

Tunable modalities in polyolefin synthesis via coordination insertion catalysis

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ABSTRACT: Metal-catalyzed coordination insertion polymerization is one of the most widely used methods to prepare polyolefins, a broad class of polymers comprising a vast majority of the synthetic materials market. To impart greater control over the polymerization process, chemists have developed innovative strategies to enable catalyst tuning by reaction engineering (e.g., changing temperature, pressure, solvent, etc.) or introducing external stimuli (e.g., redox reagents, light, boranes, or metal cations). This review article will provide an overview of the various tunable modalities employed to regulate the polymerization of olefins by transition metal complexes. We will focus on the unique capabilities and limitations of various approaches and offer our perspective on how externally regulated polymerization could have meaningful impacts on applications and future research.

Introduction

The profound impact polyolefins have on our society is undeniable. They are highly attractive commercial polymers because of their excellent chemical and physical properties, low cost, good processability, and good recyclability.[1] Polyolefins were first synthesized using heterogeneous Ziegler-Natta (Zr/Al or Ti/Al)[2] and Phillips (Cr) catalysts[3] (Chart 1) in the 1950s. The discovery by Sinn and Kaminsky in the 1970s that early transition metal metallocene complexes in combination with methylaluminoxane (MAO) are capable of polymerizing olefins with extremely high activity was an important breakthrough.[4, 5] Fujita and coworkers later found that non-metallocene early transition metal complexes exhibited living behavior and gave highly syndiotactic polymers.[6, 7] In the 1990s, this single-site catalyst technology was expanded to include late transition metal complexes. A variety of Ni and/or Pd species supported by diimine (Brookhart),[8] phenoxyimine (Johnson/Dupont, Grubbs),[9-11] and phosphine sulfonate (Drent)[12] ligands showed good tolerance toward polar additives and monomers. Many of these catalysts gave branched polymers due to their ability to undergo chain walking, which is a feature lacking in early transition metal catalysts. These seminal studies inspired several decades of research to create new catalysts with improved properties.[13-19] such as the ability to generate polymers with ultra-high molecular weight,[20, 21] multi-block microstructures,[22] or high polar monomer content.[23] Because of these extraordinary efforts, diverse libraries of catalysts are now available for polyolefin synthesis.[24-36]

Although olefin polymerization catalysis has matured significantly over the course of its 60+ years history, we still have limited control over a catalyst's behavior. For example, conventional polymer synthesis typically follows a "one catalyst one material" model because the intrinsic reactivity of a

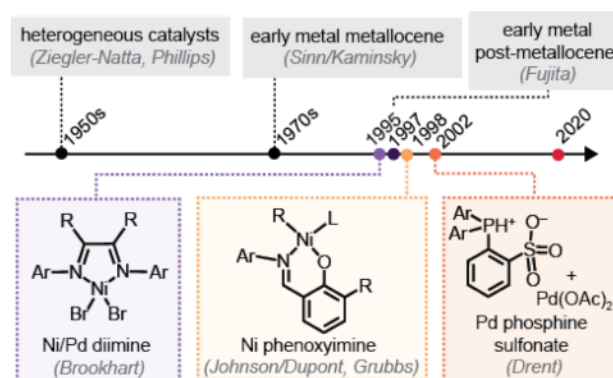


Chart 1. Brief timeline of coordination insertion olefin polymerization catalyst development.

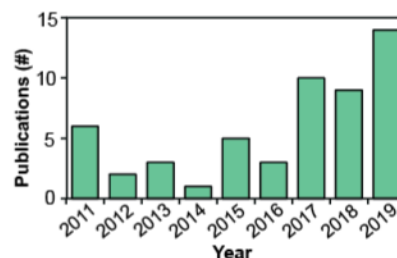


Figure 1. Publications from 2011-2019 containing either the terms "tunable" or "switchable" polymerization based on a Web of Science database search.

catalyst dictates the type of polymer it produces.[37] Without resorting to external regulations (vide infra), specialty materials such as gradient polymers[38, 39] or single-source block polymers[22] are difficult to obtain under standard polymeri-

zation conditions. Despite demonstrations that metal catalysts could be synthetically modified to alter their properties,[40-43] there are practical restrictions to what molecular structures and chemical functionalities are feasible to obtain. Thus, in our opinion, to advance polyolefin chemistry in the coming years efforts should be focused on making polymerization processes tunable and using such capabilities to synthesize previously inaccessible materials that could lead to new technologies and applications.

In recent years, chemists have devised a variety of methods to regulate polymerization reactions. One such approach is through the application of tunable catalysts,[44] which are complexes that can change reactivity when combined with external stimuli such as chemical reagents, electrical voltage, or light. Such complexes are sometimes referred to as “switchable catalysts” when used for temporal control during polymerization reactions.[45-49] Reaction engineering via modulation of environmental conditions (e.g., temperature, pressure, solvent) or mixing rates will also be considered a

form of tunable polymerization in this review. To track the emergence of the terms “tunable” or “switchable” in the polymer chemistry literature, a Web of Science database search was conducted.[50] The results showed that from 2011-2019 (Figure 1), there were greater than 50 research papers exploring externally regulated polymerization catalysis. This number is probably an underestimation since other terms, such as “stimuli-responsive” or “allosteric control,” might also be used to describe the same concept. It is clear, however, that there is a growing interest in this emerging field as chemists seek to enhance the precision of macromolecular synthesis.

Herein, we focus exclusively on user-controlled tuning of olefin polymerization by homogeneous coordination insertion catalysts. We will present representative examples from the literature to illustrate a range of modalities used to prepare polyolefins (Chart 2). The advantages and disadvantages of each strategy will be examined and factors to consider in selecting the best methods will be discussed.

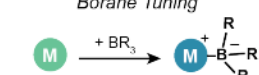
Method	Advantages	Disadvantages
Reaction Engineering 	Can be applied to most reactions. Does not require special reagents.	Environment switching is slow, can be difficult to achieve in large scale. May require specialized equipment.
Chain Transfer 	Gives good polymer molecular weight control. Produces more than one polymer per catalyst in living polymerization.	Superstoichiometric amounts of CTA often required. Cannot change branching structure.
Redox Tuning 	Tuning can be reversible. Can tune electronic environment of catalyst.	Require catalysts with redox active metal or ligands.
Borane Tuning 	Can tune both catalyst electronic and steric environments. Often enhances catalyst activity.	Borane binding tends to be irreversible. Can give polymers with broad dispersity.
Cation Tuning 	Can tune both catalyst electronic and steric environments. Many M' options are available and can serve additional functions.	Suitable catalyst design is critical. Cation metal binding dynamics can be complicated to understand.
Nuclearity Tuning 	Can give high molecular weight polymers. Can enhance thermal stability.	Difficult to control nuclearity and self-assembly processes. Can give polymers with broad dispersity.

Chart 2. Overview of tunable polymerization methods discussed in this review. M = primary catalyst, M' = secondary metal; CTA = chain transfer agent; R = alkyl or aryl groups.

Scope of Review

This article offers a tutorial on various modalities employed to regulate olefin polymerization, specifically the use of reaction engineering, chain transfer, redox tuning, borane tuning, cation tuning, and nuclearity tuning (Chart 2). Most of the examples discussed are based on nickel and palladium complexes, with the exception of several early transition metal complexes presented in the earlier sections. The diimine-, [13] phenoxy-imine-, [9] and phosphine sulfonate-based catalyst systems [17] (Chart 1) feature prominently in the examples below, which is a testament to their synthetic versatility. Our discussions of catalyst properties will rely on metrics such as catalyst activity, branching, molecular weight (MW), molecular weight distribution (MWD = distribution of polymer chains), and dispersity ($\bar{D} = M_w/M_n$). Because there are no standard conventions for classifying whether a specific characteristic is low, moderate, or high, we will adopt the ranges shown in Table 1. The ranges selected for molecular weight and branching should not be used to infer information about the macroscopic properties of the polymers since such characteristics are derived from a combination of factors (e.g., MW, MWD, branching, monomer composition, and sequence). Thus, the classification scheme presented is meant only to aid the reader in differentiating between different catalysts. It is also important to note that the values cited here represent the catalysts under optimized conditions. Finally, this review will provide a conceptual overview of the tunable polymerization catalysis subfield rather than not a comprehensive summary of the literature.

Table 1. Classification Ranges Used in this Article^a

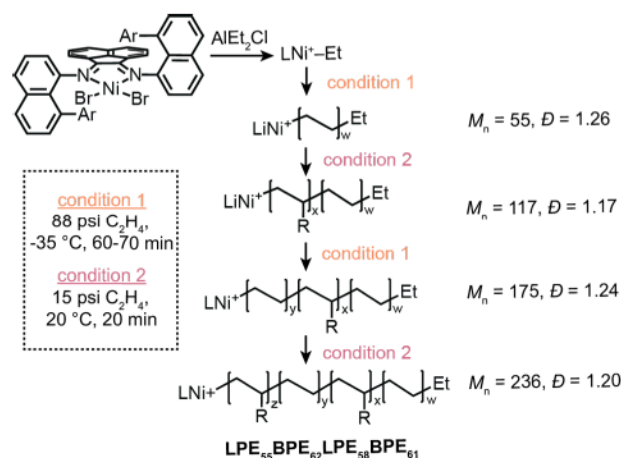
Classification	Activity (kg/mol·h)	M_n or M_w (kg/mol) ^b	Branches (/1000 C)
Low	<100	<100	0-25
Moderate	100-1000	100-500	26-75
High	>1000	>500	>75

^aThere are currently no standard conventions for classification. The ranges selected are based on our survey of the polymer chemistry literature and assessment of reasonable values for each category. ^bIn this review, M_w instead of M_n values will be used to describe the polymers if the dispersity is very large ($\bar{D} > 5$) or for comparison with other polymers in the same study.

