthesis of a well-defined Ti catalyst that exhibited rapid initiation kinetics at experimentally practical temperatures through modification of the substitution pattern on the metallacyclobutane ring [31]. For example, complex **4**, prepared via reaction of **2** with 3,3-dimethyl-1-butene, was found to mediate the ROMP of norbornene at a convenient 60 °C (see Fig. 8). At elevated temperatures, the titanacyclobutane **4** is believed to undergo a cycloreversion reaction which affords a reactive Ti methylidene and a volatile alkene. The resulting coordinatively unsaturated Ti methylidene quickly binds norbornene and undergoes another [2 + 2] cycloaddition reaction to afford **5**. At this point, the reaction vessel can be cooled to room temperature and this complex can be isolated. However, in the presence



2 **3**

Fig. 7. Synthesis titanacyclobutanes **3** from the Tebbe reagent (**2**).

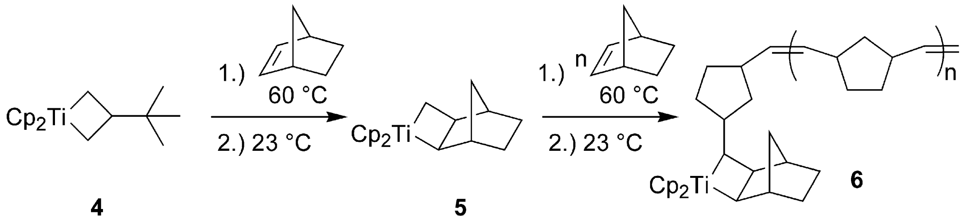


Fig. 8. Synthesis and utility of titanacyclobutanes in mediating living ROMP reactions. (Cp = cyclopentadiene)

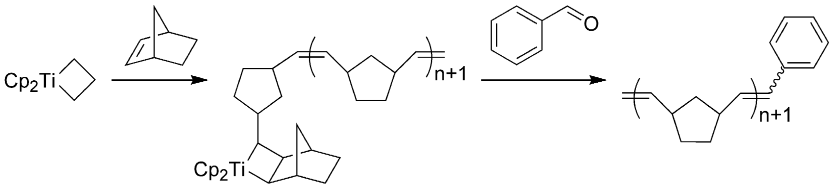


Fig. 9. Quenching a living Ti-mediated ROMP of norbornene with benzaldehyde installs a benzylidene moiety at the end of the respective polymer chain.

of excess norbornene at elevated temperatures ($>60\,^{\circ}C$), a polynorbornene with a Ti alkylidene end-group (**6**) is obtained.

Notably, these Ti catalysts provide polymers with narrow polydispersities (PDI < 1.2) and with molecular weights that scale linearly with the amount of monomer consumed. Since the rate-determining step of the ROMP is the unimolecular cycloreversion of the titanacycle noted above, the rate of the polymerization is proportional to the concentration of the catalyst (i.e. the rate equation is zero order in monomer). This provides an extremely convenient method to modify molecular weight of the polymer chains. The complexes can simply be heated in a large excess of monomer until the desired molecular weight is reached.

Like the Tebbe reagent, these Ti-based ROMP catalysts react with carbonyl containing compounds in a Wittig-type fashion to form substituted olefins and a deactivated Ti oxide species. This reactivity pattern provides a convenient method to not only terminate the polymerization but also to install functional end-groups. For example, addition of benzaldehyde to the reaction vessel at the conclusion of a polymerization selectively installs a benzylidene moiety on one terminus of the respective polymer chains (see Fig. 9).

The ability of these Ti catalysts to mediate living ROMP reactions facilitated the synthesis of macromolecular materials with advanced architectures as well as functional materials. An early example of preparing block copolymers using living ROMP is shown in Fig. 10. By sequentially adding various norbornene derivatives to a Ti-based initiator **7**, di- and triblock copolymers were prepared with very low polydispersities [32,33]. Subsequently, a variety of bifunctional and multifunctional initiators based on these Ti catalysts were also developed and used in the construction of macromolecular materials with advanced topologies [34]. Despite their low activities, most of the major requirements and advantages of living polymerizations, including a flexible catalyst design to control initiation kinetics a means to install functional and well-defined end-groups, and the ability to form block copolymers, were first demonstrated with Ti-based initiators.

2.4. *Tantalum*

Shortly after the Ti complexes were reported, a new series of ROMP-active, well-defined complexes (**8**) based on tantalum were introduced by Schrock and coworkers (see Fig. 11) [35]. These complexes were prepared in three steps from commercially-available $TaCl_5$ by sequential treatment with $Zn(CH_2CMe_3)_2$, THF, and the aryloxide ligand in excellent overall yields. While these complexes have been shown to polymerize norbornene in a well-controlled fashion, they possessed higher activities than their Ti predecessors. As a result, it was found to be necessary to monitor the ROMP reactions if materials with low polydispersities were desired [36]. For example, stopping a polymerization of norbornene ($M/I = 200$) at 75% monomer conversion provided a polynorbornene with a molecular weight of 32 100 Da and a PDI = 1.04. However, if this

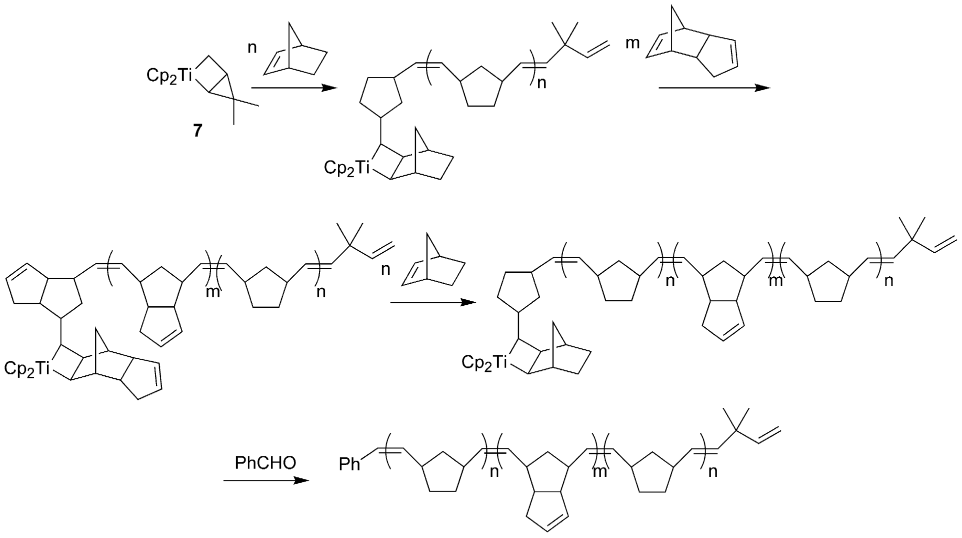


Fig. 10. Synthesis of triblock copolymers using living ROMP.

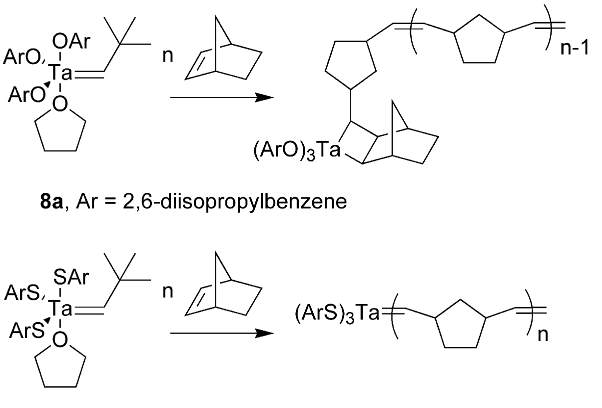


Fig. 11. ROMP of norbornene using various Ta catalysts.

same polymerization is taken to completion (i.e. complete consumption of monomer), polymers with larger molecular weights were observed but the PDI of these materials increased to values >1.6. The discrepancy has been attributed to secondary metathesis reactions as a result of the high activity of the catalyst combined with slow initiation kinetics. Thus, while the rates of secondary metathesis reactions are slower than chain propagation, they appear to become competitive as the polymerization approaches completion. The mechanism of the ROMP reaction using these catalysts is believed to proceed similarly as their Ti predecessors. Indeed, the rates of polymerization are first-order with respect to the Ta complex and independent of the concentration of norbornene, suggesting that the metallacyclobutane reversion is again the rate-determining step of the polymerization reaction.

