

Polymerization catalysis at the millennium: frontiers in stereoselective, metal-catalyzed polymerization

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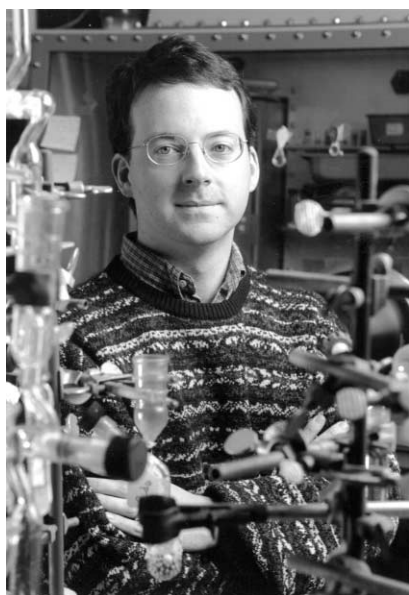
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Select recent advances in the area of stereoselective polymerization catalysis are surveyed. Although heterogeneous catalysts are the pillars of the chemical industry, homogeneous polymerization catalysts offer unmatched opportunities for the precision synthesis of new polymer architectures. In addition, these discrete 'single-site' catalysts offer extraordinary potential to examine reaction pathways at the molecular level *via* mechanistic studies. This article will examine discrete catalysts for stereoselective polymerization, with an emphasis on technologically important processes.

Introduction

Few materials have changed modern society more than synthetic polymers. The first industrial synthetic macromolecules,

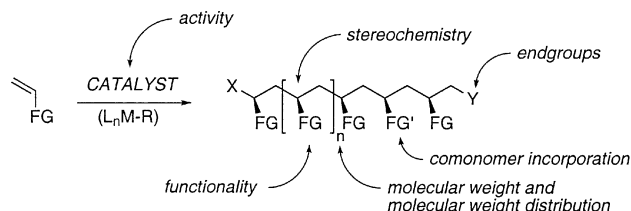
Geoffrey W. Coates was born in Evansville, Indiana in 1966. He obtained a B.A. degree in chemistry from Wabash College in 1989 and a Ph.D. in organic chemistry from Stanford University in 1994. In his thesis work, under the direction of Robert M. Waymouth, he investigated the stereoselectivity of metallocene-based Ziegler–Natta catalysts. Following his doctoral studies, he was an NSF Postdoctoral Fellow with Robert H. Grubbs at the California Institute of Technology. In 1997 he joined the Department of Chemistry at Cornell University, and was promoted to Associate Professor in 2001. His main research interests are the design, synthesis, characterization, and applications of polymers with an emphasis on catalytic transformations and the control of stereochemistry.



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such as polyamides, esters, and phenolic resins, were typically constructed from bifunctional monomers in condensation polymerizations. Addition polymers were also discovered where olefinic monomers were enchaind by controlled radical or ionic pathways. A major advance came in the 1950s when Ziegler and Natta reported that mixtures of transition metal complexes (such as TiCl_4 and AlEt_2Cl) formed highly active catalysts for the formation of linear polymers of ethylene, as well as isotactic polymers of propylene.^{1,2} This revolutionary work that launched the polyolefin industry earned Ziegler and Natta a Nobel Prize in 1963.

Over the last half decade, a tremendous amount of scientific research has focused on the development of new catalysts for polymerization. The potential applications of a polymer are determined by its physical and mechanical properties, which in turn are defined by the morphology (solid state arrangement) of the polymer. Polymer morphology largely depends on the composition and architecture of the polymer. Therefore, the development of synthetic methods for the polymerization of a wide range of monomers with control over the stereochemistry, molecular weight, and comonomer incorporation is a long-standing scientific challenge. The last two decades have witnessed impressive advances in the discovery and understanding of catalysts for controlled polymerization. While many of the industrially employed polymerization catalysts are of the heterogeneous variety, most of the catalysts that allow mechanistic studies and the synthesis of new polymer architectures are of the homogeneous type. Such catalysts are often referred to as 'single-site' catalysts, since they have the general formula L_nMR , where L_n is an organic ligand set that remains bound to and thus modifies the reactivity of the active metal center (M) during the entire chemical reaction, and R is the polymer or initiating group. By tailoring the coordination environment of the metal center, single-site catalysts are now available that can control the molecular weight, molecular weight distribution, comonomer incorporation, endgroups, and both the relative and absolute stereochemistry of a polymer in a way that is often impossible using conventional heterogeneous catalysts (Scheme 1).³ Although their commercial implementation in the



Scheme 1 Key considerations for the development of polymerization catalysts.

solution phase is often impractical, they can be heterogenized for efficient gas-phase or flow-through reactions by attaching them to a solid support.⁴ Perhaps most importantly, these defined molecular-based systems allow detailed structural and

mechanistic studies. Thus, through theoretical and empirical studies scientists can rapidly evolve new and improved generations of catalysts.

The goal of this Millennium Perspective is to highlight some of the most exciting new developments in the field of stereoselective, single-site polymerization catalysts, emphasizing processes of commercial importance. Particular attention will be given to catalysts that are living, as they allow the synthesis of new polymer architectures that are unavailable by alternate methods.

