ACS Catalysis
Perspective
Cite This: ACS Catal. 2019, 9, 11153−11188
pubs.acs.org/acscatalysis

Recent Trends in Catalytic Polymerizations

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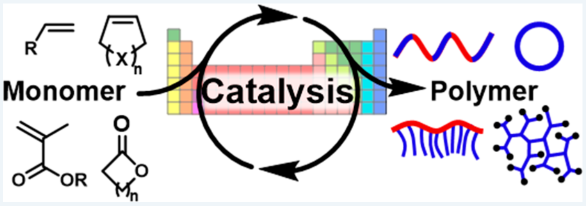
ABSTRACT: Polymers have become one of the largest and most important materials we use in daily life. Their popularity has stemmed from their wide range of material properties combined with their low cost of production. Both of these attractive traits have in part been enabled by the development of catalytic polymerizations, which provide both high levels of control while also delivering high levels of productivity. In this Perspective, we highlight recent trends and achievements made in the growing field of catalytic polymerizations.



KEYWORDS: *catalysis, polymer, polymerization, metathesis, radical polymerizations, insertion polymerizations, ionic polymerizations, ring opening polymerizations*

1. INTRODUCTION

Synthetic polymers are a diverse and tunable material that modern society has embraced for applications ranging from commodity products (e.g., house insulation, packaging, car parts) to specialty goods (e.g., bulletproof vests, drug delivery systems, hydrophobic coatings). Today, over 300 M tons of polymers are produced annually with ever-increasing societal benefit; however, some environmental issues remain to be solved.[1,2] The popularity of polymers stems from their low cost and massive chemical diversity, which enables the tuning of material properties for nearly an endless number of potential applications.[1,3] As with most chemical products, catalysis has undoubtedly played a key role in their success. In this Perspective, we focus on the recent progress made in catalytic polymerizations. The goal is to provide a broad view of the field by briefly describing the motivation of the research and the catalytic strategies employed. The Perspective will first highlight some general trends seen across the field of catalytic polymerization and then dive deeper with the following sections organized by monomer: olefin, cyclic olefin, vinyl, heterocyclic, and specialty monomers.

Prior to reviewing trends involved in catalytic polymerizations, we describe what has been considered a catalytic polymerization. IUPAC defines a catalyst as “A substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis. The catalyst is both a reactant and product of the reaction.”[4] This definition is restrictive when transposed to polymerizations; thus, the polymer community at large has employed a broader definition by considering catalytic polymerizations to be any polymerization that includes an ingredient that accelerates the rate of polymerization irrespective of whether the ingredient is regenerated. A catalyst can be used in conjunction with an initiator or may be the initiator itself. In an effort to be most inclusive, we will consider any recent advances made in polymerization based on this broader definition of catalytic polymerization.

2. GENERAL TRENDS

A polymer’s chemical structure (molecular weight, composition, and topology) directly translates into its macroscopic properties and ultimately its end applications. This direct structure−property relationship has been particularly enticing to researchers, as it enables the engineering of materials with specific properties. The most powerful strategy to engineering polymers has been through the development of synthetic protocols that can produce well-defined materials in a productive manner. Catalytic polymerizations have been among the most successful at delivering both productivity and control. As with all catalysis, productivity remains a major focus of research across all monomers, with the classical strategy (development of new ligand and catalyst structures) most often employed. Additionally, chain transfer reactions have been developed in many forms to enable one catalytic site to produce multiple polymer chains for increasing efficiency. Beyond the enhancement of catalyst productivity, control of polymer structure will be among the largest focuses of this Perspective, as there are a wide range of parameters that can be altered and a wide range of methods with which to do so. The following sections highlight general trends in tacticity, molecular weight, composition, topology, and “temporal and spatial” control.

Tacticity Control. Stereocontrolled polymerizations, reactions that control the relative orientation of a substituent in the polymer, remain an active area of research even 56 years

Received: July 31, 2019
Revised: October 15, 2019
Published: November 8, 2019

DOI: 10.1021/acscatal.9b03226
ACS Catal. 2019, 9, 11153−11188

after the Nobel Prize was awarded to Ziegler and Natta for their work on stereocontrolled polymerization.[5] Stereocontrol is highly desired as it provides a simple means to alter the melting properties, and thus processability and applications, of a polymer without modifying its chemical composition.[1,6,7] Further discussion on catalyst development for tacticity control will be found in the olefin and the heterocyclic monomer sections. The stereocontrolled catalytic polymerization of polar vinyl monomers remains challenging despite some advances made in the recent past. This limitation undoubtedly represents an exciting goal for the catalytic polymerization community.

Molecular Weight Control. Molecular weight control entails the targeting of specific polymer lengths and narrow molecular weight distributions. These properties are highly sought-after characteristics for polymerizations and are usually obtained in the form of living polymerization techniques.[3,8,9] Per the IUPAC definition, a living polymerization is "a chain polymerization from which chain transfer and chain termination are absent. In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the polymerization."[10] When a catalyst can facilitate a fast initiation and is capable of suppressing chain transfer and side reactions, the molecular weight distribution of the polymer remains narrow and the molecular weight is easily controllable through monomer conversion.[11] There has been an extensive effort to develop polymerizations that achieve the highest level of "livingness" possible, as this allows for the synthesis of materials with well-defined structures for fundamental studies into structure−function relationships.[12] Historically, improvements in control over molecular weight have come about through fundamental understanding of the polymerization mechanism which directly informs catalyst design. Today, catalyst development still seeks to attain the highest level of molecular weight control with new ligand frameworks for metal complexes and through noncovalent interactions with organocatalyzed systems.[13−15] Moreover, the nature of living polymerizations is not limited to control over molecular weight; it also underpins the recent developments in control over composition, topology, and other structural features.

Composition Control. Composition control seeks to define the placement of chemically distinct monomers within a polymer. Research in this area relies on the symbiotic development of chemically diverse monomers with functional-group-tolerant catalysts that can achieve living polymerization behavior. Much of the early work in this area began with the synthesis of random, alternating, and block copolymers, which has flourished into an invaluable tool for complex material design with applications ranging from drug delivery to nanolithography.[3,16] However, the sensitivity of certain catalysts toward functional groups limits the chemical diversity achievable. Addressing this limitation remains an active area of research. Another more recent trend is the synthesis of sequenced controlled polymers (narrowly disperse sequences) or even sequence defined polymers (monodispersed sequences).[15,17−22] This area is inspired by the astonishing structure−function relationships observed with DNA and other biopolymers, and achieving this control has been described as the synthetic polymer "holy grail".[3] Many polymerization methods have been developed to mimic the molecular precision of biological polymers. Solid-phase polymerization can achieve the precision observed in nature; however, the synthetic process remains tedious and the degree of polymerization achievable is limited.[23] The implementation of catalytic chain growth polymerizations is considerably easier, with faster production rates, and higher degrees of polymerization. However, this polymerization method is stochastic in nature, resulting in less precision.[9] Future developments in polymerization catalysts hope to bridge the gap between precision and efficiency. Finally, an emerging trend in synthetic polymer chemistry is the use of flow reactors at laboratory scale for synthesizing large libraries of polymers with precise composition.[24−30] The combination of the high throughput of automated flow reactors and the precision of catalytic polymerization promises to accelerate the establishment of new structure−function relationships.[31−33]

Topology Control. Topology control seeks to define the spatial connectivity of repeating units within a polymer. Topology control can be achieved in multiple ways, like the use of multifunctional monomers or the copolymerization of macromonomers.[3] Highly active catalysts have been particularly enabling for polymerizations of macromonomers to form high-density branched polymers (bottlebrush polymers) free of residual macromonomers.[34] Polymerizing large macromonomers in a living manner is not trivial, as the catalyst must achieve high conversions while overcoming significant steric restrictions. Today, graft through polymerizations remain limited to short lengths and low branching densities, and this restriction could be overcome with the development of more active catalysts. More uniquely, topology control can be directly achieved through the control of catalyst reactivity without requiring the implementation of a specialized monomer. Controlling the extent to which a catalyst chain walks during an insertion polymerization provides a simple means of synthesizing linear, crystalline polymer or amorphous, highly branched polymers.[1,35] A more specific trend in topological control for catalytic polymerizations has been the synthesis of ring polymers. Ring polymers have no end-groups, endowing them with unique mechanical and rheological properties when compared with their linear counterparts. The smallest presence of linear contamination has been reported to alter polymer properties, making the synthesis of "pure" ring polymers highly desirable. However, this topological control is nontrivial.[36−40] This has motivated the development of two direct catalytic polymerization strategies: ring-expansion polymerization and ring-closing polymerization.[36−40] In a ring-expansion polymerization, the initiator already starts with a small ring that grows upon monomer addition. A chain transfer reaction releases the ring and initiates a new ring on the catalyst.[41] In a ring-closing polymerization, the attraction (charge neutrality or Coulombic interaction) between the two end-groups forces them to remain in close proximity, and a rearrangement causes formation and release of the ring. For both methods, catalyst development played the central role of ensuring precision and purity.

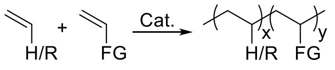
Temporal and Spatial Control. Switchable catalytic polymerizations, where a catalyst activity and/or selectivity changes upon an external trigger, represent a recent trend.[42−44] This stimuli responsiveness provides a means of modulating both temporal and spatial domains, depending on the technique being used. Common realizations of stimuli responsiveness are either turning the reaction on/off or switching between two active polymerization sites. Switchable polymerization systems tend to involve incorporating a stimuli-responsive functionality into a ligand architecture or direct alteration of the catalytic center, usually through oxidation states. Chemical, electrical, thermal, photo, and mechanical (ultrasound) stimuli have all been employed as triggers. Applications of switchable catalytic polymerizations involve controlling monomer sequences, stereoselectivity, and/or patterning surfaces.[43,45−49] This area of research is rather young, and the field can expect further development of novel strategies and a progression to more sophisticated control.

3. OLEFIN MONOMERS

Polyolefins account for over half of the polymers produced annually, of which high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), and isotactic polypropylene (iPP) are all produced via catalytic polymerizations.[1] Olefin polymerization is a mature research area with several classes of high-performance catalysts (heterogeneous, metallocene, postmetallocenes/"nonmetallocene") providing extremely high productivities and high levels of control over the polymer's molecular weight, stereochemistry, and microstructure.[14,50] This control has been achieved through extensive tuning of the steric and electronic properties of the ligands of group 3, 4, and 5 transition-metal complexes. The development of new early-transition-metal-based catalysts remains an active topic of research in academia and industry due to the societal importance of polyolefins.[14,50−54] Despite the advances made in molecular olefin catalysts, the Phillips and Ziegler−Natta catalysts remain the preferred choice for industrial production of HDPE and iPP, respectively.[55] Interestingly, the mechanism of activation for the Phillips catalyst remains intensely debated in the literature.[56−64] Today's research on polyolefins focuses on expanding architecture control and polar group compatibility through polar monomer copolymerizations, postpolymerization modifications, chain transfer polymerizations, coordinative chain transfer polymerizations, and acyclic diene metathesis polymerizations.

