Chapter 1

Introduction

Olefin Metathesis

Olefin metathesis is a versatile carbon-carbon bond rearrangement reaction, catalyzed by transition metal complexes.[1] First proposed by Chauvin in 1971, the mechanism for olefin metathesis involves olefin coordination to a metal carbene and subsequent cycloaddition to form a metallocyclobutane intermediate. This metallocyclobutane can undergo cleavage either in a productive manner to afford a new olefin and a new metal carbene complex or in a non-productive manner to regenerate starting materials (Figure 1). In general, each step in olefin metathesis is a thermodynamically controlled, reversible equilibrium process and requires a driving force, such as the release of ring strain or the loss of a volatile small molecule, to obtain the desired products.

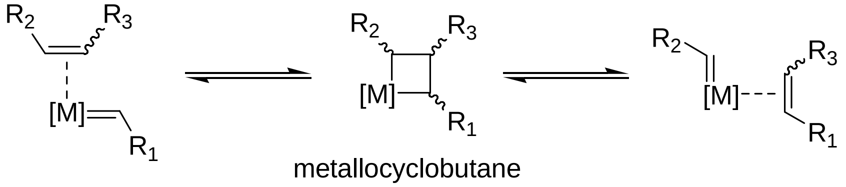
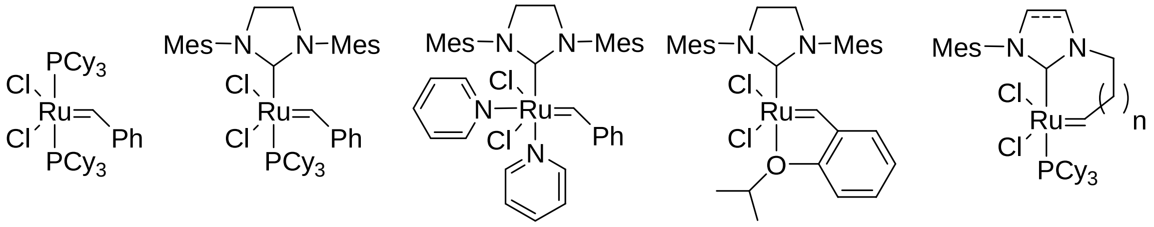


Figure 1. General mechanism of olefin metathesis.

In the first two decades of olefin metathesis (early 1960s to early 1980s), a number of ill-defined multicomponent catalysts were found active to mediate olefin metathesis.[1] The first isolated, well-defined, single-component olefin metathesis catalyst, reported by Gilliom and Grubbs in 1986, was obtained by reacting the Tebbe reagent with norbornene and it was able to catalyze living polymerization of norbornene.[2] Meanwhile, a variety of highly active, well-defined Mo and W based catalysts were developed by the Schrock group.[3] Despite their high reactivity, early transition metal-based catalysts exhibited extreme air and moisture sensitivity, low thermal stability, and poor tolerance for many functional groups, such as alcohols and aldehydes, due to the electrophilic nature of these metals.

To improve the catalyst stability and functional group tolerance, a new class of Ru-based catalysts was developed by the Grubbs group in the early 1990s.[4] Among them, the Ru(II) benzylidene complex **1** with tricyclohexylphosphine ligands (PCy_3) showed high activity as well as tolerance of air, moisture and a wide range of functional groups,[4] and is now often recognized as the first-generation Grubbs catalyst. Later in 1999, a significant improvement of catalyst activity was achieved by replacing one of the PCy_3 ligands with a strongly sigma-donating donating N-heterocyclic carbene (NHC) ligand.[5] Ru complex **2** not only maintained superb tolerance for air, moisture and organic functionalities, but also rivaled the activity of the highly active molybdenum catalysts.[6] Complex **2** is now often recognized as the second-generation Grubbs catalyst. Following the success, numerous NHC-based Ru catalysts have been synthesized and studied. Some representative examples include (1) replacing the PCy_3 ligand with pyridine to give catalyst **3** that initiated extremely fast, making it an ideal catalyst for living polymerization to produce narrowly dispersed polymers; [7] (2) incorporating an isopropoxybenzylidene ligand to give catalyst **4** to impart increased stability relative to phosphine-containing analogues;[8] (3) tethering the NHC to the Ru center to give a series of catalysts **5** that can produce cyclic polymers.[9]



1 **2** **3** **4** **5**

Figure 2. Representative ruthenium-based olefin metathesis catalysts.

Ring-Opening Metathesis Polymerization (ROMP)

As one of the most important polymerizations, ROMP is a chain-growth polymerization in which cyclic olefins are converted to polyalkenamers. The overall reaction involves breaking and reforming olefin double bonds with simultaneous opening of the unsaturated cyclic monomers. Thus, the total amount of unsaturation is retained, and the resulting polymers are comprised of repeating units that contain olefins in their backbones. The release of ring strain provides the driving force for ROMP to proceed. Typical cyclic olefin monomers for ROMP in order of decreasing ring strain include cyclobutene, norbornene, cyclooctene, cyclododecatriene, and cyclopentene, (Figure 3).