Alkene polymerization

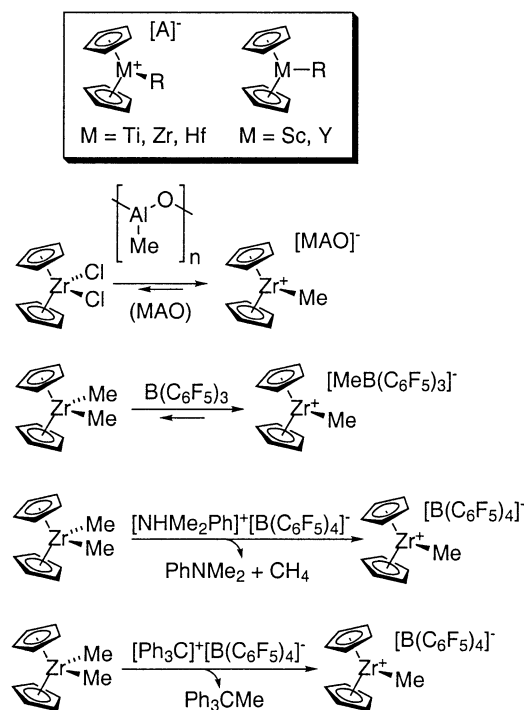
Following Ziegler and Natta's discovery of heterogeneous olefin polymerization catalysts in the mid-1950s, efforts were directed at devising homogeneous catalyst model systems that would prove more amenable to mechanistic studies. In 1957, Natta and Breslow independently reported that the metallocene Cp_2TiCl_2 (Cp = cyclopentadienyl) could be activated for olefin polymerization by Et_3Al or Et_2AlCl .⁵⁻⁷ These soluble catalysts slowly polymerized ethylene, but were basically inactive for propylene. A major breakthrough came in the early 1980s when Sinn and Kaminsky discovered that partially hydrolyzed Me_3Al , called methylaluminoxane (MAO), activated Group IV metallocenes for the polymerization of both ethylene and α -olefins.^{8,9} MAO is a dynamic and complex set of aluminium species, and is generally thought to exist as linear polymers, rings, and aggregates of the general repeat unit $[\text{Al}(\text{Me})\text{O}]_n$. The discovery of MAO stimulated a general renaissance in single-site catalysis, with olefin polymerization clearly receiving the most attention. The development of well-defined polymerization catalysts has provided the opportunity to study the mechanisms of initiation, propagation, and termination steps of Ziegler–Natta polymerization reactions. These well-defined systems also provide extraordinary synthetic opportunities in the field of polymer science.

Active species and mechanism of enchainment

Concerning the organometallic chemistry of olefin insertion, it is now clear that in most cases the active catalytic species for olefin polymerization are coordinatively unsaturated metal alkyls of the formula $[\text{L}_n\text{M}-\text{P}]^+\text{A}^-$, where P is a polymer chain, and A is a weakly-coordinating anion. An alternative to these ionic complexes are the isoelectronic, scandium and yttrium(III) alkyl complexes.¹⁰⁻¹² In both the neutral and ionic metal alkyl systems, the mechanism is thought to involve alkene coordination followed by insertion into the metal alkyl.¹³⁻¹⁸ In some cases, an interaction of a hydrogen on the alpha carbon is believed to interact with the metal center (an 'agostic' interaction) to stabilize the transition state.¹⁹ Many convenient methods for generating ionic species are now available; among the most used are reaction of a metal dihalide $[\text{L}_n\text{MX}_2]$ with MAO, or the reaction of a metal dialkyl $[\text{L}_n\text{MR}_2]$ with either fluorinated boranes, borate salts, or aluminate salts (Scheme 2).²⁰

Stereochemistry

Many polymers have stereogenic centers in the main chain, and the relative configurations of these sites is a primary determinant of mechanical and physical properties. In 1954, Natta's first propylene polymerizations using heterogeneous catalysts yielded products that were mixtures of atactic and isotactic polymer chains. Shortly thereafter, polymers were produced that consisted primarily of isotactic chains by modifying the composition of the catalyst. The modification of Group IV metallocenes to produce catalysts capable of stereoselective polymerization has developed much more slowly, but has recently seen dramatic success. Sinn and Kaminsky first found



Scheme 2 Active species for alkene polymerization.

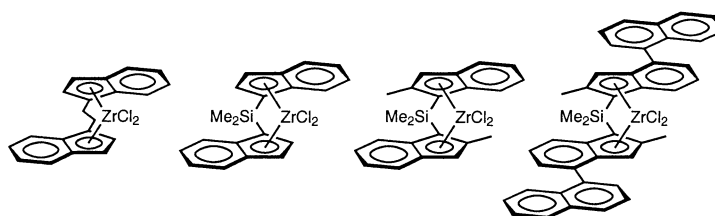
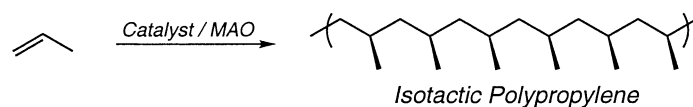
the MAO-activated Cp_2ZrCl_2 produced perfectly random atactic propylene, which was significant since heterogeneous catalysts show a tendency towards isotacticity.^{8,9} Due to the amorphous nature and low glass-transition temperature of atactic polypropylene ($T_g \approx 0^\circ\text{C}$), there are few applications for this polymer. Therefore a considerable amount of academic and industrial research was directed towards the development of metallocenes that could control polypropylene stereochemistry.²¹