3.1. Polar Monomer Copolymerization. Copolymerization of polar monomers with olefins seeks to address the intrinsic low chemical tunability and polarity of polyolefins (Scheme 1). Polar groups can endow polyolefins with important properties such as toughness, adhesion, barrier properties, surface properties (paintability, printability, etc.), solvent resistance (or its inverse), miscibility with other polymers, and rheological properties.[65,66] Unfortunately, the high oxophilicity of industrially relevant early-transition-metal and lanthanide catalysts severely limits the scope of functional comonomers.[67−69] The development of late transition-metal catalysts, primarily palladium- and nickel-based, addresses this limitation and enables copolymerization of a wide range of polar monomers.[70,71]

Scheme 1. Copolymerization of Olefins and Polar Monomers



R=alkyl

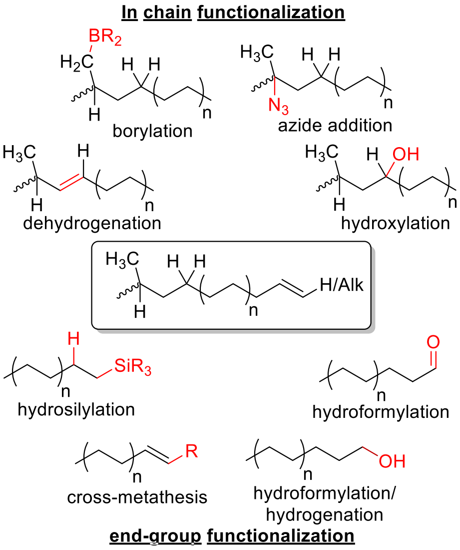
FG = Cl, OR, OAc, CN, $Si(OR)_3$

The use of late-transition-metal catalysts was first established with the development of cationic nickel and palladium diimine complexes that enable the copolymerization of ethylene with acrylates and vinyl ketone monomers.[72−74] Uniquely, these catalysts also facilitate the polymerization of ethylene into a highly branched polymer through a chain walking mechanism. This seminal work continues to inspire new reports of diimine complexes with improved copolymerization abilities.[75−78] The most noticeable achievements made with group 10 diimine-based catalysts include the control of polymer architecture, the stereoregular polymerization of olefins, the high incorporation of acrylate comonomers with palladium and vinyl siloxanes with nickel and living polymerizations.[78−84] The success obtained with cationic diimine palladium and nickel catalysts for olefin polymerization, combined with the commercial success of a neutral nickel catalyst for ethylene oligomerization (Shell Higher Olefin Process), has stimulated the exploration into new neutral and cationic catalysts.[85−94] Among the most successful catalysts, salicylaldimine nickel complexes display some of the highest activities toward ethylene polymerization in organic and aqueous media.[95−99] Simple variations in the aryl substituents of the aniline moiety drastically impact the polyethylene architecture, enabling the synthesis of a wide scope of materials ranging from highly linear polyethylene with high molecular weight, to highly branched low-molecular-weight polymer.[100−104] Phosphinosulfonate ligands are also a common ligand architecture initially developed for the copolymerization of ethylene with carbon monoxide in a nonalternating manner and ethylene with acrylates.[76,105−108] Over the past decade, phosphinosulfonate catalysts have achieved the copolymerization of ethylene with a wide range of polar monomers and the polymerization of olefins in water.[109−117] More recently, a new phosphinosulfonate catalyst has achieved moderate isospecific copolymerization of propylene and polar monomers.[118]

Despite the great advances made by these late transition-metal catalysts, the moderate catalyst productivity, the poor copolymerization efficiency (high incorporation requires high comonomer concentration), and the negative impact of the comonomer insertion on the molecular weight of the polymer precludes their industrial application. These limitations motivate the development of new catalysts.

3.2. Postpolymerization Functionalization. Postpolymerization functionalization was explored as an alternative to copolymerization for the incorporation of polar functionalities into polyolefins (Scheme 2).[119,120] Industrial-scale applications of these processes occur noncatalytically through radical reactions or ozone surface treatments with high efficiency. However, many undesirable side reactions, like chain scission, occur and erode the polymer's mechanical properties.[121] This lack of control has motivated the development of two catalytic postpolymerization functionalization strategies: end-group functionalization and in-chain functionalization.[65,122] Catalytic end-group functionalization focuses on the olefinic end-groups that form during polymerization via β-X elimination or chain transfer to monomer. A wide variety of catalytic reactions that use olefinic substrates have been implemented, including olefin metathesis, hydrosilylation, epoxidization, oxidization, hydroformylation, hydroboration, hydrocarboxylation, and aminomethylation to incorporate polar functionality at the end of the polymer chain.[123−127] Catalytic in-chain functionalization consists of performing a catalytic C−H activation, which has been successful with borylation, dehydrogenation, and azide

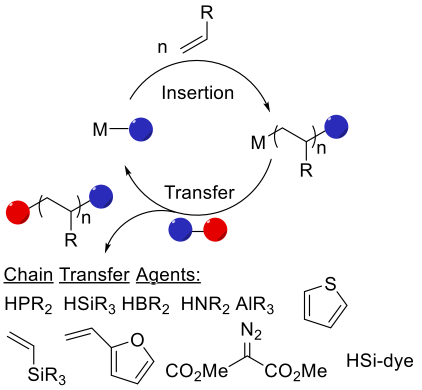
Scheme 2. In-Chain (Top) and End Group Post-Polymerization (Bottom) Catalytic Functionalization of Polyolefins



incorporation.[128−131] Nickel-catalyzed systems have been particularly successful at hydroxylating the CH_2 of polyethylene without chain scission.[132] However, the low reactivity of alkyl chains has thus far limited functionalization to low levels even with high catalyst loadings. Additionally, post-polymerization functionalization strategies in general are challenged by the high temperatures required to melt and/or solubilize polyolefins, thus limiting the possible chemical transformation options. An extension to the postpolymerization functionalization strategies is the use of functionalized polymers as an intermediary step toward the synthesis of more complex polymer architectures, such as block copolymers, to further expand the usefulness of polyolefins.[123,124,133,134]

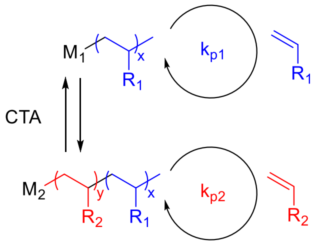
3.3. Chain Transfer Polymerization. Chain transfer polymerization (CTP) techniques were developed as an alternative strategy to copolymerization for the purpose of introducing functional groups directly during polymerization (Scheme 3). In a chain transfer polymerization, the chain transfer agent (CTA) cleaves the polymer from the metal center. One part of the CTA is introduced at the end of the released polymer and the other part is left bound to the metal center, enabling the growth of a new polymer chain.[135] This strategy allows for precise placement of the functional groups (at the polymer end) to yield (semi)telechelic polymers.[136,137] Early versions of CTPs of olefins relied on highly oxophilic catalyst systems to react with polar functional groups, such as phosphines, amines, silanes, boranes, metal alkyls, and selective insertion/H_2 systems.[135,138] Reliance on oxophilic catalysts limits the scope of end-group functionalities accessible and yields polyolefins containing at most one functional group per polymer chain. More recently, the development of CTPs catalyzed by less oxophilic late transition metals enabled the use of highly functional CTAs. For instance, nickel- and palladium-catalyzed copolymerizations of ethylene and acrylates have recently been reported to undergo chain transfer with silanes, vinyl silanes, and carbenes.[81,139,140] Silane CTA's have also been extended to a cobalt catalyst for the direct incorporation of an organic dye into a polyethylene chain.[141] While traditional chain transfer polymerizations yield polymers with a single functionalized end-group (semitelechelic), recent reports describe the synthesis of telechelic polyethylene using phosphinosulfonate palladium catalysts and 2-vinylfuran CTAs. Functionalization of both polymer ends occurs by first inserting 2-vinylfuran, which induces β-hydride elimination to functionalize the end of the polymer. Then, a second molecule of comonomer inserts preferably into the resulting M−H, functionalizing the beginning of the next polymer.[142] The functionalization of both polymeric end-groups further expands the architectures accessible with polymers synthesized by chain transfer polymerizations.[136,137]

Scheme 3. Chain Transfer Polymerization Mechanism and Various Chain Transfer Agents



3.4. Coordinative Chain Transfer Polymerization. Reversible chain transfer polymerizations or coordinative chain transfer polymerizations (CCTP) employ two or more metal complexes that can reversibly exchange polymer chains (Scheme 4).[143] One metal complex, the catalyst, grows the polymer chain while the other metal complexes, usually a zinc, aluminum, or magnesium alkyls, plays the role of a chain surrogate through a reversible exchange of the alkyl chains. This system enables the "simultaneous" growth of multiple polymer chains from the active site of a single catalyst. A recent development has been the chain shuttling polymerizations where addition of a second polymerization catalyst, in the presence of two monomers, enables the synthesis of multiblock polyolefins.[144] Multiblock polymers are formed when the two catalysts have different relative reactivities for the two monomers and the chain transfer from one polymerization catalyst to the other is slower than the propagation rate. This technique has been implemented with the copolymerization of ethylene and octene, where one catalyst incorporates high levels of octene to make a soft block (low T_g) and the other catalyst incorporates very low levels of octene to make a hard block (high T_g). This enables the synthesis of hybrid

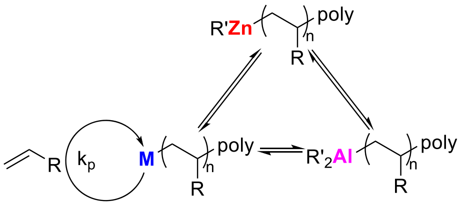
Scheme 4. Coordinative Chain Transfer Polymerization Mechanism



polyolefins with superior physical properties, such as a high melting temperature with high elasticity.[144−149]

Living coordinative chain shuttling polymerizations can be achieved when chain transfer is faster than olefin insertion, resulting in each polymer growing simultaneously at the same rate (Scheme 5). Living CCTP yields multiple living chains per catalytic metal center, overcoming the common, one-polymer-chain-per-molecule-of-catalyst limitation seen with other living olefin polymerization systems.[150−152] The fast chain transfer reaction associated with living CCTP, however, eliminates the stereoselectivity of the polymerization as the polymer shuttles back and forth between the two enantiomers of the catalyst. The use of a dinuclear catalyst for the stereoselective living CCTP of propylene was made possible by the close proximity of the two metal centers, which attenuates the rate of chain transfer and leads to multiple stereoselective insertions of the monomer prior to polymer exchange.[153]

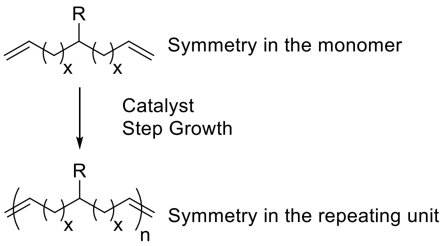
Scheme 5. Trimetallic Coordinative Chain Transfer Polymerization



Additionally, the highly reactive metal alkyl polymer chains produced during the CCTP have been leveraged for the synthesis of semitelechelic polyolefins through quenching reactions (Scheme 6).[154] One example includes the use of polynuclear zinc CTAs in synthesizing homotelechelic polyolefins for conversion into symmetrical polyolefin block copolymers.[155,156] Finally, the use of vinyl-terminated Mg alkyl CTA, or the addition of a second catalyst that performs β-hydride elimination, enables access to heterotelechelic polyolefins.[157−159]

3.5. Acyclic Diene Metathesis Polymerization. Acyclic diene metathesis (ADMET) polymerization is a step-growth polymerization reaction that implements an olefin metathesis catalyst to link α,ω diene monomers together through a cross-metathesis (and release of ethylene). These polymerizations were developed as an elegant technique for synthesizing precisely functionalized polyethylene (upon hydrogenation of the internal double bonds) from symmetric monomers (Scheme 7). While both Schrock- and Grubbs-type olefin metathesis catalysts have been used for ADMET polymerization, the compatibility of ruthenium-based catalysts with functional groups makes it the preferred catalyst for the synthesis of a large diversity of precisely functionalized polymers. Reports exist of the synthesis of ADMET polymers with aromatic groups, acids, silanes, ethers, metals, acetals, ketones, and thioethers.[160−164] Additionally, the precision of ADMET has enabled fundamental studies on the impact of spacing and functionalities of pendent groups on polymer physical properties.[17,165−167]

Scheme 7. ADMET Showing How Symmetrical Monomers Give Precise Polymers[162]

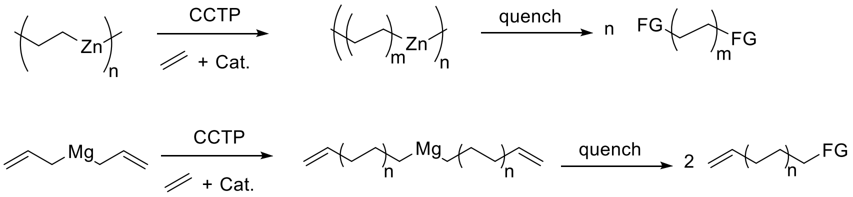


4. CYCLIC OLEFIN MONOMERS

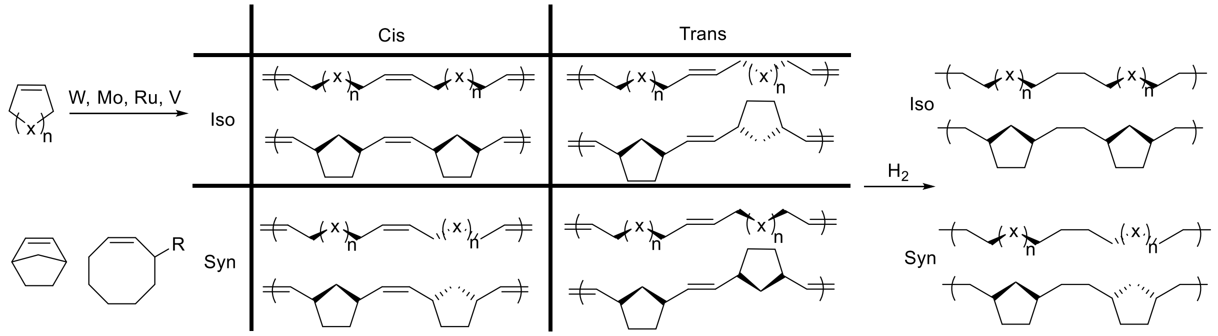
Cyclic olefins are typically polymerized through ring opening metathesis polymerization (ROMP), which involves cleavage of a cyclic double bond, formation of a metallocyclobutane intermediate, and construction of a linear double bond-containing chain. Norbornene type monomers are the most commonly used for ROMP because of their large chemical tunability and high ring strain, which results in a thermodynamically favored polymerization; specialty applications also employ cyclooctenes and other cyclic olefins.[168] There are two major families of catalysts used to perform ROMP: Grubbs type (ruthenium based) and Schrock type (tungsten- and molybdenum-based).[169,170] Grubbs catalysts, in particular Grubbs third generation, serve as the most commonly employed catalysts for ROMP because of their air and moisture stability and broad chemical compatibility.[171,172] ROMP simultaneously offers the chemical diversity accessed by radical polymerization, the living character offered by anionic polymerization, and the stereo- and regiocontrol offered by insertion polymerization, making it a powerful synthetic method. This combination of attributes enables the production of many compositionally and topically complex polymers, such as synthetically demanding bottlebrush polymers.[173,174] Recent research in ROMP focuses on the development of stereo/regio regular polymerizations, end group functionality control, sequence control, ring expansion polymerizations, and cascade catalytic reactions.

