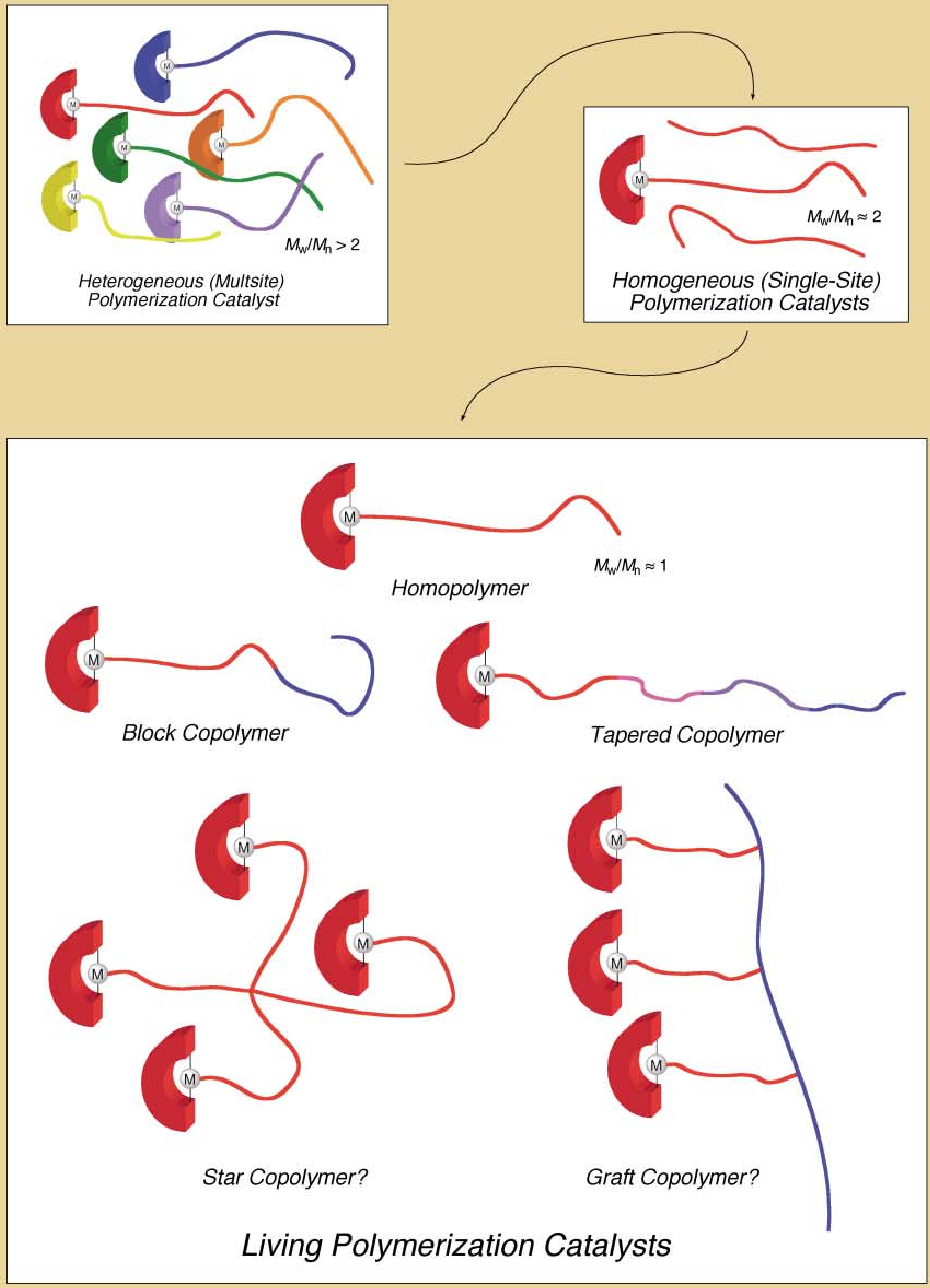

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Catalysts for the Living Insertion Polymerization of Alkenes: Access to New Polyolefin Architectures Using Ziegler–Natta Chemistry

Geoffrey W. Coates,* Phillip D. Hustad, and Stefan Reinartz

Dedicated to Professor Maurice Brookhart and Professor Robert H. Grubbs on the occasion of their 60th birthdays

Coordination–insertion polymerization systems have long been superior to their anionic, cationic, and radical polymerization counterparts with regard to stereochemical control. However, until five years ago, these metal-based insertion methods were inferior to ionic and radical mechanisms in the category of living polymerization, which is simply a polymerization that occurs with rapid initiation and negligible chain termination or transfer. In the last half decade, the living insertion polymerization of unactivated olefins has emerged as a powerful tool for the synthesis of new polymer architectures. Materials available today by this route range from simple homopolymers such as linear and branched polyethylene, to atactic or tactic poly(α-olefins), to end-functionalized polymers and block copolymers. This review article summarizes recent developments in this rapidly growing research area at the interface of synthetic and mechanistic organometallic chemistry, polymer chemistry, and materials science. While special emphasis is placed on polymer properties and novel polymeric architectures, most of which were inaccessible just a decade ago, important achievements with respect to ligand and catalyst design are also highlighted.

Keywords: alkenes · block copolymers · homogeneous catalysis · living polymerization · Ziegler–Natta catalysis

1. Introduction

Polymeric materials are currently more indispensable to modern society than at any other point in history. The potential applications of a polymer are determined by its physical and mechanical properties, which in turn are defined by the morphology (solid-state arrangement) of the polymer. Polymer morphology largely depends on the composition and architecture of the polymer. Therefore, the development of synthetic methods for the polymerization of a wide range of monomers with control over the stereochemistry and molecular weight of the resultant polymers is a long-standing scientific challenge. A primary goal of synthetic polymer chemistry that has existed for the last half century is the development of chain-growth polymerization methods that enable consecutive enchainment of monomer units without termination. Such techniques, now known as living polymerizations,[1] allow both precise molecular weight control as well as the synthesis of a wide array of polymer architectures.[2] For example, the initiation of multiple polymer chains from a central core results in the formation of a star-branched polymer, while the consecutive addition of two monomers to a single initiator produces a diblock copolymer.[3] Living methods also allow the synthesis of end-functional polymers if special initiation and/or quenching methods are employed. Of course, living polymerizations have the liability that each catalyst only forms one chain, in contrast to common alkene polymerization catalysts that can produce thousands of chains each as a result of periodic chain transfer or termination events. (Note: in this review, we refer to living species for alkene polymerization as "catalysts", not "initiators", to emphasize the fundamental catalytic event of monomer enchainment, not polymer chain formation.) The real value of living polymerization methods is that they allow the creation of virtually limitless types of new materials from a basic set of available monomers.

Based on annual production volume, polyolefins are by far the most important commercial class of synthetic polymers. Since the initial discoveries of Ziegler[4] and Natta,[5] remarkable advances have been reported concerning the control of comonomer incorporation as well as dramatic improvements in activity. Homogeneous olefin polymerization catalysts now exist that are unparalleled in all of polymer chemistry

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[*] Prof. Dr. G. W. Coates, P. D. Hustad, Dr. S. Reinartz
Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University
Ithaca, New York 14853-1301 (USA)
Fax: (+1) 607-255-4137
E-mail: gc39@cornell.edu

1433-7851/02/4112-2237 $ 20.00+.50/0

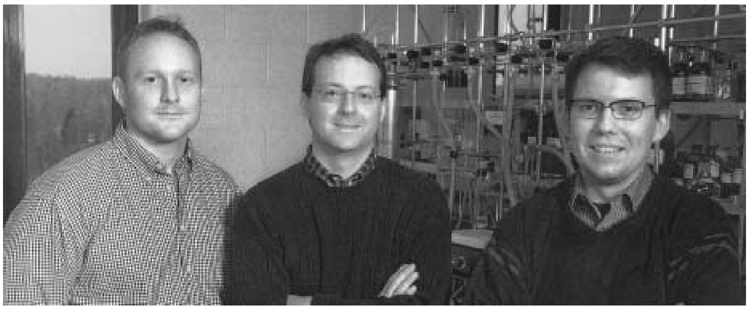
concerning the detailed control of macromolecular stereochemistry.[6] However, olefin insertion catalysts have always been inferior to their other chain-growth counterparts in one respect. While extraordinary advances in living/controlled polymerization have been discovered by using anionic,[7] cationic,[8] and radical-based[9–11] polymerization, until very recently there existed a comparative lack of living olefin polymerization systems. A significant number of advances have been reported in the last half decade, prompting us to review the area of catalysts for alkene polymerization that proceed without appreciable chain transfer or termination. In this review, we only address the living polymerization of unactivated alkenes by insertion methods; ring-opening metathesis polymerization (ROMP), the polymerization of conjugated dienes and acrylates, group transfer polymerization, and CO/alkene copolymerization will not be addressed.

The seven generally accepted criteria for a living polymerization are:

1) polymerization proceeds to complete monomer conversion, and chain growth continues upon further monomer addition;
2) number average molecular weight (M_n) of the polymer increases linearly as a function of conversion;[12]
3) the number of active centers remains constant for the duration of the polymerization;
4) molecular weight can be precisely controlled through stoichiometry;
5) polymers display narrow molecular weight distributions, described quantitatively by the ratio of the weight average molecular weight to the number average molecular weight ($M_w/M_n \sim 1$);
6) block copolymers can be prepared by sequential monomer addition;
7) end-functionalized polymers can be synthesized.[13]

Few polymerization systems, whether ionic-, radical-, or metal-mediated, that are claimed to proceed by a living mechanism have been shown to meet all of these criteria. This review will therefore include all systems that claim living olefin polymerization, providing that a substantial number of the key criteria have been met.

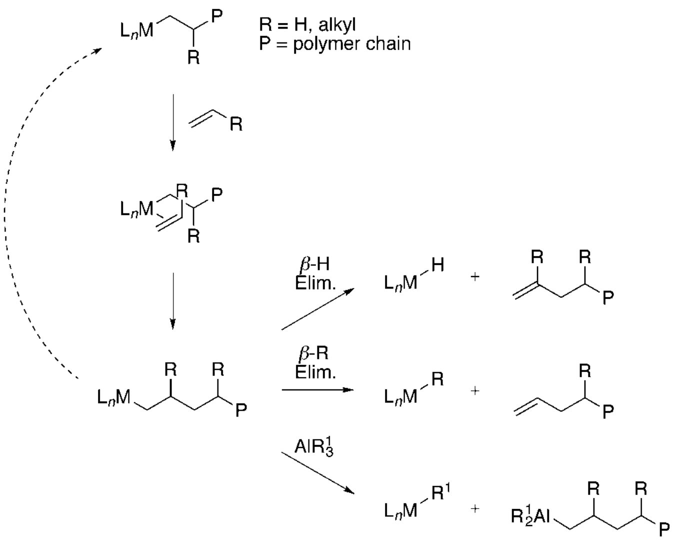
Common features of alkene polymerization catalyst systems are chain transfer and elimination reactions that terminate the growth of a polymer chain and result in the initiation of a new polymer chain by the catalyst (Scheme 1). For example, in metallocene catalysts, consecutive alkene insertion into the metal–carbon bond connecting the catalyst and polymer chain[14] proceeds until β-hydrogen and/or β-alkyl elimination occurs.[15] When alkylaluminum cocatalysts are employed, an additional termination route is chain transfer to the aluminum center.[15] In many systems, the lifetime of chain formation is on the order of seconds, rendering sequential monomer addition methods for block copolymer synthesis futile. Several strategies have been devised to decrease the rate of chain termination relative to that of propagation such that living systems can be formed. The first consideration in many cases is simply lowering the polymerization temperature of an ordinary non-living catalyst system to achieve living or at least controlled


P. D. Hustad G. W. Coates S. Reinartz

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

Phillip D. Hustad, born in Bristol, Tennessee in 1975, obtained a B.S. degree in Chemistry in 1997 from Emory & Henry College in Emory, Virginia. Inspired by undergraduate research with Prof. Koji Nakanishi at Columbia University, he then entered the Ph.D. program in Chemistry at Cornell University. He is currently working under the guidance of Geoffrey W. Coates on the development and applications of new catalysts for living olefin polymerization.

Stefan Reinartz, born in Hilden, Germany in 1972, studied chemistry at Heinrich-Heine-Universität Düsseldorf, Université de Nantes (France), and the University of North Carolina at Chapel Hill (UNC). After obtaining his Diplom in 1998, he returned to UNC, where he earned his Ph.D. in inorganic chemistry in 2001. His dissertation under the direction of Joseph L. Templeton and Maurice Brookhart focused on organometallic platinum chemistry relevant to bond activation processes. He is currently a DAAD Postdoctoral Fellow with Geoffrey W. Coates at Cornell University.



Scheme 1. Mechanisms of propagation and chain transfer in Ziegler–Natta catalyzed olefin polymerization.

behavior. Since β-hydrogen and alkyl elimination processes are unimolecular while propagation is bimolecular, a lowering in temperature more adversely affects elimination processes relative to enchainment. Since precipitation of polymers from solution at low temperatures can hinder the controlled nature of a living polymerization, it is generally advantageous to perform reactions at ambient temperature. Therefore, a second strategy for discovering living systems is to design new catalysts through empirical modification and/or computational methods.[16] By creating species that are incapable of common termination reactions at room temperature, living catalysts have been devised. A final consideration is to eliminate the use of alkyl aluminum cocatalysts that give the potential for chain-transfer reactions. In this regard, the development of weakly coordinating anions has made significant advances in living olefin polymerization possible.[17]

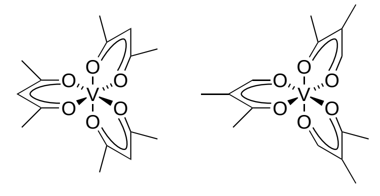
2. Vanadium Catalysts for Living Olefin Polymerization

Olefin polymerization emerged in the 1950s as a principal area of organometallic research when Ziegler and Natta and co-workers discovered that titanium chloride in the presence of alkylaluminum compounds was an efficient catalyst for polymerization of ethylene and propylene.[4, 5] Following this breakthrough, vanadium compounds in combination with alkylaluminum compounds were shown to be active catalysts for the polymerization of olefins. Through modification of ligands and activators, vanadium catalysts were also found to polymerize olefins in a living fashion at low temperatures. The utility of these living systems has been demonstrated through the synthesis of a wide variety of end-functionalized polypropylenes (PPs) and PP-containing block copolymers. However, polymerizations with these systems are limited to temperatures at or below $-40\,^{\circ}C$, and living behavior is restricted to only a few monomers.