The propensity of these Ta based catalysts to facilitate secondary metathesis reactions was successfully reduced through the incorporation of bulky, electron rich diisopropylphenoxide ligands [37] which essentially decreased their electrophilic character (see Fig. 11). As a result, norbornene was successfully polymerized to completion using this catalyst and the resultant polymers obtained at the conclusion of the reaction exhibited very narrow polydispersities (PDI > 1.1). Another distinguishing feature of this catalyst **8b** is that propagating chains appear to have alkylidene end-groups (as opposed to metallacyclobutane structures common with the aforementioned Ti complexes and Ta-based **8a**). Thus, the rates of polymerization with these catalysts are second-order and dependent on the catalyst and monomer concentration. Both catalysts **8a** and **8b** react with aldehydes and ketones in a Wittig-type fashion, which provides a convenient method for terminating the ROMP and installing functional end-groups.

The Ti and Ta complexes mentioned above are extremely Lewis acidic as a result of their high oxidation states. In addition to carbonyls, they react rapidly with most heteroatom-containing functional groups (hydroxyl, amino, etc.), placing limitations on their utility in living ROMP reactions. However, more importantly, they were an outstanding testament to the power of catalyst design in tailoring activity. Attention soon turned toward the discovery of new catalysts that maintained ROMP activity and structural tunability but also exhibited a broader range of functional group tolerance.

2.5. Tungsten

Olefin metathesis active catalysts based on tungsten have been employed for almost a half century. In fact, several commercial processes have been designed around the use of various tungsten-based metathesis catalysts. However, for most of this time, the catalysts were based on ill-defined and/or heterogeneous mixtures. While many of these catalyst systems were successful in mediating ROMP, they did not show living characteristics. Furthermore, many of these catalysts were highly Lewis acidic and were sensitive to most heteroatom-containing functional groups.

As noted above, Fischer and Casey prepared the first well-defined catalysts based on tungsten. While these catalysts were capable of polymerizing strained cyclic olefins, they did not do so in a living fashion. In the late 1970s, Schrock and Osborn were developing new classes of well-defined, tungsten-based catalysts based on the general structures of $W(=CHC(CH_3)_3)(OCH_2\text{-}t\text{-}Bu)_2Br_2$ (**9**) [38]. As shown in Fig. 12, they were found to polymerize a variety of derivatized norbornenes in a living manner at low temperatures and were also subsequently used to make block copolymers when a Lewis acid (such as $GaBr_3$) was included during the ROMP reactions [39,40].

A variety of Lewis-acid free initiators based on the general structure $W(=CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)Cl(OAr)(O(CHC(CH_3)_2)_2$ were reported by Basset and coworkers [41]. These single-component catalysts showed exceptional functional group tolerance and were reported to mediate the polymerization of a variety of functionalized norbornenes, including norborn-5-ene-2-yl acetate and norborn-5-ene-carbonitrile. Notably, complex $W(=C(CH_2)_4)(OCH_2\text{-}t\text{-}Bu)_2Cl_2$ was reported to polymerize *exo*-norborn-5-ene-2,3-dicarboxylic anhydride, which was a strong testament to the increased functional group tolerance of these catalysts [42]. As shown in Fig. 13, complex **10**, which possessed a bulky aryloxy substituent, was shown to facilitate stereocontrol over the polymerization of 1-methylnorbornene and provided high cis polymers with a strong head-to-tail preference [43]. The high activity of these catalysts promoted secondary metathesis reactions which prevented the corresponding ROMP reaction from showing living character. However, these results were an important demonstration that catalysts with increased functional group tolerance and an ability to exert stereochemical control over the ROMP could be made.

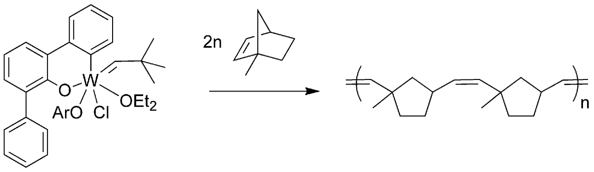


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Fig. 13. Stereoselective ROMP of 1-methylnorbornene using **10** as a catalyst provides high cis poly(1-methylnorbornene) with a head-to-tail preference in the repeating units of the polymer chain.

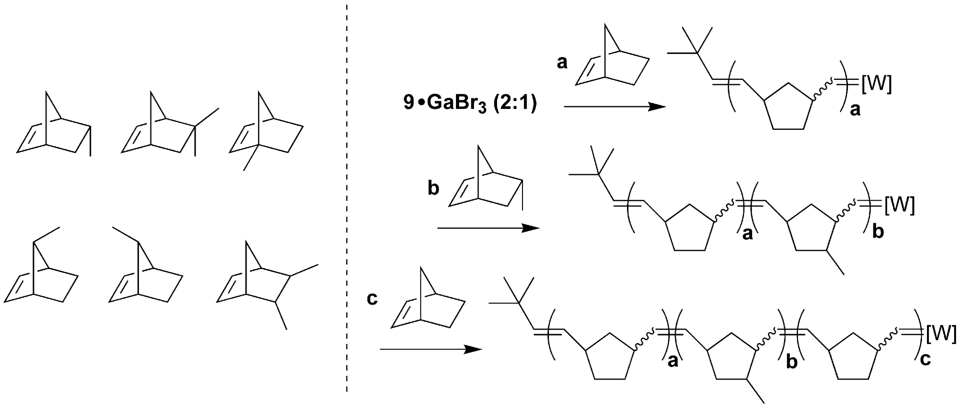


Fig. 12. (Left) Representative examples of various substituted norbornenes found to undergo living ROMP using tungsten-based catalyst **9**. (Right) An example of forming block copolymers using **9**. Note that the middle block contains a mixture of head-to-head and head-to-tail repeat units.

Schrock and coworkers modified the design of the catalyst described above to arrive at a new single-component, Lewis-acid free, imido-alkoxy based catalyst system (**11**) that showed outstanding activities in ROMP [44]. A particularly useful feature of these catalysts is their alkoxide ligands which were shown to modulate the activity of the corresponding catalysts over an impressive range. For example, addition of an excess of norbornene to **11a** resulted in a living ROMP and afforded polymers with predictable molecular weights and polydispersities as low as 1.03 after quenching with benzaldehyde [45]. Increasing the electrophilic character of the catalyst via replacement of the hydrogenated alkoxy ligands with fluorinated analogues substantially increased their activity in olefin metathesis reactions. In particular, catalysts **11b** and **11c** readily scrambled cis-2-pentene (**11a** does not) and ROMP of norbornene with these catalysts results in secondary metathesis reactions as well as slow initiation relative to propagation (see Fig. 14).

Catalysts with similar activities but increased functional group tolerance were obtained using oxo-tungsten based alkylidene complexes W(= CH-*t*-Bu)(O)(PR$_3$)(OAr)$_2$. These catalysts were found to mediate the living ROMP of 2,3-dicarbomethoxynorbornadiene and 2,3-bis(trifluoromethyl)norbornadienes [46] to give polymers with high (>95%) cis olefin content in their backbones and high (>95%) isotacticity. There was also an excellent linear relationship between the molecular weight of the polymer and the initial monomer to catalyst ratio. Notably, the catalysts appear to show very little propensity to facilitate secondary metathesis reactions as there is no change in the PDI (which can often be as low as 1.01) of the polymer even after prolonged reaction in solution. The polymerizations are extremely rapid as more than 100 equiv of monomer can be polymerized in minutes. These W catalysts were also found to display Wittig-type reactivities in analogy to their Ti and Ta precursors. As such, the addition of ketones or aldehydes can be used to terminate the polymerization and install functional end-groups.

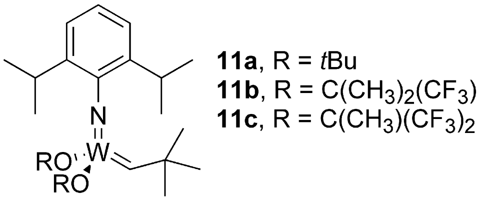


Fig. 14. Structures of W-based imido alkylidenes.

These W catalysts have been shown to mediate the living ROMP of other classes of cyclic olefins. As discussed in Section 1.1, cyclopentene is considerably less strained than norbornene which increases opportunities for various types of back-biting reactions. Thus, this monomer is considerably more difficult to polymerize in a living fashion and generally requires low temperatures. For example, a living polymerization of cyclopentene was conducted at −40 °C with **11a** and afforded a polypentenamer with a PDI of 1.08 [47]. It was important to monitor the ROMP as extended exposure to catalyst caused the polydispersity of the material to broaden over time.