4.1. Stereo/Regio Regular Reactions. ROMP of cyclic olefins yields four possible stereoregular structures that reduce to two stereoisomers (syndiotactic and isotactic) upon hydrogenation of the backbone double bonds (Scheme 8).[175] The hydrogenation, which is achievable in situ by residual ROMP catalyst, enhances the polymer's stability by preventing

Scheme 6. Postfunctionalization of Coordinative Chain Transfer Polymerization (CCTP) of Ethylene To Yield Telechelic Polyethylene



Scheme 8. Stereoselective Polymerization of Cyclic Olefins



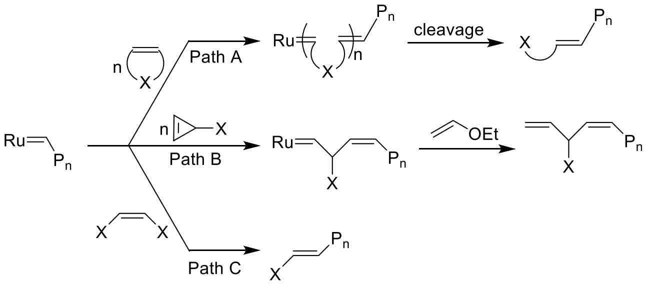
undesired side reactions of unsaturated double bonds. The diverse stereochemistry that can be generated enables access to a wide range of thermal and mechanical properties from a single monomer. Investigations of stereocontrolled ROMP primarily encompass two families of monomers: norbornenyl and substituted cyclooctene monomers, with molybdenum and tungsten catalysts providing the highest level of selectivity.[175,176] Recent work on early transition-metal catalysts focuses on expanding the monomer scope and stereoselectivity.[177−181] Recently developed vanadium catalysts also perform cis selective ROMP of norbornene.[182−184] In contrast, ruthenium-catalyzed ROMP lacks stereocontrol, and this is theorized to be due to the rotation of the metal alkylidene which relieves any steric hindrance that would favor one stereoisomer over another.[185] Nonetheless, the synthesis of cis syndiotactic-rich polynorbornene was achieved upon modification of the ligand structure of a Grubbs type catalyst.[186]

The regioselectivity of cyclic monomer addition (head to tail, tail to tail, or head to head) also serves as a focus of investigation, as it enables control over the spacing between substituents (for asymmetric monomers). The ROMP of 3-substituted cyclooctenes yields (after hydrogenation of the polymer) functionalized polyethylenes. Similarly to ADMET (vide supra), this alternative route to polyethylene is advantageous, as it does not require handling a flammable gas and is compatible with functional groups. ROMP outperforms ADMET in achieving high molecular weight polymers; however, the different regio-additions of the monomer in ROMP results in varying spacing between functional groups. This random distribution hinders crystallization and alters mechanical properties. Addressing this drawback, ROMP of 3-substituted cyclooctenes with second and third generation Grubbs catalysts deliver a high propensity for trans-selective regiospecific addition to yield precision substituted polyoctenes (stereo/regioregular), which can be hydrogenated to yield precision LLDPE (regioregular).[176,187−189] The same monomers were later reported to undergo a cis-selective regiospecific polymerization with molybdenum and tungsten catalysts.[190]

4.2. End Group Control in ROMP. Controlling polymer end groups has long served as a strategy for accessing polymers with complex compositions and architectures.[136,137] The living Ru-catalyzed ROMP enables the syntheses of semitelechelic ROMP polymers through functionalized catalyst precursors.[191−195] While successful, this approach requires advanced synthetic skills, as the isolation of organometallic complexes faces challenges with stability. The recent development of a methodology consisting of the in situ functionalization of Grubbs catalyst using alkynes significantly simplifies this synthetic challenge.[196] The success of this technique was illustrated by the synthesis of a polymer carrying two different dyes on opposite chain ends.

The use of functional olefins at the end of ROMP releases the semitelechelic polymer from the metal center (Scheme 9).

Scheme 9. Routes To Achieve End-Modified Polymers Made from ROMP[a]



[a]Path A: ROMP of a monomer with a cleavable functional group. Path B: Addition of a functionalized cyclopropene followed by termination with ethyl vinyl ether. Path C: Chain transfer to a functionalized CTA.

Many strategies have been developed around this concept: the addition of cyclic monomers that add to polymer chains without homopolymerizing (e.g., functional cyclopropenes);[197] the addition of monomers that decompose upon a trigger and yield polymer fragments with functional end-groups (including stimuli responsive group);[198−200] and through cross-metathesis with a terminating agent.[201−203] All of these techniques enable the synthesis of telechelic and semitelechelic polymers in a stoichiometric manner (one chain per metal center).[197−203]

Multiple (semi)telechelic polymers can be produced per metal center by means of a functionalized CTA, which releases a functionalized polymer chain and forms a new functionalized initiator with every CTA insertion.[204] In this chain transfer polymerization scheme, the rate of polymerization versus the rate of chain transfer dictates the molecular weight and dispersity.[205] In the case of a fast polymerization rate and slow chain transfer rate, producing telechelic polymers with narrow molecular weight distribution becomes possible.[206,207]

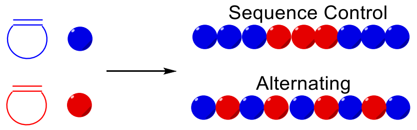
Finally, a living chain transfer ROMP of norbornenyl monomers that yields multiple polymer chains per metal center was recently developed. This strategy relies on a reversible CTA that allows shuttling of the catalyst between the active and dormant polymers.[208] The functionality of the CTA remains present at the end of the polymer chain, making the

DOI: 10.1021/acscatal.9b03226
ACS Catal. 2019, 9, 11153−11188

ROMP polymer isolatable and subsequently extendable into a block copolymer.

4.3. Sequence Control. The chemical tunability of norbornenyl monomers and the ability of ROMP to remain living at very high conversions makes it an ideal method for synthesizing polymers with complex chemical sequences. The sequential addition of different monomers serves as the simplest method of achieving sequence control (Scheme 10).[209] While successful, this methodology does not result in perfect sequence control because of the stochasticity of monomer addition. An alternative approach to synthesizing polymers with complex monomer sequences via ROMP was developed on the basis of the large difference in rates between exo and endo norbornenes, where the exo monomer polymerizes significantly faster than the endo.[210] The pulsing of exo monomer into a polymerization mixture that contains excess endo monomer yields a polymer containing exo blocks separated by a few endo monomers.[211]

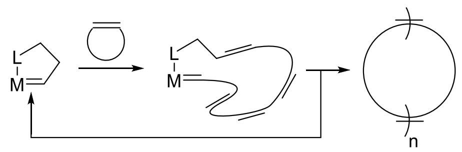
Scheme 10. ROMP of Cyclic Monomers To Give Sequence Controlled and Alternating Copolymers



The large difference in polymerization rates of norbornenyl type monomers allows for compositional control through copolymerization parameters.[34,210,212] Copolymerization of a high ring strain norbornene with a low ring strain cycloalkene yields alternating copolymers due to the very high copolymerization parameters. However, this copolymerization does not yield a perfectly alternating polymer, as the homopolymerization capability of the fast monomer necessitates a high excess of slow monomer to achieve some sequence control.[213−217] A combination of high ring strain cyclobutenes or cyclopropenes with low ring strain monomers will copolymerize quickly without homopolymerizing, enabling the synthesis of perfectly alternating structures.[218−224] Molybdenum- or tungsten-catalyzed ROMP also recently achieved stereospecific, alternating copolymerization of opposite norbornene enantiomers.[225,226] Finally, the ROMP of symmetrical cyclic olefins containing a predefined sequence of functionalities was implemented to yield polymers with complex repeating sequences.[227−230]

4.4. Ring Expansion Metathesis Polymerization. The unique physics of ring polymers has long intrigued the polymer community. Over the years, ring expansion metathesis polymerization (REMP) of cycloalkenes using tethered ruthenium catalysts has evolved as a powerful strategy for accessing ring polymers (Scheme 11).[231,232] In this reaction, cyclic olefins add to the tethered alkylidene to expand the ring. Intramolecular chain transfer results in release of the polymeric ring and regeneration of the tethered catalyst. When combined with various other polymerizations and postmodification techniques, REMP of cyloalkenes enables the synthesis of a vast array of polymers with unique architectures such as dendrimers, brush polymers, and more.[40,233−239] Tethered tungsten catalysts for alkyne polymerization have also been reported for the synthesis of stereoselective ring polymers.[240,241]

Scheme 11. Ring Expansion Metathesis Polymerization Using Tethered Catalysts



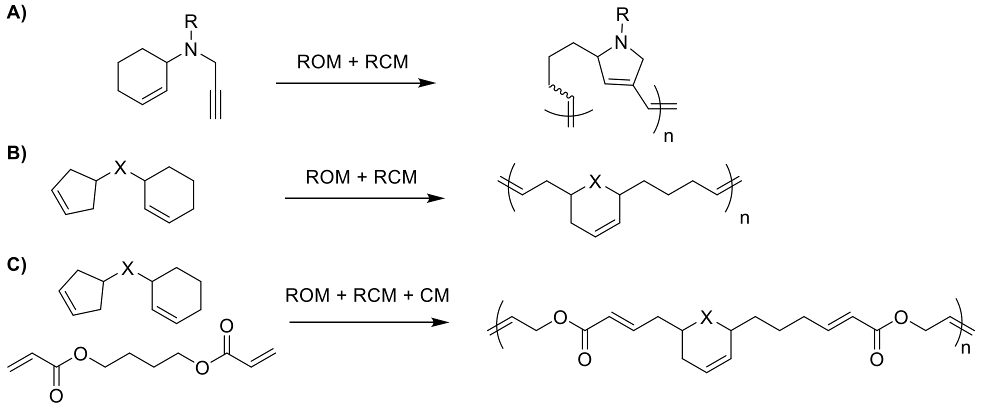
4.5. Cascade Catalytic Polymerization. Metathesis cascade reactions were developed as a means of accessing polymers with unique architectures. Metathesis cascade reactions combine sequential ring opening/closing/cross metathesis reactions (ROM/RCM/CM) in a single polymerization. Most noticeably, the use of a cyclohexene-alkyne monomer (two groups that do not readily polymerize on their own), resulted in a ring closing/opening polymerization that occurs extremely quickly (<1 min) (Scheme 12A).[242−244] The cascade ring opening/closing polymerization of a monomer containing two cycloalkenes (five- and/or six-membered rings) have also been developed (Scheme 12B), and the impact of ring size and linker groups was systematically studied.[245,246] These cascade reactions were further extended with the addition of a cross-metathesis reaction through the addition of a diacrylate. The cascade ring opening, ring closing, and cross-metathesis reactions yield polymers with precise and unique microstructures(Scheme 12C).[245,246]

5. VINYL MONOMERS

Acrylates, methacrylates, vinyl ethers, acrylamides, methacrylamides, vinyl esters, dienes, and styrene derivatives are the most widely used vinyl monomers (Chart 1). For the most part, these monomers are highly tunable, easy to handle, and are commercially available. Each of these monomers has been the subject of different advances involving catalytic polymerizations. The following section is organized by monomer (styrenic monomers, dienic monomers) followed by polymerization methods (catalyst development in ATRP, photomediated polymerizations, catalytic ionic polymerizations, Lewis pairs polymerizations, group transfer polymerizations).