2.1. Propylene Polymerization with Vanadium Compounds

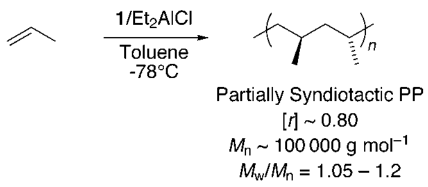
In the 1960s, Natta and co-workers discovered that vanadium tetrachloride activated with diethylaluminum chloride produced syndio-enriched polypropylenes at $-78\,^{\circ}C$.[18] The rate of polymerization was constant for long reaction times (ca. 50 h), and molecular weight increase with time was nearly linear over 25 h. The [Al]/[V] ratio had a dramatic effect on the lifetime of active chains; an increase in cocatalyst concentration was mirrored by a decrease in lifetime, implicating chain transfer to aluminum centers as a source of termination. The syndiospecificity of this catalyst was found to be the result of regioregular secondary (2,1) insertion of propylene.[19] Anisole was also found to have a dramatic effect on both catalytic activity and the average lifetime of active chains.[20] In later studies, polypropylenes from this catalytic system were found to be unimodal with narrow molecular weight distributions ($M_w/M_n = 1.4-1.9$).[21]

Although this catalytic system produced polypropylenes that were nearly living, the first true example of living olefin polymerization did not appear until over a decade later. In 1979, Doi et al. reported the first catalytic olefin polymerization system to satisfy all the requirements for a living polymerization. The catalyst, [V(acac)$_3$] (**1a**; Figure 1; acac = acetylacetonate) activated with Et_2AlCl, produced partially syndiotactic polypropylenes (81% *r* dyads; [*r*] = 0.81)[15] at $-78\,^{\circ}C$ with extremely narrow molecular weight distributions ($M_w/M_n = 1.05-1.20$; Scheme 2).[22, 23] Molecular weight increased linearly with time to values as high as 100000 g mol^{-1}, and the number of polymer chains remained constant during the course of the reaction. However, the catalyst exhibited living behavior only at temperatures below $-65\,^{\circ}C$; reactions at temperatures as low as $-48\,^{\circ}C$ resulted in polypropylenes with broadened molecular weight distributions ($M_w/M_n = 1.37-1.45$). Also, catalytic activity (ca. 4 $kg_{PP}\,mol_V^{-1}\,h^{-1}$) suffered from the fact that only about 4% of the vanadium centers were active. The nature of the aluminum cocatalyst also had a dramatic effect on polymerization activity, living



1a **1b**

Figure 1. Vanadium catalyst precursors for living olefin polymerization.

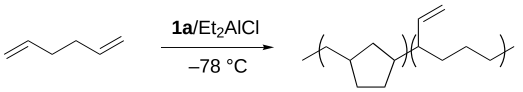


Scheme 2. Living polymerization of propylene with vanadium catalysts.

behavior, and stereoselectivity, suggesting a bimetallic active species. Particularly, use of the more electron-deficient cocatalyst $EtAlCl_2$ led to an increase in chain transfer to monomer, giving polymers with distributions approaching the theoretical value for polymerizations involving chain transfer ($M_w/M_n = 2.0$).[23, 24] The activating effect of anisole was also demonstrated for the **1a**/Et_2AlCl catalyst system.[25] The additive led to a threefold increase in the number of active vanadium centers without adversely affecting livingness or syndiospecificity.

To address the problem of activation, Doi and co-workers studied a variety of vanadium complexes and found that subtle ligand modifications had dramatic effects on catalytic behavior.[26–28] Through these studies, complex **1b** was found to be highly active (relative to **1a**) for the living polymerization of propylene (ca. 100 $kg_{PP} mol_V^{-1} h^{-1}$; Scheme 2). The increase in activity was attributed to a greater number of active vanadium centers in the reaction; the number of polymer chains per metal center approached unity for this catalytic system. Again, the polypropylene was partially syndiotactic ($[r] = 0.80$), consistent with a secondary insertion mechanism. The catalyst also displayed living behavior at temperatures as high as −40 °C, giving high molecular weight polymers with low polydispersity (M_n up to 100000 $g mol^{-1}$, $M_w/M_n = 1.2–1.4$).

Despite the success of these vanadium catalysts with propylene, living behavior is limited to only a few monomers with this catalytic system. For example, ethylene polymerizations with **1a**/Et_2AlCl at −78 °C gave high molecular weight polyethylenes (PEs; >300000 $g mol^{-1}$) with molecular weight distributions consistent with the probable distribution for a single-site catalyst ($M_w/M_n = 2.0$).[29] However, ethylene/propylene copolymerizations were living; reaction of ethylene and propylene with **1b**/Et_2AlCl at −60 °C rapidly produced a very high molecular weight copolymer ($M_n =$ 1020000 $g mol^{-1}$) with a narrow polydispersity ($M_w/M_n = 1.22$).[30] These catalysts were also found to be inactive for polymerization of higher α-olefins. For example, reaction of 1-pentene with **1a**/Et_2AlCl resulted in formation of heptane and 3-methylhexane, the products of a single 1-pentene addition to a vanadium–ethyl species with 2,1- and 1,2-regiochemistry, respectively.[31] No further reaction was detected, presumably due to the sterically congested nature of the catalytic site following the insertion. However, the vanadium system did produce living polymers with 1,5-hexadiene; at −78 °C, the diene was polymerized to low molecular weight polymer ($M_n = 6600$ $g mol^{-1}$) with a narrow molecular weight distribution ($M_w/M_n = 1.4$).[32] This polymer, however, did not possess the typical methylene-1,3-cyclopentane microstructure obtained with other insertion polymerization catalysts. By NMR analysis, the microstructure was determined to contain tetramethylene-1-vinylene units (46%) as well as methylene-1,3-cyclopentane structures (54%; Scheme 3). Copolymerization of propylene and 1,5-hexadiene also displayed living behavior. The distribution of the polymer microstructure varied with the mole fraction of hexadiene in the copolymer; high diene content gave equal amounts of the two repeat units, while lower incorporation resulted in exclusive formation of tetramethylene-1-vinylenes. However, the mechanism for formation of this unique polymer is unclear.



Scheme 3. Polymerization of 1,5-hexadiene with a vanadium catalyst.

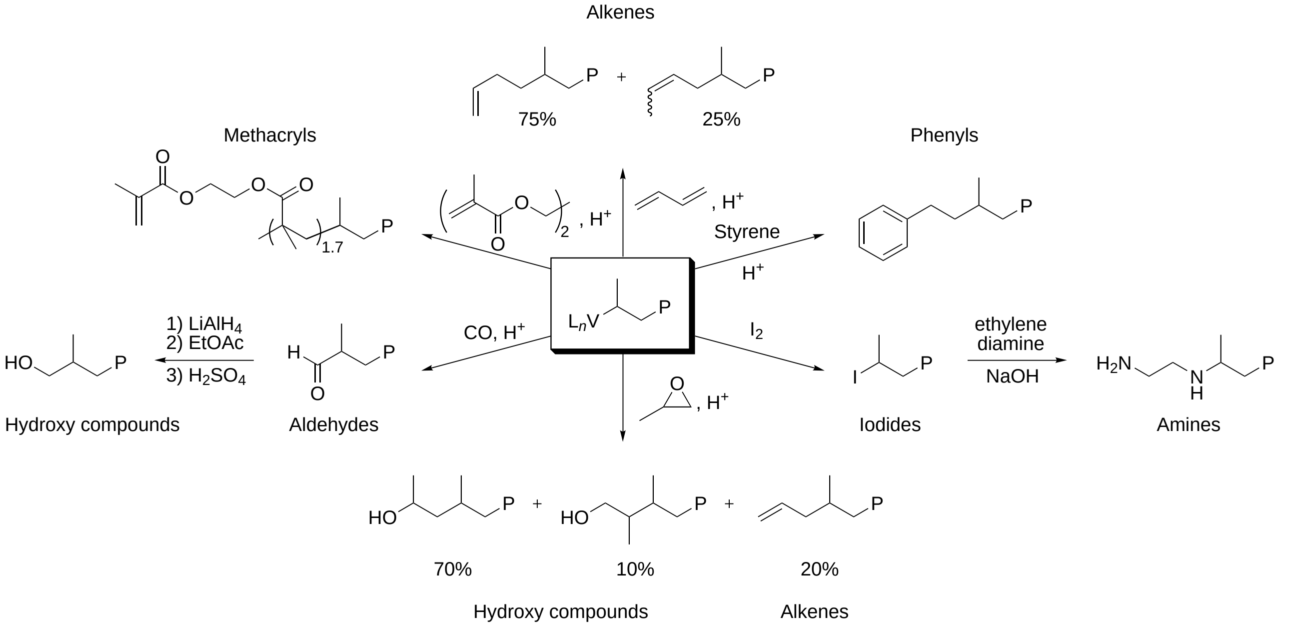
2.2. End-Functionalized Polypropylenes from Vanadium Compounds

Doi and co-workers have demonstrated the utility of the living vanadium catalysts through the synthesis of several tailor-made polymers.[33–37] By reacting active polymer chains with additives, polypropylenes with a wide variety of functional end groups can easily be prepared with these living catalyst systems (Scheme 4). In addition to providing important mechanistic information, these functional polymers display unique properties and have also been used as macroinitiators for the synthesis of block copolymers.

In an effort to synthesize new end-functionalized polymers, a living vanadium-polypropylene species was quenched with iodine at −78 °C to give a monodisperse iodine-functionalized polypropylene ($M_w/M_n = 1.15$).[33] NMR spectroscopy revealed that the structure of this end group resulted from reaction of I_2 with a secondary alkylvanadium compound, providing evidence for a 2,1 insertion mechanism. The iodine functionality was used to prepare an amine-terminated polypropylene by reacting the polymer with excess ethylenediamine in THF, followed by basic workup.[35] These polymers have also been used as macroinitiators for the preparation of diblock copolymers (see Section 2.3).

By reacting active living vanadium centers with carbon monoxide, Doi et al. have prepared aldehyde-terminated polypropylenes (Scheme 4).[38] Again, CO was found to insert quantitatively into secondary vanadium–carbon bonds. This aldehyde functionality has also been used to prepare hydroxy-functionalized polypropylenes by reduction of the aldehyde with $LiAlH_4$ in Et_2O, followed by acidic hydrolysis.[36] Hydroxy-terminated polypropylenes were also prepared with moderate success by reaction of an active vanadium species with propylene oxide.[36] The insertion of the epoxide into the growing polymer chain occurred with decent regioselectivity, preferentially adding at the unsubstituted carbon atom (7/1) to give the secondary alcohol. However, the reaction also yielded a fraction of allyl-terminated polypropylene from an undesirable elimination reaction (20%).

Polypropylene macromonomers containing methacryl functionality were prepared by addition of ethylene glycol dimethacrylate (EGDM) to a living chain end.[39] Propylene polymerization was conducted for 1 h at −60 °C with the complex **1b**/Et_2AlCl, giving a low molecular weight polypropylene ($M_n = 3100$ $g mol^{-1}$, $M_w/M_n = 1.13$). Addition of an excess of EGDM to this living chain end at −55 °C and reaction for an additional 1 h resulted in quantitative capping of the chain ends without formation of EGDM homopolymer ($M_n = 4000$ $g mol^{-1}$, $M_w/M_n = 1.10$). Both IR and NMR spectroscopy revealed the presence of the methacryl unit in the



Scheme 4. Synthesis of end-functional polypropylenes with a vanadium catalyst.

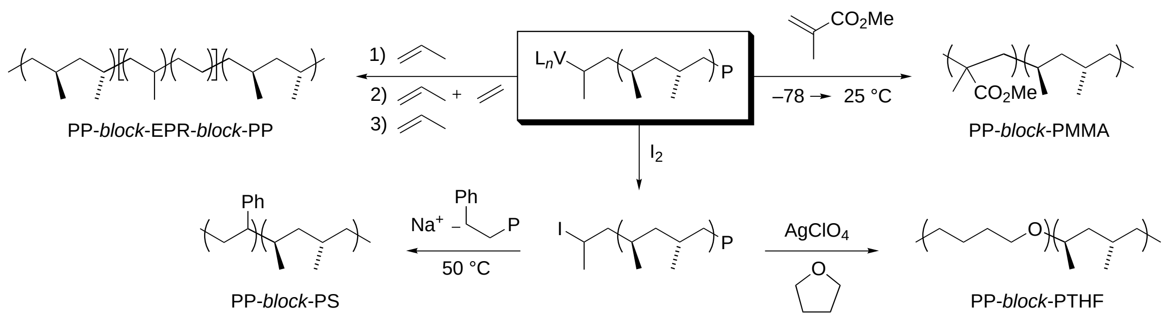
polymer; interestingly, an average of 1.7 molecules of EGDM were reported to be present per chain.

Finally, additives that produce polypropylenes with alkenyl and phenyl end groups were explored by Doi and co-workers.[36] By adding butadiene to living polypropylene prepared with **1a**/Et_2AlCl, a polymer containing alkene end groups was formed after quenching. NMR spectroscopy showed that the butadiene inserted with both 2,1 and 1,4 regiochemistry, producing polymers with both terminal (75%) and internal (25%) olefins. Phenyl-terminated polymers were also prepared in this fashion by addition of styrene to a living polypropylene, which reacts quantitatively with the growing polymer chain without formation of any styrene homopolymer.

2.3. Copolymers and Block Copolymers from Vanadium Compounds

One of the most attractive features of a living catalyst system lies in its ability to produce well-defined block copolymers by sequential monomer addition. Several methods have been described for block copolymer formation using vanadium catalysts. To this end, Doi and co-workers reported the synthesis of both AB- and ABA-type block copolymers from ethylene and propylene (Scheme 5). As described in Section 2.1, the reaction of **1a**/Et_2AlCl/anisole with propylene at −78 °C generates a living polypropylene chain end.[25] In the presence of propylene, a small amount of ethylene was added to this living chain, resulting in rapid formation of an AB-type copolymer containing syndio-enriched polypropylene and ethylene/propylene rubber (EPR) domains.[40] A sharp increase in both polymer yield and molecular weight versus time was observed following the ethylene addition. However, these rates quickly returned to values consistent with propylene homopolymerization, indicating that ethylene consumption was complete after a short time. The steady increase in yield and molecular weight following the ethylene addition indicated the continued formation of propylene homopolymer to give an ABA-type triblock copolymer (*syn*PP-*block*-EPR-*block*-*syn*PP).

In addition to providing block copolymers based on nonpolar olefins by sequential monomer addition, the vanadium catalysts have also been employed for the synthesis of block copolymers from polar monomers by transforming the living chain end to one capable of initiating a radical or cationic



Scheme 5. Synthesis of block copolymers with a vanadium catalyst; EPR = ethylene/propylene rubber.