Reaction Engineering

In synthetic chemistry, it is common practice to optimize reactions by changing environmental conditions such as temperature, pressure, or solvent. In fact, varying these parameters often has dramatic effects on olefin polymerization by coordination insertion catalysts. For example, increasing temperature typically leads to reduced polymer molecular weight due to increased chain transfer/termination. [4, 20, 51-53] In contrast, increasing ethylene pressure using bulky catalysts typically leads to increased chain lengths due to faster rates of monomer insertion. [54, 55]

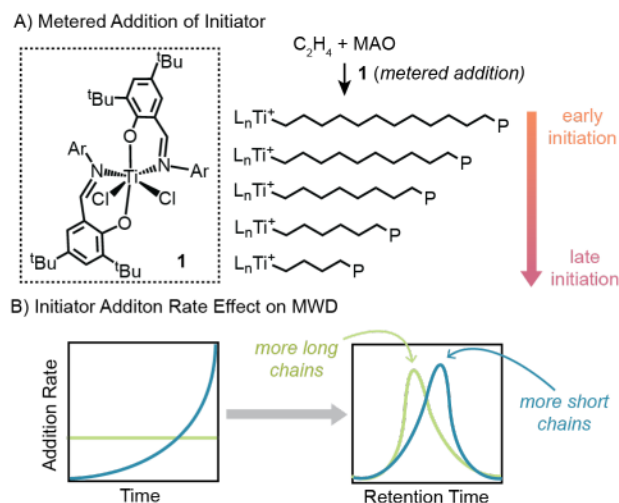
Coates and coworkers took advantage of reaction engineering to synthesize well-defined tetrablock polymers using just ethylene as the feedstock (Scheme 1). [22] The key to their success was the use of a living nickel diimine catalyst that was responsive to changes in polymerization conditions. At high pressure and low temperature (88 psi at -35 °C), linear polyethylene (LPE) was formed (~9 branches/1000 C), whereas at low pressure and higher temperature (15 psi at 20 °C),



Scheme 1. Synthesis of tetrablock polyethylene by switching reaction conditions using nickel diimine catalysts. The number average molecular weight (M_n) has the unit kg/mol. The subscripts in LPE₅₅BPE₆₂LPE₅₆BPE₆₁ indicate the M_n of individual blocks. R = H or Me.

branched PE (BPE) was formed (~112 branches/1000 C). The branches were determined to be primarily methyl groups, which presumably was the result of chain walking during polymerization. [56, 57] By alternating between two different conditions, the researchers successfully obtained a tetrablock polymer (LPE₅₅BPE₆₂LPE₅₆BPE₆₁) in a one-pot reaction. Excitingly, they observed that when just 5% of this product was blended with a mixture of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) (4:1), the new material showed a 553% increase in strain at break in comparison to polymer blends lacking the tetrablock compatibilizer.

Another elegant example of regulated polymerization is work reported by Coates, Fors, and coworkers (Scheme 2). [58] This study employed a living titanium bis(phenoxyimine) catalyst (1) in combination with MAO using metered addition to control the MWD shape of the PE product. In these experiments, solutions of the titanium com-



Scheme 2. A) Regulating polymer chain length by metered addition of titanium initiator. B) Plots showing the effect of constant (light green line) vs. exponential (blue line) initiator addition on the polymer molecular weight distribution shape.

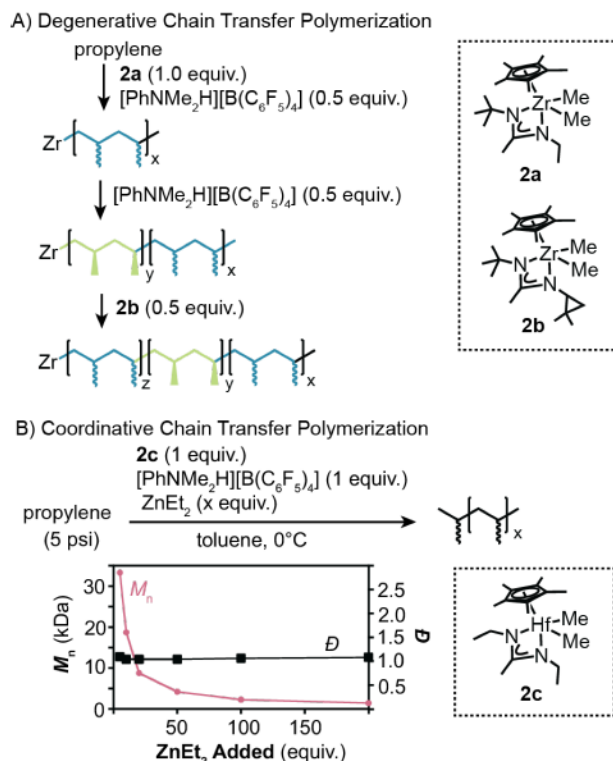
plexes were added using a syringe pump into a mixture containing fixed amounts of ethylene and MAO in toluene. A constant addition rate gave PE with a MWD skewed toward polymers with higher molar mass (asymmetry factor $A_s > 1$) because the polymer chains initiated earlier have a longer time to propagate than those initiated later. Use of exponential addition rates led to late activation of most Ti species and gave larger percentages of PE chains with low molar mass ($A_s < 1$). Remarkably, the polymers synthesized all have similar M_n (~80 kg/mol) but slightly different D (1.11-1.70) and A_s (0.43-2.61) values. Rheological testing of this unique collection of polymer samples showed that MWD shape has significant effects on complex viscosity but not mechanical integrity.

Although reaction engineering such as the examples above could in theory be applied to most polymerization catalysts (e.g., to modify polymer MW, branching, etc.), only systems that exhibit controlled chain growth (e.g., living catalysts) are compatible. Unfortunately, living polymerization is uneconomical because each catalyst produces only a single polymer chain and must operate in batch.[59] Metered addition of chain transfer agents (CTA, *vide infra*) to control MWD skewness could potentially circumvent this problem. A disadvantage of environment switching is that it is a slow process since it takes time for the reaction mixture to heat and cool and the monomer concentration must be carefully regulated. Such processes are likely problematic on industrial scales since they would require large amounts of energy, time, and cost to implement. Recent advances in flow chemistry might offer an alternative way to control MWD in the synthesis of designer polyolefins.[60]

Chain Transfer

Chain transfer describes the process in which polymeryl chains are exchanged between two metal centers and can occur intrinsically or promoted by the addition of chain transfer agents (CTA). To increase the polymer-to-metal ratio of living catalysts and control their polymer MW, CTAs were first applied to ethylene polymerization in the 1990s and are typically based on Zn or main group elements (e.g., Al). [61, 62] To be an effective CTA, chain transfer must be faster relative to propagation, reversible, and not compete with other termination processes.

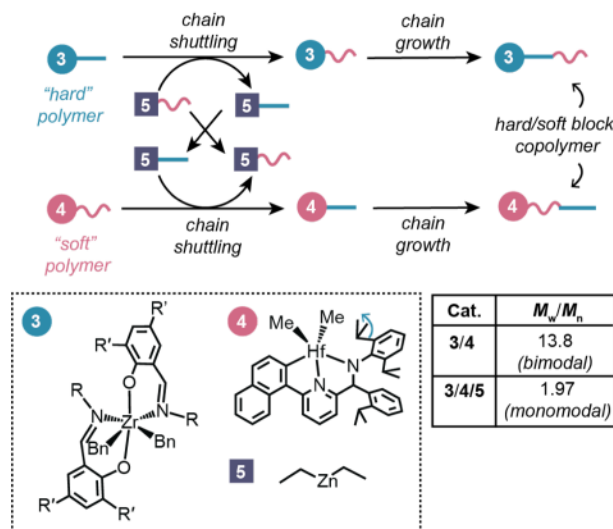
In their seminal work, Sita and coworkers elegantly demonstrated that chain transfer polymerization could be used to synthesize polyolefins with precise block microstructures. The key to their discovery was the development of half-sandwich zirconium complexes that were capable of stereo-specific living polymerization of α -olefins.[63, 64] The researchers found that when complex **2a** was activated by treatment with 0.5 equiv. of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, the resulting mixture of active cationic (ZrMe^+) and dormant neutral (ZrMe_2) species could rapidly exchange methyl groups.[64] During chain propagation, this reactivity led to loss of stereocontrol due to facile epimerization of the dormant Zr species. By turning degenerative chain transfer “on” and “off”, Sita and coworkers showed it was possible to synthesize block polymers with well-defined segments of atactic and isotactic units.[65, 66] For example, as illustrated in Scheme 3A, combining **2a** with 0.5 equiv. of an activator in the presence of



Scheme 3. Controlled propylene polymerization catalyzed by half-sandwich Zr and Hf acetamidate complexes. Degenerative chain transfer polymerization provided multi-block polymers (A) whereas coordinative chain transfer polymerization using ZnEt_2 gave varying polymer molecular weights (B).

propylene produced an atactic polymer block. When another 0.5 equiv. of the activator was added, degenerative chain transfer was turned off and a second block containing isotactic polypropylene was produced. Finally, a bulky zirconium complex **2b** was added to irreversibly transfer a methyl group to promote the formation of another atactic segment. It was found that this triblock polymer displayed higher elongation to break than either diblock or tetrablock polymers of similar molecular weight and total isotactic content. This multiblock polymer synthesis method is quite powerful because an unlimited number of stereoblock architectures could be accessed by deliberate programming of the polymerization sequence.