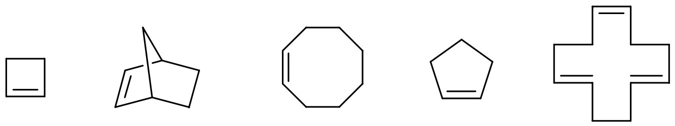


Figure 3. Representative cyclic olefin monomers used in ROMP.

Unhindered backbone olefins in the polyalkenamers can also undergo secondary metathesis since ROMP is equilibrium controlled. Intermolecular secondary metathesis leads to transfer of the active metal center from one polymer chain end to another chain and the total number of polymer chains does not change (Figure 4(a)). The active metal center at a polymer chain end can also react with an internal olefin in its own polymeric backbone, thus producing a macrocycle, and this intramolecular secondary metathesis is often referred as backbiting (Figure 4(b)).[10] To minimize the concentration of cyclic oligomers, polymerizations should be performed at conditions that minimize the relative equilibrium monomer (typically high monomer concentration and low temperatures for exothermic polymerizations). Both intermolecular chain transfer and backbiting result in broadening of the polymer molecular weight distributions, and should therefore be avoided when living polymerization is desired.

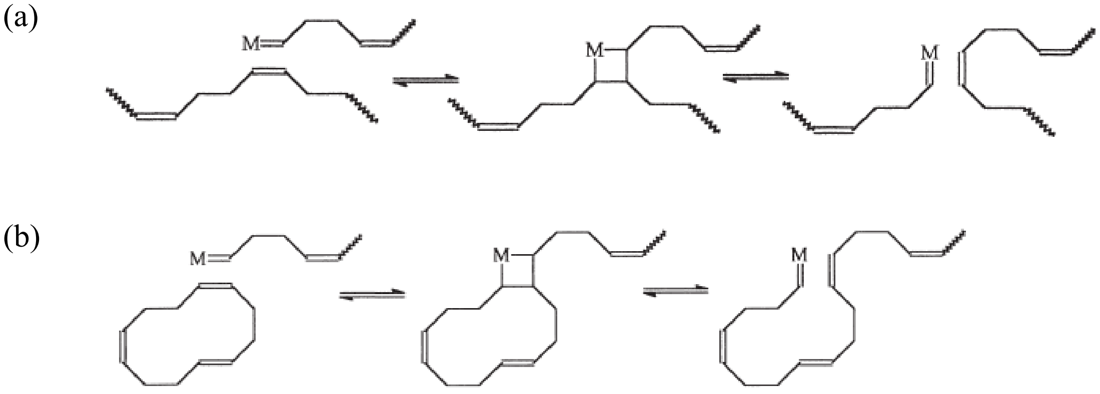


Figure 4. Secondary metathesis reations: (a) intermolecular chain transfer; (b) intramolecular back-biting.

On the other hand, intermolecular chain transfer (CT) can also be advantageous to produce telechelic polymers when an α,γ-difunctional olefin is employed as chain-transfer agent (CTA).[11] In the CT reaction with a symmetric α,γ-difunctional olefin, a propagating polymer chain is terminated with a functional group and forms a new substituted metal alkylidene. This complex subsequently reacts with monomer or a preformed polymer chain and effectively transfers the active species from one chain to another (Figure 5). This process preserves the number of active catalyst centers and leads to symmetric telechelic polymers with a number average functional groups per chain approaching 2. In the absence of chain termination (i.e., decomposition of the active metal center at the chain end), the only non-functional end group comes from the benzylidene or alkylidene in the original catalyst. Therefore, it is important to use a minimal amount of catalyst compared to the CTA. Catalysts **2** and **4** are best suited for ROMP-CT due to their extraordinary activity and high stability. If the catalyst does not decompose during the course of ROMP, the molecular weight (MW) of the polymer product is controlled by an equilibrium process. Therefore, if the catalyst concentration ($[C]_0$) is chosen such that $[CTA]_0 >> [C]_0$, then the average degree of polymerization (DP) is determined by

$DP = ([M]_0 - [M]_t) / ([CTA]_0 - [CTA]_t)$.

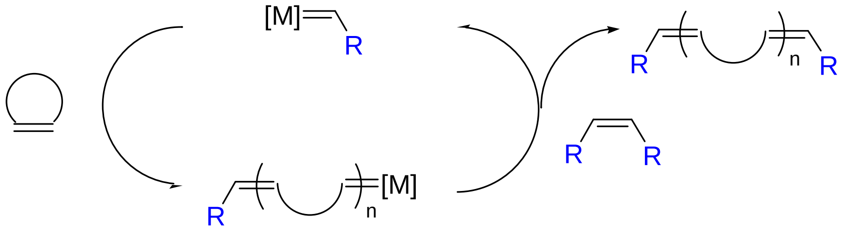


Figure 5. Generic mechanism of chain transfer in ROMP to generate telechelic polymers.