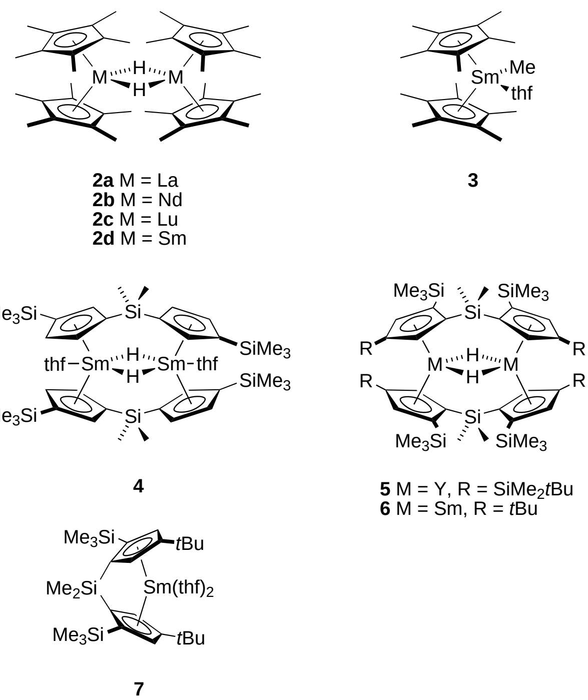
polymerization (Scheme 5). Doi et al. discovered that the polymerization of methyl methacrylate (MMA) with **1a**/Et_2AlCl at 25 °C displayed living character during the initial stages of the reaction, giving low molecular weight poly(methyl methacrylate) (PMMA) with a narrow molecular weight distribution ($M_n = 2400\,g\,mol^{-1}$, $M_w/M_n = 1.2$).[34] Copolymerizations of MMA with styrene suggested that the reaction proceeded by a radical pathway. This new method for MMA polymerization was employed for the synthesis of polypropylene/PMMA diblock copolymers. By reacting propylene with **1a**/Et_2AlCl at -78 °C, a living polypropylene chain end was formed ($M_n = 16\,000\,g\,mol^{-1}$, $M_w/M_n = 1.2$). Addition of MMA to the reaction mixture and warming to 25 °C resulted in formation of a higher molecular weight polymer containing a syndio-enriched PMMA segment (15 wt% PMMA, $M_n = 18\,000\,g\,mol^{-1}$, $M_w/M_n = 1.2$).

Another example of this strategy for block copolymer formation was demonstrated in the synthesis of a copolymer with a poly(tetrahydrofuran) (PTHF) domain. As described in Section 2.2, Doi et al. synthesized a monodisperse iodine-terminated polypropylene ($M_n = 16\,500\,g\,mol^{-1}$, $M_w/M_n = 1.15$) by addition of I_2 to a living polypropylene chain end.[33] This polymer was then dissolved in THF at 0 °C and treated with $AgClO_4$, causing immediate precipitation of AgI and concomitant formation of a cationic macroinitiator capable of THF polymerization. After 96 h, a monodisperse polymer ($M_w/M_n = 1.14$) of higher molecular weight was isolated. IR and NMR analysis revealed that the polymer contained both polypropylene and PTHF domains.

Finally, tailor-made block copolymers can be prepared by the coupling of iodine-terminated polypropylenes with monofunctional or multifunctional living polymers. Doi et al. exploited this strategy for the synthesis of a well-defined polypropylene–polystyrene diblock copolymer.[29] Addition of an iodine-terminated polypropylene ($M_n = 22\,000\,g\,mol^{-1}$, $M_w/M_n = 1.14$) to a living polystyrene anion ($M_n = 13\,000\,g\,mol^{-1}$, $M_w/M_n = 1.27$) resulted in formation of a higher molecular weight polymer ($M_n = 35\,000\,g\,mol^{-1}$, $M_w/M_n = 1.25$), consistent with the quantitative coupling of the two component polymers.

3. Rare-Earth Metal Catalysts for Controlled Alkene Polymerization

Schumann, Marks, and co-workers showed as early as 1985 that organolanthanide complexes were promising candidates for living olefin polymerization.[41] Dimeric Cp*-based hydride complexes **2a–c** (Figure 2; Cp* = pentamethylcyclopentadienyl) were extremely active for the polymerization of ethylene, with turnover numbers of more than 1800 s^{-1} for **2a** at room temperature. Molecular weight distributions of polymers from the lutetium catalyst **2c** were reproducibly less than two ($M_n = 96\,000–361\,000\,g\,mol^{-1}$; $M_w/M_n = 1.37–1.68$), and the average number of polymer chains per lanthanide center for catalysts **2a–c** was always less than one. Based on these observations, it was speculated that these systems were operating in a living fashion. Furthermore, polymerization at -78 °C with **2b** showed that temperature effects on possible chain termination reactions such as β-hydride elimination were not important ($T = 25$ °C, $t = 5$ s, $M_n = 590\,000\,g\,mol^{-1}$; $M_w/M_n = 1.81$; $T = -78$ °C, $t = 600$ s, $M_n = 648\,000\,g\,mol^{-1}$; $M_w/M_n = 1.95$). Perfectly living behavior of these hydride catalysts was believed to be impeded by mass-transport effects and initiation-limiting dissociation of the catalyst dimer.



2a M = La
2b M = Nd
2c M = Lu
2d M = Sm

3

4

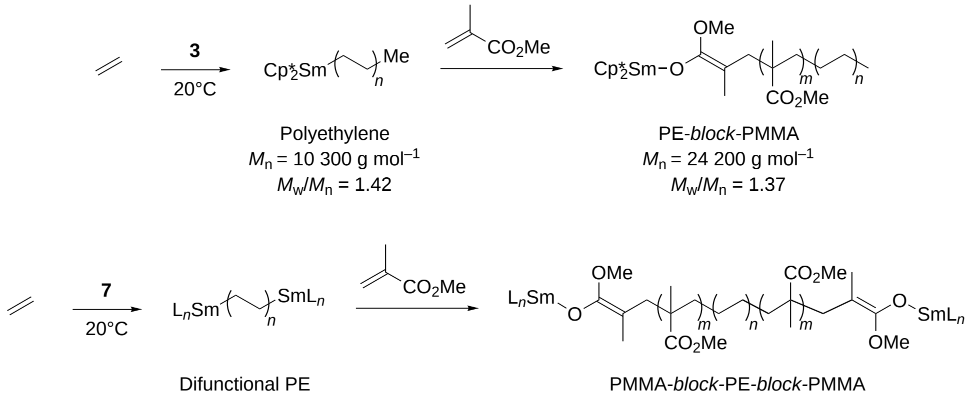
5 M = Y, R = SiMe2*t*Bu
6 M = Sm, R = *t*Bu

7

Figure 2. Lanthanide catalysts for living olefin polymerization. THF = tetrahydrofuran.

Yasuda and co-workers reported in 1992 that complex **2d** was extremely active for the living, syndiospecific polymerization of MMA ($[r] = 0.97$ at -95 °C, $[r] = 0.91$ at 0 °C) to form high molecular weight polymers (M_n up to $560\,000\,g\,mol^{-1}$) with extremely narrow molecular weight distributions ($M_w/M_n < 1.05$) via a coordination anionic polymerization mechanism.[42] Immediately following this discovery, the sequential addition copolymerization of ethylene and polar monomers was reported to give block copolymers, implicating a change of mechanism from insertion to coordination anionic during the course of the polymerization.[43] Since this material has been extensively reviewed elsewhere, we will only highlight the general concept.[44–47]

In 1992, Yasuda et al. reported that samarium catalyst **3** (Figure 2) could effect the room-temperature block copolymerization of ethylene (insertion mechanism) and several polar monomers (non-insertion mechanism) such as methyl methacrylate, methyl acrylate, ethyl acrylate, δ-valerolactone, and ε-caprolactone (CL).[43] In a typical two-step procedure, ethylene was first polymerized to a reactive polyethylene (PE) ($M_n = 6600–27\,000\,g\,mol^{-1}$, $M_w/M_n = 1.39–2.01$) in toluene under atmospheric pressure, followed by the addition of the respective polar monomer to form a linear diblock copolymer with relatively narrow polydispersity (Scheme 6). Reversal of monomer addition did not lead to block copoly-



Scheme 6. Synthesis of polyethylene/poly(methyl methacrylate) diblock and triblock copolymers with samarium catalysts.

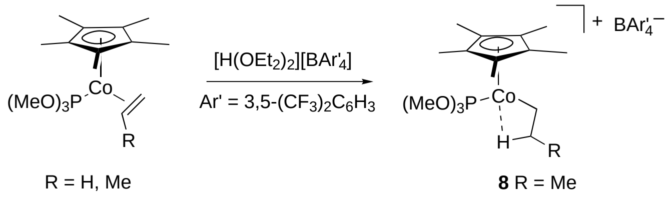
mer formation. The resulting materials, such as PE-*block*-PMMA and PE-*block*-poly(CL) showed advantageous materials properties such as deep coloration with dyes when a short polar block was present.

Recently, Yasuda and co-workers developed a binuclear samarium complex **4** (Figure 2) which exhibited high activity for the polymerization of ethylene (M_n up to 50000 g mol^{-1}; $M_w/M_n = 1.63 - 1.68$) and efficiently formed diblock copolymers such as PE-*block*-PMMA (M_n up to 70000 g mol^{-1}; $M_w/M_n = 1.67 - 1.69$) and polyethylene-*block*-poly(CL) (M_n = 70000 g mol^{-1}; $M_w/M_n = 1.65$).[48] Structurally related complexes **5** and **6** (Figure 2) were then applied in the first controlled block copolymerization of 1-hexene and 1-pentene with MMA and CL.[49] Yasuda and co-workers have also reported new divalent samarium complexes with bridging bis(cyclopentadienyl) (Cp) ligands and applied them in the polymerization of ethylene.[50] In particular, racemic complex **7** provided encouraging results not only in the formation of polyethylene but also in the polymerization of higher α-olefins to give highly isotactic poly(α-olefins) (e.g. poly(1-pentene): M_w = 10600 g mol^{-1}, $M_w/M_n = 1.48$, poly(1-hexene), M_w = 8300 g mol^{-1}, $M_w/M_n = 1.55$). Cyclopolymerization of 1,5-hexadiene resulted in the formation of poly(methylene-1,3-cyclopentane) with a *cis*-ring content of about 50% (M_w = 28500 g mol^{-1}; $M_w/M_n = 1.88$). Furthermore, since catalyst **7** operated by a mechanism involving coordination of ethylene to two samarium centers followed by electron transfer to give a telechelic ethylene-bridged dinuclear species, block copolymerization of ethylene and MMA resulted in formation of the triblock PMMA-*block*-PE-*block*-PMMA copolymer (Scheme 6).[51] Corresponding trivalent lanthanide compounds with bridging bis(Cp) ligands were not found to be superior in polymerization activity.[52]

It should be mentioned that the organolanthanide complexes discussed here do not entirely meet the generally accepted criteria for living olefin polymerization, especially with respect to molecular weight distribution. However, through the combination of living anionic polymerization of polar monomers with partially controlled olefin insertion polymerization, these systems have found exciting applications in the synthesis of new materials with interesting properties.

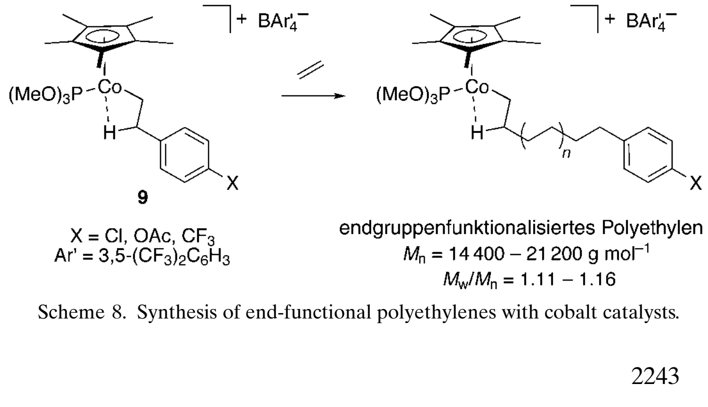
4. Cobalt, Niobium, and Tantalum Catalysts for Living Ethylene Polymerization

In the beginning of the 1990s, a number of catalyst systems for ethylene polymerization were reported in which the resulting polyethylene displayed a surprisingly narrow molecular weight distribution. The cobalt catalyst **8** (Ar′ = 3,5-$(CF_3)_2C_6H_3$), prepared by protonation of the alkene-bound precursor (Scheme 7), produced polyethylenes with narrow polydispersities for low molecular weight samples (M_n = 13600 g mol^{-1}; $M_w/M_n = 1.17$), while the polydispersity increased for samples of higher molecular weight presumably due to mass transport problems (M_n = 48500 g mol^{-1}; $M_w/M_n = 1.71$).[53] In addition, precipitation of polymer was regarded as a possible catalyst deactivation route.



Scheme 7. Synthesis of cobalt catalysts for olefin polymerization.

Based on this encouraging lead, Brookhart and co-workers subsequently reported a slightly modified cobalt catalyst for living ethylene polymerization and the synthesis of end-functional polyethylenes.[54] Highly electrophilic cobalt complexes **9**, when exposed to 1 atm of ethylene for 3 h at room temperature followed by hydrogenolysis of the Co–$C_{(alkyl)}$ bond, formed end-functional polyethylenes (M_n up to 20000 g mol^{-1}) with narrow polydispersities ($M_w/M_n = 1.11 - 1.16$) (Scheme 8). ^{13}C NMR analysis of the resulting polymer revealed a polymer microstructure with no branching. The presence of only one terminal methyl resonance signal indicated that the initiating species was the β-aryl-substituted, β-agostic complex (Scheme 8), and not its α-aryl-substituted, β-agostic isomer, in which case the corresponding polymer

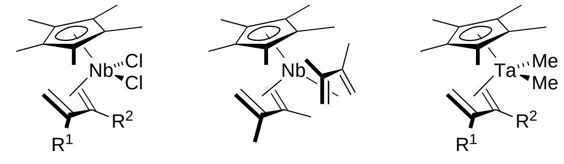


Scheme 8. Synthesis of end-functional polyethylenes with cobalt catalysts.

would have displayed two methyl resonance signals (i.e. $CH_3CH_2(CH_2CH_2)_nCH(CH_3)C_6H_4X$). Furthermore, interaction of the functional group with the cobalt center, which could lead to catalyst deactivation, was prevented since the metal center can not migrate past the aryl group. However, broadening of the molecular weight distribution was again observed for higher molecular weight polymers ($M_n >$ 40000 g mol^{-1}).