In 2008, Sita and coworkers showed that precise molecular weight control could be achieved using CTAs in combination with Cp* hafnium amidinate complexes (Scheme 3B).[67] It was reported that activation of complex **2c** provided a catalyst capable of non-stereospecific living polymerization of α -olefins. At 0°C in toluene, reaction of **2c**/[PhNMe₂H][B(C₆F₅)₄] with propylene provided atactic polypropylene (M_n is not reported at 0°C but was 122×10^3 g/mol at -10°C). It was observed that addition of increasing amounts of ZnEt₂ as a CTA (5–200 equiv. relative to **2c**), led to corresponding reduction in polymer M_n (111 – 1.45×10^3 g/mol, respectively). The linear relationship between M_n vs. $1/[2c + \text{ZnEt}_2]$, constant yield, and extremely narrow dispersity ($\mathcal{D} < 1.09$) suggested that highly efficient coordinative chain transfer polymerization was maintained in each reaction. This method was also successfully applied to the polymerization of ethylene, 1-hexene, 1-octene, and 1,5-hexadiene.[68]



Scheme 4. Chain shuttling polymerization using a dual catalyst system (**3** = Zr, **4** = Hf) in conjunction with the chain transfer agent ZnEt₂ (**5**). R, R' = alkyl, Bn = benzyl.

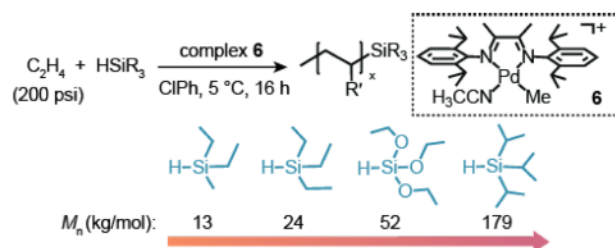
An innovative application of CTAs was reported by Arriola et. al. in 2006.[59] In this study, a novel chain shuttling process was developed to access block copolymers from ethylene and α -olefins. As depicted in Scheme 4, this method requires two distinct living catalysts, in which one gives “hard” polymers due to poor α -olefin incorporation and the other gives “soft” polymers due to efficient ethylene and α -olefin copolymerization. The CTA is responsible for exchanging growing polymer blocks between the two catalysts so that every polymer molecule has both “hard” and “soft” segments. To identify a pair of olefin polymerization catalysts with substantially different monomer selectivity and a suitable CTA to give Poisson distribution ($\mathcal{D} = 1$) of polymer molecular weights, the researchers took advantage of high-throughput technologies. Their robot-controlled screening protocol enabled testing of more than 1600 individual polymerizations over a 3-week period, which would have taken at least several months using manual labor. It was found that the use of a zirconium bis(phenoxyimine) catalyst (**3**), hafnium pyridylamide catalyst (**4**), and diethylzinc (**5**) CTA gave the desired chain shuttling products. For example, the use of **3**, **4**, and **5** produced a monomodal polymer with $\mathcal{D} = 1.97$. However, in the absence of **5**, a bimodal product was obtained ($\mathcal{D} = 13.8$). The

differences in the physical properties of the desired block copolymers compared to those of physical blends were apparent by eye. For example, solid mixtures of LDPE and HDPE were opaque due to the large HDPE crystallites and the immiscibility of the two polymers. In contrast, the use of increasing amounts of **5** relative to **3** and **4** gave materials with increasing transparency. Excitingly, the olefin block copolymers exhibited excellent elastomeric properties at significantly higher temperatures than traditional ethylene-derived elastomers. Although chain transfer using CTAs with early transition and lanthanide metal complexes has been studied in depth,[62] fewer investigations have been conducted on late transition metal complexes. In 2005, Gibson and coworkers reported that ZnEt₂ was not an efficient CTA for Ni diimine catalysts because the rate of chain propagation was faster than the rate of chain transfer to zinc by about 200–300×.[69] Later in 2014, Tonks and coworkers expanded on this study by interrogating steric effects on chain transfer efficiency between Ni diimine complexes and various MR₃ species (where M = Zn or main group metal; R = alkyl).[70] After screening a variety of catalyst combinations, it was found that only Ni diimine was compatible with CTAs ZnEt₂, AlEt₃, GaMe₃, and InMe₃ (Table 2). Although ZnEt₂ gave the highest increase in chain transfer (+640%) compared to that in the control reaction without Zn, the process was irreversible because the polymer dispersity did not narrow and the number of chains extended was much lower than the amount of CTA used. An interesting finding from this work was that less bulky catalysts and CTAs both gave faster rates of chain transfer compared to that by their more sterically bulky counterparts.

Table 2. Chain Transfer Using Main Group Metal Alkyls^a

$\text{C}_2\text{H}_4 \xrightarrow[\text{toluene, 1 h, RT}]{\text{catalyst/ligand/activator CTA}} \text{polymer}$ Increase in chain transfer?					
$\text{L} = \begin{array}{c} \diagup \quad \diagdown \\ \text{Ar}-\text{N}=\text{C}=\text{N}-\text{Ar} \end{array}$					
Cat./Activator	Mg ⁿ Bu ₂	ZnEt ₂	AlEt ₃	GaMe ₃	InMe ₃
Ni(L)Br ₂ /MAO	-	+640%	+1%	+10%	+30%
Ni(L)Me ₂ /HBAr ^F ₄	-	+640%	+1%	+70%	+25%

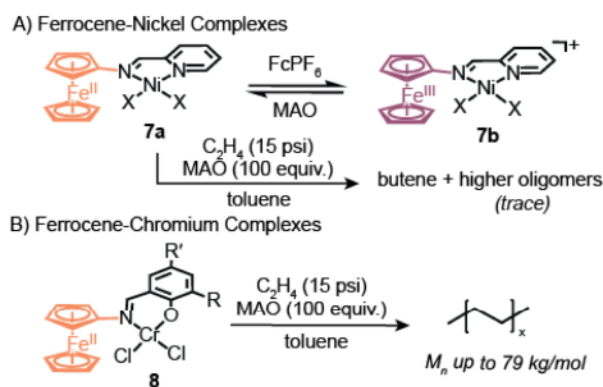
^aPercentages indicate the increase in number of chains initiated using 600 equiv. of main group metal alkyls compared to that in its absence. No polymerization activity was observed using MgⁿBu₂. HBAr^F₄ = [H(OEt)₂][BAr^F₄], Ar = 2,6-diisopropylphenyl.



Scheme 5. Control of PE molecular weight using various silane chain transfer agents. R' = H or alkyl.

In 2017, Guironnet and coworker demonstrated the use of silanes as CTAs with palladium diimine complexes (**6**) (Scheme 5).[71] They observed that addition of up to 90 equiv. of HSiEt_3 relative to **6** led to reduction in PE molecular weight from moderate to low ($M_n = 159$ to 12 kg/mol). A kinetic analysis suggests that the rate of chain propagation was only about $14\times$ faster than the rate of chain transfer from Pd to Si, which is much closer in rates than those between silanes and lanthanide or group 4 catalysts.[72] It was also found that the steric bulk of the silane influences its chain transfer kinetics, which is reflected in the M_n of the resulting PE. Finally, silane CTA was used successfully in ethylene and methyl acrylate copolymerization.

The advantages of chain transfer as a tuning modality are that it enables control of polymer MW by variations in CTA concentration and in the case of living polymerization, allows more than one polymer molecule to be generated per metal center. Some disadvantages of CTAs are that they are not universally compatible with all catalysts and cannot tune polymer branching density and branching length. Additionally, low temperatures (0°C or lower) are often needed to achieve living polymerization. For late transition metal complexes, superstoichiometric amounts of ZnEt_2 or silanes are required to obtain complete chain transfer.

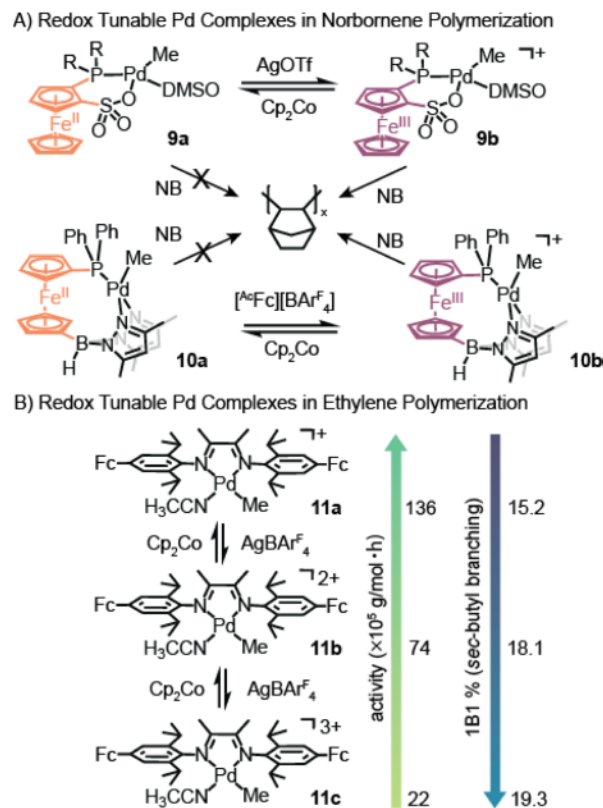


Scheme 6. Ferrocene tethered nickel pyridylimine (A) and chromium phenoxyimine (B) complexes and their reactions with ethylene.