ROMP can also be controlled to behave as a living/controlled polymerization: (1) complete and instantaneous initiation to ensure each polymer chain starts to grow at approximately the same time; (2) irreversible propagation and the propagation rate (k_p) is much smaller than the initiation rate (k_i) to ensure all the polymer chains grow simultaneously; (3) absence of chain termination and chain transfer to ensure all the propagating chain ends remain active. In order to eliminate the secondary metathesis on the polymer backbones, sterically bulky bicyclic monomers, such as substituted norbornenes, are often used. Living ROMP is also possible with monocyclic, unhindered olefins, such as cyclobutene, cyclopentene, and *trans*-cyclooctene, with the use of excess free phosphine ligands to significantly suppress the secondary metathesis.[12] Both catalysts **1** and **3** can mediate living ROMP due to their fast initiation, but catalyst **3** has become the state-of-the-art choice due to its much more improved initiation and activity. The extraordinary activity of catalyst **3** has enabled rapid synthesis of polymers with very low polydispersity indices (PDI) from norbornenes with various functionalities, and full monomer conversion is usually achieved within minutes.[13] Living ROMP has also significantly simplified the synthesis of block copolymers, simply through sequential addition of different monomers, which do not undergo chain transfer.[14]

Expansion of Polymer Chemistry Toolbox

Besides metathesis polymerizations, polymer chemistry has undergone some other important developments over the last two decades. These relatively new developments, together with the well-known ones, greatly enhanced the ability of polymer chemists to control the molecular weight distribution, functionality, microstructure, and architecture of polymers.

Living Ionic Polymerizations

Developed in the 1960s, ionic polymerizations were once the state-of-the-art living polymerization techniques (for certain types of polymers, still the best techniques to produce the highest-quality polymer products, if performed well). Cationic polymerization is suitable for olefin monomers with electron-donating substituents such as alkoxy and phenyl.[15] Anionic polymerization takes place with monomers possessing electron-withdrawing groups such as nitrile, carbonyl, and phenyl.[16]

Limited monomer functionality, rigorously purified monomer and solvent, and low temperatures are required to suppress termination and chain transfer. A suitable solvent is also important to stabilize the ionic propagating species long enough to propagate into high MW polymers. These stringent requirements make the utility of ionic polymerizations relatively limited.

Controlled Radical Polymerizations

The last 15 years have witnessed the explosive development of controlled radical polymerizations (CRPs) that mainly include atom-transfer radical polymerization (ATRP),[17] reversible addition fragmentation chain-transfer (RAFT) polymerization,[18] and nitroxide mediated radical polymerization (NMRP).[19]

All the CRP methods are based on the same idea: (1) a dynamic equilibrium is established between a low concentration of active propagating chains and a large amount of dormant chains (unable to propagate or terminate) via rapid, reversible chain-end capping or chain transfer reaction; (2) the propagation and deactivation of the active radicals, namely reversible termination or chain transfer reaction, are much faster than any irreversible termination to minimize the chance of irreversible termination and ensure that all polymer chains are growing at approximately the same rate to obtain uniform molecular weight distribution.

ATRP has been the most widely used and versatile CRP method, and it uses a catalytic amount of a transition metal complex, often copper or ruthenium, to reversibly abstract a halogen atom from a polymer chain end, and thereby transform the chain end group into an active propagating radical from a dormant state. This dynamic equilibrium strongly favors the dormant species ($K_{eq} = 10^{-9}$-10^{-7}). Therefore only a minute concentration of growing free radicals is maintained, and thus bimolecular termination and disproportionation are minimized.

Similarly, in NMRP, unstable alkoxyamine can thermally initiate and the nitroxide radicals reversibly trap the propagating radicals to maintain a low concentration of growing free radicals.

RAFT polymerizations utilize a di- or trithiocarbonyl chain transfer agent (CTA) to degeneratively chain transfer between the propagating chain ends: propagating chain end radical addition to the C=S bond in CTA is followed by rapid reinitiation through S-C bond cleavage to release another propagating chain with an active radical chain end.

