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Catalytic Chain Transfer

Versatile Pathways for In Situ Polyolefin Functionalization with Heteroatoms: Catalytic Chain Transfer

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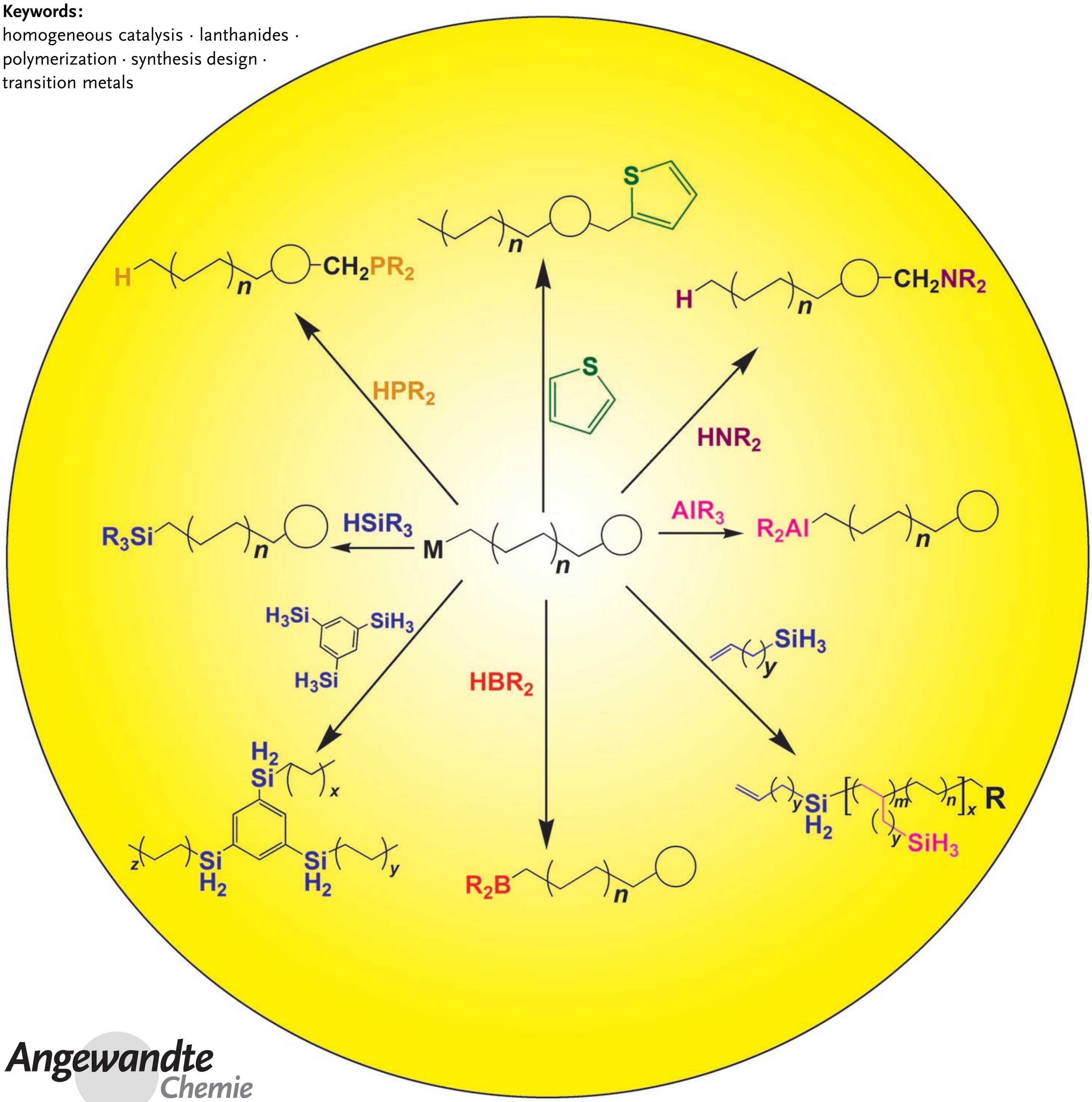

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Chain-transfer processes represent highly effective chemical means to achieve selective, in situ d- and f-block-metal catalyzed functionalization of polyolefins. A diverse variety of electron-poor and electron-rich chain-transfer agents, including silanes, boranes, alanes, phosphines, and amines, effect efficient chain termination with concomitant carbon–heteroelement bond formation during single-site olefin-polymerization processes. High polymerization activities, control of polyolefin molecular weight and microstructure, and selective chain functionalization are all possible, with distinctly different mechanisms operative for the electron-poor and electron-rich reagents. A variety of metal centers (early transition metals, lanthanides, late transition metals) and single-site ancillary ligand arrays (metallocene, half-metallocene, non-metallocene) are able to mediate these selective chain-termination/functionalization processes.

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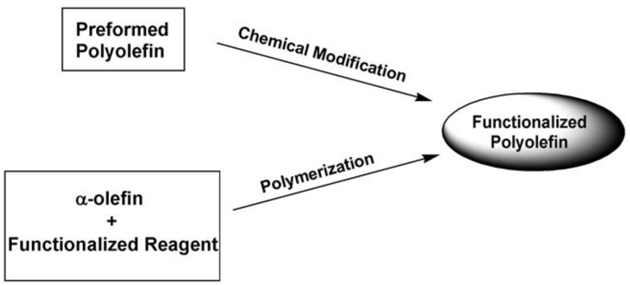
1. Introduction

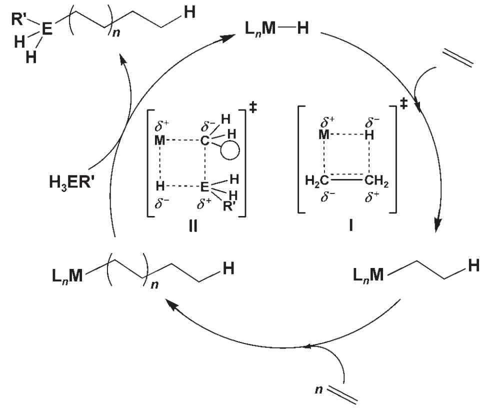
Chain-transfer agents, defined as chemical reagents which can both terminate and facilitate re-initiation of polymer chain growth, can efficiently control molecular weight and concomitantly introduce chemical functionality into polymer chains. Functionalized polyolefins[1] have many attractions versus non-functionalized polyolefins, including but not limited to, increased adhesion, paintability, and compatibility with diverse, more-polar materials.[2] Over the past decade, there have been a number of advances in methods for the functionalization of polyolefins.[1] The two conventional pathways for polyolefin functionalization are: 1) post-polymerization modification and 2) direct catalytic introduction of functional groups (Scheme 1).