Isospecific polymerization

Using chiral metallocenes first prepared by Brintzinger,²² Ewen found that C_2 -symmetric titanocenes were capable of preparing partially isotactic polypropylene, where the enantiomeric site of the active species was responsible for the inducement of stereocontrol.²³ Soon after, Kaminsky and Brintzinger used a chiral zirconocene to also produce isotactic polypropylene.²⁴ Although these chiral metallocenes stimulated an enormous amount of scientific and industrial interest, their activities as well as the isotacticity and molecular weight of polymers produced were certainly inferior to their industrial heterogeneous counterparts. In the decade following the discovery of isospecific metallocene catalysts, significant progress at developing modified versions of these original catalysts was made.²⁵⁻²⁸ Shown in Scheme 3 are a progression of catalysts that depict this evolution. The complex on the right in Scheme 3 produces isotactic polymer that is comparable to that made by the best heterogeneous catalysts.²⁷

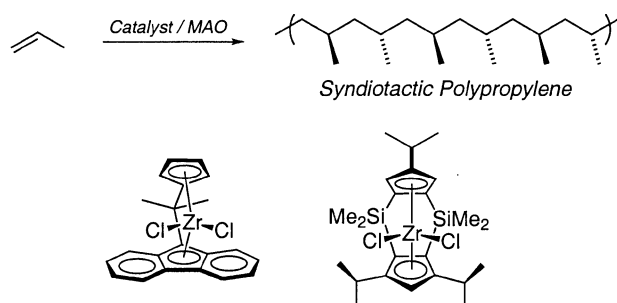
Syndiospecific polymerization

In 1962, Natta and Zambelli reported a heterogeneous, vanadium-based catalyst mixture which produced partially syndiotactic polypropylene at low polymerization temperatures.²⁹ This catalyst system suffered from both low activity and low stereoselectivity. Highly active single-site olefin polymerization catalysts have now been discovered that make syndiotactic polypropylene with nearly perfect stereochemistry. Ewen has reported a bridged cyclopentadienyl/fluorenyl zirconocene precursor that is highly active for the syndiospecific polymerization of propylene and higher aliphatic α -olefins



Year	1985	1989	1992	1994
M _w	24,000	36,000	330,000	920,000
Isotacticity [mmmm]	78%	82%	89%	99.1%
T _m	132°C	137°C	146°C	161°C
Activity [kgPP/(gM ^o h)]	2043	2088	4429	9615

Scheme 3 Advances in metallocenes for isospecific propylene polymerization.



Scheme 4 Metallocenes for syndiospecific propylene polymerization.

(Scheme 4).³⁰ It is now generally accepted that the mechanism of stereocontrol consists of the regularly alternating insertion of olefins at the enantiotopic sites of the C_s-symmetric complex.^{31–33} Bercaw has designed novel C_s-symmetric doubly-bridged zirconocenes for the synthesis of syndiotactic polypropylene (Scheme 4).^{34–37}

Stereoblock polymers

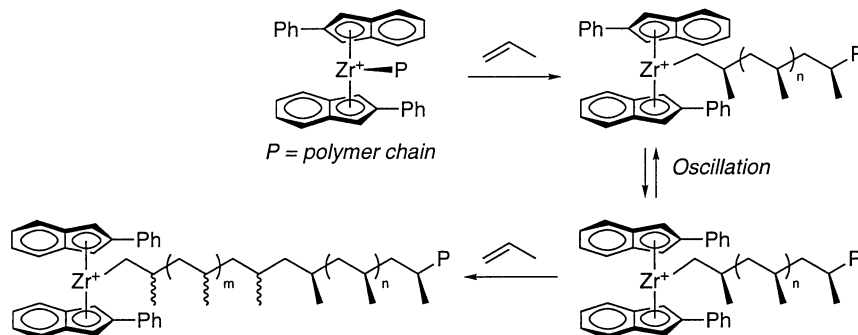
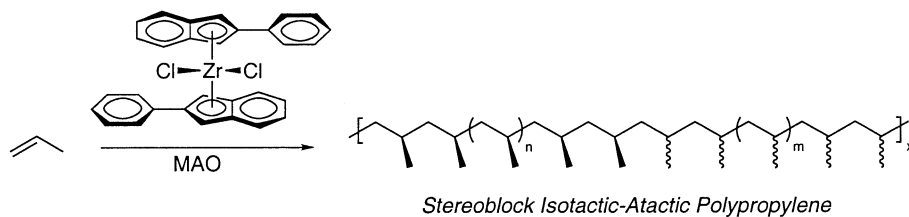
Polymers that have blocked units of varying stereochemistry have potential uses as thermoplastic elastomers as well as blend compatibilizers. Coates and Waymouth have developed a conceptually new strategy for the synthesis of stereoblock polymers.³⁸ C₁-symmetric catalysts have been reported for the synthesis of isotactic-atactic stereoblock polypropylene, however these polymers exhibit low melting points that inhibit broad applications.^{39,40} By devising a ligand isomerization strategy (Scheme 5), it is possible to control block sizes and stereoregularity (therefore melting point) by ligand design as well as reaction conditions. In this system, the relative rates of propagation and ligand isomerization control block size; the relative energies of aspecific and isospecific states and their associated rate constants determine the overall amount of units in each tacticity domain. The metallocene in Scheme 5 produces elastomeric polypropylene.³⁸ The microstructure of the polymer is sensitive to the reaction temperature, as well as monomer concentration (low temperatures and high monomer concentrations favor isotacticity). This experimental observation is consistent with an oscillation between achiral and chiral coordination geometries during propagation, which is proposed to produce the stereoblock microstructure.^{38,41}