Redox Tuning

Because redox changes can dramatically impact a complex's electronic distribution, it is an attractive means to regulate the properties of synthetic catalysts. One of the earliest attempts to incorporate redox switches into metal catalysts to modulate olefin reactivity was reported by Gibson, Long (N. J.), and coworkers in 2003 (Scheme 6A).[73] Their work involved the synthesis of Ni and Pd complexes ligated by *N*-heterocyclic imino-ferrocene chelators. The Ni species featuring reduced ferrocene (**7a**) was able to dimerize and oligomerize ethylene in the presence of MAO. Although **7a** could be chemically oxidized to **7b**, this species was proposed to revert back to **7a** in the presence of MAO. Thus, it was not surprising that the reaction of **7b**/MAO/ C_2H_4 gave products similar to those obtained from **7a**/MAO/ C_2H_4 . In subsequent work in 2005,[74] Gibson, Long (N. J.), and coworkers demonstrated that chromium phenoxyimine-ferrocene complexes (**8**) and

MAO could polymerize ethylene to PE with low MW (79 kg/mol) and monodispersity ($\mathcal{D} = 2.6$). Although it was not reported whether the oxidized form of **8** could be generated for polymerization studies, we presume that the ferrocenium group would also be susceptible to undesired reduction by MAO.



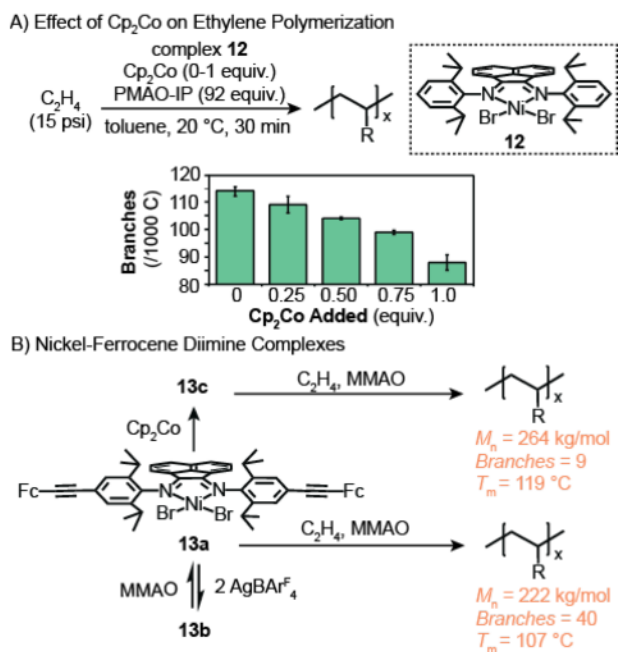
Scheme 7. Redox tunable Pd complexes for olefin polymerization. NB = norbornene, Fc = ferrocene.

The demonstration of redox tuning in olefin polymerization was achieved only recently. In 2015, Chen (C.) and coworkers created a palladium Drent-type complex by derivatizing ferrocene with phosphine and sulfonate groups.[75, 76] In ethylene homopolymerization, the reduced complex **9a** was more active than the oxidized complex **9b**, which the authors attributed to greater chemical stability of the former compared to the latter. Interestingly, **9b** was active in norbornene (NB) oligomerization ($M_n = 0.81$ kg/mol, $\mathcal{D} = 1.90$) but **9a** was not (Scheme 7A). It was demonstrated that reactions with NB could be turned on and off by the addition of AgOTf to **9a** or Cp_2Co (Cp = cyclopentadienyl anion) to **9b**, respectively.

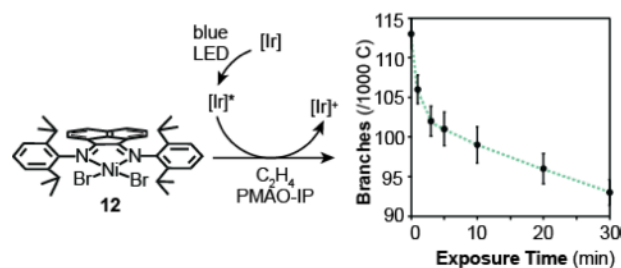
A similar redox switching capability was observed in Pd ferrocene-heteroscorpionate complexes developed by Diaconescu and coworkers in 2016 (Scheme 7A).[77] The cyclic voltammogram (CV) of **10a** showed a quasi-reversible redox couple centered around -0.27 V vs. ferrocene (Fc)/ferrocenium (Fc^+). It was reported that **10a** showed no activity in the presence of NB, even upon heating at 100°C . In contrast, the oxidized complex **10b** was capable of polymerizing NB and its derivatives ($M_n =$ up to 37 kg/mol, $\mathcal{D} = 1.5\text{--}3.6$). It was proposed that the phosphine donor in the oxidized form was more easily displaced than that in the reduced form, which allowed

more facile monomer coordination and insertion. It was demonstrated that redox switching could be achieved *in situ* by turning off **10b** upon the addition Cp_2Co or turning on **10a** upon addition of $\text{AcFcBAR}^{\text{F}}_4$ (AcFc = acetylferrocenium; BAR^{F}_4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

In 2017, Chen (C.) and coworker made Pd diimine catalysts redox switchable by installing ferrocene units to their aryl side arms (Scheme 7B).[78] The Pd-Cl precursors were characterized by NMR spectroscopy, IR spectroscopy (for the CO analogues), and cyclic voltammetry to establish that three different redox states were accessible. The CV data suggest that these Pd diimine-ferrocene species are Class I compounds according to the Robin-Day classification system,[79] which indicates that charge is localized on their redox active centers (e.g., the Fc groups). It was found that cationic **11a** could be oxidized sequentially to **11b** and **11c** using 1 and 2 equiv. of $\text{AgBAR}^{\text{F}}_4$, respectively. Addition of Cp_2Co converts the oxidized species back to their parent complexes. In ethylene homopolymerization, the activity trend was observed in the order **11a** > **11b** > **11c** (from 136 to 22 kg/mol·h at 40 °C). It was proposed that the higher charged species, **11b** and **11c**, were more prone to catalyst decomposition. The polymer products had different morphologies, including changes in molecular weight (M_n = 6.1–170 kg/mol) and branch-on-branch microstructures (1B1% = 15–19%). The different polymer products provided by **11a**, **11b**, and **11c** allowed the researchers to obtain bimodal and trimodal GPC curves by adding various equiv. of $\text{AgBAR}^{\text{F}}_4$ to **11a** during polymerization or using a mixture of partially oxidized **11a**. In ethylene and methyl acrylate copolymerization, the complexes once again showed the activity trend **11a** > **11b** > **11c** (from 13 to 3 kg/mol·h at 40 °C). Because the oxidized species are more electrophilic than their parent compound, it was suggested that they are more susceptible to catalyst inhibition by the polar methyl acrylate monomers.



Scheme 8. Redox switchable Ni complexes for ethylene polymerization.



Scheme 9. Exposure of complex **12** to light in ethylene polymerization. PMAO-IP = polyalkylaluminoxane, LED = light emitting diode.

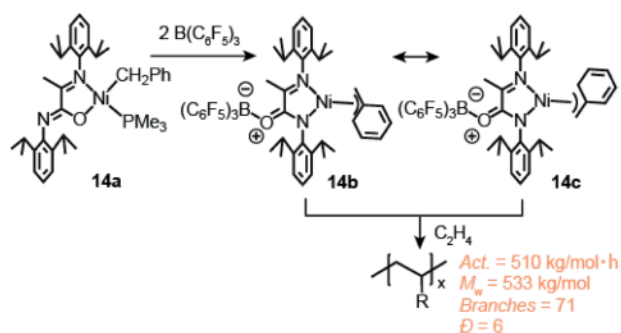
Long (B. K.) and coworkers reported in 2016 that metal diimine complexes with conjugated ligand substituents are redox tunable (Scheme 8A).[80] They showed that complex **12** containing an acenaphthene backbone displayed a quasi-reversible redox couple at -0.8 V vs. Fc/Fc^+ . Based on EPR spectroscopy, UV-vis absorption spectroscopy, and magnetic susceptibility measurements, it was determined that treatment of **12** with 1 equiv. of Cp_2Co led to reduction of Ni(II) to Ni(I). However, upon subsequent mixing with trimethylaluminum, rapid metal-to-ligand electron transfer occurred to yield a new Ni(II) species featuring a ligand-centered radical. The investigators observed that the PE produced from reaction of **12**/PMAO-IP (polyalkylaluminoxane)/ C_2H_4 could be tuned by varying the amount of reductant used from 0 to 1 equiv. relative to Ni. Although the PE molecular weight remained moderate (M_n = 200–274 kg/mol), the branching density decreased with increased addition of Cp_2Co (from 114 to 88 branches/1000 C). DFT computational studies suggest that the reduced Ni catalyst has a lower propensity for chain walking compared to that of the parent complex due to weakened metal-alkyl β -agostic interactions.[81] The application of **12**/MAO for redox control of ethylene and α -olefin copolymerization was also demonstrated.[82]

Incorporating ferrocene groups into the nickel diimine-acenaphthene framework also produced redox tunable catalysts (Scheme 8B).[83] Complex **13a** could be reduced to **13c** or oxidized to **13b** upon treatment with Cp_2Co (1 equiv.) and $\text{AgBAR}^{\text{F}}_4$ (2 equiv.), respectively. It was found that reaction of **13a**/MMAO (modified MAO)/ C_2H_4 furnished PE with characteristics nearly identical to those in PE obtained from reaction of **13b**/MMAO/ C_2H_4 . Similar to previous examples, this lack of change was attributed to MAO reducing the Fc^+ substituents back to Fc (i.e., from **13b** to **13a**). In contrast, reactivity differentiation was achieved between **13a** and **13c**. In ethylene homopolymerization, **13a** afforded PE with moderate molecular weight and moderate branching (M_n = 222 kg/mol, 40 branches/1000 C) whereas **13c** afforded PE with moderate molecular weight and low branching (M_n = 264 kg/mol, 9 branches/1000 C). Density measurements suggest that these materials should be classified as medium-density PE (0.93 g/mL) and very-low-density PE (0.90 g/mL), respectively.

