Coordination Polymerization

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Ex Uno Plures ("Out of One, Many"): New Paradigms for Expanding the Range of Polyolefins through Reversible Group Transfers

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The "mature" status presently enjoyed by polyolefins prepared with homogeneous (soluble) single-site catalysts through the transition-metal-catalyzed coordination polymerization of ethene and 1-alkenes brings with it a common impression that it is now routinely possible to obtain, with a high degree of confidence, any desired stereochemical microstructure or copolymer composition through iterative optimization employing a set of mutationally related synthetic derivatives generated from an initial molecular design. The dominant reliance on this "one catalyst, one material" strategic approach to discovery is intrinsically self-limiting, however, owing to the limited pool of molecular structures that can be reasonably synthesized and drawn upon. Recently, non-chain-terminating, reversible group-transfer processes have been purposefully introduced to olefin coordination polymerization. These processes, which are highly competitive with propagation, can be controlled externally and now provide the basis for new "one catalyst, many materials" paradigms that have the potential to greatly expand the reach of polyolefin materials for the 21st century.

1. Introduction

Global production of polyolefin-based plastics has now surpassed 110 million metric tons per year, and this number is expected to grow annually at 5–7% for the foreseeable future. By any measure, this figure represents a staggering volume of non-naturally-occurring materials upon which modern society is now wholly dependent.[1] As such, there can be no doubt that the discovery and subsequent commercialization of Ziegler–Natta (ZN) catalysts for the polymerization of ethene, propene, and higher 1-alkenes easily represents a human feat that rivals in magnitude those for which the Stone Age, Bronze Age, and Iron Age were named.[2] Against this backdrop, it is sobering to consider that even after more than 50 years of intensive worldwide academic and industrial efforts, we have only just begun to scratch the surface of the vast complexity of polyolefin structural, compositional, and architectural space that still remains to be explored. Further significant advances in the quest for new ZN catalysts and polyolefin-based materials, however, require new paradigms to drive discovery. More to the point, the successful development over the past 25 years of homogeneous (soluble), "single-center" transition-metal-based coordination catalysts of discrete molecular structure that can provide different polyolefin stereochemical microstructures and copolymer compositions with a high degree of confidence have served to establish a "one catalyst, one material" paradigm as the de facto dominant strategy by which to pursue new polyolefin-based materials through strategic design and execution.[3] The recent introduction of combinatorial methodology and robot-controlled high-throughput screening technology for the rapid and efficient evaluation of thousands of potential new homogeneous catalysts with simultaneous optimization of reaction parameters has contributed to a further entrenchment of this position.[4] If the truth be told, however, sole reliance on this paradigm is self-limiting, and, in spite of all that it has delivered to date, gaps in the polyolefin compositional and structural records will naturally exist as a result of the finite pool of molecular structures for catalysts that can be reasonably synthesized and drawn upon. As an

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illustrative case in point, Figure 1 presents structure–property relationship data for several predominately isotactic polypropene (PP) materials that possess varying levels of *rr* triad stereoerror defects as a result of differing degrees of stereoselectivities for alkene enantioface complexation and chain-growth entrainment through insertion, as mediated by a series of closely related *ansa*-bridged metallocene-based single-center coordination catalysts, some of which are depicted.[5,6] These data show that by simply increasing the level of stereoerror incorporation, a reduction in crystallinity and an improvement in elasticity can be achieved such that several grades of PP materials with different physical attributes—ranging from stiff plastics to semicrystalline flexible plastics to thermoplastic elastomers—are accessible from a single reactor process, albeit one that employs several different catalysts. On the one hand, this study by De Rosa, Resconi, and co-workers[5] beautifully epitomizes the present state-of-the-art for configurationally constrained *ansa*-bridged metallocene catalysts with respect to current knowledge regarding mechanistic processes involved in propagation and correlations between the symmetry characteristics of the active propagating species and resulting polyolefin stereochemical microstructure.[3] On the other hand, it is also apparent from Figure 1 that a continuum of catalysts and PP materials spanning the full transitional range of properties does not exist, nor does it seem likely upon inspection of the catalyst structures already employed that many new structures can be easily identified and synthesized to fill in the gaps.

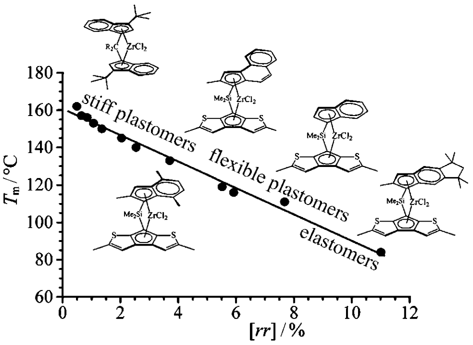


Figure 1. Classification of isotactic PP samples as stiff-plastic materials, flexible-plastic materials, and thermoplastic elastomers depending on the melting temperature and concentration of *rr* defects of stereoregularity. Reproduced from Ref. [5] with permission.