Functional group incorporation

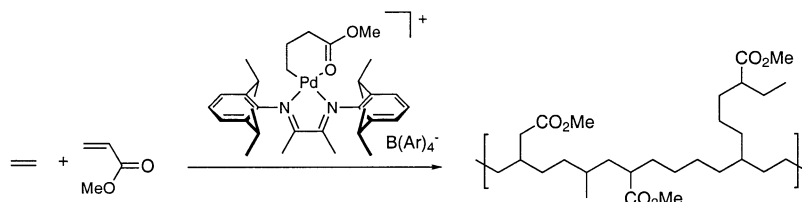
Single-site catalysts offer significant advantages over heterogeneous catalysts for the polymerization of functional olefins.⁴² One of the inherent liabilities of traditional Ziegler–Natta catalysts is that they are highly electrophilic and are easily poisoned by Lewis-base containing monomers.^{43,44} Molecular catalysts, however, offer the potential for steric protection of the active site through careful ligand design. In contrast to heterogeneous catalysts, chain-transfer mechanisms of these defined catalysts can also be modified to allow functionality to be constructed into the polymers. Although a significant amount of research has been directed toward the use of metallocene-based catalysts for the polymerization of functional monomers,⁴⁵ this strategy has the persistent disadvantage of interaction of the Lewis basic monomer with the electrophilic metal center. A recent promising advance for the synthesis of functional polyolefins is the discovery of late-transition metal catalysts that exhibit reduced interaction with the heteroatoms of functional monomers.⁴⁶ For example, Brookhart and coworkers reported that diimine ligated palladium and nickel complexes are active for the copolymerization of ethylene and functional monomers.^{47,48} The diimine-palladium complex in Scheme 6 polymerizes methyl acrylate and ethylene to give a branched polymer by a chain-walking mechanism. This development has stimulated a resurgence of activity in the area of late-transition metal polymerization catalysts, and it is clear that this field will see many exciting developments in the coming years.

Living olefin polymerization

A primary goal of synthetic polymer chemistry for the last half century is the development of chain-growth polymerization methods that enable consecutive enchainment of monomer units without termination. Such techniques, now known as living polymerizations,⁴⁹ allow both precise molecular weight control as well as the synthesis of a wide array of polymer architectures.⁵⁰ For example, the initiation of multiple polymer chains from a central core results in the formation of a star-branched polymer, while the consecutive addition of two types of monomers to a single initiator produces a diblock copolymer.⁵¹ Living methods also allow the synthesis of end-functional polymers if special initiation and/or quenching methods are employed. Although a number of olefin polymerization catalysts have been reported to produce narrow molecular weight polymers at low temperature, only in the last half



Scheme 5 Synthesis of stereoblock polypropylene and the proposed mechanism.

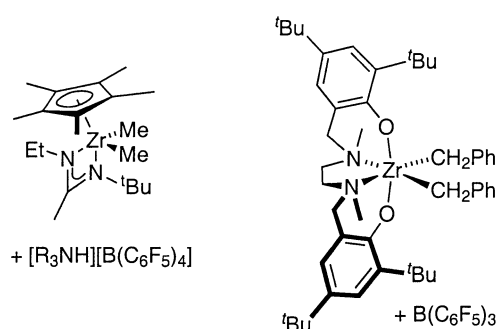
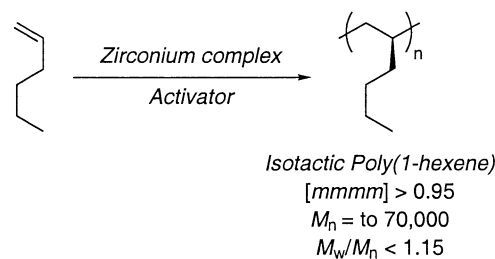


Scheme 6 Copolymerization of ethylene and methyl acrylate.

decade have truly living catalysts been reported that produce high molecular weight polymer in a living fashion at near ambient temperature.⁵² The nickel and palladium catalysts reported by Brookhart (*vide supra*) were among the first to exhibit living behavior for olefin polymerization. Subsequently, McConville⁵³⁻⁵⁵ and Schrock⁵⁶⁻⁵⁸ reported titanium and zirconium diamido complexes that made monodispersed, atactic polyhexene. Of significant recent interest are the catalysts that combine living enchainment with control of polymer stereochemistry. Sita and coworkers have reported amidinate ligated zirconium complexes that form isotactic poly(hexene), as well as block copolymers from hexene and hexadiene, and remarkably isotactic poly(vinylcyclohexane) (Scheme 7).⁵⁹⁻⁶¹ Kol, Goldschmidt and coworkers have also found a class of phenoxy-amine chelated zirconium complexes that produce highly isotactic polyhexene (Scheme 7).^{62,63} Coates and coworkers have reported a phenoxyimine ligated titanium complex that forms highly syndiotactic polypropylene in a living fashion and also produces monodisperse syndiotactic poly(propylene)-*block*-poly(ethylene-*co*-propylene) (Scheme 8).^{64,65} Researchers at Mitsui have subsequently reported a variant of this catalyst that produces living polyethylene and partially syndiotactic polypropylene.^{66,67}

Conjugated alkene polymerization

Catalysts that polymerize common olefins such as ethylene and propylene typically do not polymerize conjugated alkenes such as styrene. Ishihara first reported the synthesis of syndiotactic polystyrene (Scheme 9).⁶⁸ This polymer has an extremely high melting temperature of 270 °C, and has many promising applications as an engineering resin.⁶⁹⁻⁷¹ Although Group IV metallocenes give very low yields of syndiotactic or atactic polystyrene, mono-cyclopentadienyl titanium complexes, when activated by MAO, are highly active for the syndiospecific