Scheme 1. Pathways for polyolefin functionalization.

In general, post-polymerization modification[3] of presynthesized polyolefins avoids the issues of catalyst functional-group tolerance and catalyst poisoning. However, the unreactive nature of hydrocarbon polymers leads to difficult chemical modifications involving potentially harsh reaction conditions with a general lack of selectivity during the functionalization process. In contrast, selective and catalytic introduction of functional groups into polymerization processes offers the advantage of a controlled one-pot in situ synthesis. One effective catalytic method involves copolymerization with polar comonomers.[4] However, this approach is generally restricted to less-oxophilic late-transition-metal catalysts, which are more tolerant to polar functional groups, and turnover frequencies tend to be modest.

Another catalytic approach, which is the focus of this Review, involves incorporation of chain-transfer agents into olefin polymerization processes. Despite the potential disadvantages of catalyst poisoning or deactivation, diverse classes of chain-transfer agents and mechanisms have been discovered and shown to enable efficient, catalytic routes to functionalized polyolefins. There are two distinct classes of chain-transfer agents, electron-deficient/neutral and electron-rich, that proceed by distinctly different pathways (Scheme 2 and Scheme 3, respectively). Electron-deficient/neutral chain-transfer agents, such as silanes,[5] boranes,[6] and



Scheme 2. Catalytic cycle for single-site-mediated olefin polymerization in the presence of electron-deficient chain-transfer agents. ○ = polymer chain, E = Si, B, Al; R′ = alkyl, aryl.

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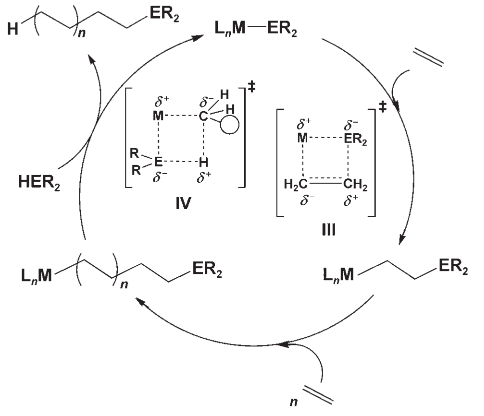
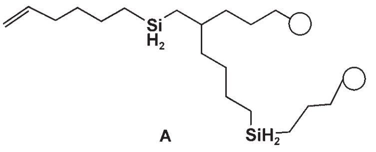


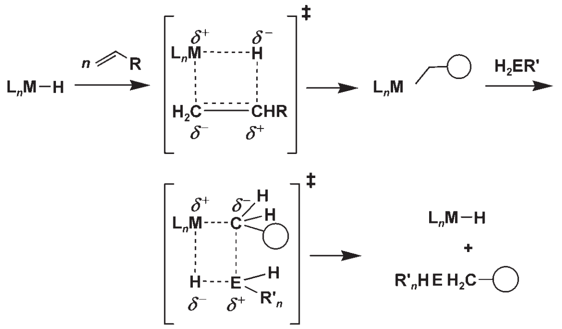
Scheme 3. Catalytic cycle for single-site-mediated olefin polymerization in the presence of electron-rich chain-transfer agents. E = P, N; R = alkyl, aryl.

alanes,[7–12] have been extensively investigated in single-site-catalyzed olefin-polymerization systems[13] with the goal of efficiently producing polyolefins having heteroatom-functionalized chain ends (Scheme 2, Figure 1). Furthermore, silane- and borane-functionalized comonomers have also successfully been implemented in a variety of copolymerization processes[5a,c,14] to catalytically access polymers with functionalized side-chains (e.g., **A**; ○ = polymer fragment).

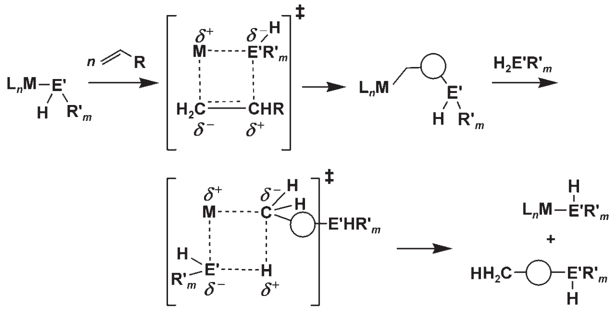


A

In addition to the electron-deficient Group 3 and Group 4 hydrides, electron-rich Group 5 and Group 6 hydrides, such as phosphines[15] and amines,[16] have also been effectively implemented as chain-transfer agents in organolanthanide-mediated polymerization systems, but proceed mechanistically by a distinctly different pathway (Scheme 3). Thus, electron-deficient/neutral and electron-rich chain-transfer agents catalytically functionalize polyolefin chain-ends in complementary ways: one through a metal hydride-based, M–C/E–H transposition cycle, the other through a metal–element-based, olefin-insertion/alkyl-protonolysis cycle [Eqs. (1) and (2), respectively; M = metal center, E = heteroatom].



(1)



(2)

The development of electron-deficient/neutral and electron-rich chain-transfer processes was founded on key reactivity and mechanistic advances in small-molecule hydrofunctionalization. For example, olefin hydrosilylation processes provide the basic stoichiometric sequences which allow organosilanes to function as chain-transfer agents in olefin-polymerization processes (Scheme 4).[17] In this case, exothermic olefin insertion into a Ln–H bond (Ln = lanthanide), for which there is substantial precedent,[18] is followed by a turnover-limiting and exothermic[19a,b] M–C/Si–H transposition[20] process. Mechanistic studies[17d] reveal that turnover frequency and selectivity for 2,1-addition regiochemistry in α-olefin hydrosilylation are enhanced by a more open ancillary-ligand sphere on the catalyst. For styrenic olefins, a rate enhancement is observed in the presence of electron-donating *para* substituents, in addition to complete regioselective delivery of the Si moiety to the benzylic position. Further-