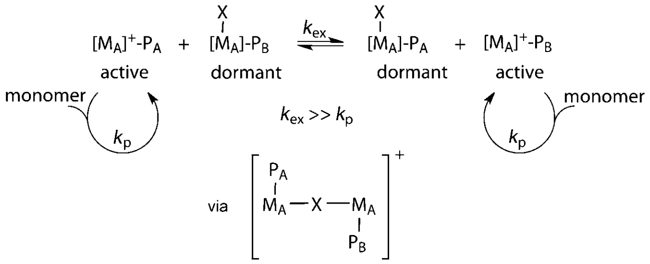
Lawrence Sita obtained his B.S. degree in 1981 from Carnegie Mellon University and studied chemistry at the Massachusetts Institute of Technology where he was a student of Satoru Masamune (Ph.D., 1985) and a postdoctoral associate with Richard Schrock (1986). He held faculty and academic positions at Carnegie Mellon University, the California Institute of Technology, and the University of Chicago before joining the faculty in 1999 at the University of Maryland, College Park, where he is professor of chemistry. His interests include nanoelectronics as well as organometallic, polymer, and surface chemistry, in particular the development of catalysts for stereoselective coordination polymerization and dinitrogen reduction.

Recently, new fundamental discoveries have identified *highly efficient, reversible bimolecular group-transfer processes* that are competitive with propagation in a manner that can have a profound impact on polyolefin structure, copolymer composition, and molecular-weight indices, including polydispersity. More significantly, external control over the rates of these second-order dynamic processes, relative to pseudo-first-order propagation in the presence of excess monomer, can be achieved with a high degree of fine granulation such that a near continuum of different polyolefin grades, and infinite varieties through different implementations, can all be generated from a single catalyst using a single reactor process.[7] Of further interest has been the introduction of fast and reversible polymeryl group chain transfer between active transition-metal centers and main-group-metal alkyl compounds that can serve as either “chain-shuttling” agents when two types of single-center coordination catalysts of differing comonomer specificities are employed[8] or as “surrogate” chain-growth sites that appear, for all practical purposes, to propagate at the same rate as the active transition-metal species.[9–13] This latter embodiment of reversible chain transfer employing multiple equivalents of a relatively inexpensive main-group-metal alkyl compound can additionally be used to provide a work-around solution for the commercial-scale production of “precision polyolefins” through living ZN polymerizations, which would otherwise suffer from a crippling “one polymer chain per metal center” cap on polymer yield.[13–15] Thus, although certainly still in their infancy, these collective findings serve to form the basis for new “one catalyst, many materials” paradigms that represent logical next steps in the continued evolution of polyolefins. Accordingly, the intent of this Minireview is to provide a brief synopsis of advances related to the introduction and control of dynamic bimolecular group-transfer processes for the single-site coordination polymerization of ethene, propene, and 1-alkenes as well as an outlook on their future prospects. For essential background material, several excellent comprehensive reviews are available covering the development of homogeneous single-site coordination catalysts,[3] the development of single-site catalysts for living ZN polymerization,[14] and the state-of-the-art of new precision polyolefins that have been prepared with the latter.[15]

2. Living Degenerative Group-Transfer Coordination Polymerization

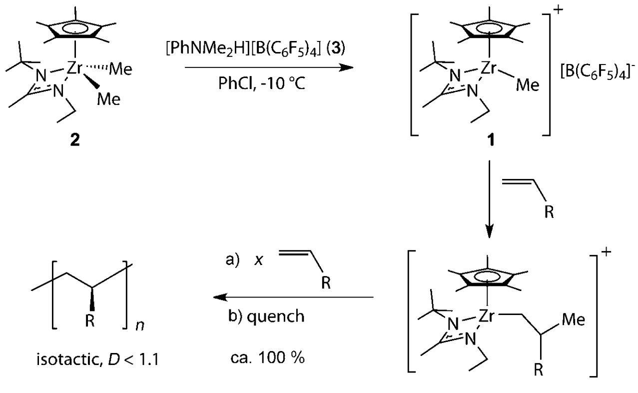
2.1. Programmable Stereoerror Incorporation

Sita and co-workers[16] first proposed, and then experimentally established, the living degenerative group-transfer coordination polymerization mechanism shown in Scheme 1, in which two populations of transition-metal species consisting of active propagating centers and nonpropagating dor-