Silyl-functionalized polyethylene could be generated in an analogous fashion with the β-agostic complex $[Cp^*\{P(OMe)_3\}CoCH_2CH(\mu\text{-}H)(CH_2)_4SiR_3][BAr'_4]$ (**10**) ($BAr'_4 = B(3,5\text{-}(CF_3)_2C_6H_3)_4$). Molecular weights and molecular weight distributions for $SiEt_3$-functional polyethylenes compared well with those of the aryl-substituted polymers. However, Me_2SiCl-functional polyethylenes showed lower molecular weight ($M_n = 10200$ g mol^{-1}) and broader molecular weight distribution ($M_w/M_n = 1.41$), presumably due to catalyst poisoning. While these cobalt complexes provided routes to end-functional polyethylenes, there are a number of drawbacks in these systems, namely the relatively low molecular weight of the resulting polymer, rather elaborate catalyst synthesis, and, especially in case of the complex **10**, their high moisture sensitivity.

The next major advance towards living olefin polymerization came in mid-1990s with the development of niobium diene based systems (Figure 3).[55–57] Since these Group 5 systems are isoelectronic with Group 4 bis(Cp) complexes, Mashima and co-workers realized that these precursors should be active in olefin polymerization. After an initial paper disclosing the validity of this idea,[55] living ethylene polymerizations with the niobium diene systems **11a–c**/MAO (MAO = methylaluminoxane) and **12**/MAO were reported in 1994.[56] Polymerization below 0 °C occurred in a living fashion to produce high molecular weight polyethylenes (M_n up to 40000 g mol^{-1}) with extremely narrow polydispersities (M_w/M_n as low as 1.05). The catalyst precursors were synthesized in low to moderate yields from $[Cp^*NbCl_4]$ and two equivalents of the respective allyl Grignard reagent. The substitution pattern of the diene moiety, which is essential for catalytic activity, influenced catalytic performance. For example, catalysts comprising 1,3-butadiene (**11a**) or 2,3-dimethyl-1,3-butadiene (**11c**) displayed approximately equal polymerization activities (38.7 versus 35.2 $kg_{PE}\,mol_{Nb}^{-1}\,h^{-1}$) at 20 °C), while catalyst **11b** containing the 2-methyl-1,3-butadiene ligand was somewhat less active (19.2 $kg_{PE}\,mol_{Nb}^{-1}\,h^{-1}$). The bis(diene) complex **12** was inactive for ethylene polymerization upon addition of $B(C_6F_5)_3$. Furthermore, changing the steric bulk of the catalyst system by replacing the Cp* ligand of **11** with the less hindered Cp ligand resulted in a significant broadening of the molecular weight distribution of the resulting polyethylene ($M_w/M_n = 1.40$), presumably due to inferior catalyst stability.



11a $R^1 = R^2 = H$
11b $R^1 = Me, R^2 = H$
11c $R^1 = R^2 = Me$

12

13a $R^1 = R^2 = H$
13b $R^1 = Me, R^2 = H$
13c $R^1 = R^2 = Me$

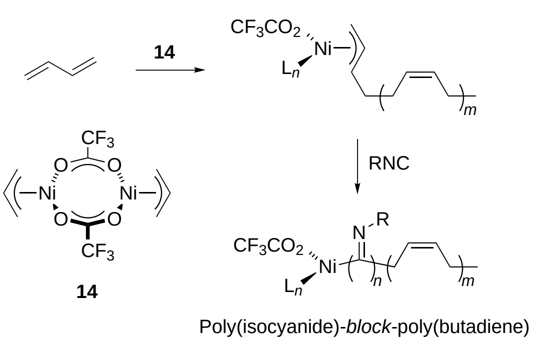
Figure 3. Niobium- and tantalum catalyst precursors for living olefin polymerization.

Following these leads, Mashima and co-workers subsequently synthesized dimethyltantalum complexes **13a–c** (Figure 3). Interestingly, the corresponding niobium complexes decomposed rapidly via carbene intermediates.[57] Although these tantalum species were inferior to niobium complexes **11** and **12** with respect to catalytic activity and molecular weight distribution of the resulting polymer, they did polymerize olefins in a controlled fashion. Addition of $B(C_6F_5)_3$ to a solution of **13b** at room temperature resulted in formation of the ion-pair $[Cp^*Ta(\eta^4\text{-isoprene})Me][MeB(C_6F_5)_3]$, as suggested by NMR experiments. The in situ generated η^4-butadiene congener **13a**/$B(C_6F_5)_3$ was found to be active for the polymerization of ethylene (1.38 $kg_{PE}\,mol_{Ta}^{-1}\,h^{-1}$), and the activity could be enhanced by adding $AlEt_3$. When activated with MAO, dimethyl complexes **13a–c** and the corresponding dichloro complexes displayed comparable activities, indicating formation of similar active species.

5. Nickel and Palladium Catalysts for Living Olefin Polymerization

The search for catalyst systems for the living polymerization of α-olefins gained additional momentum by the development of diimine nickel and palladium catalysts in the mid-1990s.[58] The advantages of these late transition metal systems are multifold. Late metal catalysts allow the copolymerization of functional monomers because of the reduced oxophilicity of the late metal center.[59] Many of the late metal catalyst precursors are easily accessible, and detailed mechanistic studies have been undertaken since key species such as alkyl olefin complexes can be cleanly generated.

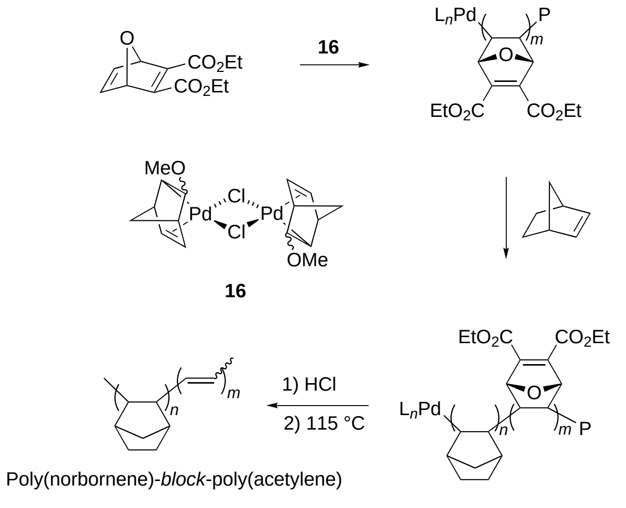
It is worth noting that more than a decade before the discovery of late transition metal catalysts for living polymerization of unactivated olefins, nickel allyl catalysts for living polymerization of conjugated dienes already existed. In 1984, Teyssié and co-workers reported that bis[(η^3-allyl)(trifluoroacetato)nickel] (**14**) promoted the living polymerization of 1,3-butadiene to poly(1,4-butadiene) with predictable molecular weight and narrow molecular weight distribution ($M_w/M_n = 1.2–2.0$) at or above room temperature.[60] Even though conversion of monomer was not complete (77% at best), the linear increase in number-average molecular weight with conversion was consistent with a living polymerization. Deming and Novak, who utilized catalyst **14** in the polymerization of *tert*-butyl-isocyanide to form the corresponding helical polymers,[61] took advantage of its living behavior in the polymerization of butadiene to form poly(butadiene)/poly(isocyanide) diblock copolymers (Scheme 9).[62] Bimetallic nickel initiators were then developed for the synthesis of hydroxytelechelic poly(butadiene) and symmetric poly(isocyanide)-*block*-poly(butadiene)-*block*-poly(isocyanide) tri-



Scheme 9. Nickel-catalyzed living copolymerization of butadiene and isocyanides.

block copolymers.[63] Allylnickel catalysts have also found applications in the living polymerization of functionalized and nonfunctionalized allenes.[64]

Risse and Mehler reported the living polymerization of norbornene using [Pd(MeCN)$_4$][BF$_4$]$_2$ (**15**). Poly(norbornene)s with number-average molecular weights up to 30000 g mol^{-1} exhibited narrow molecular weight distributions at low monomer conversions; at higher conversions, the distributions broadened.[65] Using **15**, Risse and Breunig reported the polymerization of ester-functionalized norbornenes. Depending on the nature of the ester substituent, polymers with narrow molecular weight distributions were obtained and block copolymers were synthesized.[66] Novak and Safir also demonstrated the potential of palladium catalysts for living olefin polymerization in 1995. Hydrocarbon–poly(acetylene) block copolymers were synthesized by living insertion polymerization using extremely robust, air- and moisture-stable alkylpalladium(II) complexes containing σ,π-alkyl ligands (**16**) (Scheme 10).[67] Polymerization of diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, which can be viewed as a protected acetylene monomer, occurred quantitatively with **16** to yield a polymer with an active palladium end group. Subsequent addition of norbornene to this macroinitiator led to the formation of a block copolymer. Upon heating, this material underwent a retro-Diels–Alder reaction, giving a poly(norbornene)-*block*-poly(acetylene) diblock copolymer.



Scheme 10. Synthesis of norbornene/acetylene block copolymers with a palladium catalyst.

A major breakthrough in living olefin polymerization occurred in 1995 with the discovery of a new family of late transition metal catalysts by Brookhart and co-workers. Soon after the initial report on the synthesis and polymerization activity of α-diiminepalladium and -nickel complexes,[68] a subsequent paper appeared demonstrating the use of these nickel systems for the living polymerization of α-olefins.[69] Catalyst precursor **17** (Figure 4), when activated with MAO in toluene at room temperature, was shown to be very active for the polymerization of α-olefins (turnover frequencies between 300 and 3000 h^{-1}), yielding high molecular weight materials (M_n up to 190000 g mol^{-1} for polypropylene) with relatively narrow polydispersities ($1.4 < M_w/M_n < 1.8$). At lower temperatures (−10 °C) and low monomer concentrations, polymers with very narrow molecular weight distributions were obtained because undesirable chain transfer reactions were suppressed under these conditions. Accordingly, complex **17**/MAO in toluene under 1 atm of propylene at −10 °C yielded high molecular weight polypropylene ($M_n = 161000$ g mol^{-1}, $M_w/M_n = 1.13$; Scheme 11).

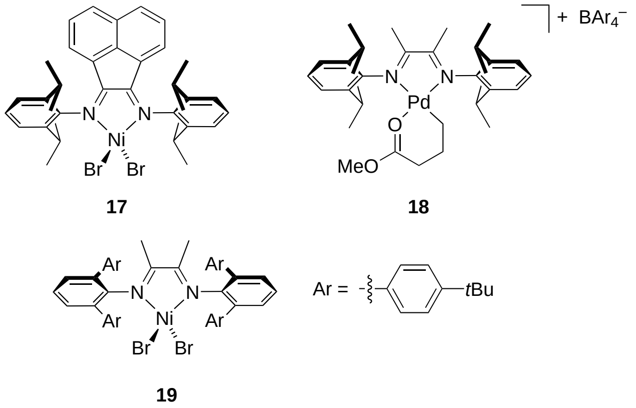
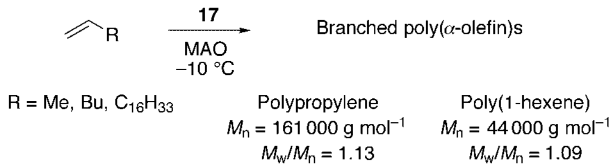
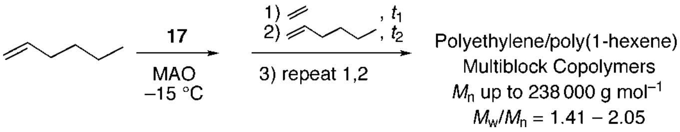


Figure 4. Nickel and palladium α-diimine catalysts and catalyst precursors for living olefin polymerization.



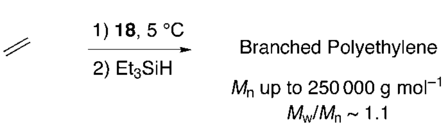
Scheme 11. Living polymerization of α-olefins with a nickel diimine catalyst system.

Since chain walking (consecutive β-hydride elimination followed by olefin reinsertion with opposite regiochemistry) is a distinguishing mechanistic feature of palladium and nickel diimine catalysts,[68, 70, 71] polymerization of ethylene results in a highly branched polymer, while polymerization of higher α-olefins leads to chain straightening, as indicated by a branching content that is lower than expected. The unique combination of living α-olefin polymerization behavior with the formation of chain straightened poly(α-olefin)s provided the basis for a new strategy for the preparation of elastomeric materials. While polymerization of propylene by **17** formed an amorphous material ($T_g = -16\,^\circ C$), polymerization of octadecene led to a polymer with unbranched, crystalline domains ($T_m = 56\,^\circ C$). Based on these amorphous and crystalline polymer domains, several diblock and triblock polymers were prepared. A poly(octadecene)-*block*-poly(octadecene-*co*-propylene)-*block*-poly(octadecene) triblock copolymer, for example, consisting of semicrystalline poly(1-octadecene) blocks and an amorphous propylene/octadecene core, displayed elastomeric properties.[69] Killian and Brookhart also exploited a similar strategy towards synthesis of ethylene/1-hexene multiblock polymers (Scheme 12).[72] Although some chain transfer in ethylene homopolymerizations with nickel catalyst **17** occurs even at temperatures below 0 °C, a successful procedure for the synthesis of these unique multiblock materials was developed. Catalyst **17** in a toluene/1-hexene solution at −15 °C was combined with MMAO (MMAO = modified methylaluminoxane), and ethylene was repeatedly added in short pulses. Since 1-hexene polymerization was living under these conditions, the main reaction product was expected to be a multiblock polymer despite some chain transfer. Depending on the time intervals for both ethylene and hexene polymerizations and the number of cycles in which this procedure was repeated, the resulting materials displayed excellent elastomeric properties (elongations of up to 1090 %, tensile strength up to 860 psi).



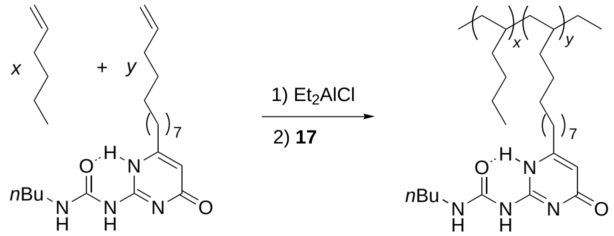
Scheme 12. Synthesis of polyethylene/poly(1-hexene) multiblock copolymers with a nickel diimine catalyst.

While nickel diimine catalysts did not polymerize ethylene in a living fashion, Gottfried and Brookhart recently reported experimental conditions under which ethylene can be polymerized by palladium catalyst **18** to give amorphous polymers with controlled molecular weights and narrow molecular weight distributions (Scheme 13).[73] Quenching the reaction mixture with triethylsilane, whereby the $Pd{-}C_{(alkyl)}$ bonds were cleanly converted to saturated end groups, proved crucial to obtaining monodisperse polyethylenes with this catalytic system. When the polymerization was quenched with acidified methanol, chain coupling frequently occurred and the resulting polyethylene displayed a bimodal molecular weight distribution. The polydispersity index of these polyethylenes remained well under 1.1 up to molecular weights of 250 000 g mol^{-1}. The resulting polymers were highly branched (100 branches/1000 C), and the branching number was independent of the polymerization conditions. However, performing the polymerization at lower ethylene pressures (1 atm) resulted in a somewhat broadened molecular weight distribution ($M_w/M_n = 1.27$). Lower ethylene pressures were believed to retard the rate of initiation relative to the rate of propagation since the palladium chelate complex **18** is favored over the corresponding chelate-opened alkyl olefin catalyst resting state. When polymerizations were performed at 27 °C, catalyst decay led to a nonlinear increase of the molecular weight over time and broadened molecular weight distributions of the resulting polyethylenes.