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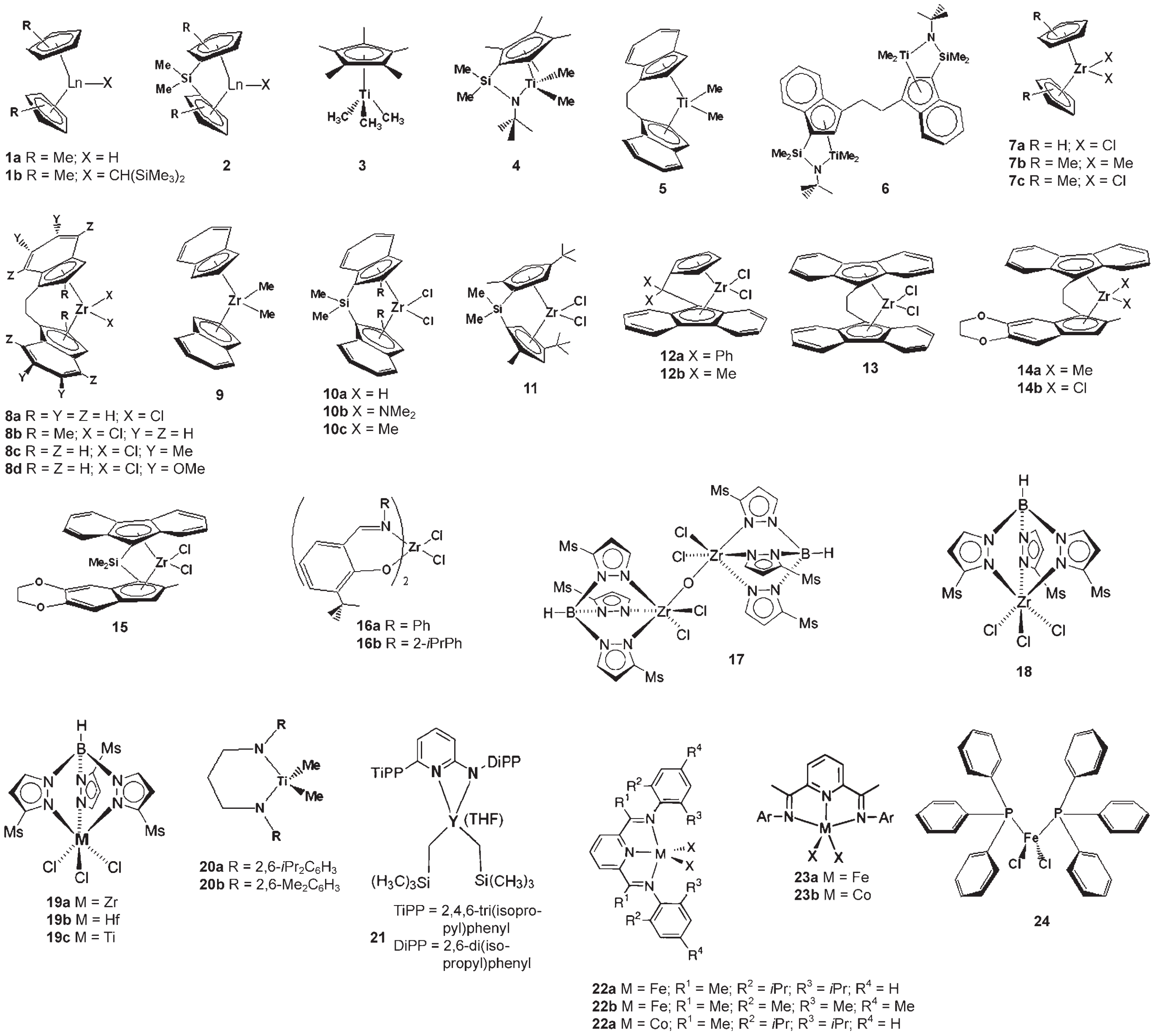
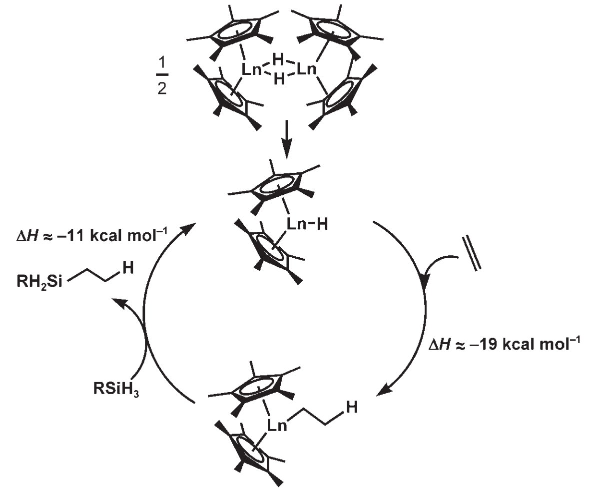


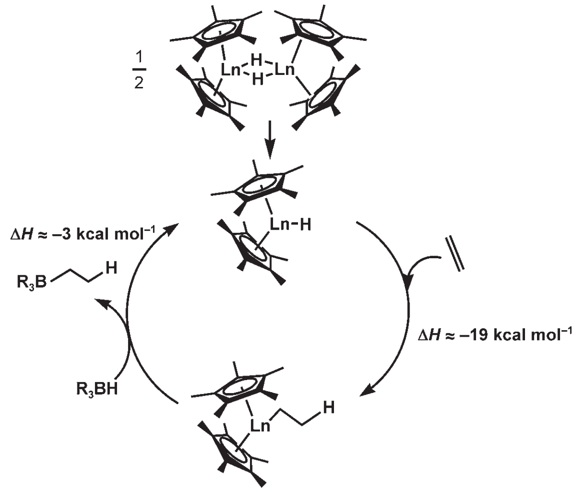
Figure 1. Representative single-site catalysts used for olefin polymerization in the presence of electron-deficient chain-transfer agents.

more, enantioselective hydrosilylation with chiral, C_1-symmetric lanthanocene catalysts affords *ee* values as high as 68%.[17d] Similarly, organolanthanide-mediated hydroboration studies[21] reveal catalytic pathways that parallel those defined for organolanthanide-mediated hydrosilylation (Scheme 5). Indeed, a wide variety of aryl- and alkyl-substituted, acyclic, and cyclic olefinic substrates can undergo efficient, catalytic hydroboration with high turnover frequencies.[21c]