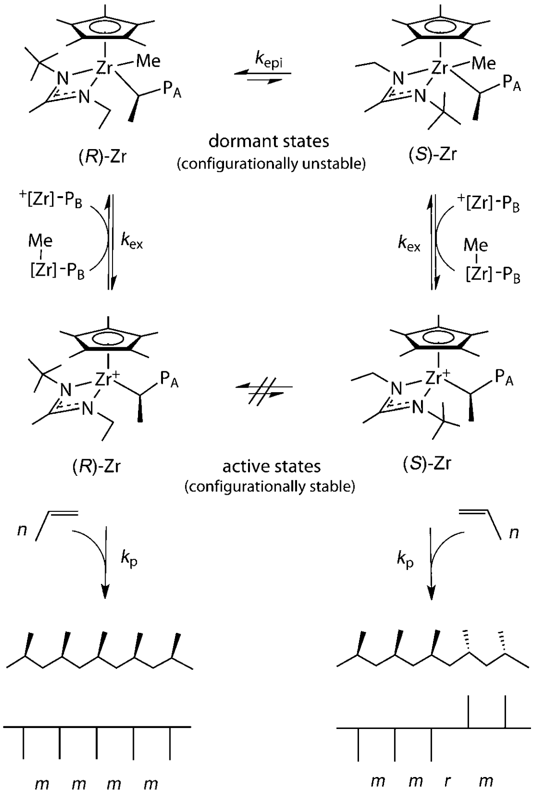
Scheme 1. Generic mechanism for degenerative group-transfer coordination polymerization. M_A is a transition-metal center that is capable of chain growth when not complexed to the transferrable group X (Me or Cl), and P_A and P_B are the associated polymeryl groups with chain length A and B, respectively. Note the absence of polymeryl group exchange in this mechanism.

mant centers undergo reversible exchange through rapid (non-polymeryl) group transfer, in particular for X = Me or Cl. The origins of this proposal trace back to a prior report that the C_1-symmetric cationic monocyclopentadienyl amidinate zirconium complex [Cp*ZrMe{N(*t*Bu)C(Me)N(Et)}][B(C_6F_5)$_4$] (**1**; Cp* = η^5-C_5Me_5), prepared through protolytic monodemethylation of neutral [Cp*ZrMe$_2${N(*t*Bu)C(Me)N(Et)}] (**2**) with a stoichiometric amount of the borate [PhNHMe$_2$][B(C_6F_5)$_4$] (**3**), can serve as an active catalyst for the highly stereoselective (stereospecific, isotactic) living ZN polymerization of 1-alkenes and α,ω-unconjugated dienes (Scheme 2).[17] Testing the hypothesis for the process depicted in Scheme 1 then simply involves employing a substoichiometric amount of the borate cocatalyst **3** to activate **2** (i.e., $[\mathbf{2}]_o/[\mathbf{3}]_o > 1.0$) so as to have a known, fixed number of metal-bound methyl groups remaining after the first few 1-alkene insertions (i.e, after complete initiation of **1**). Importantly, in keeping with the mechanistic constraints imposed by Scheme 1, these methyl groups can never engage in chain-growth propagation, but rather, they are free to participate in rapid and reversible bimolecular group transfer between the cationic (active) and neutral (dormant) metal centers. Furthermore, in the absence of irreversible chain termination, if the rate constant for group exchange is much greater than that for propagation ($k_{ex} \gg k_p$), then the molecular-weight polydispersity D (M_w/M_n) for the obtained polyolefins will be very narrow, as defined by $D \approx 1 + (\mathrm{k_p}/\mathrm{k_{ex}})$,[18] and the number-average degree of polymerization X_n will simply be inversely proportional to the initial concentration of the precatalyst **2** employed for a fixed amount of monomer, independent of the initial amount of borate cocatalyst **3** used, as long as $[\mathbf{3}]_0 \neq 0$.[16] An additional ramification dictated by these collective conditions is that, in contrast to previous expectations, only a small substoichiometric amount of an expensive borate cocatalyst is actually required to provide all the benefits of a precision polyolefin derived from a living ZN polymerization (see below).



Scheme 2. Generation of C_1-symmetric **1** and its highly stereoselective (stereospecific) living ZN polymerization of 1-alkenes.