Scheme 13. Living polymerization of ethylene with a palladium diimine catalyst.

The full potential of the nickel and palladium α-diimine systems has not yet been fully explored in the context of living polymerization, and one can only imagine the exciting possibilities for materials synthesis offered by these systems. Possible future challenges involve control over stereochemistry in living α-olefin polymerization with C_2-symmetric diimine catalysts, as well as the copolymerization of monomers containing functional groups. The following two examples are given to illustrate this point. Non-living syndiospecific polymerization of propylene by α-diimine nickel catalysts has been reported.[74–77] Rieger and co-workers recently reported the synthesis of extremely bulky C_2-symmetric nickel and palladium α-diimine complexes and their application in the formation of ultra high molecular weight polyethylenes at ambient temperature. Linear polyethylene of narrow polydispersity ($M_w = 4500000$ g mol^{-1}; $M_w/M_n = 1.3$) was obtained with catalyst **19**/MAO, providing an encouraging lead for future investigations.[78] Taking advantage of the living behavior and functional group tolerance of catalyst **17**, we explored the copolymerization of 1-hexene with a functionalized olefin capable of forming intermolecular hydrogen bonds (Scheme 14).[79] Ureidopyrimidone (UP) functionalized poly(1-hexene)s with low comonomer content (ca. 2 %) were synthesized in a living fashion ($M_n = 33000$–104000 g mol^{-1}, $M_w/M_n = 1.2$–1.4). These materials display elastomeric properties, indicating the formation of hydrogen-bond crosslinks between polymer chains. It should be pointed out that the resulting polymer is certainly more complex than shown in Scheme 14 because of chain walking.



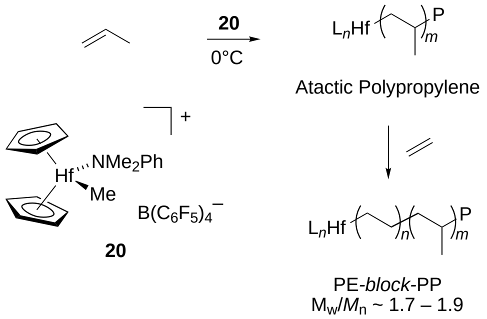
Scheme 14. Synthesis of ureipyrimidone-functional poly(1-hexene) with a nickel diimine catalyst.

6. Titanium, Zirconium, and Hafnium Catalysts for Living Alkene Polymerization

Given the key advances in the control of polymer stereochemistry and comonomer incorporation over the last two decades,[6] a significant amount of research in the quest for living olefin polymerization catalysts has centered on complexes based on the Group 4 metals. Metallocene catalyst systems have been shown to exhibit living behavior at low temperatures by suppressing undesirable β-hydride or β-alkyl eliminations. Recently, non-metallocene systems based on nitrogen and oxygen donor ligands have received considerable attention.[80] In addition to providing pathways for living olefin polymerization at ambient temperature, these systems have also made possible considerable advances concerning the control of stereochemistry in living olefin polymerization. By combining these long-sought goals, these complexes provide routes to the synthesis of polyolefin materials inaccessible by conventional polymerization methods.

6.1. Metallocene Complexes

Turner and Hlatky demonstrated the synthesis of a block copolymer of propylene and ethylene using a cationic hafnocene that was stable to chain transfer over the lifetime of the polymerization reaction (Scheme 15), even though the obtained polymer molecular weight distributions were not satisfying.[81] Propylene was first added to a solution of $[Cp_2HfMe(PhNMe_2)][B(C_6F_5)_4]$ (**20**) at 0 °C. After consumption of propylene, ethylene was added to the reactor. Based on extraction studies, it was determined that 75 % of the polypropylene chains were incorporated into diblock copolymers composed of atactic polypropylene and high-density polyethylene segments. The copolymer could also be synthesized by the reverse monomer addition, that is adding ethylene first, but the molecular weight distribution was higher in this case (1.89 versus 1.72) and the propylene content was lower (30 % versus 37 %). Due to the relatively short lifetimes of the living polymer chains, triblock copolymers were not efficiently formed.



Scheme 15. Synthesis of ethylene/propylene diblock copolymers with a hafnocene catalyst.

Bochmann and co-workers reported that $[Cp^*TiMe_3]$ (**21**; Figure 5) activated with $B(C_6F_5)_3$ was highly active for the polymerization of propylene to form high molecular weight atactic polypropylene (M_n up to 4000000 g mol^{-1}) that displayed elastomeric properties.[82] The presence of polymer fractions with very narrow molecular weight distributions ($M_w/M_n = 1.1$) in this MAO-free polymerization system was intriguing, and it was concluded that about half of the active titanium centers operated in a living fashion. Polymers with relatively narrow polydispersities ($M_w/M_n = 1.6$) were obtained at room temperature when polymerizations were performed in light petroleum despite reduced catalyst productivity in that solvent. Overall, the **21**/$B(C_6F_5)_3$ system showed several characteristics of living behavior at room temperature, such as linear increase of polymer yield with both catalyst concentration and time. Addition of $AlMe_3$ or Al*i*Bu$_3$, even in substoichiometric amounts, dramatically decreased catalytic activity and produced polymers with bimodal molecular weight distributions. Polymerization of 1-hexene under similar conditions gave atactic poly(1-hexene) with broader molecular weight distributions (M_n ca. 10000 g mol^{-1}, $M_w/M_n \sim 2.4$).[83]

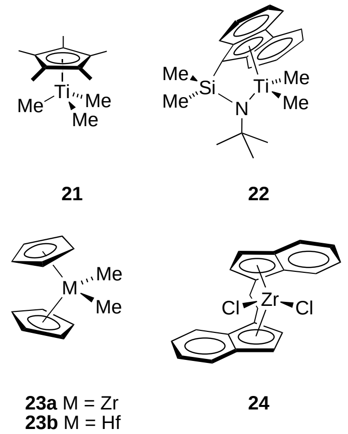


Figure 5. Metallocene catalyst precursors for living olefin polymerization at low temperatures.

Based on the notion that β-hydride elimination is negligible in comparison with propagation in standard metallocene–MAO systems at temperatures below −40 °C,[84] the research groups of Shiono and Fukui investigated olefin polymerization with metallocene or constrained geometry catalysts at very low temperatures. To avoid chain transfer to aluminum, Shiono and co-workers utilized borane activators in their initial study.[85] The titanium catalyst **22**, when activated with $B(C_6F_5)_3$ at −50 °C, produced syndio-enriched polypropylene ($[rrrr] = 0.24$) with narrow molecular weight distributions (M_n up to 20000 g mol^{-1}, $M_w/M_n = 1.15–1.40$), and polymerization of 1-hexene under similar conditions also displayed living behavior. Raising the temperature of the reaction to 0 °C resulted in complete deactivation of the catalyst system. By using rigorously dried MAO (free of $AlMe_3$ impurities), Shiono and co-workers then showed that chain transfer to aluminum caused by residual $AlMe_3$ could be efficiently suppressed in this system. Accordingly, moderately syndiotactic polypropylene ($[rrrr] = 0.42$) could be produced in a living fashion with **22**/MAO even at 0 °C ($M_n = 10100$ g mol^{-1}; $M_w/M_n = 1.35$).[86]

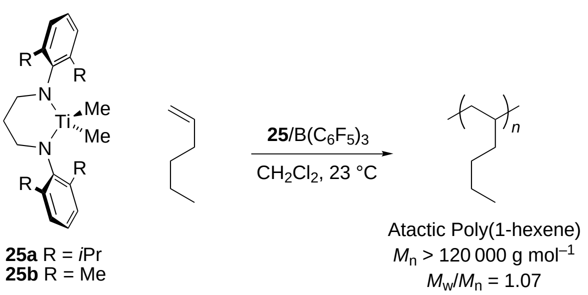
Fukui and co-workers demonstrated that the simple bis(Cp) catalyst **23a** activated with $B(C_6F_5)_3$ was capable of the living polymerization of propylene at −78 °C in the presence of Al(*n*Oct)$_3$ as scavenger.[87] The number of polymer chains was found to be constant for the course of the reaction, indicating that chain transfer did not occur at very low temperatures.

While the molecular weights of the resulting polymers were rather low ($M_w < 10000\,g\,mol^{-1}$), the molecular weight distributions were extremely narrow ($M_w/M_n = 1.06$) and polymer yields increased linearly with time. Carbon monoxide also reacted quantitatively with the living polypropylene chain ends, generating polypropylenes with terminal aldehyde functionality.[88] Similarly, the hafnium system **23b**/$B(C_6F_5)_3$, also displayed living behavior at $-50\,^\circ C$. Living polymerization of 1-hexene was also observed with the C_2-symmetric ansa-metallocene system **24**/$B(C_6F_5)_3$ at $-78\,^\circ C$, producing highly isotactic monodisperse poly(1-hexene) ($M_w/M_n = 1.2$–1.3). However, the catalytic activity for this system was low, resulting in only very low molecular weight polymers ($M_n < 5400\,g\,mol^{-1}$). Catalyst **24**/$B(C_6F_5)_3$ did not produce highly isotactic polypropylene in a living fashion at $-78\,^\circ C$, presumably due to β-alkyl elimination. Tritto and co-workers have recently shown that **24** exhibits "quasi-living" behavior for ethylene/norbornene copolymerization when activated with MAO.[89]

Very recently, Fukui and Murata employed the mixed metallocene catalyst system $[Cp_2ZrMe_2]/B(C_6F_5)_3/[Cp^*TiCl_3]$ for the living polymerization of propylene at $-50\,^\circ C$.[90] Again, reaction of carbon monoxide with a living polypropylene gave aldehyde-functionalized polypropylenes. Fukui and Murata also employed the mixed metallocene catalyst system $[Ph_2C(Cp)(fluorenyl)ZrCl_2]/Al(n\mathrm{Oct})_3/B(C_6F_5)_3/[Cp^*TiCl_3]$ for the living syndiospecific polymerization of propylene at $-50\,^\circ C$.[91] Finally, Brekner and co-workers described how "quasi-living" metallocene/MAO systems could be used in the synthesis of cycloolefin copolymers with narrow molecular weight distribution when generated at temperatures between $0\,^\circ C$ and $40\,^\circ C$ ($M_w/M_n = 1.1$–1.4).[92]

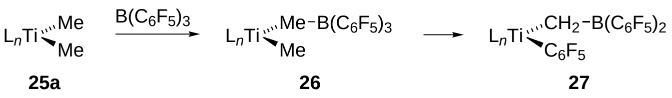
6.2. Diamido Complexes

Since the mid-1990s, several Group 4 catalysts with ancillary amido ligands for living olefin polymerization have been described. While these systems are of high academic interest since they are amenable to detailed mechanistic studies, their application in polymer synthesis has so far been limited to atactic polymers of propylene and simple α-olefins. Living polymerization of ethylene has not been reported with these catalysts, and only one example of an olefin block copolymer has been reported. In 1996, McConville and co-workers introduced a new class of diamido catalysts for living olefin polymerization. These tetrahedral dimethyltitanium complexes **25a, b** bearing ancillary propylene-bridged aryl-substituted diamido ligands proved to be highly active catalysts for polymerization of 1-hexene when activated by MAO (Scheme 16). For example, treatment of precatalyst **25a** with MAO at room temperature gave atactic poly(1-hexene) ($M_n = 47000\,g\,mol^{-1}$, $M_w/M_n = 1.73$). Chain transfer to the aluminum cocatalyst was implicated as the lone source of termination since olefinic resonances were absent from the NMR spectrum of the polymer. By activating the precatalyst with $B(C_6F_5)_3$, chain transfer reactions were eliminated and the polymerization of 1-hexene and higher α-olefins proceeded in living fashion (Scheme 16).[93] A decrease in the steric bulk of the ligand by replacement of the isopropyl substituents with methyl groups (**25b**) did not substantially influence catalyst performance. Polymerizations run in CH_2Cl_2 led to a dramatic increase in catalytic activity, yielding high molecular weight atactic polymers ($M_n > 120000\,g\,mol^{-1}$) with narrow molecular weight distributions ($M_w/M_n = 1.07$). This increase in activity was reasoned to be the result of better separation of the assumed catalyst ion-pair in the more polar solvent. On the other hand, polymerization activity decreased in the presence of toluene, presumably due to competitive binding to the active site. Mechanistic studies, including isotopic labeling and iodine quenching reactions, suggested that olefin insertion occurred in a primary (1,2) fashion.[94]



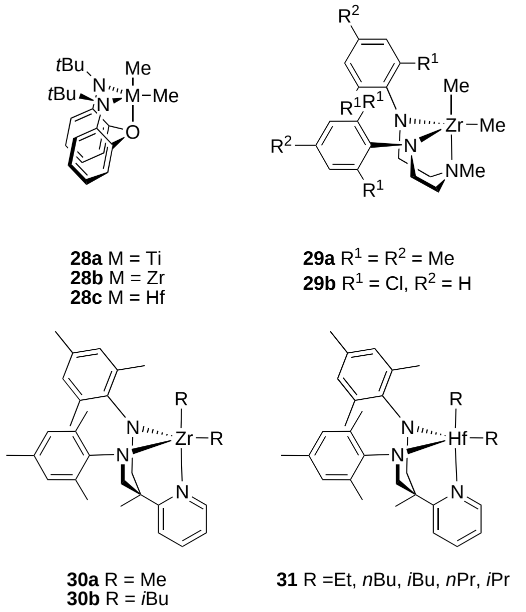
Scheme 16. Living polymerization of 1-hexene with McConville's diamidotitanium catalysts.

In a straightforward synthesis, the dimethyltitanium complexes **25a, b** were obtained by Grignard addition to the corresponding dichlorides, which in turn were best synthesized from the silylated diamines $Me_3SiArN(CH_2)_3NArSiMe_3$ and $TiCl_4$. Although attempts to isolate a cationic methyltitanium complex as a model for the presumed active species failed, a few important mechanistic issues concerning catalyst deactivation were addressed in these attempts. Addition of $B(C_6F_5)_3$ to a solution of the dimethyl complex **25a** in pentane led to the precipitation of a catalytically active borane adduct **26** (Scheme 17).[95] Suspensions of this adduct slowly evolved methane to form an inactive methylene-bridged derivative **27** that was characterized by single-crystal X-ray diffraction, thus exemplifying a possible catalyst deactivation pathway (Scheme 17). Shiono and co-workers have recently reported that **25a** also produces polypropylene with low molecular weight distribution using a modified MAO that is free of trialkylaluminum residues.[96]



Scheme 17. Deactivation pathway observed in McConville's diamidotitanium complexes.