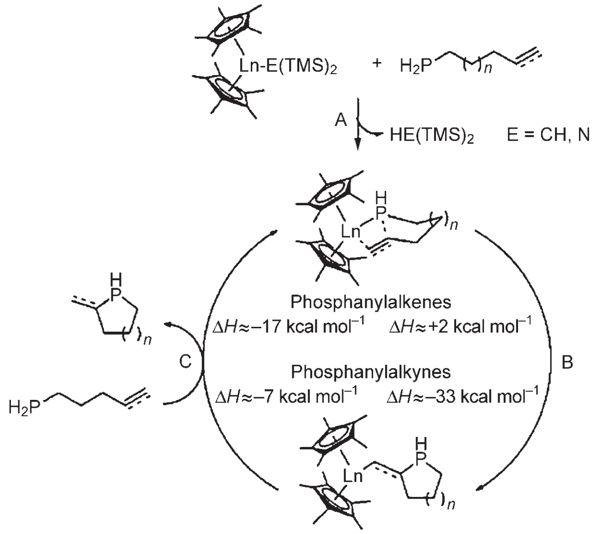
In contrast to the hydrosilylation/hydroboration systems, small-molecule hydrophosphination and hydroamination cycles proceed by completely different pathways, in part as a result of the dramatically different heteroatom Lewis basicities and bond polarities of the P–H/N–H linkages compared to those of the Si–H/B–H.[22] Mechanistic/thermodynamic analysis of organolanthanide-catalyzed hydrophosphination/cyclization pathways[19c–f] reveals that after initial precatalyst Ln–C protonolysis (Scheme 6, step A), insertion of the unsaturated C–C bond into a Ln–P bond (Scheme 6, step B) should be exothermic for alkynes and approximately thermoneutral for alkenes. This step is followed by exothermic protonolysis of the resulting Ln–C bond (Scheme 6, step C) to release the cyclized product.[23] Organolanthanide-mediated hydrophosphination/cyclization kinetic studies[23] reveal that larger metal ions and more open catalyst ancillary-ligand systems lead to increased turnover frequencies for phosphinoalkynes, whereas intermediate-sized metal ions with bis(pentamethylcyclopentadienyl) ligation lead to maximum turnover frequencies for phosphinoalkenes. At high substrate conversions, inhibition of the heterocyclic product is sometimes observed because of the competitive binding of product versus substrate. Interestingly, homoleptic lanthanide complexes (LnR$_3$) have also proven to be effective hydrophosphination catalysts with high turnover frequencies



Scheme 4. Catalytic cycle for organolanthanide-mediated olefin hydrosilylation.



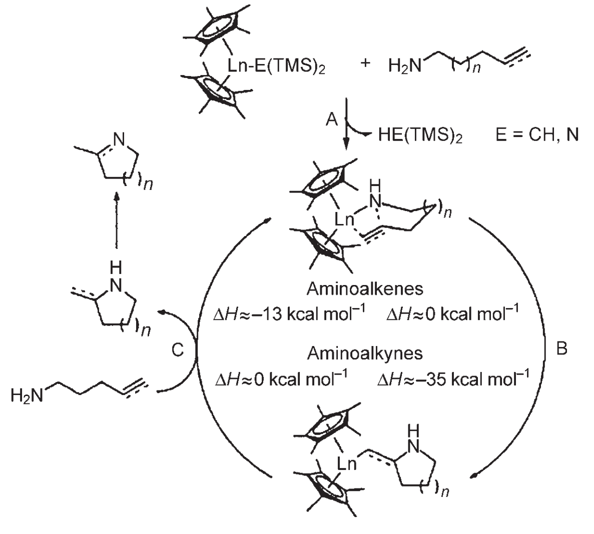
Scheme 5. Catalytic cycle for organolanthanide-mediated olefin hydroboration.



Scheme 6. Catalytic cycle for organolanthanide-mediated intramolecular hydrophosphination/cyclization. TMS = trimethylsilyl.

and good selectivities. In addition, density functional theory (DFT) B3LYP-level theoretical analysis of these hydrofunctionalization processes[24] reveals that olefin insertion into the Ln–P bond via a chair-like transition state is approximately thermoneutral for alkenes, supporting the aforementioned experimental observations, and that protonolysis by incoming phosphine to regenerate the Ln–P active species is a plausible turnover-limiting step in many cases. These theoretical studies also support the experimental observations of competitive product/unconverted substrate binding to the Ln^{3+} center, which leads to product inhibition at high conversions. Together, experiment and computation define the basic details of the processes by which phosphines will be shown to function as efficient chain-transfer agents in olefin polymerizations.

Detailed scope and mechanism studies of organolanthanide-mediated small-molecule hydroamination[25] implicate processes similar to those discussed above for hydrophosphination, and therefore suggest that amine-based polyolefin chain-transfer processes should be possible. The catalytic cycle for organolanthanide-mediated small-molecule hydroamination/cyclization proceeds by sequences of: A) quantitative protonolysis of the precatalyst by amine, B) turnover-limiting insertion of C–C unsaturation into the Ln–N bond via a chair-like transition state, and C) rapid protonolysis of the resulting Ln–C bond by incoming substrate to release the heterocyclic product and regenerate the Ln–N active species (Scheme 7). Focusing on the most relevant aminoalkene hydroamination/cyclization studies, high diastereoselectivities and turnover frequencies for formation of five-, six-, and seven-membered heterocycles have been demonstrated.[25] These processes are sensitive to the steric demands around the metal center, similar to the aforementioned hydrophosphinations, and exhibit pronounced increases in turnover frequency with larger Ln^{3+} ionic radius (La > Sm > Lu) and



Scheme 7. Catalytic cycle for organolanthanide-mediated intramolecular hydroamination/cyclization.

more open catalyst ancillary-ligand spheres. Competitive binding of product versus unconverted substrate to the Ln center sometimes results in product inhibition at high conversions. Furthermore, DFT/B3LYP-level theoretical analyses of hydroamination/cyclization[26] support rate-limiting alkene insertion into the Ln−N bond via a highly organized, chair-like four-center transition state, followed by exothermic Ln−C protonolysis to release the heterocyclic product. These results provide the groundwork for extending hydrofunctionalization to catalytic heteroatom chain-transfer processes coupled to single-site olefin polymerization.

Table 1: Organolanthanide-mediated olefin polymerization in the presence of silanes.