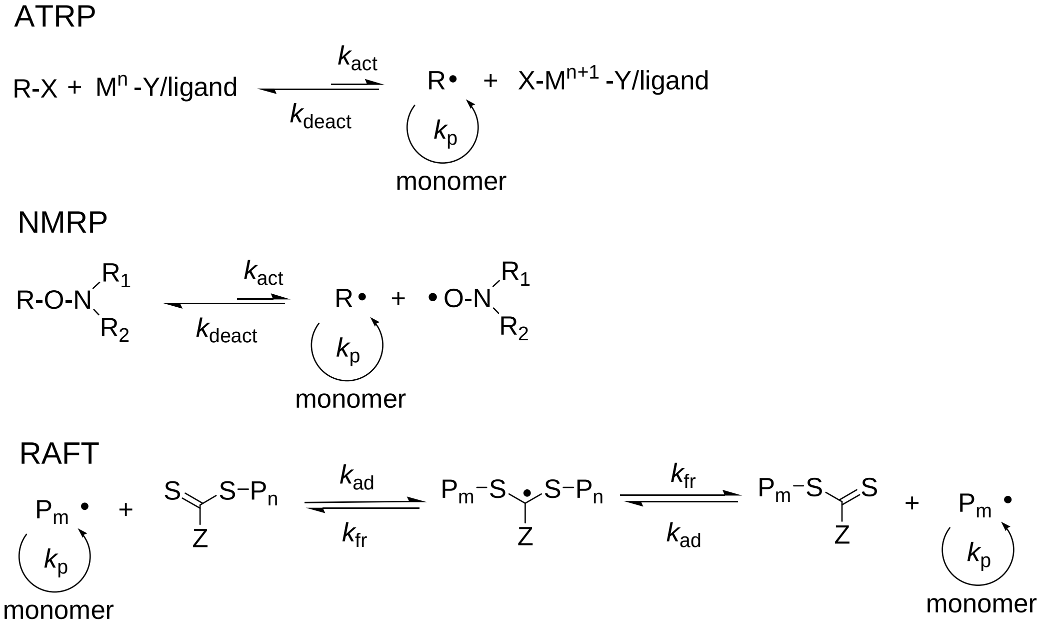


Figure 6. Generic mechanism of controlled radical polymerizations: ATRP, NMRP, and RAFT.

"Click" Chemistry

One of the most noticeable synthetic trends in the past decade is "click" chemistry, a concept first introduced by Sharpless, Kolb, and Finn in 2001,[20] which had an enormous impact on materials synthesis. The basic philosophy of "click" chemistry is to develop reactions that have

- High chemoselectivity
- Quantitative yield with little or no by-products
- Robustness to various experimental conditions

- Fast kinetics
- Functional group tolerance
- Simple and mild reaction conditions

A few modular reactions that meet these criteria involve easy-to-introduce functional groups and often have a large thermodynamic driving force to favor a single reaction product. The most notable "click" reaction is copper-catalyzed Huisgen azide–alkyne cycloadditions (CuAAC). Catalytic amount of copper(I) from various sources can be used to give exclusively 1,4-triazoles. The reaction can also be carried out in air and in water, by formation of copper(I) *in situ* using a one-electron reductant such as sodium ascorbate. In applications where residual copper may be a concern, strained cyclooctynes have been found to spontaneously undergo quantitative and selective cycloaddition with azides even in living biological systems.[21]

Other popular "click" reactions include: radical thiol-ene coupling, activated ester couplings, Michael addition, oxime condensation, anthracene-maleimide Diels-Alder cycloaddition and so on.[22]

Different from small-molecule organic reactions, reactions on or between polymers are challenging in many cases, because of the low concentrations and sterically hindered functional groups on polymers, the presence of a large amount of other functionalities, and the difficulty in purification if side or incomplete reactions occur. Simple, efficient, and selective "click" reactions are ideal to meet these challenges, and satisfy the huge need from polymer chemists to modify, functionalize, or couple polymers in a well-controlled fashion, resulting in the wide application of "click" chemistry in polymer science in the last a few years.

Control of Polymer Architectures

It has long been understood that the polymer architecture has huge implications for the physical properties and applications of polymeric materials. A central theme in polymer science over the last half century has been to develop methods for efficient and accurate control of polymer molecular weights and architectures, and to understand the structure-property relationships of polymer materials.