Soon after McConville's initial report, Schrock and co-workers reported zirconium complexes with tridentate diamido ligands based on the hypothesis that a propagating four-coordinate cationic species would be more stable than a three-coordinate species.[97] Since 1997, Schrock and co-workers have developed three different classes of compounds for use in the living, aspecific polymerization of 1-hexene (Figure 6).



28a M = Ti
28b M = Zr
28c M = Hf

29a $R^1 = R^2 =$ Me
29b $R^1 =$ Cl, $R^2 =$ H

30a R = Me
30b R = *i*Bu

31 R = Et, *n*Bu, *i*Bu, *n*Pr, *i*Pr

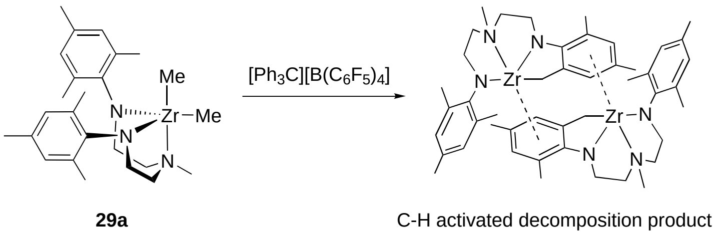
Figure 6. Diamido catalyst precursors for living olefin polymerization.

In the first two classes of compounds **28**[97–101] and **29**,[102–104] the two amido donor atoms are connected to a central donor (either oxygen or nitrogen), while in the third class **30**/**31**[105, 106] all three donors are connected to a central carbon atom. Even though living α-olefin polymerization has been restricted almost exclusively to 1-hexene with these catalysts, the resulting polymer molecular weight distributions are among the narrowest known.

In 1997, Schrock and co-workers developed a very bulky and robust tridentate diamido ligand with a central oxygen donor atom.[97] Group 4 catalyst precursors **28a–c**, incorporating the ligand $[(\{[D_6]t\text{Bu}\}\text{N-}o\text{-C}_6\text{H}_4)_2\text{O}]^{2-}$ (NON ligand) were prepared by Grignard addition to the corresponding dichloride complexes. The latter were best synthesized from the ligand dianion and $M(NMe_2)_2Cl_2$ and subsequent treatment of the bis(dimethylamido) intermediates with Me_3SiCl. The dimethyl complexes display trigonal-bipyramidal coordination geometry in the solid state with the oxygen donor and one methyl substituent in the apical positions, as demonstrated by X-ray crystallography of **28a** and **28b**.[100] Methide abstraction from the dimethyl complex **28b** by $B(C_6F_5)_3$ yielded a reasonably stable ion pair, $[(NON)ZrMe][MeB(C_6F_5)_3]$ (**32**), which was characterized in the solid state and by NMR spectroscopy. Both complex **32** as well as the dimethylaniline adduct $[(NON)ZrMe(PhNMe_2)][B(C_6F_5)_4]$ (**33**) were active for the polymerization of ethylene at room temperature (100 $\text{kg}_{\text{PE}}\,\text{mol}_{\text{Zr}}^{-1}\,\text{h}^{-1}$ for **32**, 800 $\text{kg}_{\text{PE}}\,\text{mol}_{\text{Zr}}^{-1}\,\text{h}^{-1}$ for **33**). Catalyst **33** also polymerized 1-hexene to atactic poly(1-hexene) (200 $\text{kg}_{\text{PH}}\,\text{mol}_{\text{Zr}}^{-1}\,\text{h}^{-1}$, $M_n = 45\,000\ \text{g}\,\text{mol}^{-1}$, $M_w/M_n = 1.2$). By lowering the temperature to 0 °C, chain transfer reactions were suppressed, and the polymerization occurred in a living fashion ($M_w/M_n < 1.05$ in the presence of more than 200 equivalents 1-hexene).

Insights into the polymerization mechanism were gained in a labeling study which established predominant 1,2 insertion of the olefin (1-hexene or 1-nonene) as well as β-hydride elimination as the primary mechanism of chain termination at 40 °C.[98] The rate of β-hydride elimination was slow at 0 °C, presumably due to steric crowding around the metal center which prevents the "backing up" of the bulky polymer chain towards the ligand in an olefin–hydride intermediate. Therefore, at lower temperatures, the polymerization proceeded without appreciable chain transfer. When the steric crowding about the metal center was relaxed by replacing the *tert*-butyl substituents with less bulky isopropyl or cyclohexyl groups, the corresponding activated metal dialkyl complexes only oligomerized 1-hexene.[99] Interestingly, zirconium complexes bearing the structurally-related sulfur donor ligand $[(\{[D_6]t\text{Bu}\}\text{N-}o\text{-C}_6\text{H}_4)_2\text{S}]^{2-}$ (NSN) were not active for polymerization of 1-hexene.[107]

A second class of compounds for living olefin polymerization was introduced by Schrock and co-workers in 1999. Replacing the oxygen in the ligand backbone with an amine donor resulted in the more rigid tridentate complex **29a**.[102] Activation of **29a** with $[Ph_3C][B(C_6F_5)_4]$ and subsequent reaction with 1-hexene led to the formation of poly(1-hexene) which displayed limited average molecular weight and broader molecular weight distribution than the polymer obtained with the NON system **28**. Subsequent studies revealed that this non-living behavior was caused by catalyst decomposition by C–H activation of one of the mesityl *o*-methyl substituents, producing a dimeric decomposition product that was characterized by X-ray crystallography (Scheme 18).[103] A similar decomposition pathway of a cationic zirconium complex through C–H bond activation of an adjacent methyl group had previously been uncovered by Horton and co-workers in a structurally related triamido system.[108] A simple change in aryl substitution from 2,4,6-trimethylphenyl to 2,6-dichlorophenyl prevented C–H activation of the ligand, and a living 1-hexene polymerization catalyst precursor **29b** was obtained.[103] The polymer generated with catalyst **29b**/$[Ph_3C][B(C_6F_5)_4]$ at 0 °C was of higher molecular weight than that produced with the NON catalysts **28** (M_n up to 79 000 $\text{g}\,\text{mol}^{-1}$), while the molecular weight distribution of the polymer remained extremely narrow (M_w/M_n, 1.01–1.04).

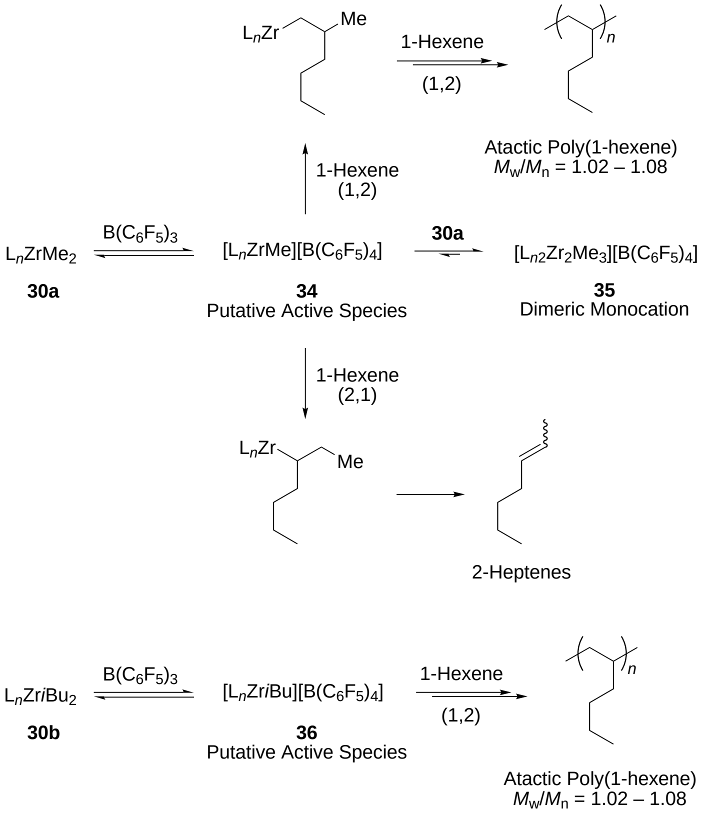


29a

C-H activated decomposition product

Scheme 18. C–H activation as a catalyst deactivation pathway observed in systems based on precursor **29a**.

In 2000, Schrock and co-workers reported a third class of compounds for living olefin polymerization. Employing the NNN framework in the form of diamidopyridine ligands (MesNpy), in which the three donor atoms are connected to a central carbon atom, the geometrically rigid zirconium complexes **30a,b** were prepared. An interesting initiator effect was uncovered in 1-hexene polymerization by complexes **30a**, **b**.[105] Methide abstraction from the dimethyl species **30a** with $[Ph_3C][B(C_6F_5)_4]$ was found to be a rather complex process, leading to the formation of the putative active species $[(MesNpy)ZrMe][B(C_6F_5)_4]$ (**34**) in equilibrium with **30a** and a monocationic dimer $[(MesNpy)_2Zr_2Me_3][B(C_6F_5)_4]$ (**35**) (Scheme 19). Solutions of **30a**/$[Ph_3C][B(C_6F_5)_4]$ were active for the polymerization of 1-hexene, but consumption of 1-hexene was not a first-order process. The average molecular weight of the resulting polymer was 10 times higher than expected assuming quantitative initiation. Furthermore, NMR studies uncovered the formation of 2-heptenes in the reaction, presumably originating from secondary (2,1) insertion of 1-hexene into the active catalyst **34** to give a 3-heptyl species that is susceptible to β-hydride elimination. The larger fraction of the 3-heptyl species β-hydride eliminates and forms heptenes and a catalytically inactive metal species, while the smaller fraction propagates by primary (1,2) insertion. Despite these mechanistic complications, the molecular weight distribution of the resulting poly(1-hexene) was surprisingly narrow with this system ($M_w/M_n < 1.08$).

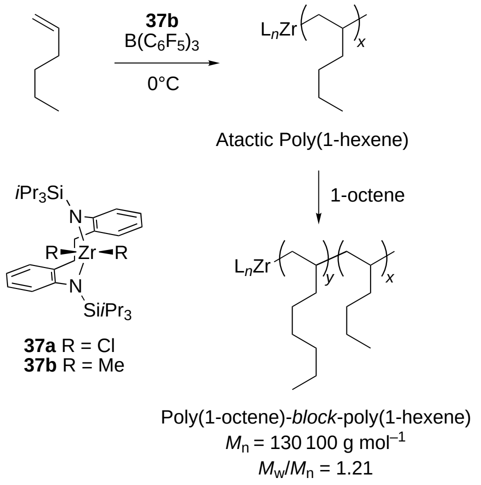


Scheme 19. Initiator effect in diamidopyridine catalysts for living olefin polymerization.

When the initiating group was changed from methyl to isobutyl (**30b**), activation with $[Ph_3C][B(C_6F_5)_4]$ cleanly generated a monomeric species $[(MesNpy)Zr\textit{i}Bu][B(C_6F_5)_4]$ (**36**; Scheme 19). Since dimer formation like in the methyl analogue **30a** did not occur, all the zirconium centers were available for polymerization and consequently no unreacted dialkyl complex **30b** was observed. Although the activated species **36** decomposed in the absence of monomer by β-hydride elimination, addition of 1-hexene led to a living polymerization. In this case, heptenes were not observed, suggesting that 1-hexene predominantly inserted into the more sterically crowded $Zr-C_{(isobutyl)}$ bond in a primary (1,2) fashion, yielding a 2-heptyl species that was relatively stable towards β-hydride elimination. Polymers produced with **30b**/$[Ph_3C][B(C_6F_5)_4]$ displayed molecular weights approximately three times the theoretical value (based on Zr) and molecular weight distributions were again extremely narrow ($M_w/M_n = 1.03$).

Most recently, Schrock and co-workers reported the synthesis, characterization, and polymerization activity of cationic hafnium complexes of the general formula $[(MesNpy)HfR][B(C_6F_5)_4]$ (**31**; R = Et, *n*Bu, *i*Bu, *n*Pr, *i*Pr).[106] These compounds displayed a surprising stability towards β-hydride elimination below 10 °C, and they promoted the living polymerization of 1-hexene under these conditions. Insertion of 1-hexene into a $Hf-C_{(alkyl)}$ bond was found to be about half as fast as for the Zr analogue **30**.

A final example of living olefin polymerization by a group IV catalyst with an ancillary diamido ligand was reported by Kim and coworkers.[109] Activated versions of these bidentate, aniline precursors **37a**, **b** were active for the polymerization of ethylene, propylene, and higher α-olefins (Scheme 20). For example, **37a**/MAO showed an activity of 5300 $kg_{PE}\,mol_{Zr}^{-1}\,h^{-1}$ under 1 atm of ethylene at room temperature. However, the polymers produced with **37a**/MAO at room temperature were polydisperse, low molecular weight materials ($M_n < 9000\ g\,mol^{-1}$, $M_w/M_n = 2.09-2.35$). Cooling the polymerization to 0 °C reduced β-elimination reactions, giving materials of higher molecular weight, but chain transfer to the aluminum cocatalyst again gave polymers with broad molecular weight distributions. However, employing $B(C_6F_5)_3$ as an activator for the dimethyl complex **37b** at 0 °C gave high molecular weight atactic polymers with relatively narrow polydispersities. The catalyst system **37b**/$B(C_6F_5)_3$ at 0 °C polymerized 1-hexene with a linear increase in molecular



Scheme 20. 1-Hexene/1-octene block copolymer synthesis with a diamido catalyst system.

weight with yield to give atactic poly(1-hexene) with a narrow molecular weight distribution ($M_n = 118300$ g mol^{-1}, $M_w/M_n = 1.23$). The living nature of the polymerization was also demonstrated by the sequential addition of two different α-olefins to form a 1-hexene/1-octene block copolymer ($M_n = 108700$ g mol^{-1}; $M_w/M_n = 1.21$) (Scheme 20).