Entry	Precatalyst[a]	Silanes[b]	Monomer[c]	Activity[d] ($\times 10^4$)	M_n[e] ($\times 10^3$)	M_w/M_n[e]	Yield [g]
1	$[\{Cp^*_2SmH\}_2]$	$PhSiH_3$	E	34.2	4.4	4.3	0.33
2	$[\{Cp^*_2LuH\}_2]$	$PhSiH_3$	E	27.4	2.6[f]	–	0.50
3	$[\{Cp^*_2YH\}_2]$	$PhSiH_3$	E	30.0	4.9	2.2	0.35
4	$[\{Cp^*_2LaH\}_2]$	$PhSiH_3$	E	82.8	4.1	3.5	0.59
5	$[Me_2SiCp'_2SmR]$	$PhSiH_3$	E	1.75	2.6	2.9	0.24
6	$[Me_2SiCp'_2SmR]$	nBuSiH$_3$	E	0.636	2.1	2.4	0.21
7	$[Me_2SiCp'_2SmR]$	$C_6F_5CH_2SiH_3$	E	0.465	2.0	2.4	0.23
8	$[\{Cp^*_2SmH\}_2]$	nBuSiH$_3$	E	50.6	2.7	1.9	0.22
9	$[Me_2SiCp'_2SmR]$	$PhSiH_3$	E/1-Hx	0.242	0.4	4.9	0.24
10	$[Me_2SiCp'_2NdR]$	$PhSiH_3$	E/S	0.257	3.3	–	1.70
11	$[Me_2SiCp'_2SmR]$	nBuSiH$_3$	E/1-Hx	1.51	1.9	2.0	1.00
12	$[Me_2SiCp'_2SmR]$	nBuSiH$_3$	E/S	0.212	1.7	2.9	1.40

[a] 10–30 μmol precatalyst. [b] 0.2–0.6 M silane. [c] E = ethylene, 1-Hx = 1-hexene, S = styrene. [d] Units = g/(mol Ln×atm ethylene × h). [e] By GPC in 1,2,4-trichlorobenzene vs. polystyrene standards. [f] By ^{1}H NMR spectroscopy.

In 1995, it was reported that, in the presence of olefins and silanes, homogeneous organolanthanide polymerization catalysts of the type $[\{Cp^*_2LnH\}_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; **1a**, Figure 1) and $[Me_2SiCp'_2LnCH(SiMe_3)_2]$ ($Cp' = \eta^5\text{-}C_5Me_4$) (**2**, Figure 1) where Ln = La, Sm, Y, Lu efficiently produce silane-terminated polyolefins with high polymerization productivities and tunable product molecular weights (up to 10^5 g polymer/(mol Ln×atm ethylene × h)).[5f,h] These initial results led to broad diversification of the applicable chain-transfer agents as well as of the catalyst systems competent for polyolefin functionalization. Herein we survey and analyze the scope of electron-deficient/neutral and electron-rich chain-transfer agents and processes which are effective in single-site-mediated olefin polymerization, focusing on research performed at both in our group at Northwestern University and in other laboratories. We begin with a summary of initial observations on organolanthanide-mediated olefin polymerization in the presence of silanes. We then show how this effort can be extended in several different directions based on the early silanolytic chain-transfer results:

1) Expansion of catalyst scope to early-transition-metal Group 4 systems
2) Simultaneous introduction of silane functional groups and branches using alkenylsilanes as chain-transfer agents
3) Exploration of silanolytic chain transfer in heterogeneous catalytic systems
4) Development of other electron-deficient/neutral chain-transfer agents and processes such as those involving boranes and alanes
5) Development of complementary approaches with electron-rich phosphine and amine chain-transfer agents

2. Silanolytic Chain Transfer

2.1. Organolanthanide-Catalyzed Silanolytic Chain Transfer[5f,h]

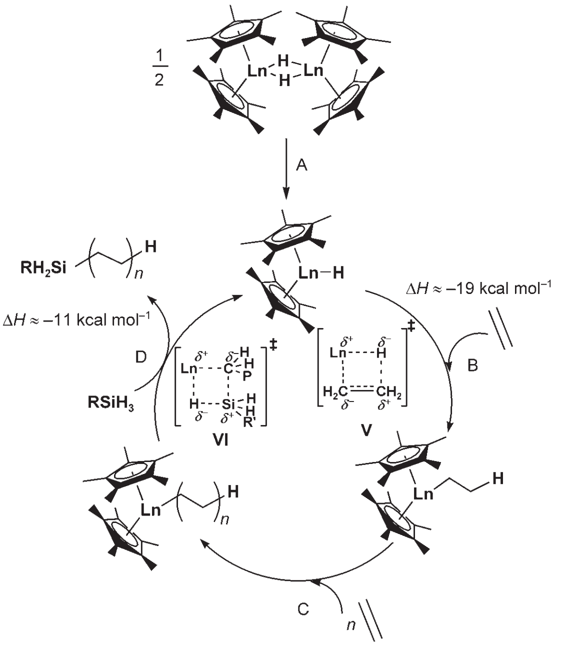
The anhydrous/anaerobic polymerization of olefins in the presence of silanes (pseudo-zero-excess) mediated by **1a** and **2** complexes proceeds efficiently and selectively (Table 1) as shown by NMR spectroscopy and gel-permeation chromatography (GPC). The approximately 1:1 ratio of the intensity of the -CH_3: -CH_2SiH_2 ^{13}C NMR signals argues that silanes readily effect intermolecular chain termination and exclusively functionalize a single terminus per polymer chain. The intensity of any vinyl chain-end resonances in these materials are below the detection limits in both the ^{1}H and ^{13}C NMR spectra, arguing that chain termination by β-hydride elimination (to metal center or to monomer)[27] is inconsequential. In addition, the resulting silane-capped polymers have relatively narrow, monomodal polydispersities (Table 1) consistent with a single-site polymerization process.[13] These catalytic polymerization systems are effective in the synthesis of silane-terminated polyethylenes, poly(ethylene-*co*-styrenes), and poly(ethylene-*co*-1-hexenes) The chain-transfer reagents used are primary alkyl- and arylsilanes which give high selectivities and activities (up to 10^5 g polymer/(mol Ln×atm ethylene × h)).