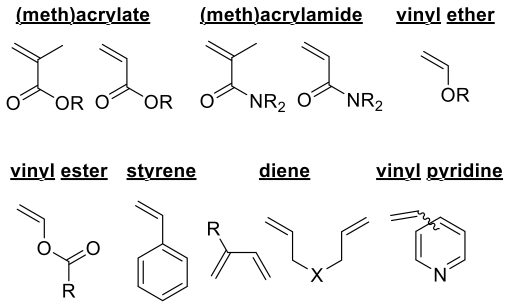
5.1. Styrenic Monomers. Commercial polystyrene is atactic because it is produced via a free radical polymerization that does not provide any stereoregularity (Scheme 13).[247] The stereocontrolled catalytic polymerization of styrene was first reported by Natta using the Ziegler catalyst, and like for propylene, the polymerization resulted in an isotactic polymer with some atactic polymer as impurities.[248] Isotactic polystyrene (iPS) has a high melting temperature (T_m ∼ 240 °C), but its low rate of crystallization limits its industrial application. It is only in 1986 that syndiotactic polystyrene (sPS) was first reported.[249] sPS also has a high melting temperature (T_m ∼ 270 °C) and low density, making it a promising specialty polymer. However, sPS produced by the titanium-based catalyst contains a small fraction of amorphous polymer and did not provide molecular weight control, motivating the development of new catalysts. A large number of group III and IV based styrene polymerization catalysts have been developed in recent years, offering high activity and good stereo- and molecular weight control.[250−256] Most of these catalysts also exhibited good reactivity toward conjugated diene polymerization, which motivated the copolymerization of styrenes and conjugated dienes. The resulting copolymers

Scheme 12. Cascade Reactions Combining Ring Opening and Closing[a]

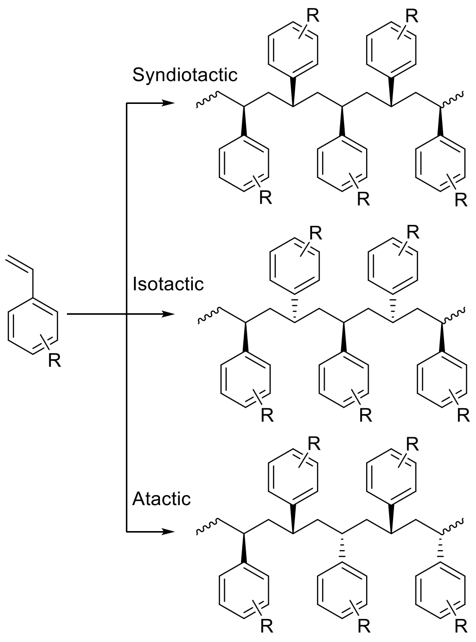


[a](A) Sequential ring opening/closing metathesis polymerization of alkyne/cycloalkane monomer. (B) Sequential ring opening/closing metathesis polymerization of dicycloalkene monomer. (C) Sequential opening/closing/cross metathesis polymerization.

Chart 1. Common Vinyl Monomers



Scheme 13. Stereoregular Polymerization of Styrenic Monomers

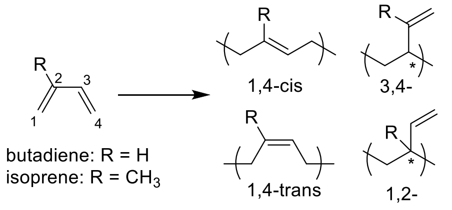


are of interest as alternative SBS elastomers or next generation ABS thermoplastics.[257,258]

The high oxophilicity of the group III and IV based catalysts employed originally limited the use of functional styrenes. The combination of in-depth experiments and computational mechanistic studies with new ligand designs has led to the development of stereoselective catalysts compatible with tertiary amine-, ether-, and thioether-containing styrenes.[257] This catalyst development was further applied to the stereospecific polymerization of vinyl-pyridine.[259,260]

5.2. Dienic Monomers. *5.2.1. Conjugated Dienes.* The polymerization of butadiene and isoprene for the production of synthetic rubbers traditionally employs Ziegler–Natta type catalysts based on titanium, cobalt, nickel, and, more recently, neodymium.[257,258,261,262] Informed by the unique mechanical properties obtained with natural rubbers, the stereo- and regioregularity of polybutadiene and polyisoprene is known to be of critical importance for controlling the properties of the corresponding vulcanized elastomers (Scheme 14). Today, neodymium-based catalysts yield polymers with the highest 1,4-cis content.[261] However, recent knowledge gained through material characterization has illustrated the benefit to access other the stereo- and regioregular polymers.[263] This has motivated the development of new catalysts for the stereoselective polymerization of dienes. Tremendous advances, primarily using group III- and IV-based metals, have enabled the selective synthesis of 1,4-trans and 3,4-polymers with high selectivity, high activity, and good molecular weight control.[257,258] The use of alkyl aluminum and alkyl magnesium to activate the catalyst led to the development of coordinative chain transfer polymerization, where multiple chains of polymers can be simultaneously synthesized with a single molecule of catalyst while maintaining stereoselectivity.[143]

Scheme 14. Regioselectivity in Polymerization of Butadiene and Isoprene[a]



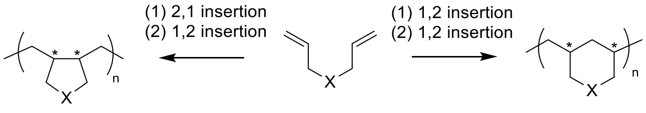
[a]* denotes a stereocenter.

In view of the inorganic fillers and other polymeric components used in rubber compounding, the introduction of polar functionalities into synthetic rubber is considered highly desirable.[264] Multiple approaches including the use of specific chain transfer agents for the direct or indirect (through postpolymerization functionalization) introduction of polar functional groups and the use of less oxophilic metal-based catalysts have been effective.[265−269] In particular, nickel-based catalysts enable copolymerization of butadiene with functionalized 1,3-diene comonomers.[270,271] Interestingly, the interaction between the metal center and the functional group led to favorable copolymerization parameters (during the copolymerization, the comonomer is consumed faster than the butadiene).[271] This is of significance, as it allows for high percentages of incorporation and complete consumption of the more expensive comonomers. Some functional group tolerance was also reported with a more industrially relevant, neodymium-based catalyst.[272] The copolymerizations of butadiene with tertiary amine- and thioether-containing monomers were achieved with high efficiency and yielded high-molecular-weight polymers without loss in stereoselectivity. However, the authors note that any monomer containing oxygen atoms led to complete catalyst deactivation.[272]

Finally, in a recent effort to decrease our dependency toward nonrenewable resources, researchers have implemented group III and IV polymerization catalysts for the polymerization of bioderived diene monomers.[273] In particular, the stereospecific polymerization of β-myrcene (a dimer of isoprene) has been successfully achieved, providing an avenue to biobased synthetic rubber.[274−278]

5.2.2. Nonconjugated Dienes. The use of bifunctional monomers in chain growth polymerization has traditionally been aimed at synthesizing cross-linked polymers. However, upon judicious choice of the diene chemical structure and polymerization conditions, bifunctional monomers can be polymerized into cyclic structures that are directly incorporated into polymer backbones.[15,279] These polymerizations are referred to as cyclopolymerization, and yield polymers with unique structures (Scheme 15). Early work in this area has focused primarily on the catalytic cyclopolymerization of unfunctionalized dienes by early transition-metal-based insertion polymerization catalysts.[280,281] These catalysts enabled control of both regio- and stereoselectivity.[255,281] The resulting polyolefins composed of cycloalkane repeating units are of interest for their high thermal stability and high transparency.[282] The properties of these polyolefins were fine-tuned through the copolymerization of the dienes with ethylene.[15] This concept of catalytic cyclopolymerization of nonconjugated dienes was extended to late transition-metal-based catalysts. These catalysts are tolerant to more chemical functionalities, enabling cyclopolymerization of functionalized dienes and yielding unique polymer structures.[105,283−286] Finally, the cyclopolymerization of bifunctional diynes catalyzed by a series of metal complexes was also developed. These polymers are of interest because the π-conjugated structures of the backbone provide them with unique physical, electrical, and optical properties.[287,288]

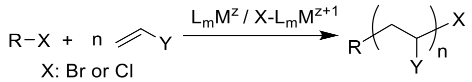
Scheme 15. Cyclopolymerizations of Nonconjugated Dienic Monomers and the Different Repeating Units Formed Based on Regiocontrol[a]



[a] * denotes a stereocenter.

5.3. Catalyst Development in ATRP. Radical polymerizations are the most common method of polymerization for vinyl monomers. Widely used, atom transfer radical polymerization (ATRP) is a controlled radical polymerization technique for synthesizing vinyl polymers with precise topology and architecture (Scheme 16).[8,289]

Scheme 16. Polymerization of Vinyl Monomers Using Atom Transfer Radical Polymerization (ATRP)



ATRP uses a dormant alkyl halide initiator, which can undergo reversible redox chemistry to reveal an active alkyl radical. The active alkyl radical can add a monomer but is more often deactivated, resulting in the uniform growth of all polymer chains.[290,291] The redox chemistry is traditionally carried out with a copper catalyst. The catalyst is employed in a reversible equilibrium reaction that facilitates the formation of the propagating radical and does not assist with monomer addition.

The synthetic opportunities offered by ATRP are endless; however, decreasing the catalyst loading from the 1 mol % originally reported is important for increasing the biological and microelectronic compatibility of the resulting polymers.[292] In-depth mechanistic studies provided quantitative design rules for ATRP catalyst development, leading to increases in catalytic activity and thus lower catalyst loadings (Figure 1).[292−295] Consequently, this decrease of catalyst loading makes the system very sensitive to unpreventable side reactions that consume the copper(I) and halt the polymerization (e.g., radical−radical recombination).[296] These side reactions originally set a limit on the copper loading that can be employed. This limit could be lowered by the introduction of a reducing step within the polymerization to regenerate the copper(I) complex. Many techniques, including the in situ catalyst regeneration step, have successfully decreased the catalyst loading over the years to ppm levels (Figure 1). Within these techniques, the use of an electrochemical cell reduced the catalyst loading to 50 ppm. Beyond the low catalyst loading, this technique is also advantageous for its temporal control over polymer growth, as the flux of current through the cell can directly control the rate of polymerization.[297]

5.4. Photomediated Polymerizations. The use of light to initiate vinyl monomer polymerization has a long and rich history leading to multiple commercial applications (e.g., dental fillings, coatings).[298] A more recent focus has been using light to mediate living polymerizations of vinyl monomers.[299−307] This focus is motivated by the desire to turn polymerization on and off with a light switch, providing temporal and spatial control over polymer growth. Photomediated RAFT (reversible addition−fragmentation chain-transfer), ATRP, and cationic polymerizations of vinyl monomers have recently been successfully achieved.