In 2018, Long (B. K.) and coworkers showed that it was possible to use light to regulate olefin polymerization through photoredox control (Scheme 9).[84, 85] In these experiments, an iridium photosensitizer was paired with complex **12** in the presence of PMAO-IP and ethylene. When the reaction mixture was irradiated with blue light emitting diode (LED) light, the photoexcited iridium species was believed to convert **12** to the one-electron reduced species. A plot of light exposure time

vs. PE branching showed that prolong irradiation led to progressive decrease in branching from 113 to 93 branches/1000 C.

Redox switching is a well-controlled catalyst regulation method that requires only stoichiometric amounts of oxidants/reductants and has the potential to be used repeatedly if the redox active unit is electrochemically reversible. However, one must be cognizant that the redox switch may not always be compatible with other chemical reagents used in polymerization, such as the tendency of MAO to react with ferrocenium. To date, up to three different catalyst states have been obtained from a common platform using redox switching. It is possible that even more reactivity states could be accessible by tethering polymerization catalysts with moieties capable of multi-electron redox chemistry (e.g., π -conjugated molecules,[86] polyoxometalates,[87] etc.).

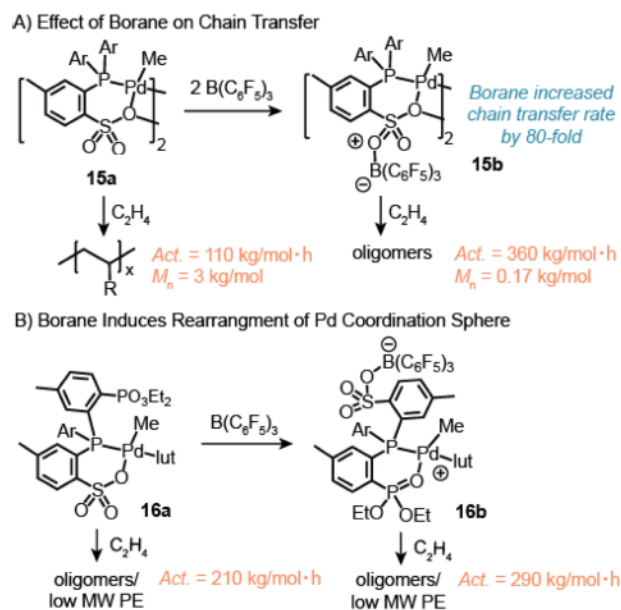


Scheme 10. Ethylene polymerization by nickel α -iminocarboxamidato complexes in the presence of boranes.

Borane Tuning

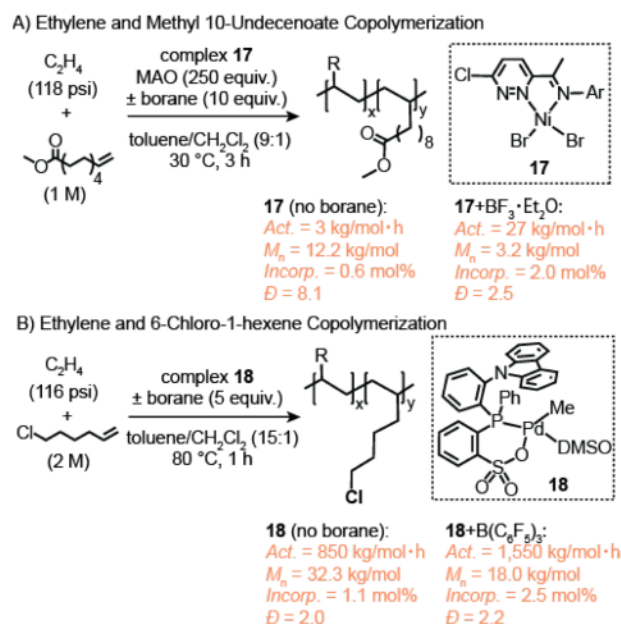
The reactivity of metal catalysts could also be tuned by the addition of Lewis acids such as boranes. In 2001, Bazan and coworkers developed olefin polymerization catalysts based on nickel α -iminocarboxamidato complexes (**14a**) (Scheme 10).[88] They reported that when $B(C_6F_5)_3$ was added to **14a**, two different isomers **14b** and **14c** were observed due to the different orientations of their benzyl ligands. X-ray crystallographic analysis of the Ni complexes revealed that rearrangement from *N,O*- to *N,N*-chelation occurred and the borane was attached to the oxygen donor. In the presence of ethylene, **14b/14c** were moderately active catalysts (510 kg/mol·h) and gave PE with moderate/high molecular weight ($M_w = 533$ kg/mol) and branching (71). Although their polymer dispersities were relatively broad ($\bar{D} = 6$), lowering the nickel catalyst concentration gave lower $\bar{D}$. Since there are no structural analogues of **14b/14c** without borane for reactivity comparison, it is unclear what is the impact of Lewis acid binding on the catalyst behavior.[89] The starting complex **14a** itself was reported to be catalytically inactive.

The application of boranes in ethylene polymerization was explored further by Jordan and coworkers. In 2012, they reported that Pd phosphine sulfonate complexes **15a** were capable of binding $B(C_6F_5)_3$ to yield the corresponding borane adducts **15b** (Scheme 11A).[90] Solutions studies by NMR spectroscopy and mass spectrometry suggest that **15a** exists as



Scheme 11. Effect of boranes on Pd ethylene polymerization catalysts. Lut = 2,6-lutidine.

a dimer in the non-coordinating solvent CH_2Cl_2 . The $B(C_6F_5)_3$ was proposed to coordinate to the sulfonate groups in **15b**, which would make the catalyst more electrophilic. This change was found to have a dramatic impact on ethylene polymerization. For example, **15b** was about $3.3\times$ more active and gave PE with $18\times$ lower MW than that of **15a**. The polymer yield and MW data suggest that the presence of borane increased the chain transfer rate by up to $80\times$. In 2014, Jordan and coworker developed a Pd phosphine sulfonate derivative that contained a phosphonate ester aryl substituent (Scheme 11B).[91] In the presence of ethylene, **16a** was moderately active (210 kg/mol·h) and gave a mixture of soluble oligomers and insoluble PE. When $B(C_6F_5)_3$ was added to **16a**, the sulfonate group was replaced by the phosphonate ester in the Pd primary coordination sphere (**16b**). This new catalyst exhibited similar activity to that of **16a** and also produced a mixture of ethylene oligomers and polymers.



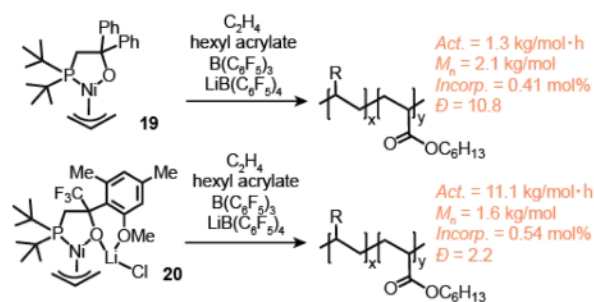
Scheme 12. Ethylene and polar olefin copolymerization catalyzed by Ni/Pd-borane complexes.

Metal-borane complexes were also shown to be active in ethylene and polar olefin copolymerization. For example, Chen (M.), Tan, and coworkers reported in 2019 that nickel pyridazine-imine complexes (**17**) could be tuned by using boranes (Scheme 12A).[92] Based on model studies, the authors proposed that boranes bind to the free pyridazine nitrogen donor in **17**, which would render the catalyst more electrophilic. In ethylene and 10-undecenoate copolymerization, it was observed that the addition of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ to **17** increased catalyst activity from 3 to 27 kg/mol·h and decreased polymer M_n from 12.2 to 3.2 kg/mol. Interestingly, the borane containing catalyst also gave polymers with higher percentage of 10-undecenoate (2 vs. 0.6 mol%) and more narrow dispersity ($\bar{D} = 8.1$ vs. 2.5) than that of the parent catalyst.

Another example of the use of the borane to modulate ethylene and polar olefin copolymerization was reported by Chen (C.) and coworkers.[93] In this contribution, the researchers constructed Ni and Pd phosphine sulfonate complexes bearing *N*-heterocyclic substituents. It was proposed that the binding of $\text{B}(\text{C}_6\text{F}_5)_3$ to the sulfonate group would increase the electrophilicity of the metal center and enhance its interactions with the pendant *N*-donor. The effects of borane were clearly observed in ethylene and 6-chlorohex-1-ene copolymerization (Scheme 12B). For example, in the absence of borane, complex **18** exhibited moderate activity (850 kg/mol·h) and produced copolymers with 1.1 mol% comonomer incorporation. When 5.0 equiv. of $\text{B}(\text{C}_6\text{F}_5)_3$ were combined with **18**, the catalyst activity increased 1.8× (1,550 kg/mol·h) and the comonomer incorporation increased to 2.5 mol%. A decrease in M_n was also noted, which was attributed to the greater rate of chain transfer due to the presence of $\text{B}(\text{C}_6\text{F}_5)_3$.