In contrast to cyclopentene, cyclobutene is considerably strained and readily undergoes ROMP. As a result, the rates of initiation are often slower than the rates of propagation, limiting control over the ROMP and leading to polydisperse materials. To enable living ROMP reactions of cyclobutenes, a donor ligand such as trimethylphosphine (PMe$_3$) must be included in the polymerization [48]. This ligand reversibly binds to the catalyst and reduces its propensity to mediate olefin metathesis. As a result, the rate of the polymerization is reduced relative to initiation and the ROMP adopts living character. Other donors such as dimethylphenylphosphine, phenyldimethylphosphine, pyridine, quinuclidine, and tetrahydrofuran may also be used, although, as a result of their weaker binding affinity, larger amounts are required. Interestingly, ROMP of cyclobutene provides polybutadiene with a "perfect" 1,4-microstructure.

The advantages and high activity of W-based catalysts were manifested in the synthesis of organic materials with promise in electronic applications. A key requirement for application of these materials in any electronic device is conductivity which necessitates an extensively unsaturated or conjugated polymeric backbone. The prototypical example is polyacetylene, which interestingly was discovered in the Natta group. As shown in Fig. 15, exposing acetylene to typical classical olefin addition polymerization catalysts (trialkylaluminum

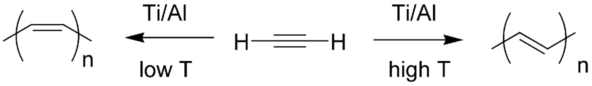


Fig. 15. Polymerization of acetylene at various temperatures using Ziegler–Natta catalysts.

reagents mixed with titanium alkoxides) at elevated temperatures produced polyacetylene as a red powder, which was later identified as the trans isomer. Performing the polymerization at low temperatures afforded the cis isomer. Unfortunately, these materials were insoluble and sensitive toward oxidation which curtailed further efforts toward studying these materials. The area was revitalized in the early 1970s when Shirakawa reported a modification of Natta's original procedure that allowed for the synthesis of a usable thin film of the polymeric material. In conjunction with Heeger and MacDiarmid, it was discovered that the electrical conductivity of this film could be drastically enhanced through the introduction of various dopants and oxidants. This outstanding discovery opened the field of organic electronics and ultimately resulted in the 2000 Nobel Prize in Chemistry [49].

As shown in Fig. 16, a wide variety of routes to prepare polyacetylene using ROMP have been developed. To solve the problem of intractability, a new monomer (**12**) was developed that upon polymerization would provide a soluble and processable precursor to polyacetylene [50]. Subsequent thermal or chemical treatment of the polymer obtained from the ROMP of **12** would eliminate a volatile small molecule and liberate polyacetylene. This route is often called the Durham route to polyacetylene. As a means to limit mass loss associated with this approach, benzvalene (**13**) was synthesized and subjected to ROMP conditions [51]. Rearrangement of the resulting polymer produced polyacetylene. In a third approach, the ROMP of cyclooctatetraene (COT) (**14**) using various W catalysts provided a "one-step" synthesis of polyacetylene from a liquid monomer, which after doping, provided a highly conductive material [52]. Limitations of the latter approach included a non-living nature of the ROMP reaction due to competing secondary metathesis reactions (e.g. benzene is one possible product that forms upon intramolecular cyclization) and the difficulties associated with processing and handling the resultant films.

2.6. Molybdenum

As noted in the introduction, metathesis catalysts that tolerate a broad array of organic functional groups have been (and still are) highly desired since the inception of the olefin metathesis reaction. While the well-defined W catalysts noted above were a strong testament of progress toward this goal, a significant advance was Schrock's introduction of well-defined Mo-based alkylidenes (**15**) [53]. Although structurally similar to W-based alkylidenes **11**, these catalysts tolerated a much broader range of functionality including monomers containing ester, amide, imide, ketal, ether, cyano, trifluoromethyl, and primary halogen-containing functional groups. The increased functional group compliance also facilitated their synthesis and use when compared to their W analogues, since they exhibited a greater tolerance toward oxygen, water, and other impurities. These complexes were also

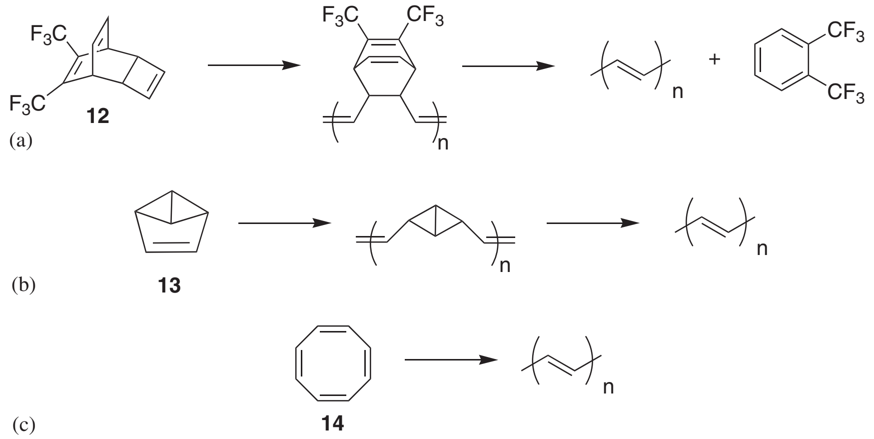
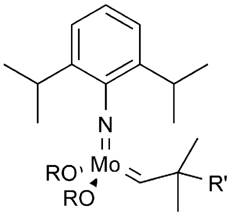


Fig. 16. Three routes to prepare polyacetylene using ROMP. (a) The Durham route. (b) ROMP of benzvalene followed by rearrangement. (c) ROMP of COT.

found to be more stable toward decomposition and other side reactions (see Fig. 17).

A representative sample of functionalized norbornene-based monomers that are amenable to living ROMP using **15a** is shown in Table 1 [54]. In general, the resultant polymers showed narrow polydispersities and good control over molecular weight was achieved by adjusting the initial monomer to catalyst ratio. It is particularly noteworthy that monomers with strong electron withdrawing groups (i.e. fluorinated moieties) and norbornene derivatives with functionalized endo substituents were amenable to living ROMP. Previously, these monomers were either reluctant to undergo polymerization or coordinated to the catalysts in a non-productive manner.

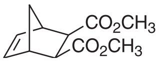
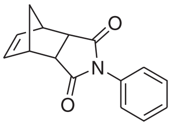
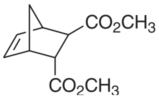
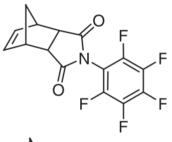
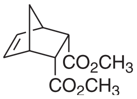
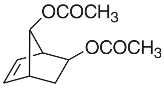
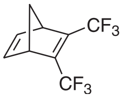
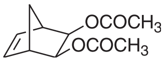
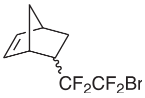
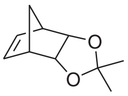
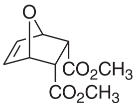


15a, R = *t*Bu
15b, R = $C(CH_3)_2(CF_3)$
15c, R = $C(CH_3)(CF_3)_2$
(R' = CH_3 or Ph)

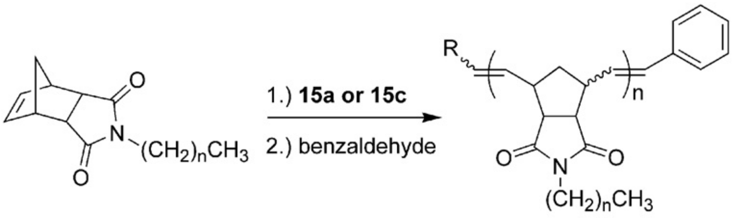
Fig. 17. Structures of Mo-based imido alkylidenes.