For almost two decades, light has been known to impact the rate of ATRP using copper catalysts.[309] The main challenge in developing a photomediated ATRP, however, has been to completely suppress the formation of the active copper catalyst through the thermally mediated equilibrium in the absence of

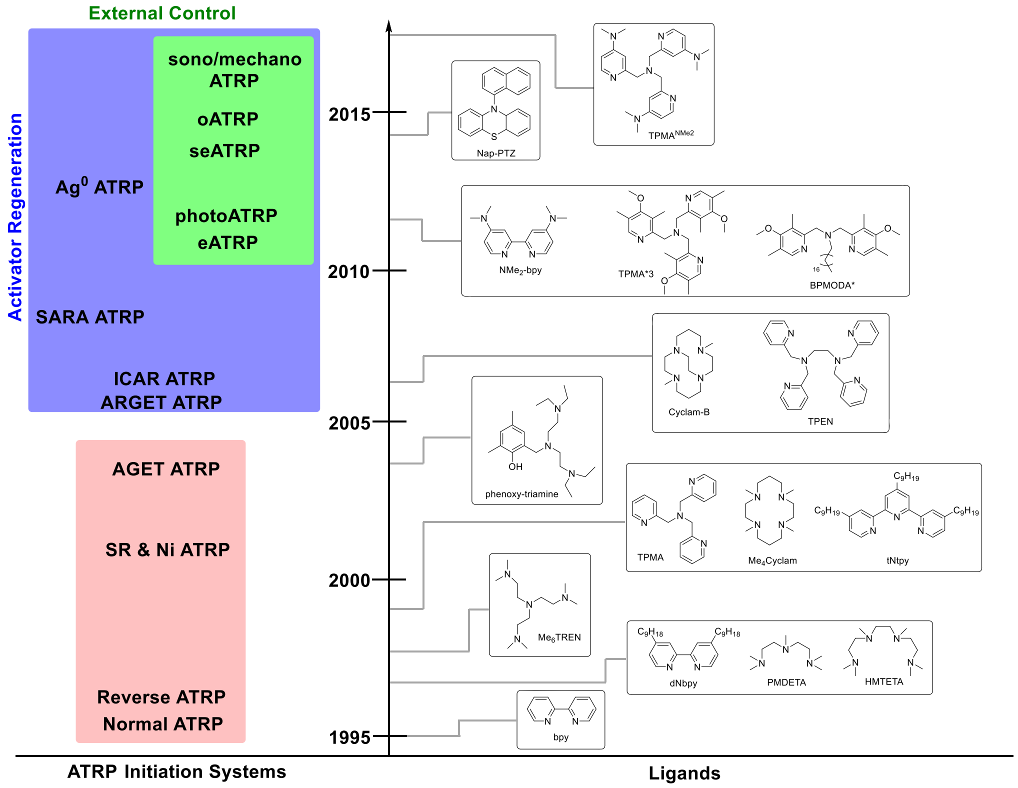
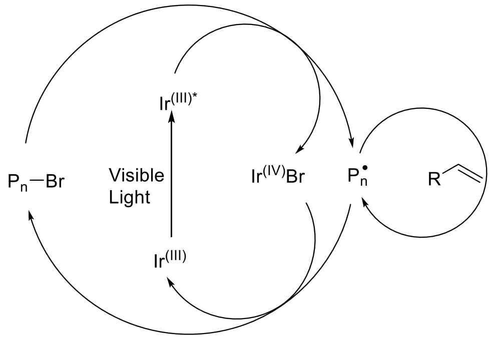


Figure 1. Timeline of ATRP initiation systems and most relevant ligands for copper-catalyzed ATRP. Modified with permission from ref 292. Copyright 2018 Wiley-VCH Verlag GmbH & Co.

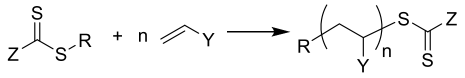
light. A fully photomediated ATRP therefore requires a means of forming the active catalyst without relying on a thermally mediated equilibrium. Inspired by work on small molecule synthesis, photomediated ATRP was achieved through a photoredox reaction for the fast and reversible formation of the propagating alkyl radical (Scheme 17).[310,311] *fac*-[Ir(ppy)$_3$] enables the polymerization of methacrylates in a controlled fashion under light while completely halting the polymerization in the dark.[308] In this process, light converts *fac*-[Ir(ppy)$_3$] into *fac*-[Ir(ppy)$_3$]*, which reduces the alkyl bromide, forming the desired alkyl radical and an iridium(IV) that reacts with the propagating radical to regenerate the initial iridium(III).

Scheme 17. Proposed Mechanism of Iridium-Photoredox-Catalyzed ATRP by Visible Light. Reproduced with Permission from Ref 308. Copyright 2012 Wiley-VCH Verlag GmbH & Co

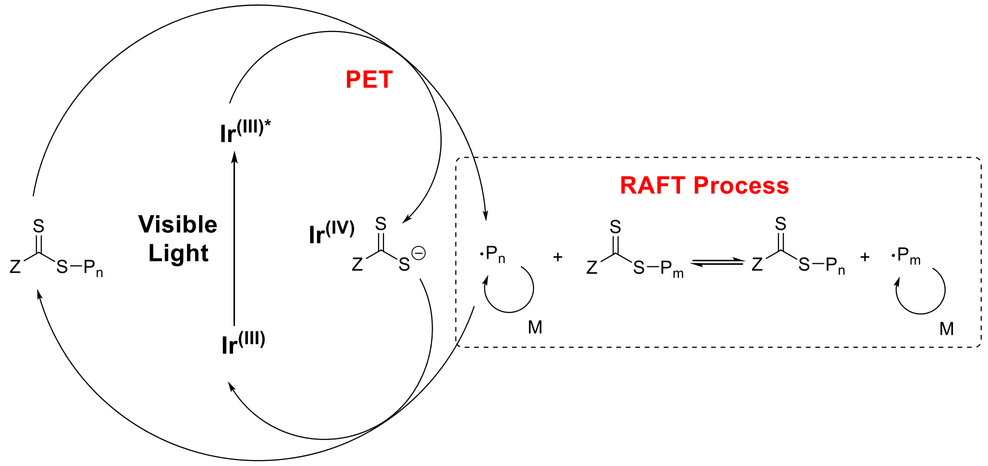


The UV absorbance of thiocarbonylthio chain transfer agents has been used for photocontrolled RAFT polymerizations (Scheme 18).[313] However, the poor end-group fidelity and molecular weight control were significantly limiting and motivated the development of a more effective method.[307] Inspired by the work on ATRP, the photoinduced electron transfer RAFT (PET-RAFT) using the same iridium complex (*fac*-[Ir(ppy)$_3$]) was developed.[312] The *fac*-[Ir(ppy)$_3$] acts as a photoredox catalyst that interacts in its excited state with thiocarbonylthios via a photoinduced electron or energy transfer reaction (Scheme 19). The polymerization was demonstrated to be compatible with a diverse set of vinyl monomers (methacrylates, acrylates, styrene, vinyl ester, methacrylamide, and acrylamide), to yield high-molecular-weight polymers, block copolymers with narrow molecular weight distribution, and most noticeably, to tolerate oxygen (a known inhibitor for radical polymerization). This oxygen tolerance was rationalized by the in situ reduction of dioxygen by the photocatalyst into an inert hydroxide. This tolerance is advantageous, as it prevents the need for the degassing of monomers. Additionally, isotactic dimethyl acrylamide was synthesized with PET-RAFT by using the coordination of a Lewis acid (Y(OTf)$_3$) to the last two repeating units of the growing polymer chains, which forces the incoming monomer to add meso (Scheme 20).[305,314,315]

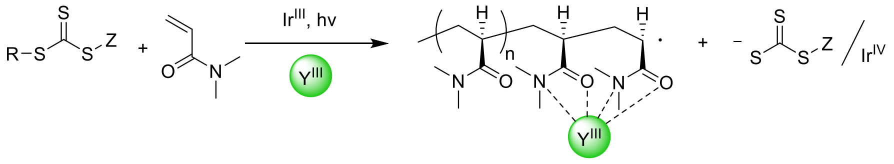
Scheme 18. Polymerization of Vinyl Monomers Using Reversible Addition−fragmentation Chain-Transfer (RAFT)



Scheme 19. Mechanism of PET-RAFT Using a fac-[Ir(ppy)$_3$] Catalyst. Reproduced with Permission from Ref 312. Copyright 2014 American Chemical Society



Scheme 20. Stereoregulation in Photoinduced RAFT Utilizing Iridium Photocatalyst and Y(OTf)$_3$ Mediator for Stereocontrol Polymer. Modified with Permission from Ref 305. Copyright 2016 American Chemical Society[a]



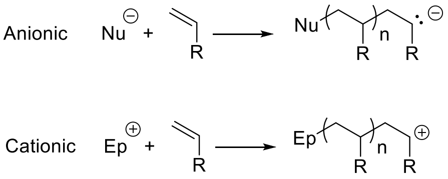
[a]See direct link at https://pubs.acs.org/doi/10.1021/acs.chemrev.5b00586. Further permissions related to this figure should be directed to the ACS.

In an effort to avoid the use of metal complexes, organocatalyzed photoinduced ATRP and RAFT were developed. Elimination of the metal catalyst was motivated by cost and by the issue that metal contaminates pose to the use of polymer in biomedical and electronic applications.[299,300,303,304] PET-RAFT has been successfully performed with a series of organic molecules as photocatalysts, with Eosin Y and fluorescein providing efficient catalysis at concentrations below 100 ppm. However, the addition of tertiary amine was required in this case to achieve the quenching of the oxygen present in nondegassed reaction mixtures.[316] ATRP of (meth)acrylate monomers with organic photocatalysts has also been successfully achieved with visible light.[317,318] Performing a metal-free ATRP represents a significant scientific achievement as, in contrast to RAFT, ATRP was originally designed with a metal complex.

The photomediated cationic polymerization of vinyl monomers has also been the topic of serious progress recently.[319] Electron-rich vinyl monomers and cyclic olefins have been successfully polymerized in a living manner using photocatalysts.[320−323] In particular, the development of a reversibly switchable system has enabled the transition of a controlled radical polymerization of methacrylate to a controlled cationic polymerization of vinyl ether in situ.[324]

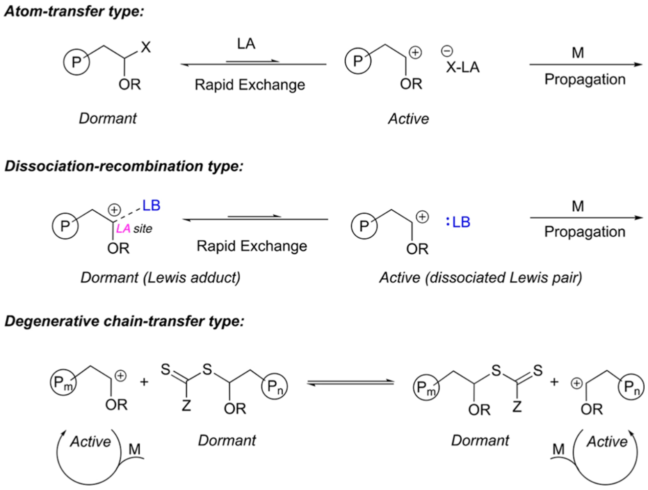
5.5. Catalytic Ionic Polymerizations. Lewis base-catalyzed anionic polymerization has been a significant achievement in the past few years (Scheme 21).[325] The use of N-heterocyclic carbenes and other organic bases has enabled the controlled catalytic polymerization of methacrylate derivatives.[326−329] Variations in the chemical structure of the catalyst have been shown to result in different polymerization mechanisms, leading to polymers with different topologies and end-groups.[325] The controlled polymerization of (meth)-acrylate monomers initiated by a NHC in combination with an alcohol was reported; however, the molecular weight achieved remained relatively low.[330] Lewis base initiated polymerizations are superior to radical polymerization for the polymerization of bioderived vinyl monomer, such as γ-MMBL (γ-methyl-α-methylene-γ-butyrolactone), with high rates being achieved at low catalyst loading.[331,332] These monomers offer a promising alternative to the petroleum based (meth)acrylates.[333]

Scheme 21. Anionic and Cationic Polymerization Using Nucleophile (Nu) and Electrophile (Ep) Initiators



Cationic polymerizations are most commonly employed for electron-rich monomers such as vinyl ether, styrene, isobutene, dienes, and *N*-vinylcarbazole derivatives. Current research has focused on achieving molecular weight control and stereo-selectivity.[325,334,335] The high reactivity of the growing cationic polymer chain results in a high tendency for chain transfer and other side reactions, hampering control of the molecular weight. Three strategies have been successfully developed to achieve molecular control; two of them consist of controlling the Lewis pair interaction (vide infra) while the third method proceeds through a degenerative chain-transfer type similar to RAFT (Scheme 22). In this "cationic RAFT", the thiocarbo-

Scheme 22. Three Types of Living Cationic Polymerization Systems According to Mechanistic Classifications.[a] Reproduced from Ref 325. Copyright 2018 American Chemical Society



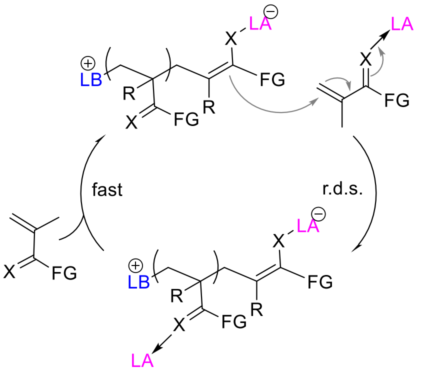
[a] LA: Lewis Acid, LB: Lewis Base, M: Monomer.

nylthio compounds are activated through the addition of a small amount of Brønsted acid. The polymerization proceeds through a reversible chain transfer of the growing carbocationic species to the dormant thioester bond.[336] As stated earlier, the thiocarbonylthiol chain transfer agents are also compatible to radical polymerization, enabling the synthesis of block copolymers made via radical and cationic polymerizations.[324]

Another direction of high interest for cationic polymerization of vinyl monomer is the development of stereoselective polymerization methods. Stereospecific living cationic polymerizations of *N*-vinylcarbazole has been achieved through the interaction of the propagating carbocation and the counterion at low temperature to yield polymer with high isotacticity.[337] More recently, the catalyst-controlled stereoselective cationic polymerization of vinyl ethers has produced semicrystalline polymers in high yield.[338]