A curious feature of the reversible degenerative group-transfer proposal of Scheme 1 is that, as long as the rate of group-transfer exchange ν_{ex} is much greater than the rate of propagation ν_p ($\nu_{ex} \gg \nu_p$), *there should be no obvious indication of the existence of the reversible group-transfer process if no specific effort is made to experimentally detect it.* However, in the case of living degenerative *methyl* group-transfer coordination polymerization based on the C_1-symmetric precatalyst **2**, the stereochemical microstructures of the PP materials that were obtained had a much higher frequency of *mmrm* pentad[19] stereoerror incorporation than those from the highly stereoselective (isotactic, *mmmm*) propagation that occurs when **2** is fully activated by cocatalyst **3**.[7,16a,17a] This degradation in stereochemical integrity under substoichiometric activation conditions was traced to the spectroscopically validated differences in configurational stability of the cationic (active) metal centers and the neutral methyl, polymeryl (dormant) metal centers (Scheme 3). More specifically, the active propagating metal centers are configurationally stable for the entire time of polymerization, while the dormant metal centers are configurationally unstable towards a metal-centered epimerization that has a very small associated energy barrier. Thus, the rate of configurational epimerization of dormant sites ν_{epi} is greater than that of methyl group transfer and far greater than that of propagation ($\nu_{epi} > \nu_{ex} \gg \nu_p$). In practical terms, this situation means that the frequency of *mmrm* pentad stereoerror incorporation into the polyolefin stereochemical microstructure is directly proportional to the concentration of dormant metal centers undergoing epimerization. Indeed, the data reproduced in Figure 2 serves to validate this hypothesis; a large number of new stereochemical grades of PP with very narrow polydispersities—ranging from stiff plastics to semicrystalline flexible plastics to amorphous materials—can be produced in programmed fashion through controlled stereoerror incorporation by simply adjusting initial levels of substoichiometric activation of **2** by **3**.[7a] If we now consider that further fine-tuning about a particular microstructure can be achieved by simply varying solvent volume and hence the absolute concentrations of the active and dormant species, then a near continuum of PP microstructures of varying stereoerror incorporation (solid line in Figure 2) can conceivably be rapidly obtained from just a single catalyst. Clearly, the ease with which this continuum of polyolefin grades can be generated relative to the substantial synthetic effort that would be required following a "one catalyst, one material" approach lends substantial credence to the future potential of



Scheme 3. Mechanism of stereoerror incorporation that occurs under living degenerative methyl group-transfer conditions. P_A and P_B refer to growing polymer chains, and *m* and *r* denote *meso* and racemic (*rac*) stereochemical relationships, respectively, between adjacent stereocenters of the polymer backbone.[19] Depicted relative and absolute configurational relationships for the metal centers and the polymer chains are for illustrative purposes only. Note the absence of polymeryl group exchange in this mechanism.

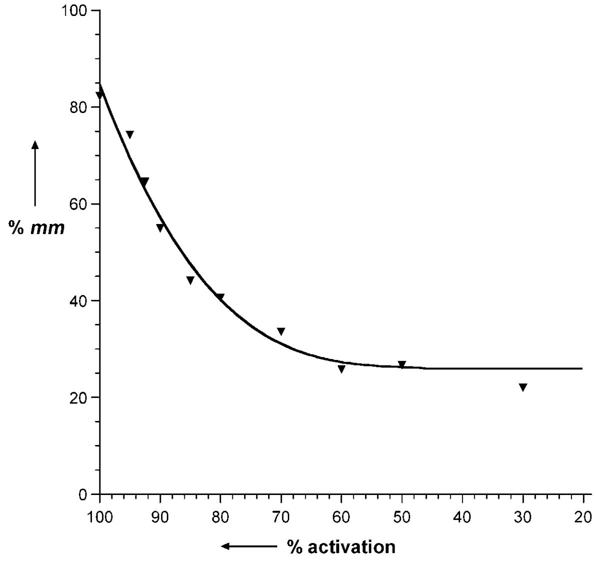


Figure 2. Proportion of *mm* triads (at the triad level of ^{13}C NMR spectroscopic stereoerror analysis) of predominantly isotactic PP materials obtained as a function of activation of the precatalyst **2** by the borate cocatalyst **3** under identical polymerization conditions. Reproduced from Ref. [7a] with permission.

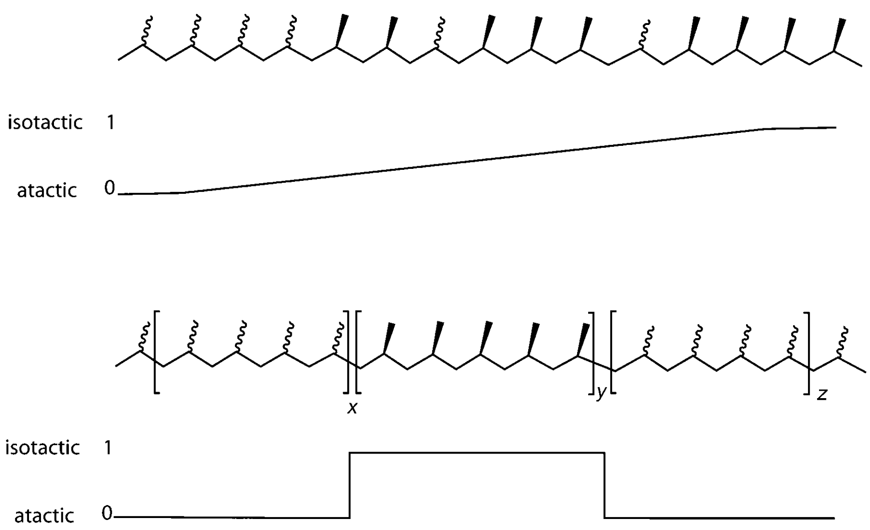
an alternative "one catalyst, many materials" paradigm based on external control of dynamic bimolecular processes.