One common feature that these catalysts shared with their W precursors is that their activity could be tuned through modification of the alkoxide ligand. In general, complex **15a** does not readily react with acyclic olefins, limiting their ability to mediate secondary metathesis reactions when used in a ROMP. In contrast, their fluorinated derivatives **15b** and **15c** showed markedly increased activities and were found to rapidly isomerize 2-pentene and other acyclic olefins. The difference in activities of these catalysts in ROMP was demonstrated in a comparative study using various n-alkyl exo- and endo-norbornene dicarboximides [55]. As shown in Fig. 18, ROMP reactions catalyzed by **15a** afforded polynorbornenes with lower polydispersities than analogous reactions catalyzed with **15c**. The differences were ultimately attributed to the higher activity of the latter, but also to its relatively poor initiation characteristics. Thus, when used in ROMP applications it is important to monitor the polymerization to find timescales that optimize the rate of polymerization over rates of chain transfer reactions.

Table 1
ROMP of various monomers using **15a**

Functional group	Monomer structure	PDI	Functional group	Monomer structure	PDI
Ester		1.07	Imide		1.07
		1.04	Imide		1.05 (M/I = 50)
		1.12	Cyano		1.07
Carbonate		1.11	Halo		1.05
		1.19			1.06
Ether		1.07	Ether/Ester		1.17

Unless otherwise noted, [*M*/**15a**] = 100.



catalyst	monomer	polymer PDI
15a	exo (n = 6-11)	1.05 - 1.1
15c	exo (n = 6-11)	1.3 - 2.1
15a	endo (n = 8)	1.3
15c	endo (n = 8)	1.8

Fig. 18. Comparison of catalysts **15a** vs. **15c** in ROMP reactions.

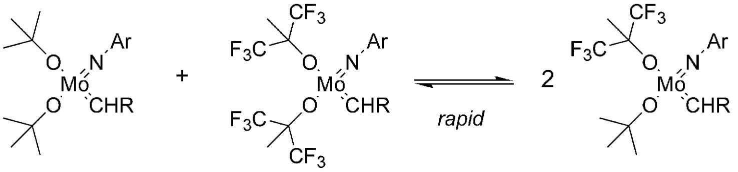


Fig. 19. Rapid alkoxy ligand exchange leads to an equilibrium of Mo catalysts. Since each catalyst exerts a different control over the stereochemistry of the resultant polymer, this equilibrium can be used to tailor cis/trans ratios along the backbones of polyalkenamers.

Notably, the high functional group tolerances combined with the high activities of the Mo-based catalysts enabled the preparation of synthetic analogues to biological polymers through the ROMP of endo-5-norbornene-2,3-dicarboximides obtained from the methyl esters of amino acids [56]. Star polymers were also obtained [57].

Another advantage of the Mo systems is their ability to provide stereoregular polymers. While certain conventional catalysts were well known to produce highly substituted polymer chains with high stereoregularity, it was discovered that well-defined Mo alkylidenes could also exert control over polymer stereochemistry [58]. For example, Schrock, Feast, and Gibson found that polymers obtained from the living ROMP of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene catalyzed by **15a** were highly tactic with a >98% trans olefin geometry exhibited along the polymer backbone. Interestingly, when the same ROMP reaction was catalyzed with **15c**, the resultant polymer was found to have >98% cis content (but was also highly tactic). Furthermore, they found that alkoxy ligand exchange was rapid on the timescale of the polymerization (see Fig. 19), enabling the synthesis of polymers with pre-determined amounts of cis/trans contents by initiating the ROMP with varying mixtures of **15a** and **15c**. Notably, these ROMP reactions were living and provided materials with tunable molecular weights and low polydispersities. A kinetic-based mechanism that balances the rates of interconversion of cis and trans rotamers of the alkylidene moiety with the rate of polymerization has been proposed to describe the origin of the stereochemical control in these catalysts [59]. This mechanistic knowledge was later used to create Mo-based catalysts based on C_2-symmetric diolate ligands, ultimately providing highly isotactic polymers via an enantiomorphic site-control mechanism [60].

In addition to norbornene based architectures, Mo-based catalysts were found to polymerize a range of cyclic olefins with varying degrees of ring-strain and functionality [61]. Polycyclopentene with controllable molecular weights and narrow polydispersities (PDI < 1.1) was obtained using catalyst **15a** [62]. As with the W mediated ROMP reactions noted above, a strong donor ligand (e.g. trimethylphosphine) was required. However, the Mo catalyst mediated the ROMP reaction in a living fashion at room temperature whereas use of the W catalyst required low temperatures. This feature enabled

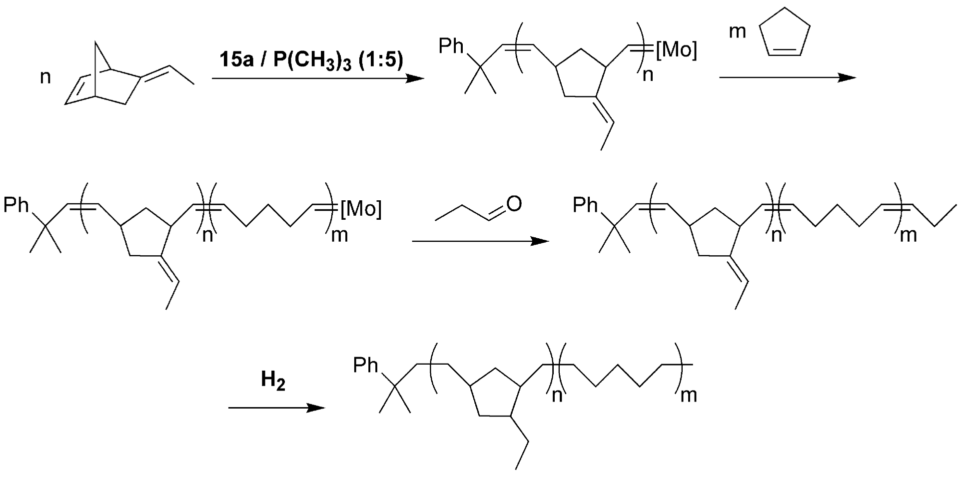


Fig. 20. Synthesis of crystalline/amorphous diblock copolymers via sequential ROMP of ethylidenenorbornene/cyclopentene followed by hydrogenation. Note that trimethylphosphine is necessary to achieve control over the ROMP of cyclopentene.

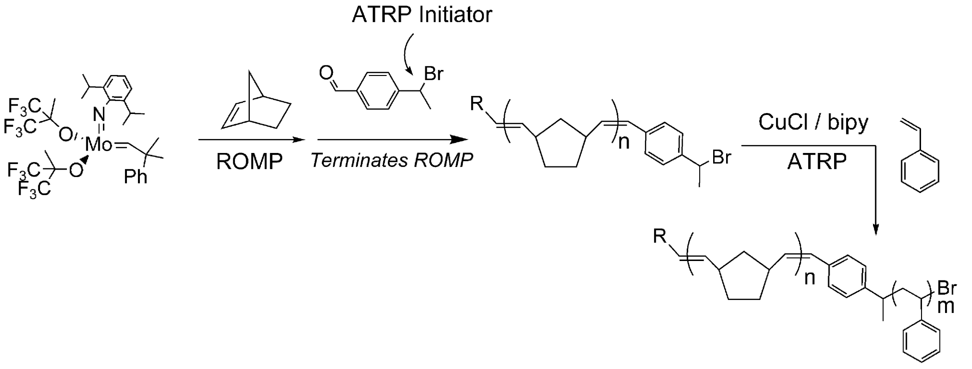


Fig. 21. Synthesis of poly(norbornene)-*b*-poly(styrene) block copolymers by combining ROMP with ATRP.

estimation of the equilibrium monomer concentration (at room temperature) for cyclopentene (1.3 M). Thus, performing the ROMP reactions at relatively high monomer concentrations (>2.8 M) and low catalyst loadings (initial monomer to catalyst up to 10 000) enabled the synthesis of polycyclopentenes with molecular weights up to 67 800 Da with PDIs as low as 1.04. The living nature of this ROMP enabled the synthesis of well-defined diblock copolymers comprised of polycyclopentene and polyethylidenenorbornene which, after hydrogenation, afforded a new diblock copolymer with crystalline and amorphous regions (see Fig. 20).

While this sequential monomer addition method was found to be useful for preparing diblocks, both monomers must be amenable to the same polymerization method. If two (or more) desired monomers cannot be polymerized by the same polymerization mechanism, then multiple steps are required. For example, poly(styrene)-*b*-poly(norbornene) and poly(methyl acrylate)-*b*-poly(norbornene) diblock copolymers have been prepared by combining atom-transfer radical polymerization (ATRP), a metal-mediated method for controlling radical polymerizations [63], with ROMP [64]. Norbornene was polymerized using ROMP and capped with an agent that was subsequently used as an initiator for the ATRP of styrene or methyl acrylate (see Fig. 21).