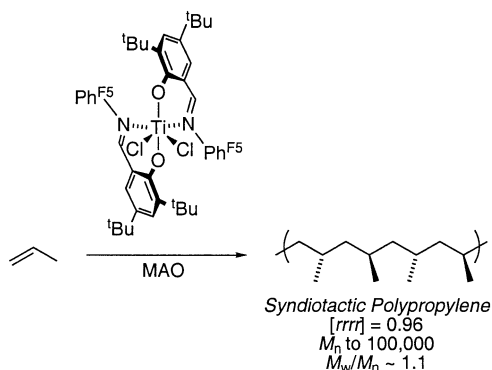


Scheme 7 Isospecific living polymerization of hexene.

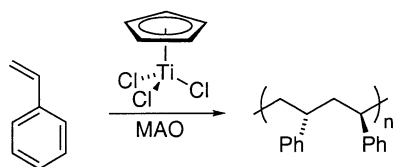
polymerization of styrene. These catalysts are also active for the stereoselective polymerization of conjugated dienes; depending on the reaction temperature, either isotactic, *cis*-1,4 or syndiotactic-1,2 polymers are produced.⁷²

Alkene/CO polymerization

The synthesis of alternating copolymers from carbon monoxide (CO) and olefins using palladium catalysts has been an active area of research throughout the last two decades. It should be



Scheme 8 Syndiospecific living polymerization of propylene.



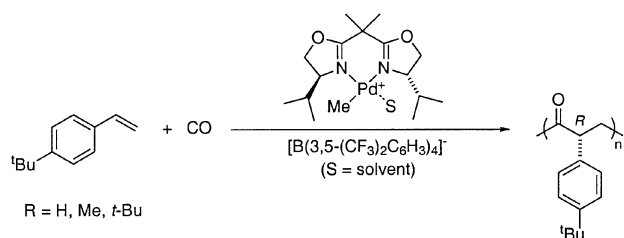
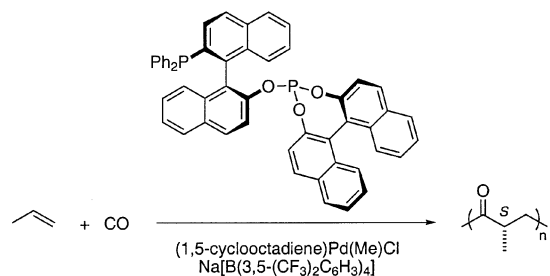
Scheme 9 Synthesis of syndiotactic polystyrene.

noted that, despite impressive advances in catalyst discovery and polymer synthesis, Shell has discontinued their effort to commercialize this class of polyketones. In cases where α -olefins are used, the regiochemistry (head/tail orientations) and stereochemistry (tacticity) of olefin insertion have a strong influence on the properties of the polymers. Unlike regioregular α -olefin homopolymers, these copolymers have a directionality along the polymer backbone due to the incorporation of CO. Therefore isotactic, regioregular CO/olefin polymers are chiral by virtue of their main-chain stereochemistry; in contrast, their syndiotactic counterparts are achiral.

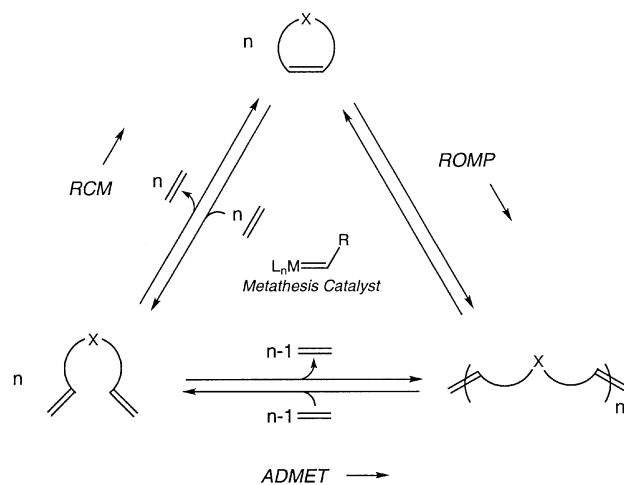
In the early 1980s, it was discovered that cationic palladium catalysts with bidentate tertiary phosphines exhibited remarkable reaction rates for olefin/CO copolymerization.^{73,74} Although initial studies using bidentate arylphosphines produced CO/propylene polymers with poor regioregularity, it was later revealed that bidentate alkylphosphines and/or chiral phosphines produced polymers with a much higher degree of regioregularity. In the early 1990s, the first reports concerning the use of enantiopure, C_2 -symmetric ligated catalysts for the enantioselective, isospecific copolymerization of α -olefins and CO began to appear.⁷⁵ Although several excellent systems for the enantioselective copolymerization of alkenes with CO have appeared, one of the best regarding propylene was reported by Nozaki and Takaya.^{76,77} Using a phosphine–phosphite bidentate ligated complex a copolymer with the highest reported specific optical rotation was produced (Scheme 10). Again, several systems have been reported for the asymmetric copolymerization of styrenes and CO; notably Brookhart and coworkers reported a bisoxazoline ligated palladium complex that produces highly isotactic and optically active polymer from CO and *p*-*tert*-butyl styrene (Scheme 10).⁷⁸ Brookhart and Wagner have also described a clever ancillary ligand exchange, where the chiral bisoxazoline ligand is replaced with an achiral bipyridine ligand during chain formation to create an isotactic–syndiotactic stereoblock polymer.⁷⁹