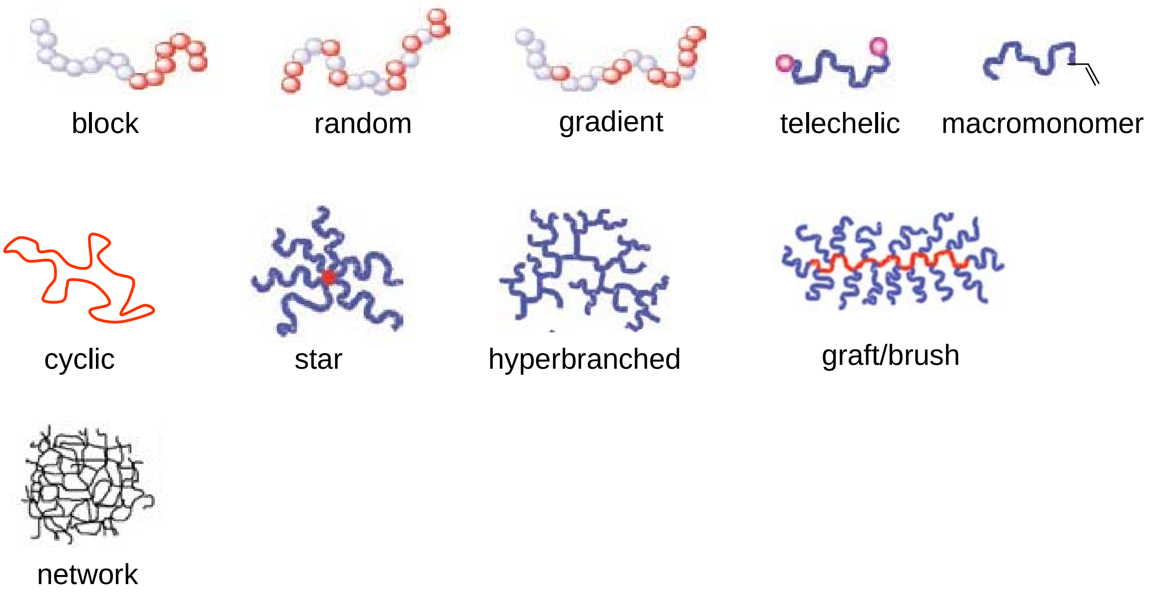


Figure 7. Representative polymer architectures. Partly adapted from reference 25b.

Linear Copolymers

The simplest examples of linear polymer architectures include copolymers of two types of different monomers, A and B. A and B can be arranged in a "block", "random", "alternating", or "gradient" fashion in a linear chain. With the same overall chemical compositions, the arrangement of A and B monomers can dramatically affect the materials properties, such as the viscosity, the solubility, phase transitions temperatures, mechanical properties, optical properties, and association behavior in the melt and solution states.[23]

Telechelic Polymers

The ends of a polymer chain are obviously important positions. Polymers with reactive or functional terminal groups are called telechelic polymers. Polymer terminal groups most often originate from the initiation and the termination steps, and from chain transfer process in some cases.[24] A wide variety of controlled polymerization methods, such as anionic, controlled radical, and metathesis polymerizations, provide precise control of the chain ends. Using functionalized initiators,[25] modifying the existing end groups,[25] and end-capping with functional terminating agents[26] are the most common ways to achieve the desired chain end functionalities.

The end groups of telechelic polymers can be used to attach polymers onto surfaces or to form hybrid conjugates only at the chain ends.[27] The end groups can also be designed to form associating supramolecular polymers or networks.[11c,11d,28] Telechelic polymers are also important precursor polymers for the synthesis of triblock copolymers through chain extension,[29] and for the syntheses of cyclic polymers[30] and model networks[31] through end-linking.

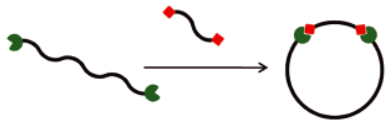
In a special case, when a polymer chain is terminated at only one end with a polymerizable group, this monotelechelic polymer is often referred as “macromonomer” (MM).[32] Macromonomers can be polymerized to prepare more complex polymer structures.

Cyclic Polymers

While end groups of polymers have demonstrated a significant role in many of their properties, the absence of end groups in cyclic polymers make them a unique architecture, mostly for scientific curiosity, but they may find commercial applications if unique properties can be found from cyclic polymers or mixtures of cyclic and linear polymers. For example, (1) cyclic polymers can be used to test the existing theories of polymer physics established on linear chains, such as the reptation theory in polymer melt and the glass transition of polymers; (2) the absence of end groups may be an advantage in some cases, considering that end groups often affect surface properties and degradation; (3) threaded cyclic polymers may act as mechanical crosslinks in a mixture with linear chains.[33]

Synthetic strategies of cyclic polymers can be divided into two main categories: ring-closure approach and ring-expansion approach.[30,33] The ring-closure approach involves cyclization reaction of telechelic polymers under high (or pseudo-high) dilution conditions to suppress the intermolecular end-linking. Successful macrocyclization has been achieved in both bimolecular coupling of a symmetric telechelic polymer and a bifunctional coupling agent[34] and unimolecular coupling of an asymmetric telechelic polymer with complementary functional end groups[35] (Figure 8). Clean, fast, and high yield coupling reactions are commonly used in macrocyclization to boost the conversion of the coupling step.

Bimolecular cyclization using a symmetric telechelic polymer



Unimolecular cyclization using an asymmetric telechelic polymer

Figure 8. Synthesis of cyclic polymers via cyclization of telechelic polymers. Adapted from reference 30a.