The Mo-based catalysts have also been used to polymerize a variety of 3-substituted cyclobutenes [65]. For example, 3-methylcyclobutene and 3,3-dimethylcyclobutene were independently polymerized using catalysts **15a–c**. After hydrogenation, these materials are effectively poly(ethylene-*alt*-propylene) and poly(ethylene-*alt*-isobutylene) copolymers which are very difficult to obtain using other

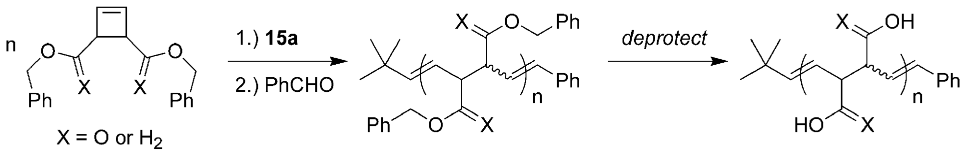


Fig. 22. Living ROMP of 3,4-difunctionalized cyclobutenes followed by deprotection.

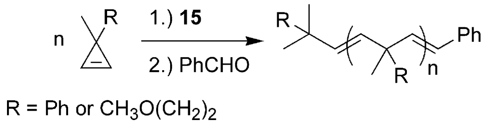


Fig. 23. Living ROMP of various 3,3-disubstituted cyclopropenes using various Mo based catalysts.

polymerization methods. Unfortunately, the high degree of ring-strain associated with this monomer prevented control over the ROMP and relatively polydisperse materials were obtained. As with the W catalysts, the rate of propagation is generally faster than the rate of initiation, leading to polydisperse materials. In contrast, the ROMP of 3,4-disubstituted cyclobutenes has been reported to be living and provides polymeric materials with well-defined structures [66]. For example, cis-cyclobutene-3,4-dicarboxylate and cis-3,4-bis(2-oxa-3-phenylpropyl)cyclobutene were polymerized using **15a**. Excellent control over the polymerization was observed and materials with very low polydispersities ($PDI < 1.15$) were obtained. However, in order to obtain living character, it was found essential to use catalyst **15a** in these polymerizations as the more active derivatives (e.g. **15c**) lead to extensive chain transfer and relative broad PDIs of the resultant materials. As shown in Fig. 22, these polymers were deprotected to provide a variety of high-strength adhesive materials.

Most recently, the living ROMP of cyclopropenes was reported using Mo catalysts [67]. As shown in Fig. 23, addition of a 3,3-disubstitutedcyclopropene to catalysts **15a–c** afforded the corresponding polycyclopropenamers in excellent yields ($>94\%$) after quenching the ROMP with benzaldehyde. Polymers obtained from these ROMP reactions exhibited molecular weights of approximately 10,000 Da (determined by GPC calibrated with polystyrene standards) with extremely narrow polydispersities ($PDIs < 1.05$). ^1H NMR spectroscopy suggested that the geometry of the olefins along the polymer backbones was predominately trans. Considering the paucity of examples reported in the literature on the polymerization of cyclopropenes, this result should provide a method for studying the thermodynamics of a new class of cyclic olefin amenable to ROMP and may lead to new elastomeric materials. Notably, reaction of 3,3-disubstitutedcyclopropenes with W alkylidenes **11** did not afford polymer and instead resulted in the corresponding W allylidenes (W = CH–CH = CHR) [68].

2.7. Ruthenium

Like most late transition metals, Ru shows low oxophilicity, which makes it inherently stable toward many polar functional groups. However, Ru also readily forms bonds with carbon which opens opportunities for mediating olefin metathesis reactions. Despite these advantages, the popularity and extensive utility of ruthenium in olefin metathesis has risen only recently [69]. Early reports on the use of Ru stem from the 1960s when it was discovered that $RuCl_3$ salts in protic media facilitated the polymerization of various norbornene derivatives [24,70]. Over two decades later, the use of this metal was reinvestigated for preparing charged polymers via ROMP [71]. During these studies, it was discovered that while the hydrates of $RuCl_3$ or Ru(*p*-toluenesulfonate)$_2$ were successful in mediating the non-living ROMP of various oxanorbornenes in aqueous or protic media, long initiation periods were required when the reactions were performed in organic solvents or when anhydrous conditions were employed [72]. Regardless, these catalysts were found to mediate the ROMP of functionalized norbornenes, 7-oxanorbornenes, and norbornadienes. More importantly, the ability to conduct these polymerizations in aqueous or protic media exemplified their extraordinary tolerance toward polar functionality. Attention soon shifted toward isolating a well-defined Ru alkylidene, since it was assumed that Ru based ROMP reactions proceeded by the same mechanism as for early metals [73]. For example, it was found that including various acyclic olefins during ROMP reactions resulted in polymeric materials with end-groups containing functional groups from the added olefins [74]. Additional evidence stemmed from detailed NMR analyses, indicating that the microstructure of the polymers produced from Ru catalysts were similar to those produced from well-defined metal alkylidenes (ruling out radical, ionic, and other types of chain addition polymerizations processes).

The first well-defined, single-component Ru complex that showed activity in ROMP was $(PPh_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$ (**16**) [75]. The synthesis of this complex was facilitated by adopting synthetic methodology used to prepare some of the W-based alkylidene complexes mentioned above. Specifically, treatment of $(PPh_3)_3RuCl_2$ or $(PPh_3)_4RuCl_2$ with 3,3-diphenylcyclopropene afforded **16** in nearly quantitative yields. The complex is stable in degassed and dry organic solvents (benzene, dichloromethane, etc.) for extended periods of time (>weeks). It is stable indefinitely in the solid state. The complex also does not show appreciable decomposition after exposure to water, various alcohols, or ethers and does not react with aldehydes and ketones in a Wittig-type fashion. This well-defined Ru complex was found to mediate the ROMP of norbornene in a living fashion with outstanding activity. For example, as shown in Fig. 24, addition of norbornene to **16** resulted in a polymer chain with a propagating alkylidene species observable by ^1H NMR spectroscopy ($\delta = 17.79$ ppm). However, upon the addition of 2,3-dideuterionorbornene, the signal disappeared. Introduction of additional (2,3-diprotio-) norbornene restored the signal and effectively produced a triblock copolymer of the two monomers. The polymerizations were terminated through the addition of ethyl vinyl ether which replaced the Ru alkylidenes on the termini of the polymer chains with a methylidene and formed a metathesis inactive Fischer carbene complex ([Ru] = CHOR) [76]. Although the rate of initiation was found to be slower than the rate of propagation, quantitative initiation was accomplished through the addition of excess monomer. Importantly, secondary metathesis reactions were minimal. Catalyst **16** was also found to mediate the living ROMP of bicyclo[3.2.0]heptane and trans-cyclooctene, and block copolymers of these monomers with norbornene were successfully prepared [77].

While Ru catalyst **16** showed an impressive tolerance to a broad array of functionality and was capable of mediating living ROMP reactions of norbornene and cyclobutene derivatives, the catalyst did not show appreciable activity toward other olefins. In accord with the studies on other catalyst

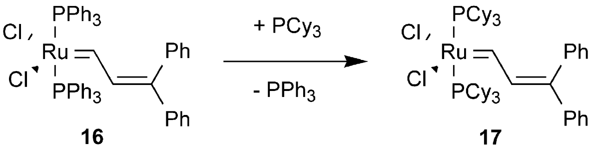


Fig. 25. Structures of various Ru vinylidene complexes and conversion to a more active derivative via phosphine exchange.