2.2. Discrete, Isotactic–Atactic Stereogradient Polyolefins

One of the more intriguing aspects of living degenerative group-transfer coordination polymerization according to Schemes 1 and 3 is the ability to use external control to directly manipulate the frequency of stereoerror incorporation as a function of time in a number of different ways that, in turn, provide access to a wide range of previously unknown stereochemical microstructures for polyolefins. Thus, as the upper schematic representation in Scheme 4 indicates, application of a decreasing linear gradient of dormant sites through continuous addition of the borate cocatalyst **3** up to a full stoichiometric complement, after initially starting at a 60% level of activation of **2**, provided the first example of an atactic–isotactic stereogradient PP material of narrow polydispersity; its stereochemical microstructure is graphically depicted in Scheme 4.[7a] Significantly, this stereogradient PP material was found to be stereochemically homogeneous among all polymer chains by difference ^{13}C NMR spectra of aliquots taken at timed intervals throughout the gradient chain-growth process. It is further essential to note that reports of stereogradient microstructures for polymers are extremely rare.[7a,20] In the present case, stereogradient polyolefins can only be produced through living ZN polymerization, as the chain transfer and irreversible chain termination that occur in nonliving systems would produce stereochemical heterogeneity within the final isolated material. Finally, by programming different ramp profiles that includes "reversing" the direction of the ramp through selective methylation of cationic active sites (see below), it is clear that by applying external temporal control over living degenerative methyl group-transfer coordination polymerization, an infinite variety of new stereogradient polyolefin materials can be envisioned and prepared—and once more, all from a single catalyst!

2.3. Discrete, Isotactic–Atactic Stereoblock Polyolefins

By alternatively turning living degenerative group transfer "on" and "off" as a function of time through partial methylation of cationic active sites and full demethylation of neutral dormant sites, respectively, the synthesis of discrete, isotactic–atactic stereoblock polyolefins with well-defined block junctions and tunable block lengths and block architectures can be conducted in programmed binary fashion, as schematically shown by a representative dormant-site concentration profile (Scheme 4, bottom).[7b] In this way, a family of discrete, stereochemically homogeneous, atactic–isotactic stereoblock PP materials possessing narrow polydispersities were prepared for the first time and shown to have desirable elastomeric characteristics that depend upon the specific stereoblock architecture (i.e., diblock vs. triblock vs. tetrablock). For instance, a freshly prepared sample of a 30-20-30-20 atactic-isotactic-atactic-isotactic tetrablock stereoblock PP



Scheme 4. Schematic representation of programmed discrete stereochemical microstructures for atactic–isotactic stereogradient PP (top) and atactic-isotactic-atactic stereoblock PP (bottom).

($M_n = 172400$ Da, $D = 1.19$) displayed an ultimate elongation to break of 1227 %, with 91 % recovery after break. However, after initial strain-induced annealing, this material proved to be an exceptional elastomer, and no irreversible deformation was detected within subsequent stress–strain cycles involving a maximum strain of 250 %. A freshly prepared sample of a 30-40-30 atactic-isotactic-atactic triblock stereoblock PP ($M_n = 167500$ Da, $D = 1.19$), on the other hand, displayed the highest ultimate elongation to break of 1530 %, with 70 % recovery after break. Clearly, however, the potential now exists to design and synthesize an unlimited variety of different stereoblock architectures all from the same catalyst, including architectures that superimpose stereomodulation of block microstructure and the architecture of block copolymer polyolefins prepared from two or more different monomers polymerized in sequential fashion. In other words, by now incorporating atactic—isotactic stereomodulation of microstructure for each block, the three possible regiochemical permutations for an ABC triblock copolymer (i.e., ABC, BAC, ACB) now dramatically expand to 24 possible regio-stereochemical permutations (i.e., (i-A)(i-B)(i-C), (i-A)(i-B)(a-C), (i-A)(a-B)(i-C), (a-A)(i-B)(i-C), …, (a-A)(a-C)(a-B)).

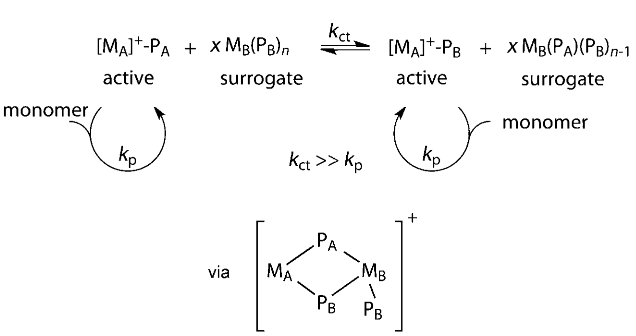
2.4. Degenerative Chloride Group Transfer