Metathesis polymerization

In the late 1950s, heterogeneous catalysts based on Mo, Ru, W, or Re oxides and halides were discovered that were capable of breaking open the double bond of a cyclic olefin, then converting the ring-opened molecule into a polymer with olefins in the main-chain.⁸⁰ This process, called ring-opening metathesis polymerization (ROMP), has been studied in great deal since these initial discoveries (Scheme 11). It is now known that olefin



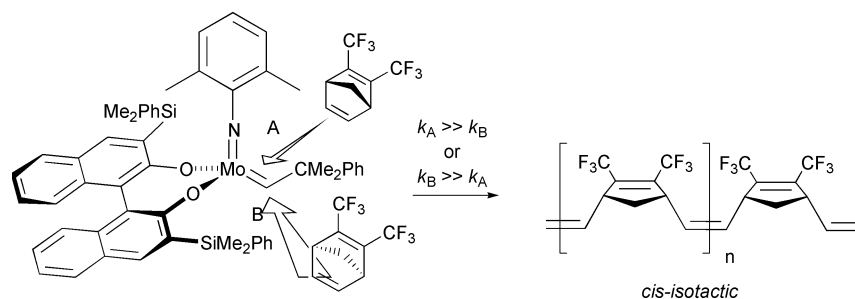
Scheme 10 Enantioselective, isospecific copolymerization of propylene and styrene with carbon monoxide.



Scheme 11 Metathesis processes.

metathesis reactions are catalyzed by metal carbene complexes that are composed of a metal atom that is covalently bound to a CR_2 group by a double bond. Reaction of this carbene with an olefin can effectively interchange the double bond substituents of the two species *via* a metallacyclobutane transition-state or intermediate.⁸⁰ An alternate mode of polymer formation using these metal carbenes is the coupling of α - ω -diolefins in a step growth mechanism. This process, known as acyclic diene metathesis polymerization (ADMET) occurs when a ring-closing metathesis (RCM) is disfavored due to enthalpic or entropic factors (Scheme 11). Since the early heterogeneous catalysts were difficult to characterize and modify, a tremendous amount of research has been directed toward the development of single-site metal carbene complexes. These compounds, which have the general formula $L_nM=CHR$, allow the synthesis of new polymer microstructures with exceptional precision, and perhaps more importantly, allow the detailed study of the factors that dictate stereochemical control. Two representative catalysts that have emerged over the last decade are based on molybdenum and ruthenium.⁸¹

In the late 1980s Schrock and coworkers reported a major advance concerning the development of well-defined catalysts for ROMP.⁸² Molybdenum and tungsten carbene complexes have since been discovered that exhibit high activities for ROMP, and produce polymers with exceptional control of molecular weight and stereochemistry, and have been used in



Scheme 12 Enantiomeric-site control in ROMP of a norbornene.

many types of ring-opening metathesis polymerization.⁸³ One of the advantages of these compounds is that they have successfully been used to make both *trans*-syndiotactic and *cis*-isotactic polynorbornenes. A distinct disadvantage is their relative lack of functional group tolerance. Since the original Schrock molybdenum complexes were achiral and only able to effect modest stereochemical control over the polymerization, complexes with C_2 -symmetric diols were synthesized to create asymmetric catalysts (Scheme 12).^{84,85} The molybdenum complex in Scheme 12 exerts an exceptionally high degree of stereochemical control in the polymerization of norbornenes, producing polymers that are >99% *cis* and have >99% isotactic (*mm*) triads. A considerable amount of research has been directed toward understanding the mechanisms of stereocontrol in these molybdenum-based catalyst systems. When the alkoxide ligand is chiral, there will be a preferential diastereofacial attack on the carbene regardless of the polymer's chain end configuration (Scheme 12). Again, if the barrier to enchainment at one face is significantly lower in energy, an isotactic polymer will form.

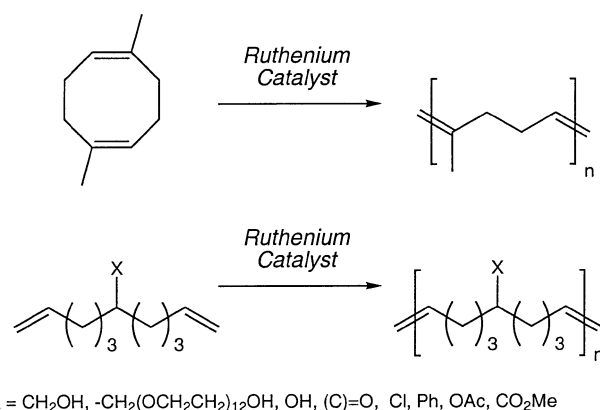
In the early 1990s, Grubbs and coworkers reported a new class of well-defined ruthenium carbenes of the form $(Cl)_2(PR_3)_2Ru=CHR$ that were moderately active for ROMP.^{86–88} A remarkable feature of these complexes was that they were active for olefin metathesis in the presence of a wide range of functional groups, including esters, amides, alcohols, and ammonium salts. This feature opened countless opportunities for the synthesis of functional polymers. One disadvantage of these catalysts is that they have, to date, not been found capable of stereochemical control in ROMP.