A general issue with the ring-closure approach is that cyclization yields dramatically decreas with increasing MW of the telechelic precursor polymers. Inevitable intermolecular end-linking reactions during macrocyclization lead to the formation of linear chain impurities, which are often difficult and laborious to separate from the cyclic product. Although, a few methods have been developed to strongly favor the intramolecular macrocyclization, such as using biphasic coupling, [36] electrostatic interaction,[37] and addition of poor solvent,[38] and high cyclization efficiencies (>90%) have been reported in some systems. A second limit with the ring-closure approach is the small quantity of cyclic materials that can be produced as a result of the high dilution conditions. Reported macrocyclization reactions are often carried out at milligram scale, making many physical measurements and applications of the cyclic polymer product difficult.

The second strategy toward cyclic polymers is the ring-expansion approach. Ring-expansion polymerizations typically involve a catalyst or initiator that yields a growing cyclic polymer chain, held together by a relatively labile bond (i.e., organometallic or electrostatic). Propagation by insertion of new monomer into this weak bond is driven by thermodynamic factors, such as ring strain in the monomer. The resulting macrocycle may either retain this initiating species or release the catalyst by an intramolecular chain transfer.

The key advantage of the ring-expansion approach is that high dilution is not required to yield cyclic polymers. As a result, this approach is amenable to large scale syntheses. Also, because the cyclic structure is maintained throughout propagation, high molecular weight polymers can be easily prepared without the entropic penalty associated with the ring-closure approach. The complication of the ring-expansion approach is that, as a catalytic process, the rates of initiation, propagation, chain transfer, and catalyst release (when possible) have to be fine tuned in order to control the MW and purity of the produced cyclic polymers. Furthermore, linear monomer, linear catalyst, or undesired initiator may have to be absent from the reaction system to avoid ring opening during the ring-expansion polymerization.

The cyclic nature of the polymer products is often supported either by molecular characterizations, such as matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, to confirm the absence of end groups, or by materials characterization, based on known properties of cyclic polymers, such as lower intrinsic viscosity and smaller hydrodynamic radius of cyclic polymers compared to their linear analogs *at the same MW*.

However, these characterizations may not reveal the overall purity of the cyclic polymers. Furthermore, the lack of the exact linear polymer analogs may complicate the comparison of the properties. As a result, in most of these studies, the purity of the cyclic polymers was not claimed and protocols to ensure high purity were not studied.

Some of the most important examples using this approach are highlighted below:

In an early example, the Shea group has developed a cyclic borane to initiate the polyhomologation of dimethylsulfoxonium methylide (Figure 9). Methylene insertion occurs only on the two less-hindered carbon-boron bonds on the macrocycle to produce low MW cyclic polymethylene (0.6–2 kDa) with PDIs between 1.1 and 1.6.[39]

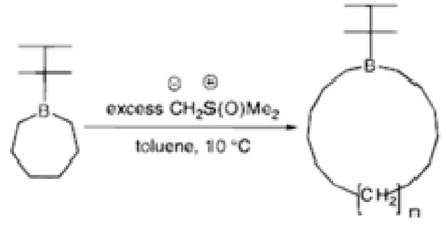


Figure 9. Synthesis of cyclic poly(methylene) from cyclic boranes. Adapted from reference 39.

The groups of Jérome and Kricheldorf have used cyclic tin alkoxide initiators to make cyclic polyesters from lactone monomers.[40] At the end of the polymerization, the tin initiator remains in the cyclic polymer and is subject to hydrolysis. To stabilize the cyclic structure, a small amount of crosslinkable caprolactone was polymerized after the first caprolactone polymerization was finished. Photo-crosslinking the cyclic block copolymer under dilute conditions produced more stable linkage (Figure 10).[40d]

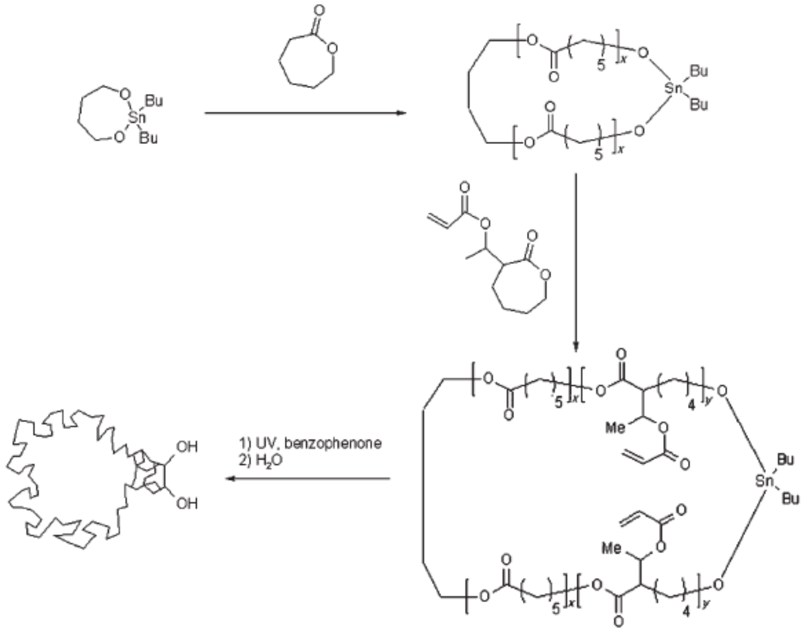


Figure 10. Synthesis of cyclic polycaprolactone block copolymers from a cyclic tin alkoxide initiator and photo-crosslinking to stabilize the cyclic structure. Adapted from reference 40d.