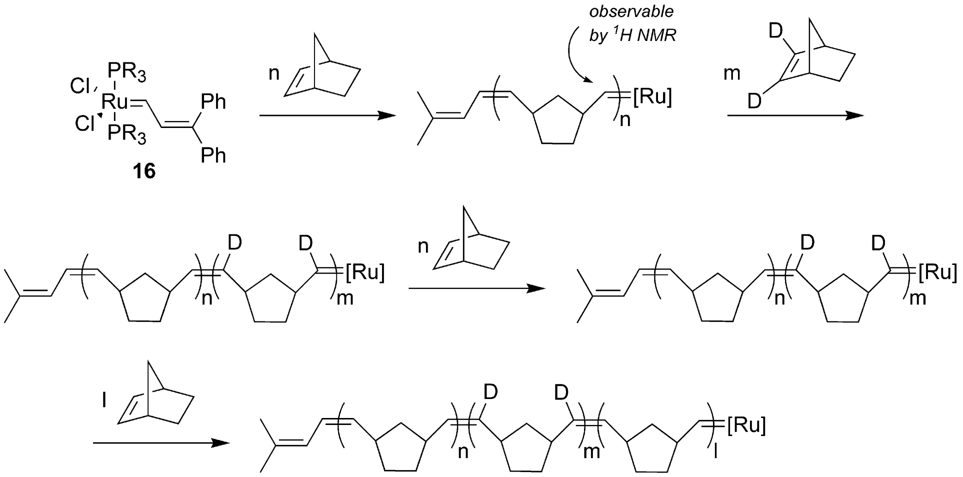


Fig. 24. Sequential living ROMP of norbornadiene and 2,3-dideuterionorbornene using a well-defined Ru alkylidene effectively affords a triblock copolymer. Note that the ROMP is quenched with ethyl vinyl ether which installs a methylidene unit on the terminus of a polymer chain and forms a Fischer-type carbene ([M] = CHOR) with very low metathesis aptitude.

systems mentioned above, attention soon shifted toward optimizing the ligand environment of the Ru center. The most convenient method to optimize activity was to vary the nature of the phosphine ligand. Ultimately, it was discovered that the use of bulky and electron rich phosphines (e.g. PCy_3) lead to highly active catalysts. This trend contrasts the Schrock catalyst in which higher activities were found with electron withdrawing ligands. Synthetically, this phosphine exchange reaction was relatively simple to perform and was accomplished by adding an excess of PCy_3 (or $P(iPr)_3$) to **16** [78] (see Fig. 25). The resultant complexes $(PPCy_3)_2Cl_2Ru{=}CH–CH{=}CPh_2$ (**17**) were found to be more stable and exhibit a broader range of tolerance toward functionality than their precursors. For example, in addition to water and alcohols, these complexes were found to be stable toward organic acids (acetic acid) as well as solutions of strong inorganic acids (diethyl ether solutions of HCl). While these complexes were found to polymerize norbornene, they did not show significant control over the reaction. Their highly active nature exasperated the differential between the rate of initiation versus the rate of propagation. In addition, there was some evidence that chain transfer reactions were occurring [79]. Thus, polynorbornenes obtained from the ROMP of norbornene using catalyst **17** generally exhibited high molecular weights ($M_n > 10^5$ Da) with broad polydispersities (PDI > 2). However, these catalysts opened new opportunities in the living ROMP of functionalized monomers that were less reactive than norbornene. For example, as shown in Fig. 26, block copolymers of monomers containing Si functionalities were prepared using these Ru catalysts [80].

Large quantities of metathesis-active Ru alkylidenes were soon available once an alternative

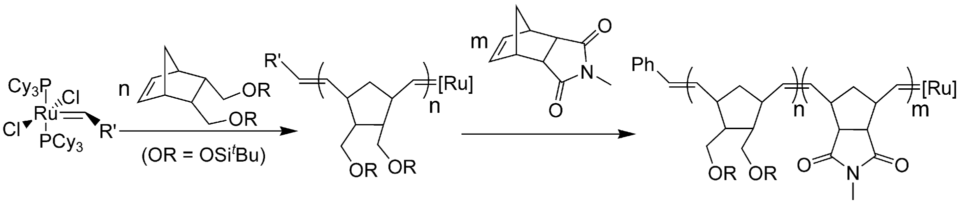


Fig. 26. Synthesis of block copolymers using Ru alkylidenes.

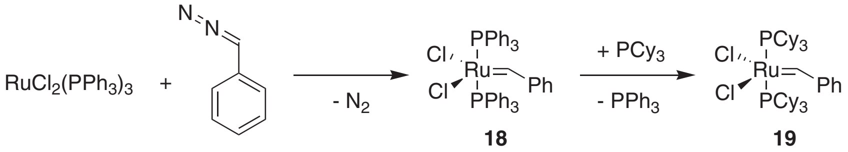


Fig. 27. Synthesis of well-defined Ru benzylidene complexes.

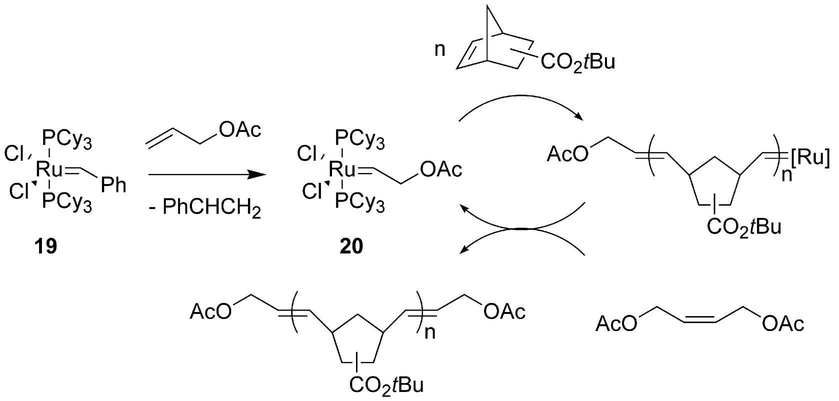


Fig. 28. Synthesis of telechelic polymers using an acetoxy-functionalized Ru initiator.

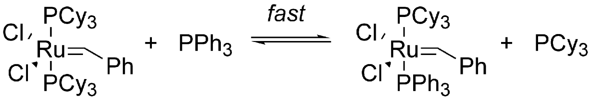
synthesis involving the treatment of $(PPh_3)_3RuCl_2$ with diazobenzylidene was developed (see Fig. 27). The resulting complex **18** can be readily converted into its more active derivative **19** via phosphine exchange and also converted to other alkylidene catalysts by simply adding the corresponding terminal olefin, which was found to have important influences over initation efficiencies in ROMP reactions [81]. (The parent benzylidene complex appears to have the most favorable initiation kinetics in ROMP reactions.)

The ability of these Ru catalysts to react with terminal olefins also provided a convenient method for functionalizing the end-groups of polymer chains. For example, as shown in Fig. 28, Gibson prepared a series of end-functionalized polymers using Ru complex **20** (prepared by reacting **19** with allyl acetate). This ROMP initiator effectively placed an acetoxy group on one terminus of the polynorbornene chain and an active Ru alkylidene at the other end. Upon the conclusion of the polymerization (i.e. after all the monomer was consumed), 1,4-diacetoxy-2-butene was added, effectively installing an acetoxy group on the growing end of the polymer chain and re-forming the functionalized initiator. Ultimately, this produced a polymer with acetoxy groups on both ends of the polymer chains (a so-called "telechelic polymer") [82].

Complex **19** was also found to polymerize a wide variety of functionalized norbornenes and cyclobutenes, many of which contained pendant alcohol, amino, ester, amido, and keto functional groups, in a living manner and in protic media [83]. In addition to exhibiting a high tolerance for most functional groups, **19** was also found to be relatively thermally stable with a half-life of over a week at 55 °C [84].

The ability to prepare designer Ru catalysts was used to address a fundamental problem in the synthesis of block copolymers composed of segments that cannot be prepared by the same polymerization mechanism. While a variety of coupling or chain transfer strategies have been put forth, from a practical standpoint it would be ideal to use a single component catalyst to mediate multiple mechanistically distinct reactions to form block copolymers directly. As shown in Fig. 29, this was effectively accomplished through the synthesis of a difunctional initiator that effectively mediated the ROMP of cyclooctadiene and the Ru-mediated ATRP of methyl methacrylate to form a variety of poly(butadiene)-*b*-poly(methyl methacrylate) block copolymers in a single step [85].

As noted above, the more active Ru alkylidenes possessing trialkylphosphine groups were unable to polymerize norbornene and many of its derivatives in a highly-controlled manner due to poor initiation characteristics and (slow) secondary metathesis reactions. One solution to this problem was reported by Gibson who capitalized on the ability to readily exchange the ligands on these catalysts and produced a catalyst with increased initiation characteristics [86]. However, as a direct result of extensive mechanistic analyses, it was determined that the rate of phosphine exchange was significantly faster than the rates of reactions with olefins in the bisphosphine Ru alkylidene complexes. In addition, the triphenylphosphine derivatives of these catalysts exhibit elevated rates of initiation. Collectively, this suggested an alternative solution to the problem of slow initiation. It was envisioned that addition of relatively labile phosphines such as PPh_3 to complexes **19** during a ROMP would enhance the initiation efficiency of these complexes. Since phosphine exchange is fast, complex **21** should form in situ and exhibit better initiation



19 **21**

Fig. 30. In situ synthesis of mixed phosphine Ru alkylidenes (**21**) that show high initiation kinetics in ROMP reactions.