The proposed catalytic cycle for silane-mediated chain transfer (Scheme 8) is envisioned to proceed via coupled, well-precedented sequences of: A) precatalyst dimer dissociation,[18g] B) initial C=C insertion into the Ln−H bond (**V**),[18] C) multiple chain propagating C=C insertions into the Ln–alkyl bond,[18] and D) silanolytic chain termination, presumably through a σ-bond metathesis-type transition state (**VI**),[17,20,28] to regenerate the catalytically active organolanthanide hydride and close the cycle. As mentioned in Section 1 the theoretical results for the steps in this cycle are consistent with the experimental evidence for such reaction sequences.[19]

Under steady-state conditions, the number-average degree of polymerization (P_n) is equal to the sum of all rates of propagation (ΣR_p) divided by the sum of the rates of competing chain-transfer pathways (ΣR_{ct}) [Eq. (3)]. A kinetic

$$P_n = \frac{\sum R_p}{\sum R_{ct}} \tag{3}$$

analysis of the chain-transfer process (Figure 2), assuming constant concentrations of silane, ethylene, and catalyst for any given reaction and that rapid re-initiation occurs after chain transfer, where silanolysis is the dominant chain-



Scheme 8. Catalytic cycle for organolanthanide-mediated olefin polymerization in the presence of silanes.

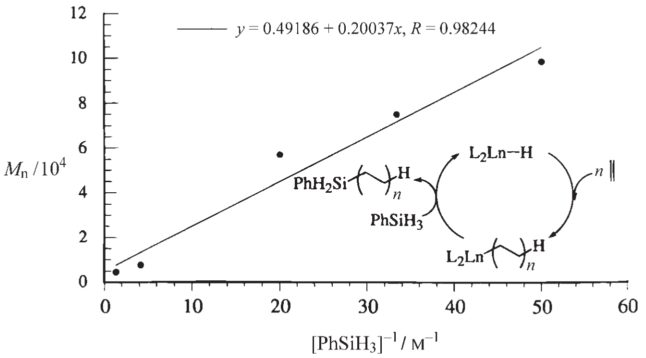


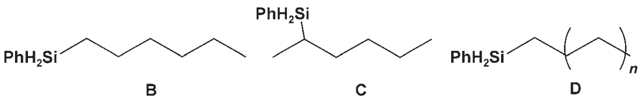
Figure 2. Relationship of polyethylene number-average molecular weight (M_n; GPC versus polystyrene standard) to inverse concentration of $PhSiH_3$ chain-transfer agent for fixed organolanthanide catalyst $[\{(Me_5C_5)_2SmH\}_2]$ and ethylene concentrations. Inset: Proposed catalytic cycle for this process.

transfer pathway, reveals that the number-average degree of polymerization P_n at ideal steady-state should obey Equation (4). In this case, the product polymer number-average

$$P_n = \frac{\sum k_p[\text{olefin}]}{\sum k_{ct}[\text{chain-transfer agent}]} \tag{4}$$

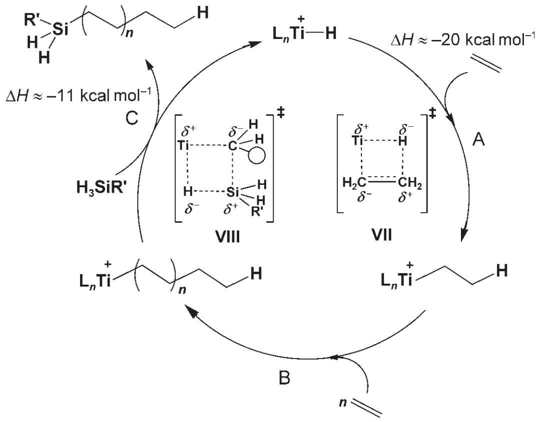
molecular weight (M_n) should decrease linearly with increasing silane concentration, typifying an ideal chain-transfer process and indicating that silanolytic chain transfer is the dominant chain-termination pathway; k_p is the rate constant for chain propagation and k_{ct} is the rate constant for chain transfer.

The present olefin-polymerization rates in the presence of silanes are appreciably sensitive to catalyst steric encumbrances, similar to trends observed with the same catalysts for α-olefin polymerizations in the absence of silanes.[18g] Thus, polymerization rates increase with increasing Ln^{3+} ionic radius (La ≫ Sm = Y = Lu). Interestingly, simple organolanthanide-mediated hydrosilylation of α-olefins with $PhSiH_3$ yields a mixture of 1,2- and 2,1-regiochemistries (e.g., **B** and **C**, respectively in the case of 1-hexene), whereas the terminus-only regiochemistry of the silane-capped polyolefin (e.g., **D**) argues that Si–C bond formation arises from direct chain transfer (Scheme 8, step D) rather than from hydrosilylation of a previously formed β-H elimination product. As discussed in Section 1, high selectivity for 2,1-regiochemistry in olefin hydrosilylation increases with more open catalyst ancillary-ligand spheres, resulting in products such as **C**.



2.2. Group 4 Mediated Alkyl/Arylsilane Chain Transfer[5e,g]

The success of organolanthanide-mediated silane chain transfer led us to inquire whether analogous chain-transfer processes in Group 4 mediated polymerization systems are viable. Organotitanium complexes **3**, **4**, and **5** (Figure 1) efficiently produce a diverse spectrum of silane-terminated polyolefins, which have been characterized by GPC as well as by $^1H/^{13}C/^{29}Si$ NMR spectroscopy. Silanolytic chain transfer doubtless proceeds by an essentially similar mechanistic scenario to that of the organolanthanide-mediated polymerization systems (Scheme 9) with rapid ethylene insertion/chain propagation and turnover-limiting silanolytic chain transfer (Scheme 9, step C). There is extensive precedent for this type of M–C/Si–H four-center transposition reaction as noted in Section 1.[20,28] Similarly, high activities (up to 10^6 g polymer/(mol Ti×atm ethylene × h)) are observed for propylene, 1-hexene, ethylene/styrene, ethylene/1-hexene, propyl-



Scheme 9. Catalytic cycle for organotitanium-mediated olefin polymerization in the presence of silane chain-transfer agents. R' = alkyl, aryl.

ene/1-hexene, and styrene polymerizations in the presence of silanes, with no detectable formation of β-H elimination-derived vinyl-terminated polymer contaminants. A wide variety of silane-capped stereoregular and random homo- and copolymers as well as block copolymers can be selectively synthesized (Figure 3). These silane-terminated polyolefins contain versatile, reactive C–Si functionalities that can further undergo a diverse range of subsequent and useful transformations.[29] One example of such a transformation is the protodesilylation and oxidative cleavage of arylsilane-terminated atactic polypropylenes to produce hydroxy-terminated atactic polypropylenes [Eq. (5)].[5e]