5.6. Lewis Pairs Polymerizations. Lewis pair polymerizations (LPPs) have been developed as a means to polymerize vinyl monomers (and others) with the goal of achieving stereocontrol. LPPs proceed through the cooperative effect of a Lewis pair where both elements are actively involved in the polymerization process. The use of a mixture of a Lewis acid and a Lewis base to initiate the polymerization of vinyl monomer was first reported in 1960.[325] The polymerizations showed some level of stereoregularity, but the rates were very slow. More recently, the discovery of frustrated Lewis pairs has enabled the rapid and efficient polymerization of conjugated linear and cyclic acrylic monomers, with the polymers exhibiting moderate levels of tacticity.[339] From a mechanistic standpoint, it was determined that strong Lewis acids cause uncontrolled terminations (e.g., cyclization via a backbiting mechanism), preventing the polymerization from being living (Scheme 23). The addition of a Lewis base helped lower the reactivity of the acid and prevented this undesired termination.[340−342] Today, multiple Lewis pairs have been reported to catalyze the living polymerization of acrylic, vinylpyridine, and vinyl phosphate monomers with high efficiency.[325] In contrast to controlled radical polymerization, LPPs of vinyl monomers can be performed to complete conversion without negatively affecting the dispersity.[342] Furthermore, the use of Lewis pair polymerizations has shown a unique ability to polymerize biomass-derived cyclic acrylic monomers in a living manner.[343,344]

Scheme 23. Proposed Propagation "Catalysis" Cycle for the LPP of Polar Vinyl Monomer. Modified with Permission from Ref 325. Copyright 2018 American Chemical Society



r.d.s. = rate-determining step

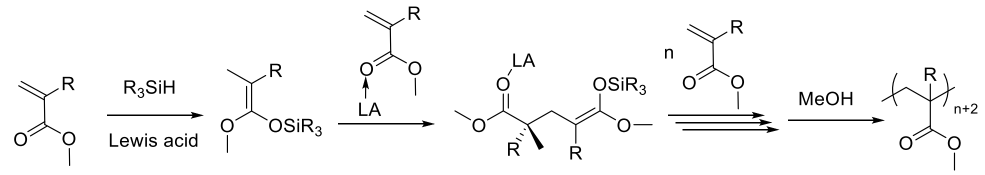
5.7. Group Transfer Polymerizations. Group transfer polymerization (GTP) was first developed at Dupont in 1983 as an alternative to the low-temperature anionic polymerization method for the polymerization of methacrylates.[345,346] GTP traditionally employs a silyl ketene acetal initiator and a Lewis acid catalyst. It has since been expanded to include acrylate and acrylamide with great levels of control over molecular weight and fast kinetics.[325,346] However, the reaction mechanism and rate of polymerization differ based on the catalyst family.[325,347,348] More recently, a tandem group transfer polymerization has been reported, where the silyl ketene acetal is synthesized in situ through a Lewis acid-catalyzed hydrosilylation reaction (Scheme 24). The Lewis acid then subsequently catalyzes the living GTP. This method is advantageous, as it bypasses the need to isolate the reactive silyl ketene acetal and shows good initiation efficiency and high polymerization rates exclusively from commercially available reagents. Block copolymers and heterotelechelic polymers of acrylates have been successfully accessed through this reaction mechanism.[349−352] However, molecular weights of the polymers reported thus far are limited, and the catalyst ($B(C_6F_5)_3$) is not compatible with Lewis base containing monomers.

6. HETEROCYCLIC MONOMERS

Heterocyclic monomers are polymerized via a chain growth ring opening polymerization (ROP) involving the cleavage of a C−X or X−X bond, where X is not carbon. The ROP of heterocyclic monomers results in polymers containing at least one heteroatom within the polymer backbone. The five most common elements are oxygen, nitrogen, sulfur, phosphorus, and silicon. The term "catalyst" in the context of ROP has been used to describe many different reagents (organic, inorganic, organometallic, and enzymes) added to a polymerization to facilitate the ring opening process. The three most common ROP mechanisms are anionic, cationic, and coordination insertion (sometimes referred to as anionic coordination polymerization) (Figure 2).[353−355]

General trends across heterocyclic monomers include lowering catalyst loadings, controlling molecular weight, and

Scheme 24. Tandem Group Transfer Polymerization of Methyl (Meth)acrylates Initiated by a Hydrosilane and Catalyzed by a Lewis Acid



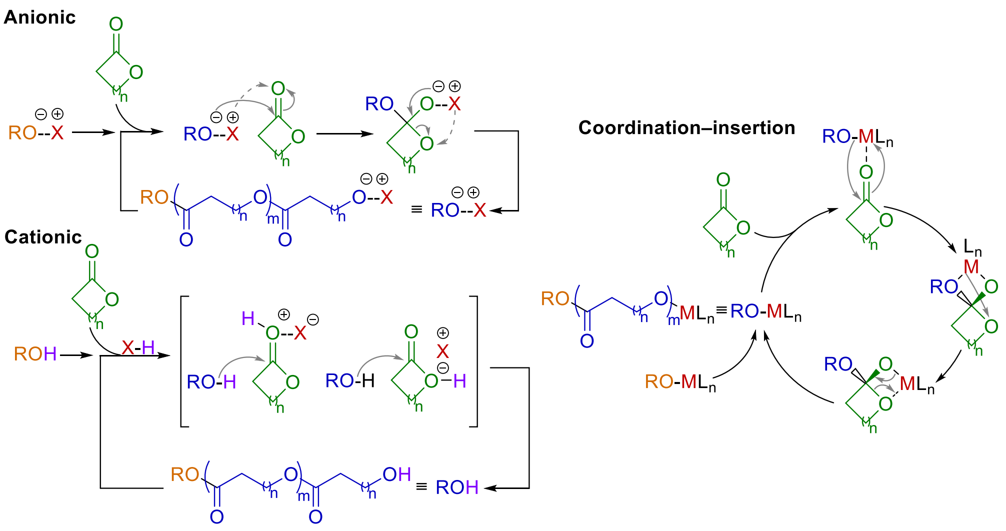


Figure 2. Anionic (top, left), cationic (bottom, left), and coordination−insertion (right) mechanisms for the ring opening polymerization of lactones.

controlling stereoselectivity. Low catalyst loadings can be achieved by the quick shuttling of catalyst between multiple growing polymer chains. This technique is referred to as an immortal polymerization (Figure 3).[356] Molecular weight control is achieved by implementing catalytic systems that minimize side reactions, enabling the synthesis of compositionally and topologically complex macromolecules. Stereochemistry of polymers is controlled either through using enantiopure monomers with stereoretentive catalysts or by implementing stereoselective catalysts with racemic monomer mixtures. Stereoregularity enables the crystallization of polymer chains, providing superior mechanical properties and higher melting temperatures. For example, amorphous atactic PLA has a glass transition temperature (T_g) of ~60 °C, while isotactic PLA is semicrystalline with a melting temperature (T_m) of ~170 °C.[357] Additionally, there has been significant interest in the formation of polymeric stereocomplexes (cocrystallization of two polymer chains having different stereochemistry), as this further increases physical properties beyond that of enantiopure polymers (stereocomplexes of PLA have a T_m = 220 °C). Stereocomplexation has been shown to occur with a wide range of polymers made via ROP of hetercocylic monomers.[357−362]

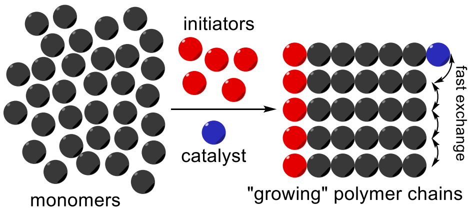
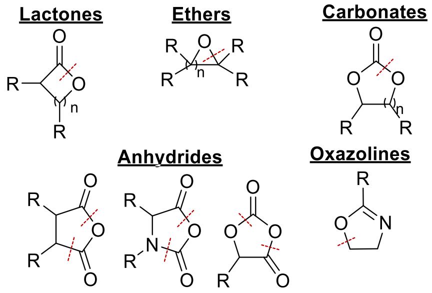


Figure 3. Immortal polymerization.

6.1. Oxygen−Carbon Bond Cleavage. Heterocyclic monomers where the oxygen−carbon bond is cleaved during polymerization are the most widely researched monomer group. We will cover these monomers by dividing them into the following groups: lactones, ethers, carbonates, anhydrides, oxazolines, and copolymerizations (Chart 2).

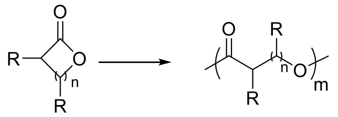
Chart 2. Heterocylic Monomers in Which ROP Results in Cleavage of the Oxygen−Carbon Bond[a]



[a] Bond cleavage represented by red dotted line.

6.1.1. Lactones. The development of the ROP of lactones saw a large surge in popularity in the 1990s with the growing public awareness of environmental issues and rising prices of petroleum (Scheme 25).[354] The periodic table in Figure 4 highlights any element that bonds or coordinates with an active site for lactone polymerization, and illustrates the massive number of catalysts reported for the ring opening polymerizations of lactones.[354,363−391] The most commonly used

Scheme 25. Ring Opening Polymerization of Lactones



metals are zinc, aluminum, tin, yttrium, and lanthanides. New metal catalysts providing higher polymerization rates at lower loadings, while maintaining molecular weight and stereocontrol are continuously being reported.[355,392−403] Additionally, the development of highly active catalysts has enabled the polymerization of novel monomers, like (un)substituted butyrolactones, that can be easily depolymerized, opening up new possibilities for fully recyclable polymeric systems.[404−408]

Organocatalysts have become more popular recently due to their ease of use, commercial availability, and lower toxicity.[409] Chart 3 depicts the most common acid and base catalysts in which the use of (thio)urea-mediated ROP serves as a significant recent advancement in this area.[365,385,391,410−414] (Thio)urea activators, in the presence of a base catalysis, act as hydrogen bond donors providing high levels of control over molecular weight with extremely fast polymerizations (<10 s).[364,415,416] Overall, the precision of organocatalyzed ROP of lactones has enabled the synthesis of polymers with controlled composition, topology, and incorporation of a wide range of functionalities.[417−425] Additionally, the use of organocatalysts for stereocontrol of PLA has seen the development of site control polymerizations vs chain end controlled polymerizations.[426−432]

Stimuli-responsive polymerizations have recently been developed for ROP. Among the early examples in 2005 was the thermally reversible NHC, which was active at 90 °C, and dormant at 20 °C through the formation of a triazolylidene-alcohol adduct.[433] Redox-sensitive catalysts through the modulation of the ligands or the metal center have also been developed.[42,434−437] Reversible inhibition is another avenue recently explored, as the active site can be blocked by the addition or removal of a ligand or competing coordinating agents (such as CO_2 with DBU).[438,439] Most recently, light has been used to control the ROP through photocyclization or photoisomerization modulation.[320,440−444]

6.1.2. Ethers. Epoxides are the most prevalent cyclic monomer, with ethylene oxide (EO), propylene oxide (PO), and butylene oxide (BO) reaching a production scale of more than 33 million tons per year (Scheme 26).[445] Poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) have found applications as lubricants, plasticizers, dispersants, nonionic surfactants, and building blocks of polyurethanes.[445,446] The high water-solubility and very low immunogenicity, antigenicity, and toxicity have made PEO the "gold standard" for any biocompatible applications.[445,447] Epoxide polymerizations typically occur through an anionic polymerization initiated by metal alkoxides, as this methodology can achieve precise molecular weight control over a wide range. Additionally, the development of metal-free polymerizations has seen renewed interest with amine-, NHC-, phosphazene-, and N-heterocyclic olefin (NHOs)-based catalysts, with newer catalysts providing higher polymerization rates and accessing higher molecular weights by eliminating side reactions.[400,448−457]

Coordination insertion polymerizations of epoxide have historically achieved either high molecular weights (>30 000 g/mol) or control over stereochemistry, but not both.[445,458−461] Recent work implementing a bimetallic chromium catalyst with a diol chain shuttling agent has provided both moderate MW with narrow dispersities and enantioselectivity.[462] Additionally, the catalytic polymerization of functionalized epoxide with the Vandenberg catalyst (acetylacetone-chelated aluminum) and other organoaluminum catalysts has sought to expand the chemical versatility of ROP catalysts while maintaining control of the polymerization.[463−466]