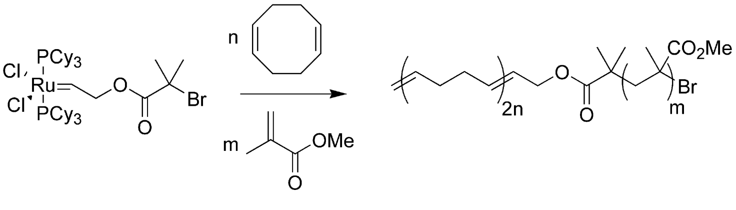


Fig. 29. Synthesis of block copolymers composed of two mechanistically distinct segments through a tandem living ROMP—living ATRP reaction using a single component catalyst.

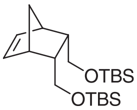
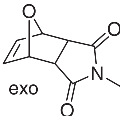
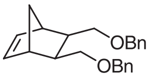
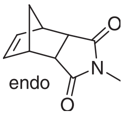
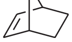
characteristics. In essence, phosphine would compete with monomer for the propagating species and effectively lower the rate of propagation. Indeed, inclusion of triphenylphosphine (1–5 equivalents) in the ROMP of various norbornene derivatives reduced the PDIs from 1.25 to as low as 1.04 [87] (see Fig. 30).

Simultaneous to studies involving the use of these catalysts in various ROMP reactions, tremendous effort was directed toward understanding the mechanism of these Ru catalysts [88]. It was determined that the mechanism to the olefin metathesis reaction was dissociative in nature. Thus, a phosphine ligand must separate from the catalyst before olefin coordination (and subsequent reaction) may occur. Stabilization of these coordinately unsaturated intermediates was also necessary to prevent premature catalyst decomposition. N-heterocyclic carbenes (NHCs) were known to be strong σ-donors yet less labile than phosphines [89]. They are less likely to dissociate from the catalyst but also provide increased electron density to stabilize intermediates. Ultimately, a mixed-ligand system (**22**) was designed and synthesized through a phosphine exchange type reaction [90] (see Fig. 31).

Complex **22** was shown to possess exceptional activities in a large number of ROMP reactions [91]. For example, **22** was found to polymerize cis-cyclooctadiene at higher rates than Schrock's Mo-based catalysts and could also ROMP 1,5-dimethyl-cyclooctadiene as well as 1,3,5,7-cyclooctatetraene [92]. However, this catalyst generally provides polymers with uncontrollable molecular weights and broad polydispersities. This has been attributed to relatively slow rates of initiation coupled with competing secondary chain transfer reactions. By tuning the ligand environment, a new class of Ru-based metathesis catalysts (**23**) containing strongly ligating NHCs with weakly coordinating pyridines was developed (see Fig. 32) [93]. These catalysts displayed not only extremely high activities in ROMP but also exhibited fast initiation kinetics as a result of the labile nature of the pyridine ligands. As a result, living ROMP reactions were achieved with Ru catalysts ligated to N-heterocyclic carbenes.

As summarized in Table 2, a wide range of monomers have been polymerized using catalyst **23**. Notably the PDIs of the resultant polymers were extremely low. It is also notable that a

Table 2
ROMP of a variety of cyclic olefins mediated by catalyst **23**

Monomer	M_n (GPC)	M_n (theo)	PDI
	24500	38300	1.06
	29100	18000	1.05
	30400	33500	1.05
	22900	17800	1.08
	28700	19900	1.10
	9000	9500	1.09

In all cases, the initial monomer to catalyst ratio was 100:1. The theoretical molecular weights assume quantitative conversion. The last example (norbornene) was performed at −20 °C.

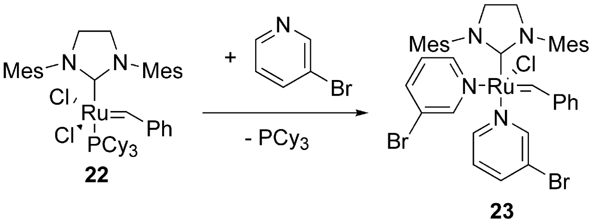


Fig. 32. Synthesis and structure of Ru alkylidene ligated to a N-heterocyclic carbene that exhibits rapid initiation kinetics.

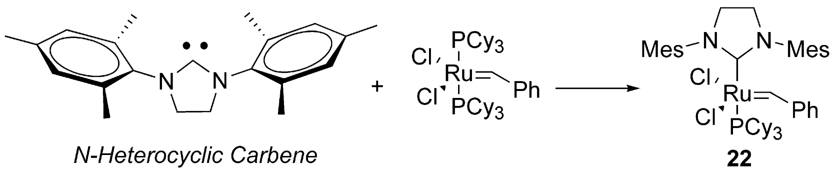
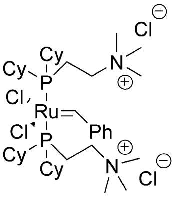


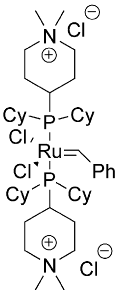
Fig. 31. Synthesis of well-defined a Ru alkylidene ligated to a N-heterocyclic carbene.

polynorbornene was prepared with a PDI as low as 1.06. However, it was important that in this case the ROMP was conducted at −20 °C to suppress secondary chain-transfer reactions. As a testament to the living nature of these polymerizations, a variety of diblock copolymers were also prepared using this catalyst.

The ability to readily replace phosphines on the catalysts also led to the development of water-soluble Ru-based catalysts for aqueous ROMP applications. By incorporating charged phosphines, water soluble Ru complexes **24** and **25** were obtained (see Fig. 33) [94]. While both of these catalysts are metathesis active, they do not mediate living ROMP reactions because the propagating species are unstable and rapidly decompose. However, it was later determined that decomposition was enhanced in the presence of base which prompted the notion that the catalyst instability was due to the presence of a small amount of hydroxide in solution. This limitation was readily resolved by adding a strong Brønsted acid (e.g. HCl) during the ROMP reaction. Interestingly, the acid not only sequesters any hydroxide that may be present in solution, but it has the added effect of promoting initiation through phosphine protonation. Ultimately, this led to living aqueous ROMP reactions. In particular, as shown in Fig. 34, the living ROMP of water soluble norbornene derivatives afforded homopolymers with PDIs of <1.24 as well as block copolymers of these two monomers. Water soluble quenching agents such as triethyleneglycol methyl vinyl ether were found to effectively terminate these polymerizations. More recently, water soluble catalysts bearing NHC ligands have been prepared and were found to show extremely high activities in aqueous ROMP reactions [95].



24



25

Fig. 33. Water soluble, well-defined Ru alkylidenes that show high metathesis activity in aqueous media.

3. Challenges and perspectives for the future

The ability to exert exquisite control over macromolecular structure and function remains a central aim in polymer chemistry. As noted in the introduction, the advent of living polymerizations has resulted in a significant step toward this goal by providing a method to tune the size and polydispersity of many types of macromolecular materials. However, advancement of the field will continually require the development of new synthetic methodologies.

The introduction of well-defined catalysts that mediate living ROMP has pushed the frontier of living polymerization. As a result of these catalysts, an impressively broad range of monomers, many of which are densely functionalized, may now be polymerized to nearly any shape or size. Another advantage of living ROMP reactions is an ability to prepare a wide range of copolymeric materials as well as materials with advanced topologies. Indeed, many of these materials have found utility in biological and electronic applications. However, living ROMP is not a solved problem. Several remaining challenges are listed below.