Grubbs and coworkers have recently found a mixed phosphine/*N*-heterocyclic carbene ruthenium complex (Scheme 13) that exhibits unprecedented activity for alkene metathesis.⁸⁹ For example, this is the first complex to ROMP 1,5-dimethyl-1,5-cyclooctadiene (Scheme 13).⁹⁰ As another representative example of the value of this versatile metathesis catalyst, Wagener and coworkers have found that it enchains hydroxyfunctional diolefins in an ADMET polymerization.⁹¹ Polymers with degrees of polymerization as high as 150 are obtained, indicating high conversion of the metathesis reaction.

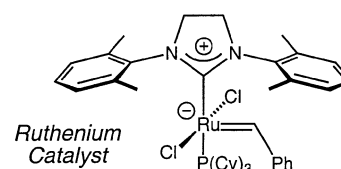
Polymers from biorenewable resources

At the present time, tens of thousands of chemical compounds are produced worldwide from a basic set of around 300 chemical intermediates. The predominant source of carbon for these raw materials comes ultimately from fossil fuels. Since these resources are limited, there is significant interest in finding new routes to important chemicals from biorenewable resources, especially polymers. Two areas of promise in this regard are polymerizations involving CO_2 as well as the cyclic diester of lactic acid, lactide.

Although remarkable advances have been reported concerning the development of single-site metal catalysts for olefin polymerization, relatively few well-defined metal catalysts are available for the ring-opening polymerization of lactones.⁹² Prior to the 1990s most catalysts for lactone polymerization



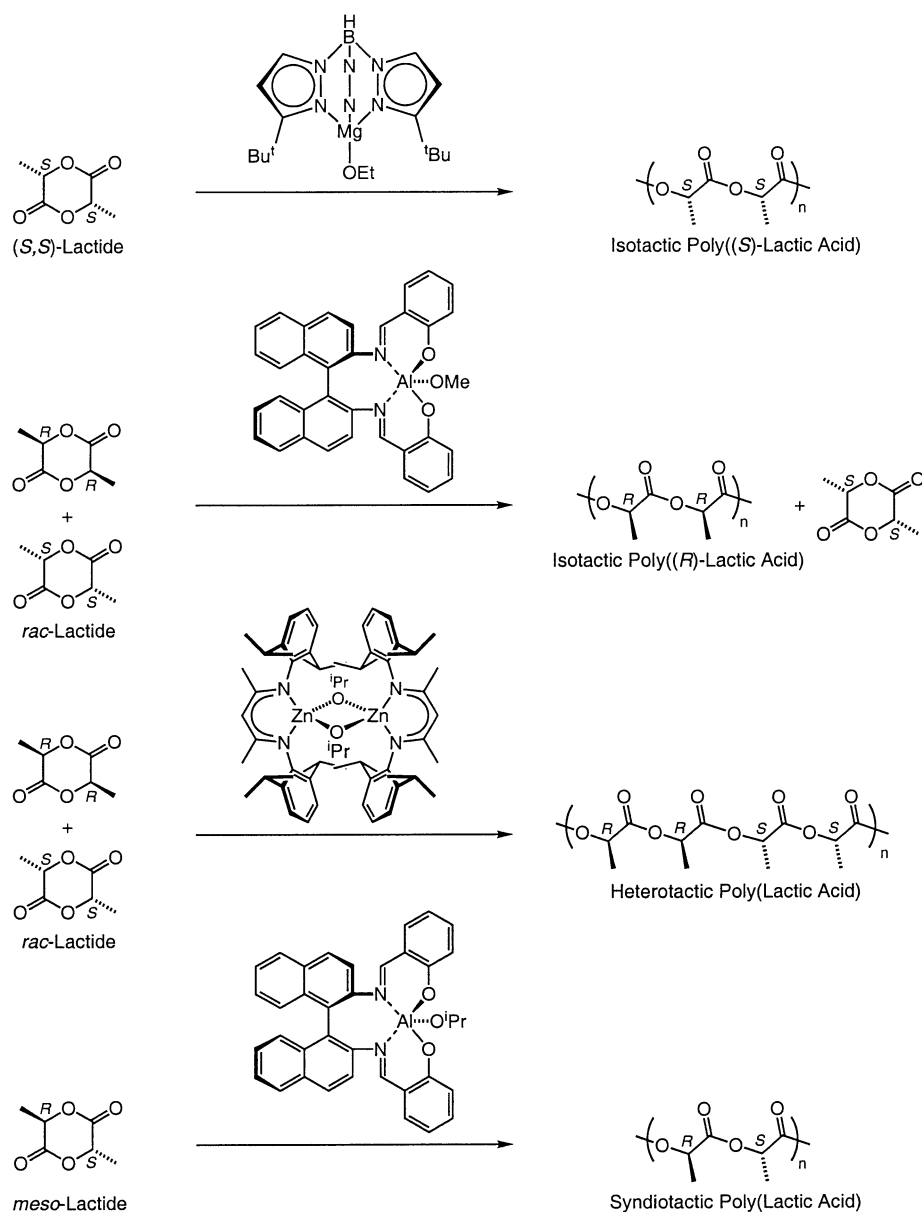
X = CH_2OH , $-(CH_2(OCH_2CH_2))_{12}OH$, OH, (C=O), Cl, Ph, OAc, CO_2Me



Scheme 13 Metathesis polymerization of sterically bulky and functional monomers.