In the examples above, the addition of borane to polymerization reactions often boosted catalytic rates while reducing

chain growth. The latter phenomenon is similar to the effect of chain transfer agents, albeit via different mechanisms. Some potential challenges in using boranes to regulate polymerization processes are that the catalysts must have Lewis basic sites to interact with BR_3 and borane-binding might be irreversible due to strong boron-donor linkages.[94] The application of boranes in polymerization switching has not yet been demonstrated.



Scheme 13. Incorporation of lithium cations into Ni olefin polymerization catalysts.

Cation Tuning

Given the large number of elements in the periodic table and the distinct properties they possess (e.g., they have different charges, Lewis acidity, atomic radii, redox potentials, coordination geometries, etc.), external metal binding offers virtually endless possibilities for catalyst fine-tuning. In 2003, Johnson, Brookhart, and coworkers were the first to demonstrate that pairing alkali ions with olefin polymerization catalysts had beneficial effects (Scheme 13).[95] For example, it was found that nickel-lithium alkoxy phosphine complex **20** was about 8.5× more active than mononickel **19** in ethylene and hexyl acrylate copolymerization. Because **19** lacked a well-defined secondary metal binding site, the addition of excess Li^+ salt to its reaction mixture most likely had minimal impact (the reaction of ethylene with **19** without Li^+ was not reported). In contrast, the Li^+ ion in **20** is directly interacting with the nickel primary coordination sphere, which would render the Ni center more electrophilic. It is notable that **20** gave copolymers with significantly more narrow dispersity than that of **19** ($\bar{D} = 2.2$ vs. 10.8, respectively). The control reaction using complex **20** without the coordinated Li^+ ion was not reported.

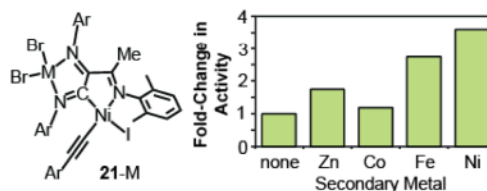
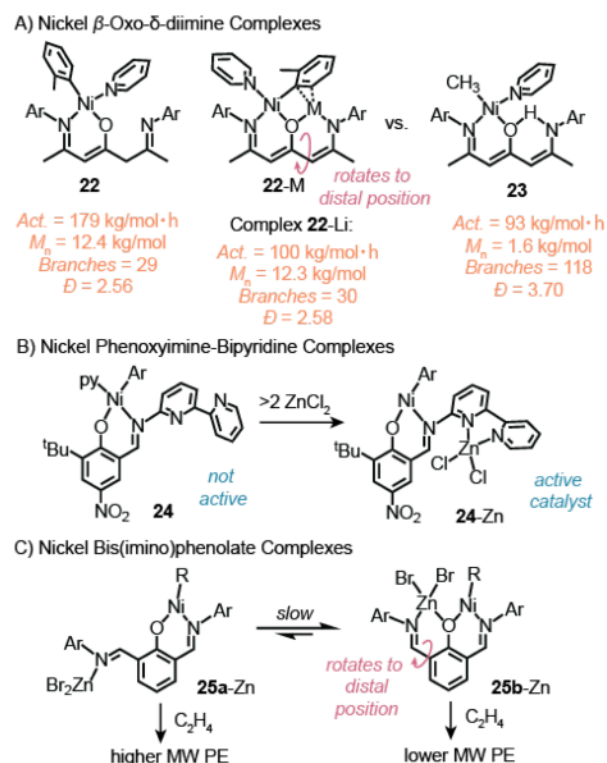


Figure 2. Effect of secondary metals on ethylene polymerization by azanickellacyclic catalysts. The polymers produced by **21-Fe** and **21-Ni** were bimodal, whereas the others were monomodal.

In 2005, Nagashima and coworkers reported their study of azanickellacyclic **21** derived from trimerization of isocyanide with nickel (Figure 2).[96] This complex is unique because it has a bis(imino) group available for coordinating secondary cations. The authors showed that **21** could be combined with various metal salts to yield the corresponding heterobimetallic species **21-M**. The molecular structures of **21-Zn** and **21-Co** were characterized by X-ray crystallography. As shown in Figure 2, the addition of MBr_2 salts (where $M = Zn, Co, Fe, \text{ or } Ni$) to **21** led to enhancement in ethylene polymerization activity in the order $Ni > Fe > Zn > Co$. The **21-Zn** and **21-Co** catalysts produced monomodal PE whereas **21-Fe** and **21-Ni** produced bimodal PE. Because iron, cobalt, and nickel are known to be capable of polymerizing ethylene, it is possible that both metals in the bimetallic species are active in polymerization, particularly **21-Fe** and **21-Ni** since they provided bimodal polymers. Additionally, since both **21** and **21-M** yielded PE with $\bar{D} \geq 2.9$, these complexes do not exhibit ideal single site catalyst behavior. Studies to investigate the polymerization behavior of the secondary metals were not reported, although it would probably require inhibiting the activity of the primary nickel center to minimize competing reactions.

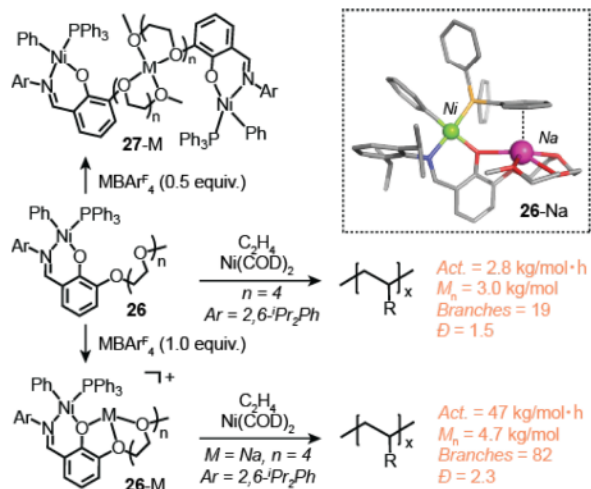
Tonks and coworkers also explored the effects of secondary metals on olefin polymerization catalysts. In 2016, they prepared nickel complexes from β -oxo- δ -diiminate ligands that can exist in two tautomeric forms, either as imine **22** or enamine **23**.^[97] Although both species were formed during synthesis, pure **22** and **23** were separated successfully from the crude reaction mixture via crystallization. Solution studies by 1H NMR spectroscopy revealed that **22** and **23** are kinetically stable and do not interconvert. Interestingly, deprotonation of **22** with $M(HMDS)$ (where $M = Li, Na, \text{ and } K$, HMDS = hexamethyldisilazide) yielded the corresponding heterobimetallic species **22-M** (Scheme 14A). Reactivity studies with ethylene showed that **22** and **22-M** produced similar PE products ($M_n = \sim 12$ kg/mol, Branches = $\sim 30/1000$ C). The authors hypothesized that this similarity was due to the ability of the alkali-enamine arm in **22-M** to rotate away from the nickel center so that it essentially has the same coordination environment as that of **22**. Interestingly, the enamine tautomer **23** afforded PE with lower molecular weight ($M_n = 1.6$ kg/mol) and higher branching (118/1000 C) than that of **22**. Although cation-tuning was not successful in this example, it illustrates the difficulty in designing pre-organized ligand platforms that maximize the beneficial effects of secondary metals.

A cation-responsive catalyst **24** based on the nickel phenoxyimine platform was reported by Tonks and coworkers in 2016 (Scheme 14B).^[98] The key feature of this complex is the presence of a 2,2'-bipyridine moiety that was designed to capture external secondary metals. The researchers discovered that **24** was inactive toward ethylene but could be turned-on in the presence of zinc salt. Crystallographic studies showed that combining **24** with $ZnCl_2$ furnished a discrete bimetallic nickel-zinc species (**24-Zn**). In ethylene polymerization, complex **24** and $ZnCl_2$ (50 equiv.) exhibited low activity (10.3 kg/mol·h) and generated PE with low molecular weight ($M_n = 37.1$ kg/mol). The use of smaller amounts of $ZnCl_2$ led to greater polymer dispersity (e.g., $\bar{D} = 11$ when 1 equiv. of $ZnCl_2$ was added). Interestingly, polymerizations conducted in the presence of other Lewis acids such as $CuCl_2$ and $AlCl_3$ were not as effective as those using $ZnCl_2$.



Scheme 14. Effects of secondary metals on nickel N,O -ligated complexes.