6.3. Zirconium Amidinates

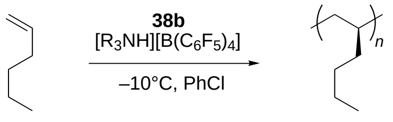
Although the living vanadium catalysts developed by Doi et al. gave syndio-enriched polypropylenes (Section 2.1), the first catalyst to simultaneously achieve the highly sought goals of livingness and stereoselectivity was reported by Jayaratne and Sita in 2000.[110] Using an amidinate zirconium catalyst, the living isospecific polymerization of 1-hexene was achieved with high stereoselectivity. By addition of carbodiimides to the Zr–C$_{(methyl)}$ bond in [Cp*ZrMe$_3$], catalyst precursors **38a–d** (Figure 7) were easily prepared. When $R^1 \neq R^2$, the resulting compounds are chiral but variable-temperature ^{1}H NMR revealed low barriers to racemization. Upon activation with [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in chlorobenzene at 0 °C, symmetric complex **38a** was active for the polymerization of 1-hexene, giving a monodisperse polymer ($M_n = 11000$ g mol^{-1}, $M_w/M_n = 1.10$). The narrow molecular weight distribution and the lack of olefinic resonances characteristic of chain transfer indicated the living nature of the polymerization. However, microstructural analysis by ^{13}C NMR revealed the lack of stereochemical control in the polymerization.

38a $R^1 = R^2$ = cyclohexyl
38b R^1 = *t*Bu, R^2 = Et
38c R^1 = *t*Bu, R^2 = cyclohexyl
38d R^1 = *t*Bu, R^2 = 2,6-*i*Pr$_2$C$_6$H$_3$

39a $R^1 = R^2$ = cyclohexyl
39b $R^1 = R^2$ = *i*Pr
39c R^1 = *t*Bu, R^2 = cyclohexyl

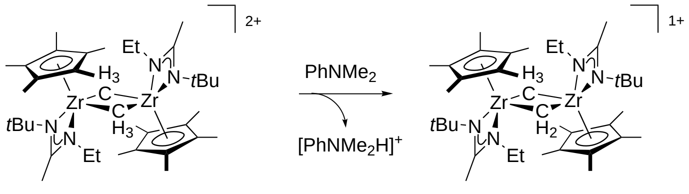
Figure 7. Amidinate catalyst precursors for living polymerization of 1-hexene.

With this encouraging lead, the catalytic properties of C_1-symmetric compounds **38b–d** were evaluated.[110] Precursors **38c**, **d** displayed poor activity toward 1-hexene, presumably due to the sterically encumbered nature of the complex. However, the activated complex **38b** proved to be a superior catalyst for the polymerization of 1-hexene at 25 °C (Scheme 21). In addition to an increase in activity and molecular weight, the polymer was also highly isotactic ([*mmmm*] > 0.95). The increase in activity was unfortunately accompanied by a broadening of the molecular weight distribution ($M_w/M_n = 1.50$). However, lowering the polymerization temperature to −10 °C led to higher molecular weight polymers with extremely narrow polydispersities ($M_w/M_n = 1.03–1.10$) and high stereoselectivities ([*mmmm*] > 0.95). The living character of the polymerization was demonstrated by the linear increase of number-average molecular weight (M_n) with conversion. Furthermore, addition of a second portion of 1-hexene (180 equiv) to a living polymer chain end ($M_n = 20700$ g mol^{-1}, $M_w/M_n = 1.03$) resulted in formation of a higher molecular weight polymer ($M_n = 35400$ g mol^{-1}, $M_w/M_n = 1.13$).



Isotactic Poly(1-hexene)
[*mmmm*] > 0.95
M_n = 32 600 – 69 500 g mol^{-1}
M_w/M_n = 1.03 – 1.10

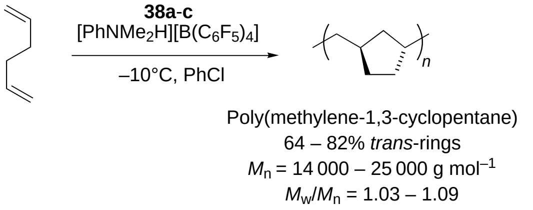
Scheme 21. Living isospecific polymerization of 1-hexene with zirconium amidinate catalysts.



Scheme 22. Potential deactivation pathway in amidinate catalyst systems.

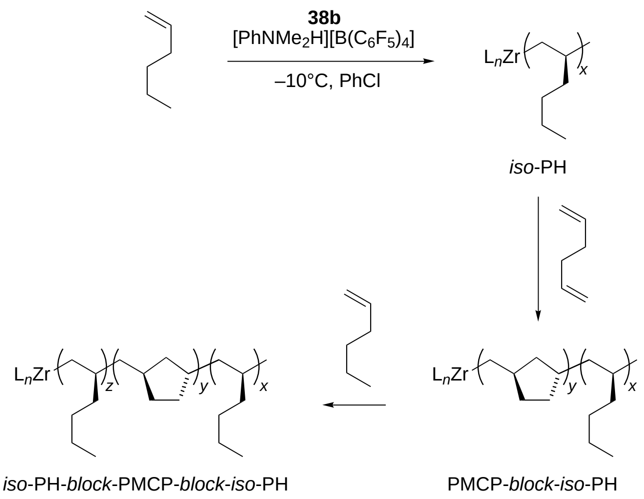
Although this catalytic system displayed excellent selectivity for production of isotactic poly(1-hexene), the mechanism of stereocontrol was unclear. NMR spectroscopy revealed a small resonance attributed to a *mmmr*-pentad as the only visible stereoerror, consistent with an isotactic stereoblock microstructure.[110] The high selectivity demonstrated by this system was remarkable considering the low barrier to racemization of precursor **38b**. Sita et al. suggested that the barrier might be higher in the activated complex and the structural defects in the polymer were a consequence of amidinate ring flipping. To shed light on the origin of stereocontrol in this unique system, crystallographic analyses of **38b** and **38b**/[B(C$_6$F$_5$)$_4$] were performed.[111] Indeed, the more electrophilic metal center of the activated complex resulted in a shortening of the Zr–N bonds, providing evidence that suggests a higher barrier to racemization in the active species. Also, coordination of diethyl ether to the activated complex occurred on the more sterically encumbered face of the catalyst, suggesting that olefin coordination might be preferred at that site. Crystallization in the absence of Lewis bases at low temperatures (−10 °C) provided a dimer with bridging methyl groups comprising a planar four-membered ring, inside of which reside two bridging agostic hydrogen atoms (Scheme 22). The elongated Zr–C$_{(methyl)}$ bond length demonstrated the stabilizing effect of these α-agostic interactions. It was suggested that these bridging α-agostic interactions in dimeric cations might serve to lower the barrier to migratory insertion, as has been proposed for mononuclear complexes.[14] On the other hand, crystallization of activated complex **38b**/[B(C$_6$F$_5$)$_4$] at 25 °C revealed the formation of a μ-CH$_2$, μ-CH$_3$ monocationic species, resulting from reduction of one of the metal centers (Scheme 22). This species, presumably the result of deprotonation of the dimer by dimethylaniline introduced from the cocatalyst, revealed a viable pathway for termination of active centers during the polymerization with this catalytic system.

The enormous potential of this living and stereoselective catalyst system lies in its potential for the synthesis of well-defined olefin block copolymers with both crystalline and amorphous domains. Due to the microphase separation of such blocks, these materials have numerous applications as compatibilizers and elastomers. In a demonstration of the utility of this living catalyst system, Sita and co-workers explored the cyclopolymerization of nonconjugated dienes to give living polymers with high melting transitions.[112] To this end, 1,5-hexadiene was polymerized by the catalyst system **38a**–**c**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in chlorobenzene at $-10\,^{\circ}$C to give poly(methylene-1,3-cyclopentane)s (PMCP) with narrow molecular weight distributions ($M_w/M_n = 1.03-1.09$; Scheme 23). The lack of olefinic resonances in the polymers and the linear kinetic relationship ($\ln([M_o]/[M_t])$ versus time) were consistent with a living polymerization. Analysis of the PMCP microstructures showed that the catalysts displayed high selectivity for cyclization (>98%). Selectivity for formation of *trans* rings was mediated by the steric bulk of the catalyst precursor; increasing bulk of the amidinate ligands in the series **38a**→**38b**→**38c** was mirrored by an increase in *trans* ring content and thus the degree of crystallinity ($T_m = 98-102\,^{\circ}$C). Furthermore, the ligand structure had a huge influence on the tacticity of the PMCP. While precursor **38a** gave an atactic polymer, complex **38b** displayed a high degree of stereocontrol, giving highly isotactic PMCP.



Scheme 23. Living cyclopolymerization of 1,5-hexadiene with zirconium amidinate catalysts.

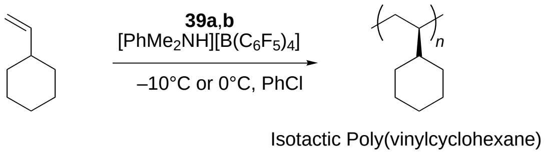
Sita and co-workers exploited the ability of the amidinate zirconium catalysts to produce living polymers with crystalline domains through the synthesis of block copolymers from 1-hexene and 1,5-hexadiene (Scheme 24).[112] Addition of 1-hexene to the activated complex **38b**/[PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in chlorobenzene at $-10\,^{\circ}$C gave a living isotactic poly(1-hexene) ($M_n = 12\,200$ g mol^{-1}, $M_w/M_n = 1.03$). Addition of 1,5-hexadiene to this living chain end resulted in formation of a higher molecular weight polymer ($M_n = 22\,800$ g mol^{-1}, $M_w/M_n = 1.05$). The ^{13}C NMR spectrum of the material was consistent with both PH and PMCP and showed the highly isotactic nature of the diblock material. This strategy was also applied to the synthesis of a triblock copolymer ($M_n = 30\,900$ g mol^{-1}, $M_w/M_n = 1.05$) by addition of a second portion of 1-hexene to a living diblock (Scheme 24). Through AFM imaging, the block nature of this unique triblock material was demonstrated. A thin film of the material phase-separated into a morphology composed of PMCP cylinders embedded in a PH matrix.



Scheme 24. Synthesis of poly(1-hexene)/PMCP diblock and triblock copolymers with a zirconium amidinate catalyst.

In 2001, Sita et al. reported a modified class of amidinate catalysts for living olefin polymerization (**39a**–**c**; Figure 7).[113] Employing the less bulky Cp ligand, the activated complexes displayed enhanced activities relative to their Cp* counterparts. For example, complex **39b**/[PhNMe$_2$H]-[B(C$_6$F$_5$)$_4$] polymerized 1-hexene (200 equiv) to 79% conversion in only 2 min and proceeded to completion in under 10 min to give a monodisperse polymer ($M_n = 20\,800$ g mol^{-1}, $M_w/M_n = 1.03$). A kinetic study of 1-hexene polymerization with **39c** revealed a linear relationship consistent with a living polymerization, and GPC traces of all reported polymers showed narrow distributions ($M_w/M_n = 1.03-1.09$). While the more exposed nature of the metal center was beneficial in regard to catalytic activity, it had a detrimental effect on stereoselectivity. Unlike complex **38b**, which produced highly isotactic poly(1-hexene)s, polymers from both the achiral compounds **39a**, **b** and the C_1-symmetric, chiral complex **39c** were atactic, demonstrating the importance of the bulky Cp* ligand for stereodifferentiation.

Given the enhanced activities of these catalysts toward polymerization of 1-hexene, Sita et al. reasoned that these complexes might be capable of polymerization of more sterically encumbered monomers such as vinylcyclohexane.[113] Indeed, activation of **39a**, **b** at $-10\,^{\circ}$C in the presence of vinylcyclohexane resulted in nearly complete conversion to polymer (Scheme 25). Despite the achiral, C_s-symmetric nature of catalyst precursors, the poly(vinylcyclohexane) microstructures in each case were highly isotactic

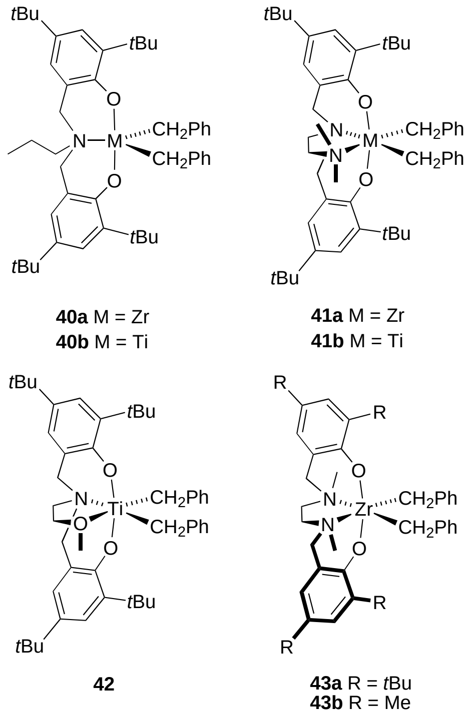


Scheme 25. Isospecific living polymerization of vinylcyclohexane with a zirconium amidinate catalyst.

([*mmmm*] > 95 %), indicative of a chain-end control mechanism. The linear kinetic relationship and the narrow polydispersities of the polymers ($M_w/M_n = 1.04-1.10$) demonstrated the living nature of the polymerization. This living polymerization was also applied to the synthesis of a new triblock copolymer composed of poly(vinylcyclohexane) and polyhexene domains through a sequential addition approach.

6.4. Amine Bis(phenolate) Complexes

In 1999, a new family of Group 4 complexes bearing amine bis(phenolate) [ONO]- and [ONNO]-type ligands was introduced by Kol, Goldschmidt, and co-workers.[114] Initial investigations of the C_s-symmetric zirconium compounds **40a** and **41a** (Figure 8) demonstrated the dramatic effect of the extra donor arm on catalytic activity.[115] When activated with $B(C_6F_5)_3$ at room temperature, complex **40a** bearing the tridentate [ONO] ligand displayed low activity toward 1-hexene (23 $kg_{PH} mol_{Zr}^{-1} h^{-1}$), producing only 1-hexene oligomers (< 20 units/chain). On the other hand, complex **41a**/$B(C_6F_5)_3$ based on the tetradentate [ONNO] ligand was extremely active for the polymerization (15 500 $kg_{PH} mol_{Zr}^{-1} h^{-1}$), giving high molecular weight poly(1-hexene) with polydispersities consistent with a single-site catalyst ($M_n = 170000\ g\,mol^{-1}$, $M_w/M_n = 2.2$). The catalytic performance of the titanium complexes **40b** and **41b** was also investigated.[116] In this case, the activated complex **40b** bearing the [ONO]-type ligand was slightly more active than the [ONNO] complex **41b**, but the polymerization quickly attained a maximum value of molecular weight ($M_n = 1500\ g\,mol^{-1}$, $M_w/M_n \sim 2$). However, the polymerization of 1-hexene with **41b**/$B(C_6F_5)_3$ bearing the amine donor proceeded in a living fashion ($M_n = 14000\ g\,mol^{-1}$, $M_n/M_n = 1.18$), giving poly(1-hexene) with a linear increase in molecular weight with time (Scheme 26). As anticipated, NMR spectroscopy revealed the absence of olefinic end groups and the atactic microstructure of the polyhexene. In this case, the presence of the extra donor arm served to suppress chain transfer reactions.