were based on poorly defined and aggregated metal alkoxides and carboxylates. Early work by Inoue and Spassky showed the promise of well-defined porphyrin and salen aluminium alkoxide complexes for lactide polymerization.^{93,94} More recently, Chisholm has reinvigorated the field by reporting a new class of magnesium alkoxides for lactide polymerization (Scheme 14).^{95,96} Notably, the catalyst is highly active for polymerization of optically-active lactide without appreciable epimerization, and produces isotactic poly(lactic acid) of controlled molecular weight. Spassky has developed a highly selective aluminium complex for the kinetic resolution of racemic lactide that prefers the *R*-enantiomer of lactide over its antipode with a selectivity of 20 : 1 (Scheme 14).⁹⁷ Coates has recently reported a diiminate ligated zinc complex that forms a heterotactic polymer from racemic lactide (Scheme 14).^{98,99} Using Spassky's chiral aluminium alkoxide, Coates has also reported the synthesis of highly syndiotactic, semicrystalline poly(lactic acid) from meso-lactide (Scheme 14).^{100,101}

Carbon dioxide is an ideal synthetic feedstock since it is abundant, inexpensive, nontoxic, and nonflammable. Although it is estimated that Nature uses CO_2 to make over 200 billion tons of glucose by photosynthesis each year, synthetic chemists have had little success in developing efficient catalytic processes that exploit this attractive raw material. Therefore there has been considerable recent interest in the development of catalysts for the alternating copolymerization of carbon dioxide with epoxides to produce aliphatic polycarbonates.¹⁰² Due to the low cost and accessibility of the monomers and the attractive properties of polycarbonates, the development of new, efficient initiators for this polymerization process is a significant scientific goal. Several complexes have been reported that can

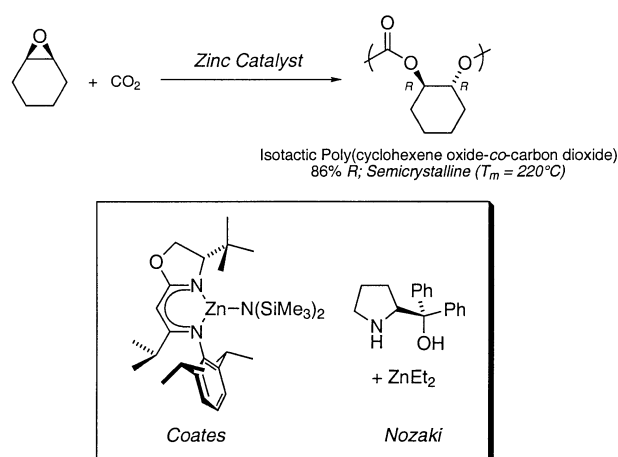


Scheme 14 Stereoselective polymerization of lactide.

polymerize CO_2 and epoxides; among the most active are those based on zinc and chromium.^{103–106} Despite the recent intense interest in developing enantioselective catalysts for the synthesis of optically-active polymers, there are only few examples of meso-desymmetrization in polymerization reactions. Coates¹⁰⁷ and Nozaki¹⁰⁸ have recently reported chiral zinc-based complexes for the asymmetric polymerization of CO_2 and epoxides (Scheme 15). In addition to imparting crystallinity to the typically amorphous aliphatic polycarbonates, these catalysts provide a route to optically active diols upon polymer hydrolysis.

Outlook

The last half-century has witnessed impressive advances in the field of stereoselective polymerization catalysis. Progress during the last decade has been particularly rapid, with notable achievements in stereochemical and molecular weight control being reported. Given the growing need for inexpensive plastics for use in ordinary applications, the future for metal-catalyzed polymerization is certainly bright. However there are many important goals still remaining in this field. Perhaps the biggest general challenge facing the field is the development of new methods for producing copolymers of controlled sequence, functionality, and stereochemistry. One obvious way



Scheme 15 Asymmetric copolymerization of CO_2 and cyclohexene oxide.

to achieve this goal is the development of living olefin polymerization catalysts. Although living methods are now available for the synthesis of stereoregular olefin block copolymers, this approach has the significant disadvantage

that only one polymer chain is formed from one metal complex. For economic reasons, it is essential that methods are developed that not only allow the synthesis of block copolymers in a controlled fashion, but also significantly increase the polymer/catalyst ratio. One solution to this problem is to develop "multi-state" catalysts that can exist in more than one state; if the different states exhibit different propagation characteristics, then block polymers are formed. Another remaining goal is the copolymerization of monomers previously considered to be incompatible, such as simple alkenes and acrylates, in a sequence- and stereo-controlled fashion.

Since the development of new polymerization catalysts will have a profound impact on the achievement of the above-mentioned goals, appreciable work must center on advancing the rate at which these future complexes are discovered. Historically, catalyst discovery has been the product of hard empirical work and serendipity. In the future, these traditional methods must be supplemented by combinatorial and high-throughput methods, as well as computational studies.

One of the overarching trends of the future of chemistry is the development of environmentally-benign methods for chemical synthesis. Since, by far, the largest volume of chemicals produced are polymers, it will be essential that new catalysts and processes are developed that reduce the energy and chemicals needed to produce a given amount of polymer. In addition, due to dwindling petroleum reserves, it is crucial that renewable resources are used when possible.

It is likely that Ziegler and Natta, forefathers of the field of stereoselective olefin polymerization, could never have foreseen the exciting advances over the last several decades. It is perhaps even more difficult now to predict the advances that will occur over just the next half decade. However, based on the current trajectory, it is safe to conclude that the coming years will produce countless exciting and currently unimaginable discoveries.

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