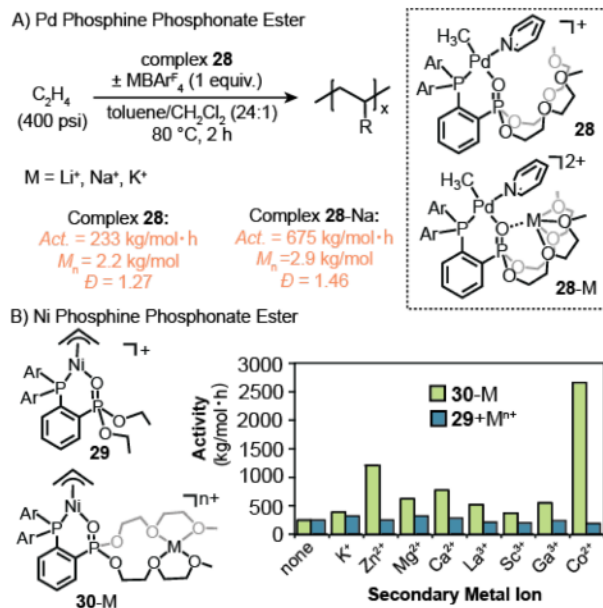
To pursue their goal of integrating secondary metals into olefin polymerization catalysts, Tonks and coworkers also synthesized nickel bis(imino)phenolate complex **25**.^[99] 1H NMR spectroscopic studies in THF suggested that metallation of **25** with $ZnBr_2$ occurred through a two-step process involving first binding of Zn^{2+} to the imine arm followed by chelation to the phenolate donor. In the absence of zinc, **25** was catalytically inactive. Surprisingly, ethylene polymerization by **25**/ $ZnBr_2$ at 35 °C gave bimodal PE, whereas at 50 °C monomodal PE was obtained. It was proposed that at low temperature, the active species exists in two forms, **25a-Zn** and **25b-Zn** (Scheme 14C). The former is believed to be responsible for yielding longer polymer chains whereas the latter is believed to be responsible for yielding shorter polymer chains. Computational studies suggest that β -hydride elimination from **25b-Zn** is essentially barrierless, which is consistent with the experimental observation that **25b-Zn** undergoes more facile chain termination than **25a-Zn**. At 50 °C, the equilibrium favors the thermodynamically more stable **25b-Zn** so polymerization occurs predominantly from this species and thus, gave rise to monomodal PE.



Scheme 15. Effect of alkali ions on ethylene polymerization by nickel phenoxyimine complexes. The molecular structure of 26-Na obtained from X-ray crystallographic analysis is shown in the dotted box. M = Li⁺, Na⁺, or K⁺.

In 2015, our research group's foray into cation-tunable polymerization began with studies of nickel phenoxyimine complexes bearing polyethylene glycol (PEG) side chains (26) (Scheme 15).[100] Based on solution titration studies, we found that the phenolate-PEG unit can bind alkali ions to give either bimetallic (26-M) or trimetallic (27-M) species (M = Li⁺, Na⁺, K⁺). The distribution of various mixed-metal complexes depends on the nickel:alkali ratio used and size match between the PEG chains and the alkali ions. The heterometallic structures of 26-Na, 26-K, and 27-Na were confirmed by X-ray crystallography. When tested in ethylene polymerization, 26 exhibited low activity (2.8 kg/mol·h) and produced PE with low molecular weight (3.0 kg/mol) and branching (19/1000 C). Upon addition of Na⁺ to 26, the activity increased 17× and PE branching increased 4× while maintaining similar MW. A correlation was observed between the catalyst activity and the association constant for 26+M⁺, which suggests that the active species most likely contains both nickel and alkali metals. We also showed that synthetic modifications could be applied to enhance the catalyst properties of 26-M even further.[101]

Our strategy of PEGylating catalysts to make them cation-tunable was tested in other catalyst platforms. We found that two PEG chains could be attached to a Pd phosphonate ester complex to afford 28 (Scheme 16A).[102] Secondary metal binding studies indicated that 28 is capable of coordinating alkali ions in a 1:1 stoichiometry. Crystallographic characterization of 28-M (M = Li⁺, Na⁺, K⁺) could only be obtained for a nickel-sodium derivative containing a bridging chloride. Without a chloride bridge, such as in the activated form of 28-M, it is unclear whether M⁺ could maintain close proximity to the nickel center. Our ethylene polymerization results showed that at 80 °C, 28 is a moderately active catalyst (233 kg/mol·h) that gave low molecular weight PE (2.2 kg/mol). Interestingly, when 28 was combined with M⁺, the catalyst activity increased 3× but the polyethylene product had similar morphology to that obtained without secondary metals. Complex 28-Na was found to have excellent thermal stability, displaying moderate activity even up to 140



Scheme 16. Ethylene polymerization by Pd (A) and Ni (B) phosphine phosphonate-PEG complexes in the presence of secondary metal ions. The structure of 28-M was proposed but it is possible that the phosphonate ester oxygen donor does not interact with M⁺.

°C. Both 28 and 28-M provided PE with Đ ≤ 1.7, suggesting that they are both single site catalysts. Although 28-M was active in ethylene and alkyl acrylate copolymerization, its activity (<90 kg/mol·h) and acrylate incorporation (<2 mol%) were relatively poor.

Since nickel complexes often exhibit greater activity than their palladium counterparts, we prepared complex 30 for comparative studies.[103] Similar to our previous PEGylated complexes, 30 binds M⁺ ions in a 1:1 stoichiometry to afford 30-M (M = Li⁺, Na⁺, K⁺). The solid-state structure of 30-Na revealed that Na⁺ is coordinated by the PEG chains as expected but has no interactions with the phosphonate oxygen donor. As a consequence, the Ni-M distance is long (~7 Å apart) and the presence of M⁺ has minimal impact on the steric and electronic environment of the nickel center. Surprisingly, we discovered that the nickel complexes were active for ethylene polymerization in 100% THF, which allowed us to test polymerizations using a wide range of secondary metals such as M²⁺ and M³⁺ ions (Scheme 16B). After surveying various alkali, transition, and post-transition metals, we found that addition of Zn²⁺ and Co²⁺ to 30 provided the most significant boost in catalyst activity (1210 and 26600 kg/mol·h, respectively) compared to that in reactions without secondary metals (250 kg/mol·h). The importance of the PEG chains in 30 to cation binding was demonstrated by showing that a conventional nickel derivative 29 was unaffected by the presence of M⁺. Interestingly, the PE products obtained from both 30 and 30-M had similar MW and branching density. We hypothesize that this lack of differentiation is due to the nickel and secondary metal being too far apart in 30-M to have any synergistic interactions.

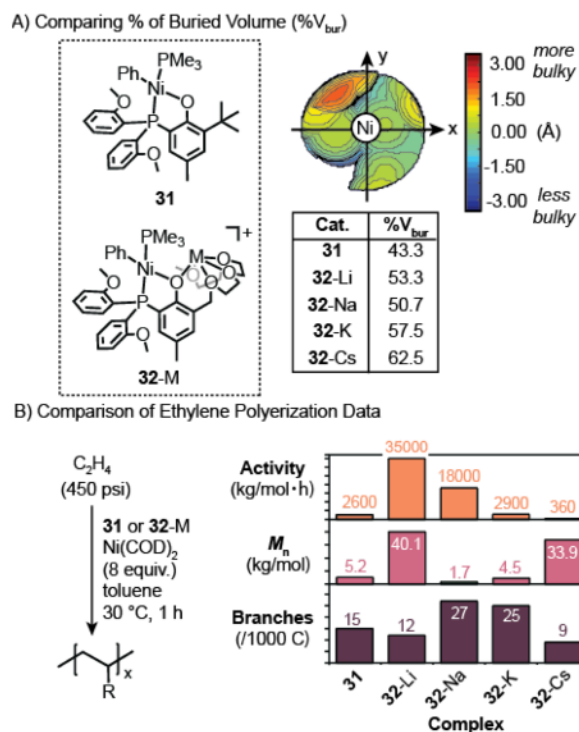
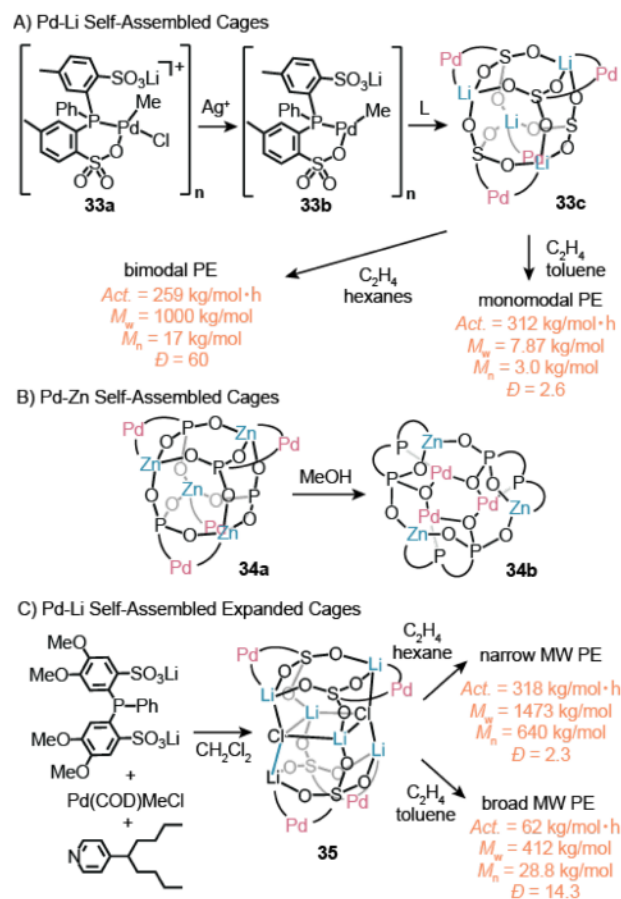


Figure 3. Characterization of Ni phenoxyposphine complexes (A) and their ethylene polymerization performance at 30 °C (b).