In their research on organocatalysis of lactone polymerization, the groups of Waymouth and Hedrick have found that, in the absence of any alcohol initiators, NHC can mediate the polymerization of lactones to produce cyclic polyesters.[41] The polymerization was believed to occur by nucleophilic attack of the carbene on lactone to generate an alkoxide and acylimidazolium zwitterions, which subsequently propagates by the addition of monomer to the alkoxide of the zwitterionic intermediate. Efficient macrolactonization occurs rapidly as a result of the enforced proximity of the zwitterionic chain ends to generate macrolactones (Figure 11). The produced cyclic polyesters had MW of 7-26 kDa, which was controlled by the ratio of monomer to NHC ([M]/[NHC]), and PDIs < 1.3. Recently, the Zhang group also reported narrowly dispersed cyclic homo and block poly(α-peptoid)s (PDI < 1.2) from NHC catalyzed polymerization of *N*-carboxylanhydrides, presumably operated by the same zwitterionic mechanism.[42]

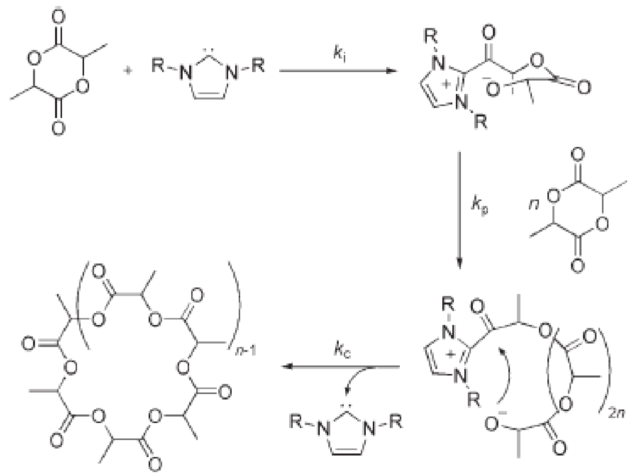


Figure 11. Proposed mechanism for NHC-mediated zwitterionic polymerization of lactide. Adapted from reference 41a.

The Grubbs group has developed a series of cyclic Ru-alkylidene catalysts (Catalyst **5** in Figure 2) that were able to mediate ring-expansion metathesis polymerization (REMP) of cyclic olefins to produce cyclic polymers.[43] A portion of this thesis is devoted to the study of REMP mechanism and synthesis of cyclic polymers via REMP.

Star Polymers

Star polymers have a globular three-dimensional structure consisting of multiple linear polymers (arms) radiating from the central moiety (core). The preparation of star polymers is usually achieved via living ionic polymerizations, controlled radical polymerizations, and ring-opening polymerizations. The synthetic strategies can be divided into three general synthetic methods: (1) “core-first” approach, where a multifunctional initiator is employed to simultaneously initiate the polymerization to form the arms of the star polymer (Figure 12a); (2) “arm-crosslinking” approach involves the reaction of a macroinitiator or a macromonomer, pre-prepared as the arm, with a difunctional (or higher) crosslinker to form a densely cross-linked core (figure 12b). (3) “Arm coupling” approach involves coupling of end-functionalized polymers or living polymer chains with a multifunctional coupling agent (Figure 12c).[44,45,46]

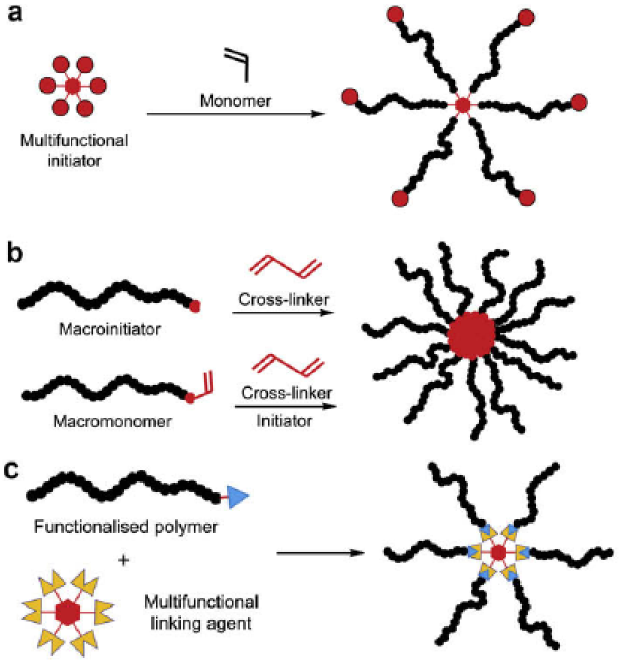


Figure 12. Synthetic approaches toward star polymers. Adapted from reference 45.