In the above examples of living degenerative methyl group-transfer coordination polymerization, the intrinsic configurational instability of the dormant metal centers was exploited to access a broader range of polyolefin stereochemical microstructures with technologically promising physical properties. It is interesting to speculate, however, that incomplete activation of other known classes of transition-metal precatalysts by main-group-element cocatalysts might give rise to unforeseen degradation of stereoselectivity during living or nonliving coordination polymerizations in which similar degenerative group-transfer exchange processes and metal-centered configurational instabilities might be operative. On the other hand, if both the active and dormant sites are configurationally stable during the entire polymerization, it should be feasible to use reversible deactivation by the degenerative group-transfer mechanism of Scheme 1 to dramatically reduce the required amount of an expensive main-group-element cocatalyst without affecting the level of stereocontrol. In this regard, the concept of living degenerative group-transfer coordination polymerization was successfully extended to include rapid and reversible chloride group transfer (X = Cl in Scheme 1).[16b] Accordingly, after substoichiometric activation of [Cp*Zr(Cl)(*i*Bu){N(*t*Bu)C(Me)N(Et)}] (**4**), which is a closely related analogue of **2**, through chemoselective chloride abstraction by the borate cocatalyst $[Et_3Si][B(C_6F_5)_4]$,[21] the living degenerative chloride group-transfer coordination polymerization of 1-alkenes could be conducted in a stereospecific fashion. Once again, the success of this stereospecific process relies on the fact that both cationic (active) and neutral chloro polymeryl (dormant) metal sites are configurationally stable during propagation. It is also interesting to note that the same high degree of stereospecificity was maintained even when using only 50 % of the stoichiometrically required amount of main-group-element cocatalyst.

In summary, it is rather striking that such a large and virtually infinite range of new polyolefin stereochemical microstructures are now routinely accessible from a single catalyst by taking advantage of the configurationally instability (for X = Me) or stability (for X = Cl) of dormant sites that are involved in living degenerative group-transfer coordination polymerization of 1-alkenes according to Scheme 1.

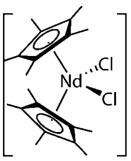
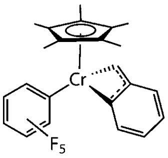
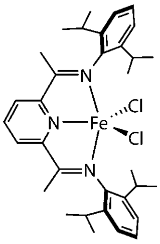
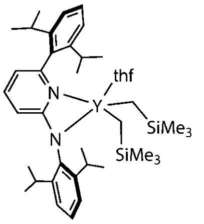
3. Reversible Chain-Transfer Coordination Polymerization

Although living degenerative group-transfer coordination polymerization can be used to access a greater range of polyolefin materials and to reduce the cost associated with expensive main-group-element cocatalysts, both of which are issues of significance for commercialization efforts, the critical limitation of "one polymer chain per active metal center" for a living process must still be addressed. In this respect, the introduction of a very different reversible group-transfer process to living ZN polymerization may hold the key.[13] More specifically, coordinative chain-transfer (CCT) polymerization involves nonterminating, reversible polymeryl group (chain) transfer between active transition-metal propagating centers and chain-growth-inactive "surrogate" main-group-metal alkyl species according to Scheme 5.[9–13] In this scheme, the surrogate sites cannot be classified as "dormant", as there is no mechanism by which these species



Scheme 5. Reversible coordinative chain-transfer polymerization of ethene and 1-alkenes. M_A is an active transition-metal propagating center and M_B is an inactive main-group metal alkyl (polymeryl) species, where n is the number of equivalent alkyl (polymeryl) substituents. P_A and P_B are polymeryl groups of chain lengths A and B, respectively.

Table 1: Representative single-site precatalysts for the coordinative chain-transfer oligomerization of ethene.

Precatalyst	Ref.	Cocatalyst	Main-group-metal alkyl
 $[Li(OEt_2)_2]^+$	[9]	none	$Mg(nBu)_2$
	[10d]	none	$AlEt_3$
	[11]	MAO[a]	$ZnEt_2$
	[12a]	$[R_2NMeH][B(C_6F_5)_4]$	$(iBu_2Al)_2O$

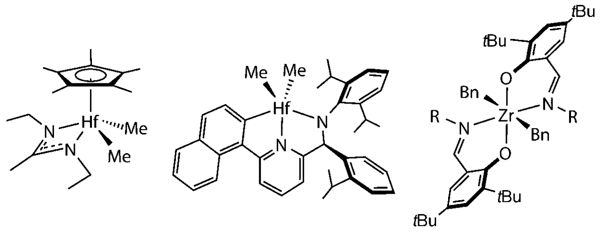
[a] MAO = methylaluminoxane.