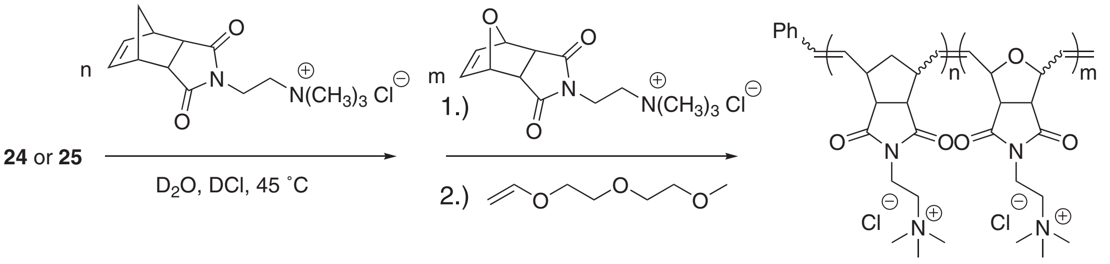
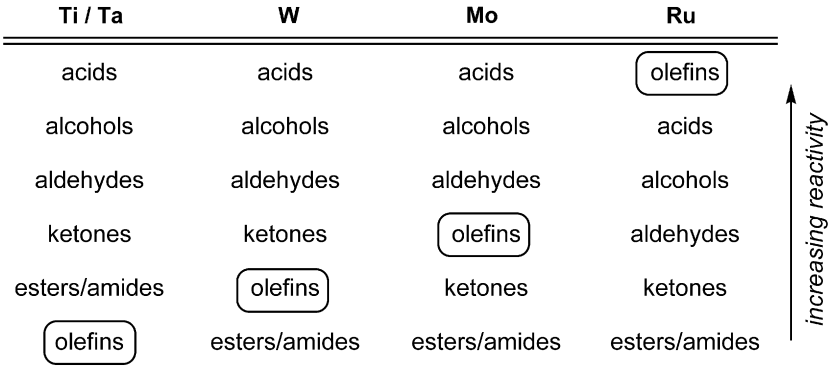
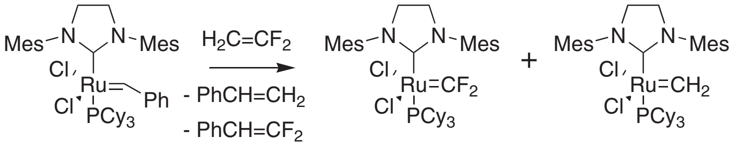


Fig. 34. Examples of living ROMP reactions that were conducted in aqueous media.



Ti / Ta	W	Mo	Ru
acids	acids	acids	olefins
alcohols	alcohols	alcohols	acids
aldehydes	aldehydes	aldehydes	alcohols
ketones	ketones	olefins	aldehydes
esters/amides	olefins	ketones	ketones
olefins	esters/amides	esters/amides	esters/amides

Fig. 35. Functional group tolerance of various olefin metathesis catalysts based on early vs. late transition metals.



22 **26**

Fig. 36. Synthesis of Ru difluoromethylidenes (**26**) via reaction of **22** with 1,1-difluoroethene. Note that complex **26** was found to be active in initiating the ROMP of 1,5-cyclooctadiene.

3.1. Development of new catalysts

Nearly every advance in ROMP can be traced to an advance in catalysis. As such, the future of living ROMP is critically dependent on the development of new catalysts which includes finding new transition metals and new ligands. It has been shown that late transition metals are inherently more stable toward polar functional groups (for a summary, see Fig. 35) and, through proper ligand choice, can often exhibit activity in ROMP reactions comparable to their predecessors based on early transition metals. This trend suggests that future generations should look toward other late transition metals such as Fe or Re. However, this will be challenging as Fe alkylidenes generally prefer to cyclopropanate olefins and there are only a handful of examples demonstrating that Re catalyzes metathetical reactions [96]. For Ru-based catalysts, it is clear that highly donating ligands enhance activity. Efforts should continue to focus on finding new ligands that exceed the electron donating abilities of NHCs. Ultimately, the ideal catalyst for living ROMP reactions will react with cyclic olefins exclusive to all other types of functionality. This will be a challenging task, however, as often high activity equates to increased chances for secondary metathesis reactions, which limits their potential in living ROMP reactions.

3.2. Polymerization of "new" and "old" monomers

The field of living ROMP will also be dependent on an ability to polymerize new monomers. For example, one area that has been underdeveloped is the ROMP of highly halogenated cyclic olefins. It has been shown that Ru catalysts react with 1, 1-difluoroethylene to afford Ru difluoromethylidene complex **26**. This complex was subsequently found to be active in initiating the ROMP of 1, 5-cyclooctadiene (see Fig. 36) [97]. With the right ligand environment (or transition metal), ROMP may one day be used to polymerize highly halogenated olefins such as perfluorocyclobutene. Another challenging area is the polymerization of tri- and tetrasubstituted cyclic olefins. The synthesis of tetrasubstituted olefins has recently experienced considerable growth due to advances in ring-closing and cross metathesis reactions. This results may offer clues for exploring the ROMP of substituted cyclic olefins.

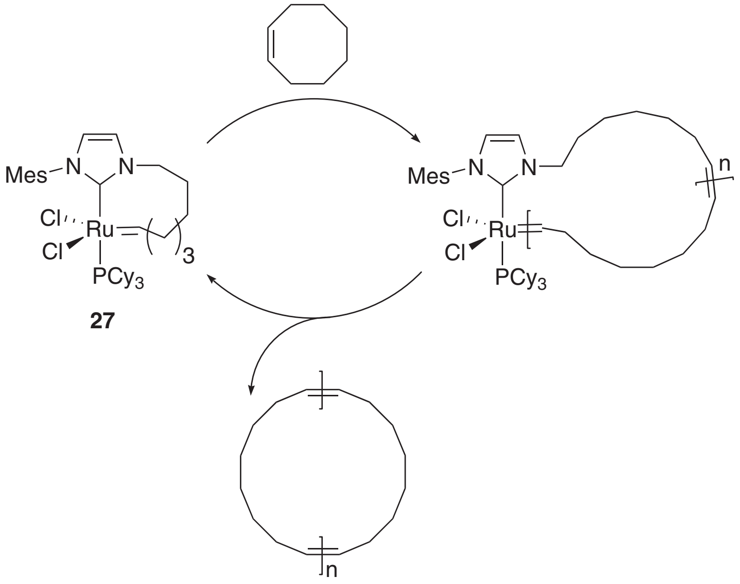


Fig. 37. Synthesis of cyclic polymers using ROMP. Addition of cis-cyclooctene to **27** resulted in the formation propagating species where both ends of the polymer chains are connected to the same metal center. Subsequent intramolecular chain transfer provides cyclic polymer and regenerates **27**.

Another means to push the frontier of living ROMP is to develop new catalysts to obtain polymeric materials with interesting topological features from "old" monomers. The Ru catalysts discussed above are particularly suited for such application as both the alkylidene and the phosphine/NHC ligands can be extensively modified. This concept was demonstrated in the synthesis of water soluble catalysts through the incorporation of water soluble phosphine ligands which enabled living ROMP in aqueous media. More recently, this concept was used to design a catalyst that provided cyclic polymers [98]. As shown in Fig. 37, the addition of cis-cyclooctene to complex **27** affords a propagating species where both ends of the polymer chains remain attached to the metal center. At some point later in time, an intramolecular cyclization reaction occurs and effectively provides a cyclic polymer. This approach effectively eliminates the need for linear polymeric precursors and high dilution which were drawbacks of traditional strategies for preparing these materials.

4. Conclusion

Fifty years ago, Szwarc introduced the concept of a "living" polymerization. This technique changed the way polymer chemists think about preparing well-defined macromolecular materials and has resulted in numerous scientific advances, many of which can be found in contemporary society. Coincidentally, the olefin metathesis reaction was also introduced about fifty years ago. In some ways, this reaction also changed the way polymer chemists think about preparing macromolecular materials.

The original metathesis catalysts were ill-defined mixtures consisting of several metals, additives, and specialized conditions. As the direct result of advances in the field of catalysis, a series of well-defined catalysts based on a range of metals including titanium, tantalum, tungsten, molybdenum, and ruthenium have been prepared. Through subsequent optimization, living ROMP catalysts based on each of these metals have been synthesized. These catalysts have found utilities in numerous applications, most notably in the synthesis of macromolecular materials with interesting biological, electronic, and mechanical properties.

Finally, it is important to note that a "universal" catalyst does not exist and each of the aforementioned catalysts possesses their own inherent advantages and disadvantages. Considering the broad range of catalysts available, it should be possible to find one that meets a specific need or application. If not, the synthetic diversity available to each of these catalysts should facilitate the necessary modifications.

Acknowledgements

The authors wish to thank the researchers who have made significant contributions to living ROMP and related areas. In addition, the support of the NSF and ONR of the author's research in the area is particularly appreciated.

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