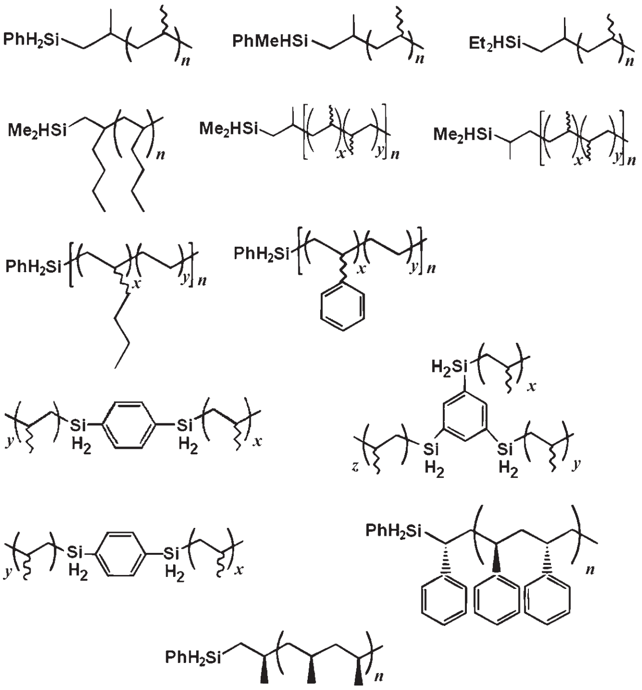
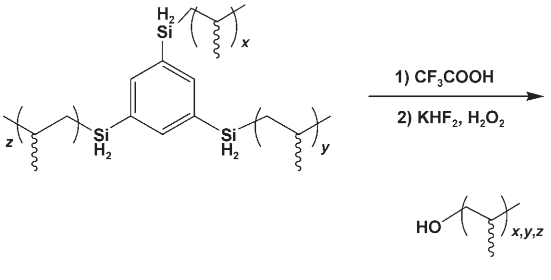
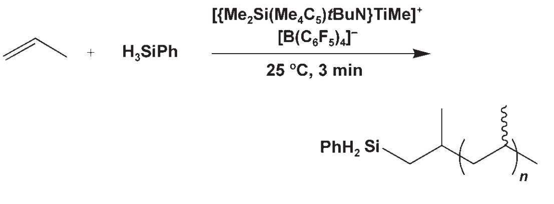


Figure 3. Silane-functionalized polyolefins accessible by catalytic olefin polymerization and silane chain-transfer processes mediated by organotitanium catalysts.



(5)

Secondary silanes used as chain-transfer agents in these organotitanium-mediated systems exhibit somewhat diminished reactivity versus primary silanes. However, as the concentration of secondary silane is increased in these systems, the yield of silane-capped polymer produced increases linearly. Note that the hydrosilylation of the analogous vinyl-end-group-terminated polyolefins (produced by β-H elimination in the absence of silane chain-transfer agents) under identical reaction conditions, yields silane-capped polymers only after 20 h of reaction time [compare Eq. (6) and Eq. (7)], arguing that this pathway makes negligible contribution to the catalytic production of silane-terminated polyolefins.



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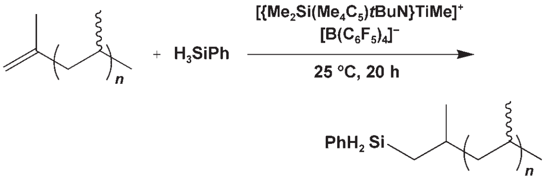


(7)

The chain-transfer behavior of silanes in organotitanium-mediated systems is well-behaved, as supported by the linear decrease in product polymer M_n value with increasing silane concentration at constant catalyst and monomer concentrations [Figure 4, Eq. (4)]. Silanolytic chain termination is clearly the dominant chain-transfer pathway in these organotitanium-mediated polymerization systems. Interestingly, silane-capped polyethylenes proved to be conspicuously difficult to synthesize at 25 °C using primary and secondary alkyl- and arylsilanes, which is likely to be due to complex competing kinetic and steric effects, suggested by the observations that: 1) silane-capped polyethylenes are produced at −25 °C, and 2) silane-capped poly(ethylene-*co*-1-hexene) and silane-capped poly(ethylene-*co*-styrene) are produced efficiently at 25 °C. These results suggest that

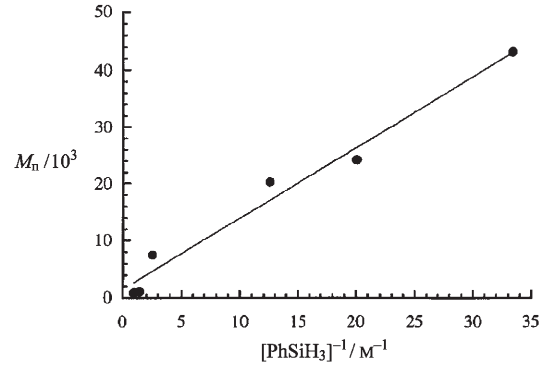
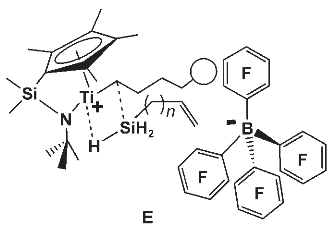


Figure 4. Relationship of polypropylene number-average molecular weight (GPC versus polystyrene standard) to inverse concentration of $PhSiH_3$ chain-transfer agent in the $[\{Me_2Si(Me_4C_5)tBuN\}TiMe]^+[B(C_6F_5)_4]^-$-mediated capping of atactic polypropylene (at constant catalyst and olefin concentrations).

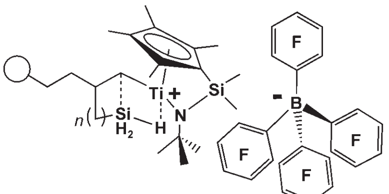
ethylene propagation and β-hydride elimination are rapid at 25 °C compared to the slower silanolytic chain termination, resulting in vinyl-terminated polyethylenes. In addition, the transition state **VIII** (scheme 9) is more sterically congested for an organosilane compared to that for β-hydride elimination, again resulting in vinyl-terminated polyethylenes.