Hyperbranched Polymers

Similar to star polymers, hyperbranched polymers are relatively compact and have lower viscosity than their linear counterparts with the same MW because of their small hydrodynamic radius. There are two major approaches to preparing hyperbranched polymers: (1) condensation polymerization of AB_n-type of monomers, where the A group can react with B, and create a branching point; and (2) "self-condensing polymerization" of inimers which contain both a polymerizable group (carbon–carbon double bond) and a group able to initiate polymerization, in the same molecule.[47]

Graft/Comb/Brush Polymers

Graft/comb polymers are a special type of branched polymers in which side chains or side groups are attached to the backbone polymer at various points. Brush polymers are commonly referred to as high MW graft polymers with very dense side chains placed on every backbone repeating unit. For simplicity, the name "brush polymer" is exclusively used to represent this type of graft polymer architecture. In brush polymers, the high steric crowding of sides chains leads to an extended backbone conformation, instead of random coil as in a linear polymer. The nonspherical macromolecular geometries and molecular lengths that can be up to a few hundred nanometers make brush polymers an attractive unimolecular nano-object to study.[48]

Brush polymers are usually prepared by three grafting methods (Figure 13): "grafting from", "grafting onto", and "grafting through" (i.e., the macromonomer approach): (1) The "grafting from" approach involves the growth of side chains from polymer backbones containing initiation sites (macroinitiators) and has been most explored for a variety of monomers. Importantly, the initiation efficiency from the macroinitiators may be limited due to the high density of initiation sites. (2) The "grafting onto" method allows separate preparation of backbone polymers and side chains, but the grafting becomes progressively difficult with conversion, leading to limited grafting density, even in large excess of side chains. (3) The "grafting through" approach guarantees complete grafting (i.e., one side chain per repeating unit), and it can also afford the most precise and easiest control of side chain length and main chain length, provided that the polymerization of MM is efficient and controlled. However, this is often difficult because of the inherently low concentration of polymerizable groups and the demanding steric hindrance of side chains.[46, 49]

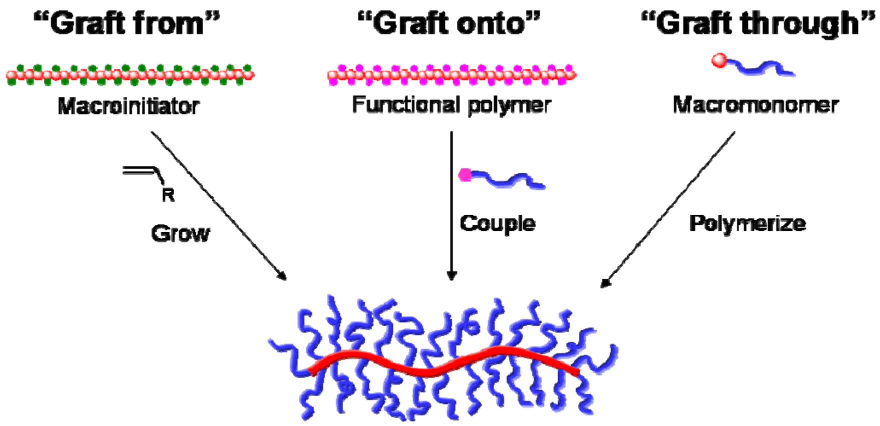


Figure 13. Synthetic approaches toward brush polymers.

A portion of this thesis addresses the challenges to synthesize brush polymers with *ultrahigh MW* and *low PDI*, in *high conversions* and *large quantities*.

Additionally, hybrid polymers combining different architectures are also of great interest for current research.

Thesis Research

To design and synthesize well-defined polymeric materials efficiently with predetermined properties is a constant goal for polymer scientists. This thesis research explores the use of powerful olefin metathesis reactions in the syntheses of complex polymer structures and investigates the physical properties enabled by the resultant new materials.

Chapters 2 and 3 describe the study of a homologous series of "cyclic" catalysts that can mediate REMP to produce cyclic polyalkenamers, including the polymerization mechanism and characterizations of cyclic polymer products.

Chapters 4 and 5 describe the synthesis of various linear brush homopolymers and copolymers via living ROMP of macromonomers and the synthesis of cyclic brush polymers. Several morphological characterizations revealed the extended conformation of individual brush polymers and the highly ordered self-assembly structures formed by brush copolymers.

Chapter 6 describes the synthesis of well-defined liquid crystalline (LC) networks from telechelic precursor LC polymers. These networks exhibited fast, reversible, low-threshold electro-optic response, revealing the importance of network parameters on the materials performance.

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