can ever engage in direct chain growth through alkene insertion into a metal–carbon bond. However, if the rates for forward and reverse chain transfer ν_{ct} are much greater than the rate of propagation ν_p ($\nu_{ct} \gg \nu_p$), then both the active and surrogate metal species will appear to propagate at the same rate. Under these conditions, X_n is inversely proportional to the total population of initial active transition-metal species and surrogate main-group-metal alkyl species for a given amount of monomer consumed: $X_n = [\text{monomer}]_o/\{[\text{active}]_o + [\text{surrogate}]_o\}$. Furthermore, if coordinative chain-transfer polymerization proceeds in a living fashion with no irreversible chain termination arising from β-hydrogen transfer processes, then polydispersity of the final polyolefin materials will once again be established according to $D \approx 1 + (k_p/k_{ct})$.[18] Finally, if each initial surrogate main-group-metal alkyl site possesses several equivalent alkyl groups that are equally available for exchange, then final polymer yield can be significantly amplified based on x, the total amount of initial surrogate main-group-metal alkyl compound employed (relative to the transition-metal catalyst) and n, the number of equivalent alkyl groups that can engage in reversible chain transfer according to Scheme 5.

In practice, the use of main-group-metal alkyl compounds, such as diethylzinc ($ZnEt_2$), as effective chain-transfer agents for controlling polyolefin molecular weights during the ZN polymerization of 1-alkenes is well-established.[22] Detailed investigations have also shown that polymeryl group chain transfer between active propagating centers and main-group-metal alkyl species can be reversible.[23] Indeed, the presence of dynamic chain transfer can lead to formation of isotactic–atactic stereoblock polypropene components in stereochemically heterogeneous product mixtures when two transition-metal catalysts with differing stereospecificities are used simultaneously for propene polymerization in the presence of main-group-metal alkyl cocatalysts.[23a,c–e]

Of more recent vintage are detailed investigations of coordinative chain-transfer polymerization that proceeds in the manner depicted in Scheme 5. However, it is critical to note that until just recently, successful demonstrations of the coordinative chain-transfer polymerization of 1-alkenes have been limited to the controlled oligomerization of ethene, in which pseudo-living character is imparted by virtue of the stability of the polymeryl groups residing on the surrogate main-group-metal centers that are less prone to undergo terminating β-hydrogen transfers to either metal or monomer.[9–12] Table 1 presents an overview of these studies by providing details of some of the different precatalysts, cocatalysts, and main-group-metal chain-transfer agents that have been utilized to date.[11c,12b]

In terms of establishing truly living coordinative chain-transfer polymerization for a given 1-alkene, past investigations of nonliving systems have pointed out the substantial difficulties associated with identifying the right combinations of precatalyst, cocatalyst, chain-transfer agent, and polymerization conditions under which effective reversible chain transfer can occur according to Scheme 5.[8a,11c] Attempts to extend coordinative chain-transfer polymerization to propene and higher 1-alkenes have been few but promising.[23h,i] However, in early 2008, Zhang and Sita [13] reported the first definitive example of living coordinative chain-transfer polymerization of propene, in which a large molecular-weight range of atactic polypropene materials possessing extremely narrow polydispersities could be produced using the hafnium complex $[Cp^*HfMe_2\{N(Et)C(Me)N(Et)\}]$ (**5**; Scheme 6) as precatalyst and the borate **3** as cocatalyst in the presence of varying amounts of $ZnEt_2$ as the surrogate main-group-metal



5 **6** **7**

Scheme 6. Single-site precatalysts for living coordinative chain-transfer polymerization of ethene, propene, and 1-alkenes (**5**)[13] and chain-shuttling copolymerization of ethene and 1-octene (**6** and **7**). Bn = benzyl.[8]

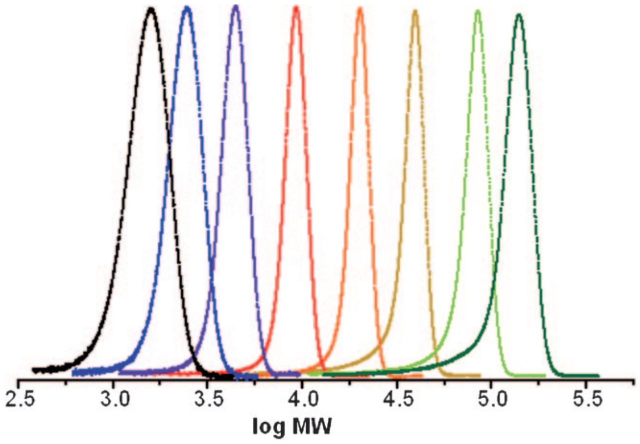
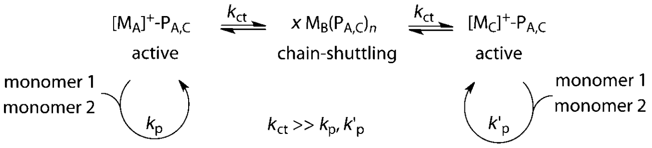