6.1.3. Carbonates. Polycarbonates are known for their low toxicity, biocompatibility, and biodegradability (Scheme 27). Much of the research in this area focuses on producing functionalized polycarbonates for biomedical applications, with the six-membered TMC (trimethylene carbonate) being the most common monomer.[459,467−472] Recent work has shown the potential of N-substituted, functionalized, eight-membered cyclic carbonates as a simpler and more efficient route to

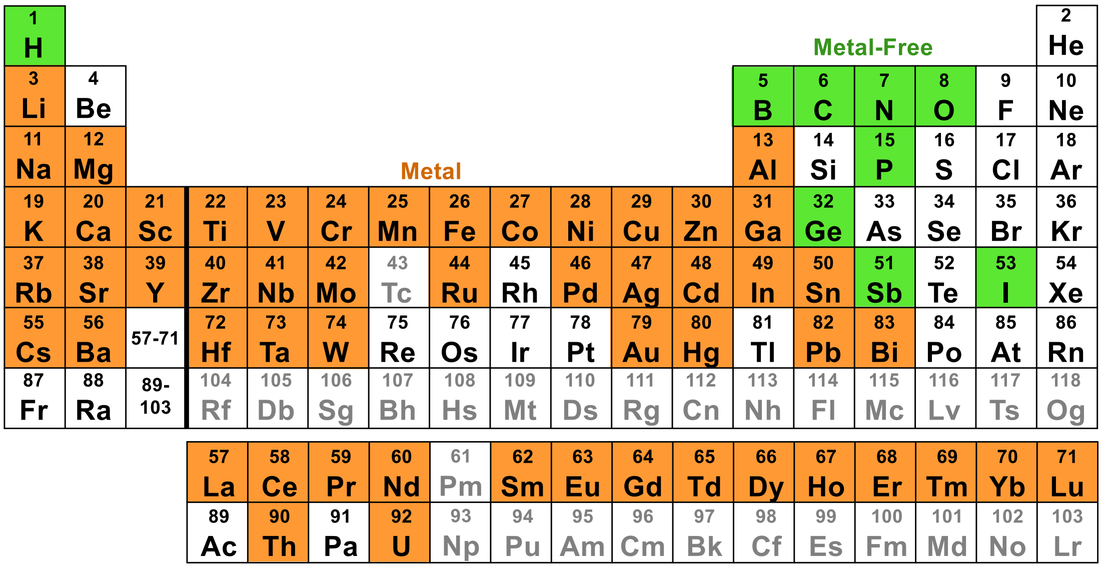
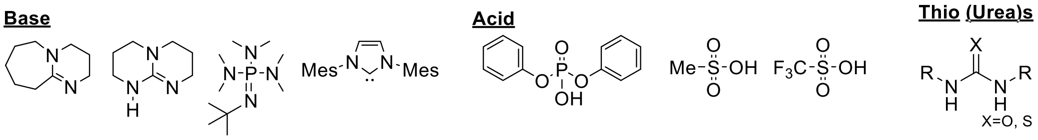


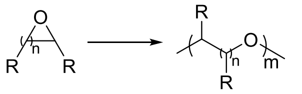
Figure 4. Elements with catalytic activity for the ROP of lactones (colored), including metals (orange) and nonmetals (green). Gray lettering designates synthetically prepared elements.[354,363−391]

Chart 3. Key Organic-Catalysts for the Polymerization of Lactones[a]

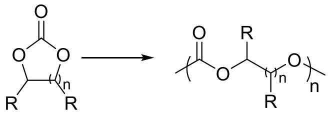


[a]DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), TBD (triazabicyclodecene), phosphazene, NHCs (N-heterocyclic carbine), DPP (diphenyl phosphate), methanesulfonic acid, and triflic acid.

Scheme 26. Ring Opening Polymerization of Ethers



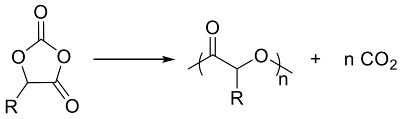
Scheme 27. Ring Opening Polymerization of Carbonates



accessing functionalized polycarbonates.[473,474] Interestingly, most of the catalysts active for lactone polymerization also display activity for ROP of carbonates; therefore, advances made for the former traditionally results in advances for the latter. More particularly, recent efforts have focused on transposing the organocatalysts developed for the ROP of lactones to carbonates as they are more biocompatible than their metal counterparts (Chart 3).[416,475−481] Today, the organocatalyzed ROP of carbonates achieves high levels of control over molecular weight.

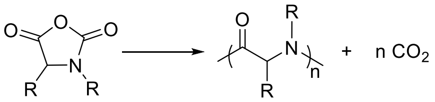
6.1.4. Anhydrides. *O*-Carboxyanhydrides (OCAs) are a class of five-membered cyclic anhydrides that release CO_2 upon opening of a five-membered ring, resulting in polyester formation (Scheme 28).[482−485] The rich variety of side-chain functionalities of *O*-carboxyanhydrides enables access to polyesters that are difficult to obtain directly from the ROP of lactones. Organocatalyzed ROP of OCAs has recently been developed with bases and nucleophiles, such as DMAP and NHC, that provide good levels of control.[486−495] A large number of metal catalysts have also been applied for the ROP of OCAs, with hafnium and zirconium alkoxide and photoredox nickel/iridium/zinc system catalysts recently achieving the first examples of stereoselectivity with high molecular weights and narrow dispersities.[496−504]

Scheme 28. Ring Opening Polymerization of *O*-Carboxyanhydrides



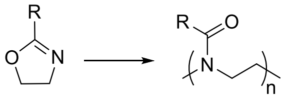
N-Carboxyanhydrides (NCAs) are a class of cyclic anhydrides with a nitrogen within the ring (Scheme 29). Upon polymerization, the five- or six-membered ring opens, and CO_2 is released, resulting in the formation of polyamides, which are polypeptide analogues.[505−510] The similarity of polyamides to natural peptides has prompted significant biomedical and pharmaceutical interest in polymerizing NCAs.[505] The recent use of organosilicon amines, like HMDS (hexamethyldisilazane), or organosilicon sulfides has been demonstrated to enable the controlled polymerizations of a moderate range of NCAs.[511−514] The addition of acids, guanidines, thioureas, or polyamines molecules has also been shown to further enhance control over the polymerization.[515−519] Metal catalysts, in general, offer moderate stereoselective control over the ROP of NCAs through kinetic resolution.[520] Most unique to this monomer, the formation of secondary structure (α-helix) during its polymerization significantly increases the polymerization rate.[446] Recently, it was reported that the rate of ROP of NCAs in a graft-from synthesis of a bottlebrush polymer can be further accelerated by the cooperative interactions between the macrodipoles of neighboring helical polypeptides.[521,522]

Scheme 29. Ring Opening Polymerization of *N*-Carboxyanhydrides



6.1.5. Oxazolines. Oxazolines are a class of five-membered cyclic imino ethers where cleavage of the C−O bond results in polypeptide analogs (Scheme 30). Similar to NCAs, their biomimicking structure motivates significant research in biomedical and pharmaceutical applications. The benefit of this family of polymers over other biomimetic polymers includes their facile and tunable monomer syntheses as well as their broad compatibility with numerous polymerization methods. For instance, the ROP of 2-oxazolines through the cationic polymerization by Lewis acids, strong Brønsted acids, acid halides, silyl halides, chloroformates, supercritical CO_2, and alkylating agents have been performed.[523−526] High levels of control have been achieved, enabling the synthesis of compositionally and topologically complex polymers.[527−532]

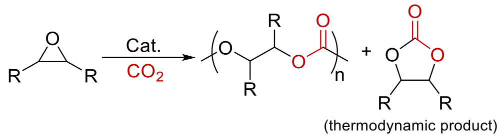
Scheme 30. ROP of Five-Membered Oxazolines To Produce a Polypeptoid



6.1.6. Copolymerization. Copolymerization of oxygenated heterocyclic monomers has been a growing trend as polymer chemists seek to access a larger variety of polymers. Oxygenated heterocyclic monomers are particularly amenable to copolymerization as there is significant overlap in catalyst compatibility which gives copolymerization access to a broad range of polymer properties, topologies, and compositions.

The copolymerization of epoxides with CO_2, an abundant and nontoxic biorenewable molecule, has gained significant attention recently as an attractive route to accessing polycarbonates (Scheme 31).[533−535] Most catalysts for this copolymerization fall into one of two categories: bicomponent or bimetallic.[536] One of the most successful catalysts (salen-based) for the copolymerization of CO_2 and epoxides is also highly effective at producing stereoregular polymers.[459,537−543] There has also been interest in the copolymerization of CO and epoxides to produce polyesters as a low-energy and atom-economical route to form lactones in situ.[544−549] This tandem monomer synthesis and ROP can be done either with one catalyst or with the use of compatible epoxide carbonylation and lactone polymerization catalysts. More recently, there has been interest in copolymerizing carbonyl sulfide (COS) and carbon disulfide (CS_2) with epoxides for the production of high-performance materials with excellent electrical, mechanical, and optical properties.[550−562] The alternating copolymerization of epoxides with anhydrides yields polyesters and has recently achieved high levels of control with organometallic complexes or metal-free Lewis pairs.[563−566]

Scheme 31. Copolymerization of CO_2 and Epoxide Forming Polymer and Cyclic Carbonate



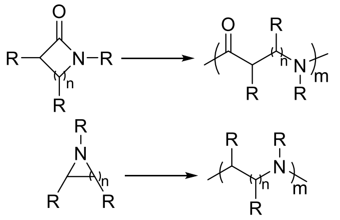
Terpolymerizations (copolymerization of three monomers) focus on the development of selective polymerization catalysis that can create a single, well-defined polymer structure from a complex mixtures of monomers.[567,568] This area focuses on "one-pot" polymerizations of any combination of CO_2, epoxide, anhydrides, and lactones and has recently been accomplished with high levels of selectivity with bimetallic zinc alkoxide complexes, modified aluminum or chromium salen catalysts, or phosphazenes.[569−578]

Switchable ring opening copolymerizations have recently been explored for compositional control in oxygenated polymers.[42,46,579] Two redox switchable copolymerization systems were developed to switch between ROP of lactones and the ROP of epoxides.[435,580−583] Photoswitchable ROP catalyst systems have been recently reported as capable of switching polymerization preference between lactones and carbonate.[441,442]

6.2. Nitrogen, Sulfur, Phosphorus, and Silicon-Containing Bond Cleavages. The following section covers monomers where nitrogen, sulfur, phosphorus, and silicon are involved in polymerization breaking bond. They will be divided into the their respective groups on the basis of the element involved in the bond cleavage (Chart 4).

6.2.1. Nitrogen. The ROP of lactam is known mostly for the industrial production of Nylon-6 from ε-caprolactam (Scheme 32).[584] Recently, the development of the metal-free anionic ROP of lactams has been effective with NHC and phosphazenes, with phosphazenes being a more moisture- and functional-group-tolerant system.[585−591]

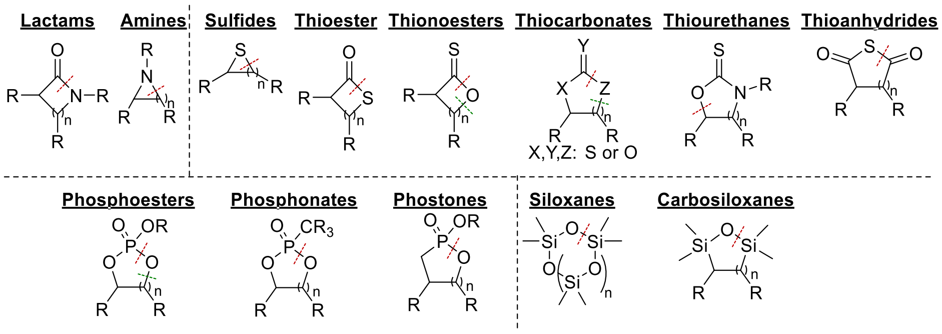
Scheme 32. ROP of Lactams (Top) and Amines (Bottom)



The ROP of cyclic amines yields polyamines which have found use as antibacterial and antimicrobial coatings, CO_2 adsorption, materials templating, and nonviral gene transfection.[446,592] A recent development in the polymerization of cyclic amines has been the use of the electron-withdrawing sulfonyl group on the nitrogen, which has made the anionic polymerization of cyclic amines possible for the first time.[593] Anionic polymerizations of aziridines typically are initiated by strong alkali nucleophiles or metal-free systems, such as NHCs and phosphazenes.[594−603]

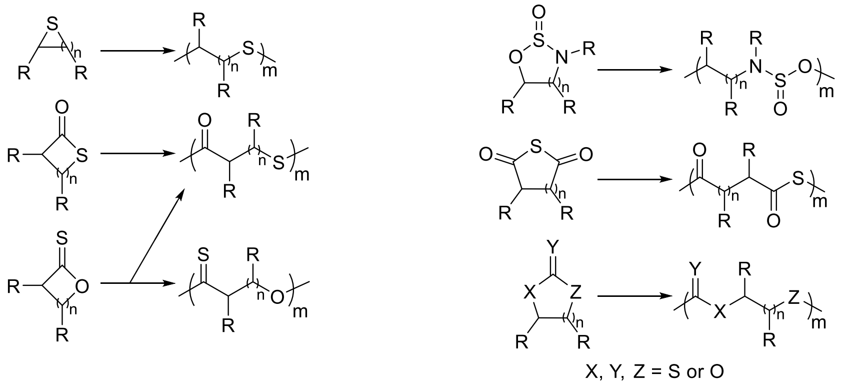
6.2.2. Sulfur. Sulfur-containing polymers are of great interest for their degradable and biocompatible properties for biomedical applications, their high refractive index for optical applications, and their sorbent properties for wastewater treatment (Scheme 33).[604] A recent development for the ROP of sulfides has been the use of thioester, thiourethane, and trithiocarbonate as initiators, which provides well-controlled polymerizations. Additionally, this has enabled the development of a switchable polymerization system, as trithiocarbonates can be used as RAFT transfer agents, to control polymer composition on demand with external stimui.[21,605−609] Recently, a purely alternating polymerization of episulfide with carbon disulfide was reported with a salph

Chart 4. Common Monomers Used in Which Polymerization Results in Bond Cleavage between Nitrogen, Sulfur, Phosphorous, and Silicon[a]



[a]Bond cleavage represented by red or green dotted line.