Although our work above provided useful insights into cation-tunable complexes, we wanted to develop catalysts that were fast and gave distinct polymer products in response to M^{nt} addition. This objective led us to pursue the creation of nickel phenoxyposphine-PEG complexes (32).[51, 104] We established that when combined with alkali salts, 32 formed discrete heterobimetallic species (32-M, M = Li⁺, Na⁺, K⁺, Cs⁺). Using structural data obtained from X-ray crystallographic analysis of 32-M, we calculated their percentage of buried volume (%V_{bur}), which took into account the fraction of the primary coordination sphere occupied by the phenoxyposphine-PEG ligand and alkali ion (Figure 3A). The results suggest that the steric bulk of the catalysts are in the order 32-Na < 32-Li < 32-K < 32-Cs. The %V_{bur} of 32-Cs is 19% greater than that of 31, a conventional catalyst featuring a *tert*-butyl substituent. These findings were remarkable because they indicated a wide range of steric protection could be achieved simply by selecting the appropriate secondary metal. Another notable advantage of our approach is that secondary metal binding can change the nickel redox potential, which will impact the catalyst's electrophilicity and corresponding reactivity. The effects of alkali ions on 32 were quite dramatic (Figure 3B). In the absence of secondary metals, 32 was catalytically inactive. However, upon addition of M⁺ to 32/Ni(COD)₂ (COD = 1,5-cyclooctadiene) under 450 psi of ethylene, large amounts of PE were obtained. At 30 °C, the highest activity was exhibited by 32-Li (35000 kg/mol·h), which places it among one of the most efficient late transition metal catalysts reported to date. At 90 °C, 32-Cs showed the highest activity (23000 kg/mol·h), which we attributed to its greater thermal stability compared to the other nickel-alkali species in the series. Importantly, the different 32-M catalysts produced PE with different polymer MW (M_n = 2-40 kg/mol) and branching

(9-27/1000 C) while maintaining narrow dispersity ($\mathcal{D} = \leq 2$). Our investigations suggest that both steric and electronic factors must be considered to understand the unique reactivity of the 32-M catalysts. Furthermore, the ability of M⁺ to participate in coordination interactions with external substrates or metal-bound ligands might also play important roles during catalysis.

The examples presented in this section illustrate that cation-tuning could be a highly effective way to regulate polymerization processes. Its major advantages are that many catalyst states are potentially accessible due to the large number of M^{nt} salts available and it can produce changes in structure and function that might not be possible to achieve through synthetic modifications. The difficulties in developing cation-tunable catalysts, however, are that it can be challenging to design catalysts that maintain well-defined heterometallic structures in solution,[105, 106] exhibit distinct reactivity in response to M^{nt} binding, and display high catalytic efficiency and robustness.



Scheme 17. Palladium caged complexes as ethylene polymerization catalysts. The cage structures are drawn in cartoon form for simplicity; each Pd atom is ligated by a phosphine sulfonate ligand. L = 4-(5-nonyl)pyridine.

Nuclearity Tuning

Unlike in the previous section in which attempts were made to avoid formation of higher order structures, it has been

demonstrated that controlling the self-assembly of molecular catalysts could be a useful strategy to modulate their reactivity. In 2010, Jordan and coworker investigated the ethylene polymerization capabilities of multinuclear palladium cages (Scheme 17A).[107] It was reported that Pd phosphine sulfonate complexes bearing lithium phenylsulfonate groups (**33a** and **33b**) spontaneously formed multinuclear species. To make them more soluble, 4-(5-nonyl)pyridine was combined with **33b** to yield a tetranuclear complex **33c**, which was characterized by X-ray crystallography. Upon exposure to ethylene under heterogeneous conditions in hexane, **33c** produced bimodal PE ($\bar{D} = 60$) that showed greater amounts of high molecular weight fractions ($M_w = 1000$ kg/mol). These results suggest that in its tetranuclear form, **33c** is not a single site catalyst. In contrast, when **33c** was dissolved in toluene, it converted into mononuclear species and produced narrowly dispersed PE ($\bar{D} = 2.6$) with low molecular weight ($M_n = 3.0$ kg/mol). In-depth studies to understand the complicated nature of these palladium-lithium cages revealed that molecular rigidity is a key factor in controlling their self-assembly behavior.[108]

Efforts to develop structurally robust catalyst clusters led Jordan and coworker to investigate the self-assembly of Pd phosphine sulfonate complexes in the presence of Zn^{2+} rather than Li^+ (Scheme 17B).[109] Using a stepwise synthesis procedure, they were able to obtain both tetranuclear (**34a**) and trinuclear (**34b**) palladium-zinc cages. Their structures were confirmed by both NMR spectroscopy and X-ray crystallography. When **34a** was suspended in either toluene/chlorobenzene or hexanes/chlorobenzene (49:1) and then activated by treatment with 1 equiv. of $B(C_6F_5)_3$, PE with moderate/high molecular weight and broad dispersity was obtained (in toluene/PhCl: $M_w = 436$ kg/mol, $\bar{D} = 15$; in hexanes/PhCl: $M_w = 1031$ kg/mol, $\bar{D} = 6.6$). Interestingly, **34b**+ $B(C_6F_5)_3$ in toluene/chlorobenzene (49:1) gave higher MW polymer ($M_w = 691$ kg/mol) with more narrow dispersity ($\bar{D} = 2.7$) compared to that for **34a**+ $B(C_6F_5)_3$, which is characteristic of single site catalysts.

Building on previous work, Jordan and coworker constructed a bulky lithium bis(phenylsulfonate) phosphine ligand to assemble tetrapalladium complex **35**, which features an expanded cage structure (Scheme 17C).[110] Variable temperature NMR spectroscopic studies indicated that **35** had excellent thermal stability. For example, only 6.5% of **35** was dissociated in $CDCl_2/CDCl_2$ at 80 °C. In contrast, the first generation cage **33c** showed about 38% dissociation under similar conditions. The resistance of **35** to cage disassembly led to favorable ethylene polymerization results. It was observed that in hexane, **35** furnished high molecular weight PE ($M_n = 640$ kg/mol) with monomodal distribution ($\bar{D} = 2.3$). However, the polymer dispersity broadened in other solvents such as toluene or CH_2Cl_2 . The authors suggested that formation of higher MW polymer is a general feature of Pd_4 cage catalysts because their bulky structures could inhibit associative chain transfer. It was also proposed that the Li^+ ions coordinated to the sulfonate groups could enhance the electrophilicity of the catalyst and the close proximity of Pd centers to each other might allow for cooperative effects.

Molecular self-assembly is an appealing catalyst tuning strategy because it provides access to sterically protected structures that are not possible to achieve through ligand de-

sign. In fact, the use of monomeric building blocks to create complex quaternary structures is commonly employed in nature with great success.[111] However, this approach can be challenging to implement because it is not always straightforward to control the self-assembly process and caged structures are prone to dissociate in the presence of polar solvents and additives.

Method Selection and Applications

The diverse strategies available to modulate coordination insertion catalysts give chemists tremendous flexibility in polyolefin synthesis. Selection of the best tuning modality for a particular application requires consideration of a variety of factors. First, some methods employ superstoichiometric amounts of additives (e.g., zinc alkyls, silanes, boranes, etc.), which would add cost to the process and is not ideal in terms of green chemistry.[112] However, for small-scale synthesis of designer polymers, this limitation may not be a major problem. Second, some methods are easier to implement than others. Reaction switching that relies on rapid environmental changes or metered addition requires specialized equipment that may not be readily available in a typical laboratory. In contrast, batch reactions using pre-mixed components could be run in standard reaction vessels. Third, some tuning modalities are more suitable for reaction switching than others. For example, borane switching could be difficult to achieve more than once because formation of borane-Lewis base adducts tends to be strong and irreversible.[94] On the other hand, it has been demonstrated that redox switching could toggle between two different catalyst states multiple times during the course of a reaction.[113] Alternatively, the use of secondary cations might offer the possibility of continuous reaction switching by exploiting metal binding dynamics.

Tunable polymerization catalysis aims to provide either more efficient ways to obtain known materials or easy access to novel ones. Unlike conventional catalysts, which are essentially “pre-programmed” to produce a specific type of polymer, tunable catalysts allow chemists to customize polymer products by providing more precise control over the polymerization process. For example, difficult to synthesize materials such as gradient polymers or non-uniform block copolymers might be attainable. Although the physical, mechanical, and thermal properties of novel polymers are sometimes difficult to predict *a priori*, being able to create them is the first step to improving our general understanding of synthetic materials. Furthermore, tunable catalysts might be useful in advanced applications such as in tandem or switchable catalysis.[114, 115] For example, in multi-catalyst reactions, being able to turn certain catalysts on and off at specific times could overcome incompatibility issues or allow cascade transformations to occur. Ultimately, tunable catalysts provide new tools with which to test the limits of our synthetic imagination.

Future Outlook

Polyolefins comprise an integral part of our material world today. The discovery of coordination insertion catalysts that provided economical routes to these materials from simple olefins was a major scientific breakthrough. Although coordination insertion polymerization is now considered a relatively mature research field, the examples in the preceding sections illustrate that it is by no means exhausted of fresh ideas. In

fact, the development of tunable/switchable polymerization is still in its infancy. All of the tunable modalities discussed in this review have advantages and disadvantages. Some of their limitations might be possible to overcome with further research and development. For example, the range of tunability for most methods is somewhat limited. Redox tuning has so far achieved up to 3 different states, but perhaps could be expanded by installing multi-electron redox units to polymerization catalysts. Cation tuning also has great potential to achieve more graduated catalyst control simply due to the large number of different metal ions in different oxidation states that exist. However, cation tuning requires catalysts that have exquisitely engineered secondary metal binding pockets and could form single site catalyst structures. Some other challenging features to incorporate into tunable catalysts include achieving high activity, polar molar incorporation, and thermal stability. Practical considerations such as cost and ease of use would also be important for general applications. We anticipate that the creativity and enthusiasm that had driven advances in polyolefin synthesis for the past several decades will continue to fuel the next generation of polymer chemistry research. These efforts will undoubtedly lead to an exciting future for tunable polymerization catalysis and the creation of new polyolefin-based technologies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Graphical Abstract