Figure 3. Molecular-weight distributions for atactic PP samples obtained under living coordinative chain-transfer conditions employing **5** as the precatalyst, **3** as the cocatalyst, and $ZnEt_2$ as the main-group-metal alkyl species. D values are below 1.1 for the first seven samples (from left to right) and 1.15 for the last. Under identical conditions, the first six samples were produced using a decreasing number of equivalents of $ZnEt_2$ relative to **5**: 200, 100, 50, 20, 10, 5. Reproduced from Ref. [13a] with permission.

alkyl species. The data presented in Figure 3 confirm that highly efficient and reversible polymeryl group transfer indeed occurs according to Scheme 5. A further important distinction of this study is that coordinative chain-transfer polymerization is equally efficient with as little as five molar equivalents of $ZnEt_2$ and as many as several hundred equivalents (Figure 3).[13] Such a large range of precise molecular-weight control has not been previously demonstrated for coordinative chain-transfer polymerization. Finally, this study addresses the critical question of whether the scaled production of polyolefins through a living process can be achieved with a significant reduction in the required amount of transition-metal precatalyst. In this respect, using living coordinative chain-transfer polymerization based on the present system, 60 g of a targeted oligomeric atactic polypropene with $M_n = 920$ Da ($D = 1.10$) could be prepared using a 99% reduction in the amount of **5** that would otherwise be required in the absence of reversible chain transfer.

4. Chain-Shuttling Coordination Polymerization

In 2006, Arriola et al.[8a] at Dow Chemical reported using $ZnEt_2$ as an effective "chain-shuttling" agent (CSA) for mediating polymeryl group transfer between two different transition-metal active sites derived from the precatalysts **6** and **7** (Scheme 6) within a continuous process for the copolymerization of ethene and 1-octene. Of academic and commercial significance, the process of chain shuttling, which is depicted in Scheme 7, provides the means to produce multiblock, "blocky" poly(ethene-*co*-1-octene) materials by virtue of differing capabilities for 1-alkene incorporation between the two active propagating centers. More specifically, after chain growth with low comonomer incorporation at the active center derived from precatalyst **6**, chain shuttling of the resultant polymeryl group via the main-group-metal alkyl CSA to the active center derived from precatalyst **7** yields a block structure after resumption of chain growth with high comonomer incorporation. Reversible repetition of this process during polymerization ensures that a multiblock architecture will be embedded into the final polyolefin material. Since chain shuttling is highly competitive with propagation at each of the two different active metal sites, monomodal molecular-weight distributions for the "blocky" poly(ethene-*co*-1-octene) materials are insured, in contrast to the bimodal distribution observed in the absence of a CSA.[8c] Finally, in a more recent demonstration of the commercial potential of reversible chain shuttling for the scaled production of polyolefin block copolymers, the Dow group employed the single catalyst derived from **6** with $ZnEt_2$ as a CSA in a tandem dual-reactor continuous process in which different poly(ethene-*co*-1-octene) block compositions were generated from different monomer feed ratios in each reactor.[8b] In this single-catalyst-based continuous operation, it is critical that the CSA serves as a temporary "place holder" for the polymeryl chains to reside during transport from the first reactor to the second, in which active chain growth is resumed upon addition of more of the precatalyst **6**. In terms of fitting within the context of a "one catalyst, many materials" paradigm, it is clear that chain-shuttling polymerization using two different catalysts certainly has the potential to produce new polyolefin structures and compositions that are not accessible through the more traditional "one catalyst, one material" approach.



Scheme 7. Coordinative chain-shuttling copolymerization of ethene and 1-octene. P_A and P_C are polymeryl groups of differing poly(ethene-*co*-1-octene) compositions.[8]

5. Outlook

After decades of intense worldwide focus, the subject of homogeneous single-site catalysts for alkene polymerization, and for preparation of polyolefins in general, has been classified, with all the best intentions, as being a "mature" field.[24] While this label may be taken to imply that little new is left to be discovered, it is actually through the benefit of such maturity that bold new directions can be explored. The identification and harnessing of dynamic bimolecular processes that are competitive with propagation can provide not only the basis for new "one catalyst, many materials" paradigms for further polyolefin discovery and development but can also provide the mechanisms by which precision polyolefins prepared under living conditions can potentially be brought to commercial realization. Significantly, all of the bimolecular processes considered to date can be carried over to new single-site coordination catalysts with different polyolefin structural and compositional capabilities, and here, high-throughput screening techniques will likely prove instrumental for the rapid evaluation and optimization of reaction parameters. With the increasing availability of these methods and of instrumentation for supporting academic and industrial research efforts alike, the prospects for further development of the "one catalyst, many materials" paradigm seem secure. In this respect, the maturity presently enjoyed by the field of polyolefins derived from the coordination polymerization of 1-alkenes is simply that of "middle age", and a long continued life of new discoveries still lies ahead.

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