Scheme 33. ROP of Sulfides (Top Left), Thiourethanes (Top Right), Thioesters (Middle Left), Thioanhydrides (Middle Right), Thionoesters (Bottom Left), and Amines (Bottom Right)

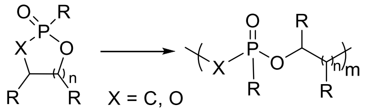


ligand chromium catalyst to produce polytrithiocarbonates.[610] Thioanhydrides have also been copolymerized with episulfides by means of both organocatalysts and metal catalysts.[611−613] Trithiocarbonates have been polymerized through a radical ROP when used as a RAFT chain transfer agent.[614−616]

Thioesters, which contain a carbonyl and a sulfide linkage, have recently been polymerized by organocatalyzed systems with the use of strong bases (DBU, TBD, MTBD) in conjunction with thioureas or cysteine methyl esters.[617,618] Thionoesters, which contain a thiocarbonyl and an ether, have been polymerized using organic bases to produce solely polythionoesters, which is often not the product due to rearrangement of the thionoester to the more stable thioester in situ.[613,619−621]

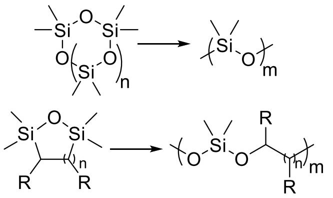
6.2.3. Phosphorus. The ROP of cyclic phosphorus monomers is attractive, as the phosphorus ancillary unit enables easy functionalization and tuning of physical properties over a massive range (Scheme 34).[485,622−627] Among the possible ancillary units, the phosphoesters are by far the most popular. The recent development of organocatalyzed ROP has been applied to phosphoesters with DBU, TBD, DBU/TU, and NHCs, providing well-controlled polymerizations.[628−631] The implementation of organocatalyzed ROP has enabled the recent exploration of polyphosphonates, polyphostones, and thionophosphoester, providing more hydrolysis, thermal, and photostable materials from less toxic starting materials.[632−636]

Scheme 34. ROP of Phosphorous-Containing Monomers



6.2.4. Silicon. Silicones are known for their very low glass transition temperature, biocompatibility, low-temperature sensitive viscoelatic behavior, and extreme resistance to heat (Scheme 35).[637−639] Recently, the ROP of siloxanes and carbosiloxanes has been achieved with organocatalysts, such as TBD and NHCs. These catalysts have been able to minimize side reactions and produce polymers with narrow dispersities.[640,641]

Scheme 35. ROP of Siloxane (Top) and Carbosiloxane (Bottom)



7. SPECIALTY MONOMERS

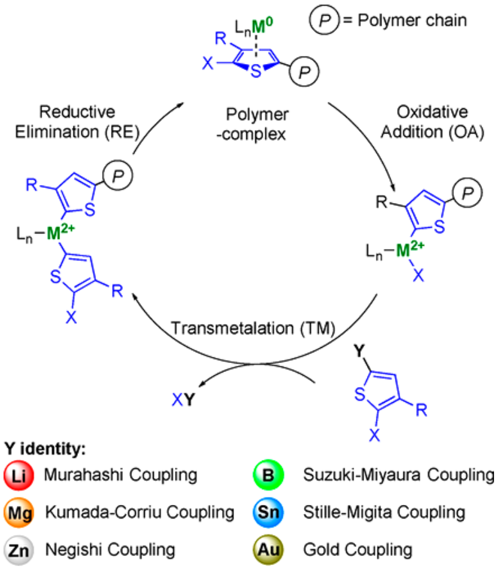
7.1. Conjugated Polymers.

Conjugated polymers are composed of alternating single and double bonds that give rise to semiconducting properties. Research in this area has been motivated by the ease of processing polymers for photovoltaics, organic light-emitting diodes, and flexible electronics.[642−644] Today, many conjugated polymers are synthesized through transition-metal-catalyzed cross coupling reactions.[645−649] Traditionally, a step-growth polycondensation is performed by repetitive cycles of oxidative addition, transmetalation, and reductive elimination to produce a polymer following a step-growth kinetic (high conversion is necessary to reach high molecular weight).[650] A transformative development in this field was the synthesis of poly(3-hexylthiophene) via a nickel-catalyzed cross-coupling polycondensation reaction that followed a controlled chain growth kinetics (Scheme 36).[651−655] This unique kinetic behavior implies that the polymer end-group is more reactive than the same functional group on the monomer.[650] This higher reactivity was rationalized by the complexation of the catalyst to the conjugated π electrons of the growing polymer chain, thus preventing the transfer of the catalyst to a new monomer forming a new polymer chain.[656,657] This catalytic chain growth polycondensation is more formally known as a catalyst transfer polymerization. Chain growth polymerizations are of interest, as it enables the tailoring of primary polymer structure (e.g., copolymer sequences, end-group functionalities) and molecular weight (e.g., targetable molecular weight and narrow dispersity).[645−649] Since its first report, many types of catalytic cross-coupling reactions have been reported when specific monomer and catalyst pairs are employed.[645−649] The identification of these pairs has remained mostly empirical, and this process is complicated by the continuous development of new, more complex monomers that are ever more difficult to polymerize. However, recent work probing the stability and ring-walking capability of many catalysts seeks to accelerate the development of new controlled chain transfer polymerizations.[658−660]

7.2. Silicone Polymers.

Hydrosilylation, the addition of a silane across an olefin, alkyne, carbonyl, or imine, enables the

Scheme 36. Proposed Catalytic Cycle for Polymerization of Thiophene by CTP. Reproduced with Permission from Ref 645. Copyright 2018 Wiley-VCH Verlag GmbH & Co



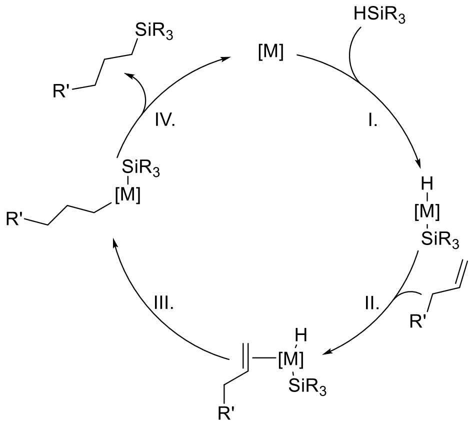


Figure 5. Chalk−Harrod mechanism. I. Oxidative addition; II. Olefin coordination; III. Olefin insertion into the Pt−H bond; IV. Reductive elimination.

catalytic cross-linking of silicone polymers to produce silicone elastomers, with applications including release coatings, sealants, lubricants, and silicone rubber (Scheme 37).[661,662] Platinum-based hydrosilylation catalysts, and Karstedt's catalyst more specifically, have become the industry standard due to their high activity and selectivity.[661,663] Recent advances through coordination of ligands to the platinum metal have helped improve the stability and compatibility toward functional groups of the catalyst.[664] Hydrosilylation with platinum- and other metal-based catalysts follows the Chalk−Harrod mechanism (Figure 5), which involves the oxidative addition of hydrosilane followed by insertion of olefin into the metal hydrogen bond and reductive elimination of the hydrosilylation product.[661,662,665,666] In depth mechanistic studies leading to the establishment of the Chalk−Harrod mechanism have helped establish that the reaction is homogeneously catalyzed and not catalyzed by metal nanoparticles.[666−670]

More recently, hydrosilylation catalysis trends have shifted from precious metals toward earth-abundant transition-metal catalysts, such as iron, nickel, and cobalt. These metals offer the promise of lower cost and greater environmental sustainability.[663,671] For instance, tridentate pyridine-(diimine)-containing iron complexes, such as $[(^{Me}PDI)Fe(N_2)]_2(\mu_2\text{-}N_2)$, have been reported to exhibit comparable activity and superior selectivity over Karstedt's catalyst.[671,672] However, discoloration caused by trace uncoordinated pyridine(diimine) ligands and high air and moisture sensitivity of the catalyst hampers industrial adoption. Structurally similar, pyridine(diimine)-containing cobalt and nickel catalysts have also been prepared and provide the benefits of milder activation conditions, high anti-Markovnikov selectivity, and tolerance for oxygen-containing functional groups.[671,673] However, air instability of the active catalyst species remains a challenge.

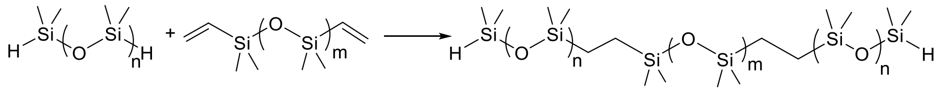
The shift toward lower costs and improved sustainability has also included the development of metal-free hydrosilylation catalysts. A notable example is the use of perfluorarylborane Lewis acid catalysts, such as $B(C_6F_5)_3$, in which borane Lewis acids activate silicon-hydride bonds.[325,674] Hydrosilylation with other Lewis acids, such as organophosphonium cations, has also been reported as part of the metal-free trend.[663,674]

8. OUTLOOK

Decades of research into catalytic polymerizations have enabled the production of polymers at a scale that has transformed modern society. This article captures the recent advances across the entire field of catalytic polymerizations. In general, the past two decades have seen the progression toward the synthesis of more and more complex polymers with higher levels of control over molecular weights, chemical composition, and topology. These higher precision polymers have facilitated the development of fundamental structure function relationships, thus accelerating the engineering of materials.

Catalytic polymerizations will undoubtedly remain at the core of polymer research as we attempt to synthesize macromolecules with the precision achieved for small molecules; however, broader challenges remain for polymers. Perhaps the most pressing of these challenges is the accumulation of plastics in the environment. Further catalyst development has the potential to play a key role in alleviating this societal issue by enabling the synthesis of biodegradable polymers, producing more robust polymers with higher recyclability, and/or synthesizing new polymeric compatibilizers to reduce the need for sorting plastics for recycling. Additionally, the continued development of polymerization catalysts for biobased polymers could reduce our reliance on fossil fuels and further mitigate the impact on the environment. Alternatively, catalytic depolymerization or upcycling of

Scheme 37. Hydrosilylation of Polysiloxanes



polymers into higher value materials by catalytic postpolymerization functionalization are also promising approaches to address environmental issues. However, for any of these proposed solutions, a total life cycle analysis will be an important step for ensuring a positive environmental impact. Finally, concerns about the residual catalyst in polymers remains a topic of conversation. Not only the toxicity associated with the use of transition metals but also residual catalyst (organic or organometallics) can accelerate undesirable polymer degradation during its processing. This can ultimately limit its application and reduces the recyclability of polymers, which further incentivizes the community to seek exceptionally productive catalysts. Given the incredible progression of the field, catalytic polymerizations will undoubtedly keep providing sustainable solutions to societal needs.

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Funding

The authors thank the NSF DMR 17-27605, NSF CHE 18-00068, and NSF CBET 17-06911 for funding. We also acknowledge Dow for funding through the University Partnership Initiative.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Tianwei Yan, Brian Van Dyke, and Danielle Harrier for the fruitful comments they provided about the manuscript.

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