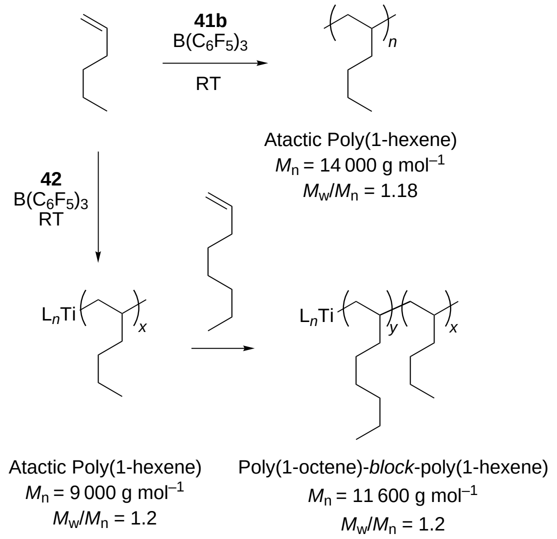
40a M = Zr
40b M = Ti

41a M = Zr
41b M = Ti

42

43a R = *t*Bu
43b R = Me

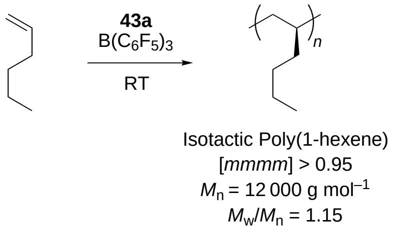
Figure 8. Amine bis(phenolate) catalyst precursors for living olefin polymerization.



Scheme 26. Living polymerization of 1-hexene and block copolymerization of 1-hexene and 1-octene with amine bis(phenolate)-type catalysts.

With the successes of the extra donor arm of these complexes, Kol, Goldschmidt, and co-workers recently reported a new ligand in this family.[117] Incorporating an extra oxygen donor, this [ONOO]-type ligand gave the analogous C_s-symmetric titanium species **42** (Figure 8). When activated at room temperature by $B(C_6F_5)_3$, complex **42** proved to be active for polymerization of 1-hexene (20–35 $kg_{PH} mol_{Ti}^{-1} h^{-1}$) (Scheme 26). The living behavior of this system was evident by the narrow polydispersities ($M_w/M_n = 1.07-1.12$) and the linear increase of molecular weight with time. Amazingly, this linear relationship was still observed after extremely long reaction times (31 h), giving a high molecular weight poly(1-hexene) ($M_n = 445000\ g\,mol^{-1}$, $M_w/M_n = 1.12$). The polymerizations also had living character at elevated temperatures, with reactions as high as 65 °C giving relatively monodisperse polymers ($M_n = 22000\ g\,mol^{-1}$, $M_w/M_n = 1.30$). The livingness of this system was also demonstrated through the synthesis of a block copolymer of 1-hexene and 1-octene (Scheme 26). Addition of 1-hexene to **42**/$B(C_6F_5)_3$ in chlorobenzene at room temperature gave poly(1-hexene) after 3.5 h ($M_n = 9000\ g\,mol^{-1}$, $M_w/M_n = 1.2$). After an additional 1.5 h, addition of 1-octene to this living chain end resulted in formation of a higher molecular weight polymer ($M_n = 11600\ g\,mol^{-1}$, $M_w/M_n = 1.2$) with a ^{13}C NMR spectrum consistent with atactic poly(1-hexene-*block*-1-octene).

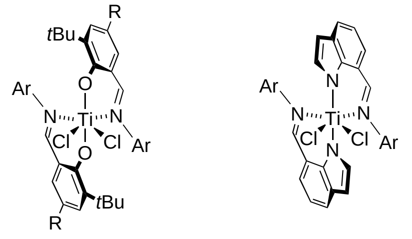
With the promising lead of living behavior mediated by an extra amine donor, Kol and co-workers targeted complexes with a new type of [ONNO] ligand with similar functionality but different connectivity, providing catalysts with C_2 symmetry capable of stereocontrol in α-olefin polymerization.[118] The diamine bis(phenolate) ligands proved excellent for this task, providing C_2-symmetric complexes (**43a,b**) analogous to the ansa-metallocenes. Complex **43a**, when activated at room temperature by $B(C_6F_5)_3$, proved to be an active catalyst for the polymerization of 1-hexene ($18\,kg_{PH}\,mol_{Zr}^{-1}\,h^{-1}$) (Scheme 27). The linear increase in molecular weight (M_n up to 12000 $g\,mol^{-1}$) with conversion and the narrow molecular weight distribution of the polymers ($M_w/M_n = 1.11-1.15$) demonstrated the living nature of the polymerization. Furthermore, ^{13}C NMR spectroscopy revealed that the polymer possessed a highly isotactic microstructure (>95%). The bulky *tert*-butyl substituents of **43a** were crucial to both the livingness and stereoselectivity of the catalytic system; polymerization of 1-hexene with the methyl-substituted complex **43b**/$B(C_6F_5)_3$ yielded atactic poly(1-hexene) with a broader molecular weight distribution ($M_n = 23000\,g\,mol^{-1}$, $M_w/M_n = 1.57$).



Scheme 27. Living isospecific polymerization of 1-hexene with a diamine bis(phenolate) catalyst.

6.5. Bis(phenoxyimine) and Bis(indolideimine) Complexes

Scientists at Mitsui have discovered that Group IV complexes bearing phenoxyimine ligands are a remarkable class of catalysts for olefin polymerization.[119] Based on these initial discoveries, several advances in the area of stereoselective as well as living olefin polymerization have been reported. For example, Tian and Coates targeted Mitsui-type complexes (**44a**) for isospecific propylene polymerization. Due to their structural similarities with the ansa-metallocenes, they reasoned that these C_2-symmetric complexes might be suitable precursors for the isospecific polymerization of α-olefins through a site-control mechanism. Surprisingly, compound **44a**/MAO (Figure 9) produced polypropylenes that were substantially syndiotactic ($[rrrr] = 0.78$).[120] Microstructural analysis of the resulting polymer revealed that a chain-end mechanism was responsible for the observed stereocontrol. Subsequent studies revealed that this extreme chain end control was enhanced by an unusual secondary insertion mechanism.[19, 120, 121] However, GPC analyses revealed the lack of molecular weight control in this system ($M_w/M_n \sim 2$).

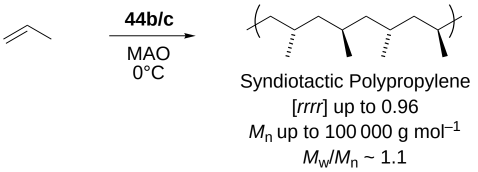


44a Ar = C_6H_5, R = *t*Bu
44b Ar = F_5C_6, R = *t*Bu
44c Ar = F_5C_6, R = H

45a Ar = C_6H_5
45b Ar = 2,6-$F_2C_6H_3$
45c Ar = 2,4,6-$F_3C_6H_2$

Figure 9. Bis(phenoxyimine) and bis(indolide-imine) catalyst precursors for living olefin polymerization.

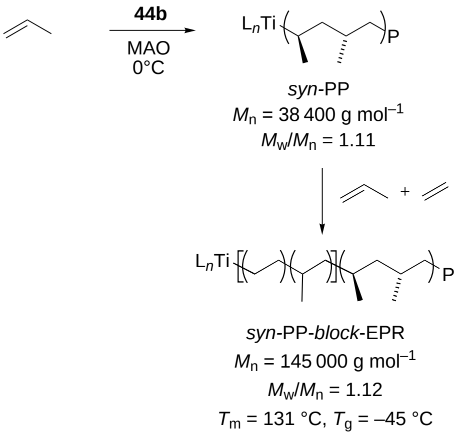
In an effort to develop improved versions of these phenoxyimine catalysts, Coates and coworkers discovered that simple fluorination of the aniline moiety had a beneficial effect on both catalytic activity and stereoselectivity.[122] The catalytic system **44b**/MAO was an order of magnitude more active than **44a** and provided highly syndiotactic polypropylene ($[rrrr] = 0.96$; Scheme 28). The polymer exhibited a peak melting temperature of 148 °C, among the highest values reported for syndiotactic polypropylene. These polymers also displayed narrow molecular weight distributions ($M_w/M_n \sim 1.1$) and were free of olefinic end groups. Not only were β-hydride and β-methyl eliminations suppressed, but the polymerization also proceeded without transfer to the aluminum cocatalyst, a common source of chain transfer in catalytic systems activated by MAO. The living nature of the reaction was demonstrated by the linear relationship of molecular weight and polymer yield. Although a slight deviation from the initial linear relationship was observed at longer reaction times, molecular weight distributions remained narrow ($M_w/M_n = 1.11$) to molecular weights approaching 100000 $g\,mol^{-1}$. Furthermore, the molecular weight of the polymer was close to the value calculated from the monomer/initiator ratio obtained from the mass of the polymer produced, indicating that each molecule of catalyst produces exactly one polymer chain during the polymerization. Remarkably, polymers with $M_n > 300000\,g\,mol^{-1}$ were synthesized with fairly narrow molecular weight distributions ($M_w/M_n = 1.34$), and the reactions were also living at room temperature ($M_w/M_n = 1.13$). Fujita and co-workers concurrently reported that the fluorine-containing catalyst system (**44c**/MAO) is also living for propylene polymerization (M_n up to 108000 $g\,mol^{-1}$, $M_w/M_n = 1.07-1.14$).[123] Polymers from this bis(phenoxyimine)



Scheme 28. Highly syndiospecific and living polymerization of propylene with bis(phenoxyimine) catalysts.

catalyst, which incorporates a single *tert*-butyl substituent on the phenoxy moiety, exhibited somewhat lower syndiotacticity ($[rrrr] = 0.76$) and peak melting temperature ($T_m = 137\,°C$) than polymers from **44b**/MAO, although low molecular weight oligomers ($M_n = 2000\ g\,mol^{-1}$) are nearly perfectly syndiotactic.

Coates and co-workers demonstrated the utility of this living and stereoselective catalyst system through the synthesis of well-defined ethylene/propylene copolymers with crystalline, syndiotactic polypropylene domains (Scheme 29).[122] Addition of **44b** to a solution of propylene and MAO at 0 °C resulted in the formation of a living polypropylene after 2 h ($M_n = 38\,400\ g\,mol^{-1}$, $M_w/M_n = 1.11$). Addition to a slight overpressure of ethylene to this living chain end resulted in rapid formation of a higher molecular weight polymer ($M_n = 145\,100\ g\,mol^{-1}$, $M_w/M_n = 1.12$). The polymer, a *syn*-PP-*block*-EPR diblock copolymer, displayed a T_m of 131 °C, while the T_g of the EPR domain was $-45\,°C$. Fujita and co-workers have also reported the remarkable, above room temperature living polymerization of ethylene[124] (M_n up to $400\,000\ g\,mol^{-1}$, $M_w/M_n = 1.05-1.13$) and copolymerization of ethylene and propylene using the modified phenoxyimine system **44c**.[125] Monodisperse ethylene/propylene copolymers with varying propylene content (15–48 mol %) were prepared with **44c**/MAO at 25 °C ($M_n > 80\,000\ g\,mol^{-1}$, $M_w/M_n = 1.07-1.13$). Diblock and triblock copolymers composed of polyethylene, polypropylene, and ethylene/propylene blocks have also been synthesized with this catalyst system.[124, 125] For example, a *syn*-PP-*block*-EPR diblock similar to that described above by Coates and co-workers was prepared from reaction of ethylene with a living polypropylene chain ($M_n = 27\,000\ g\,mol^{-1}$, $M_w/M_n = 1.13$). The resulting copolymer ($M_n = 161\,000\ g\,mol^{-1}$) displayed a broader molecular weight distribution ($M_w/M_n = 1.51$).[125]



Scheme 29. Synthesis of ethylene/propylene diblock copolymers with a bis(phenoxyimine) catalyst; EPR = ethylene/propylene rubber.

Fujita and co-workers have also developed a new class of compounds bearing indolide-imine ligands for the living polymerization of ethylene.[126] When activated by MAO at 25 °C, complexes **45a–c** produced polyethylenes with narrow molecular weight distributions ($M_n = 11\,000-41\,800\ g\,mol^{-1}$, $M_w/M_n = 1.11-1.14$). Increasing electrophilicity of the metal center through fluorination of the ligand led to an increase in activity, with **45c** providing the most active precursor. The living nature of the polymerization was demonstrated for **45c**/MAO by the linear increase in molecular weight with polymer yield. Notably, polymerization with **45c**/MAO at 50 °C also produced polyethylene with a fairly narrow polydispersity ($M_w/M_n = 1.24$).

7. Outlook and Summary

The last half-decade has witnessed a renaissance in living olefin polymerization, building rapidly on the foundation set solidly by Doi and co-workers over two decades ago. Today, we have many efficient and selective catalysts available for living olefin polymerization. Polyethylene, as well as atactic, isotactic, and syndiotactic poly(α-olefins) can now be efficiently synthesized in a living manner, allowing the creation of unlimited new polymer architectures, such as block copolymers and end-functional macromolecules. The ability to synthesize such polymers will allow the detailed study of structure–property relationships and their influence on mechanical and physical properties of this new class of materials.

Perhaps the main challenge facing this new field is that these sophisticated (and therefore usually expensive) metal complexes only form one polymer chain during the polymerization reaction, rendering the displacement of current commodity polyolefins by these new materials economically nonviable. Therefore, significant research must be conducted to develop new strategies for the production of multiple polymer chains per initiator. Such approaches will include the development of agents that can cleave the growing polymer chain from the metal but regenerate the catalyst in an active form that can propagate a new polymer molecule. Alternately, other methods for the synthesis of block copolymers from non-living systems must also be pursued. These include: 1) the development of oscillating catalysts that can change their geometries during chain growth;[127] 2) the transfer of chains between catalysts of differing stereospecificities;[128] 3) the change of polymerization conditions that affect stereochemistry or comonomer incorporation on a time scale faster than chain growth; and 4) the development of stopped-flow techniques.[129]

Undoubtedly, the future will witness continued research at this exciting interface of organometallic chemistry and polymer science to the benefit of both fields. It is clear that living systems will allow detailed mechanistic studies of catalysts due to their discrete nature; in return these new catalysts will allow the synthesis and study of a wide range of new polymeric materials.

G.W.C. gratefully acknowledges a Packard Foundation Fellowship in Science and Engineering, a Dreyfus New Faculty Award, an Alfred P. Sloan Research Fellowship, an Arnold and Mabel Beckman Foundation Young Investigator Award, a NSF

CAREER Award, and a Camille Dreyfus Teacher-Scholar Award. S.R. thanks the DAAD for a postdoctoral fellowship.

Received: November 7, 2001 [A 499]

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