2.3. Organotitanium-Mediated Alkenylsilane Chain Transfer[5a–c]

As presented in Section 2.2, organotitanium-mediated silanolytic chain transfer has one significant drawback. Unlike organolanthanide catalytic systems, selective and efficient synthesis of silane-capped polyethylenes by organotitanium catalysts has remained elusive, making their applicability to one of the most commonly used synthetic polyolefins limited. This limitation appears to derive from the complex competing steric and electronic effects noted in the Section 2.2. To investigate the possibility of a selective, catalytic synthesis of silane-capped polyethylenes, a series of α,ω-alkenylsilanes was investigated as C–C unsaturated comonomers for copolymerization with ethylene. It was envisioned that coordination/insertion of the alkenylsilane olefinic end groups would increase the effective local silane concentration in close proximity to the electrophilic Ti center, thus making silanolytic chain transfer kinetically more efficient (e.g., **E** vs. **F**). Interestingly, alkenylsilanes are extremely selective and efficient chain-transfer agents for organotitanium-mediated ethylene polymerization with activities as high as 10^6 g polymer/(mol Ti × atm ethylene × h). Compared to alkylsilanes, alkenylsilanes are far more effective chain-transfer agents during ethylene polymerization (k_{ct}/k_p for alkenylsilanes is up to 150-times greater than that for alkylsilanes; Figure 5). Intriguingly, silane chain transfer is inefficient for styrene homopolymerization mediated by **4**; however, polymerization activities are dramatically increased in the presence of silanes, which is likely to be due to the interaction of the weakly basic Si–H moiety with the electrophilic Ti center. This interaction would effectively disrupt the hypothetical "back-biting" deactivation of the catalyst by the styrene π-system (e.g., **G** vs. **H**) and promote monomer enchainment (that is, incorporation of the monomer into the growing polymer chain).[5b]



E



F

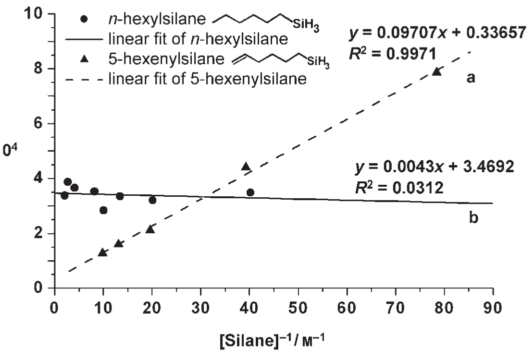
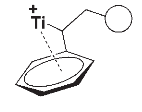
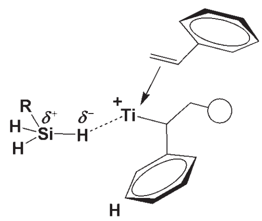


Figure 5. Relationship of polyethylene number-average molecular weight (GPC versus polyethylene standard) to: a) inverse 1-$C_6H_{11}SiH_3$ concentration at fixed catalyst and ethylene concentrations, and b) inverse n-$C_6H_{13}SiH_3$ concentration at fixed catalyst and ethylene concentrations.

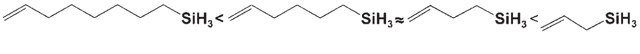


G

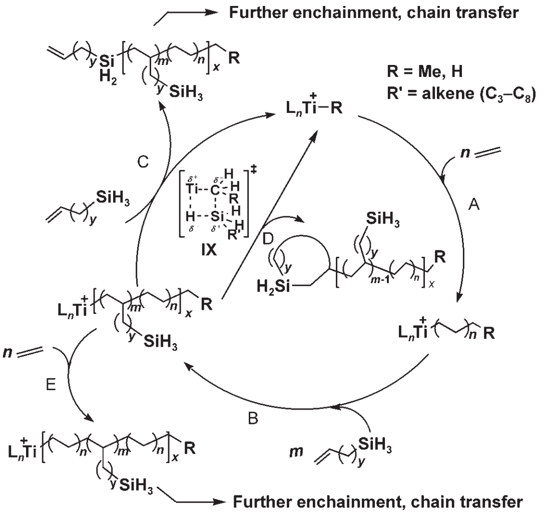


H

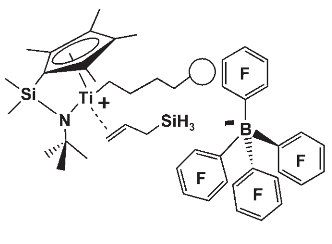
These same organotitanium/alkenylsilane polymerization systems effect the controlled introduction of short- and long-chain branching by silane-branch chain-transfer processes as demonstrated by copolymerization of alkenylsilanes with ethylene using catalysts **4** and **6** and $[Ph_3C]^+[B(C_6F_5)_4]^-$ as the cocatalyst. The proposed catalytic cycle for mononuclear titanium-mediated ethylene/alkenylsilane copolymerization is envisioned to proceed as shown in Scheme 10 by sequences of : A), E) multiple insertions of C=C unsaturations into titanium–alkyl bonds, B) C=C insertion of the alkenylsilane into the growing polymer chain, and/or C) intermolecular silanolytic chain transfer to the copolymer chain, and/or D) intramolecular silanolytic chain transfer to the copolymer chain, to complete the cycle. In this case, alkenylsilane incorporation and branch formation trends parallel those of α-olefin/ethylene copolymerization, where decreasing alkenylsilane chain length is accompanied by increased comonomer incorporation and branch formation in the sequence:



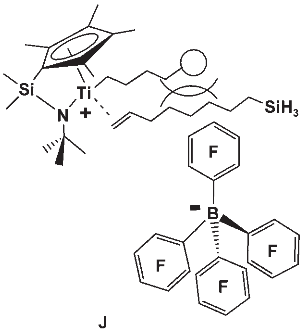
This observation is reasonably attributed to the more sterically facile coordination/insertion of smaller alkenylsilanes (e.g., **I**) versus the more sluggish coordination/enchainment of longer alkenylsilanes (e.g., **J**) as a result of nonbonded repulsions involving the ancillary ligands, the poly-



Scheme 10. Catalytic cycle for organotitanium-mediated alkenylsilane/ethylene copolymerization.



I

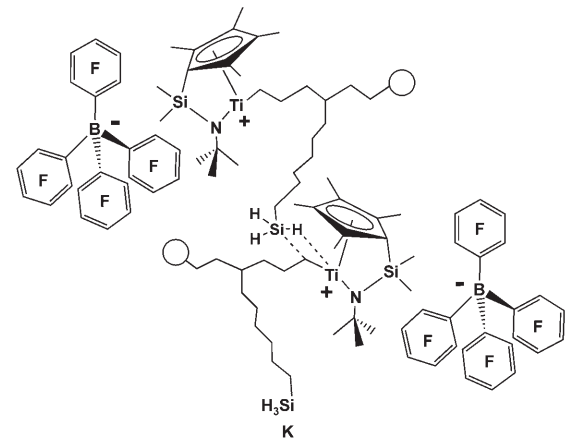


J

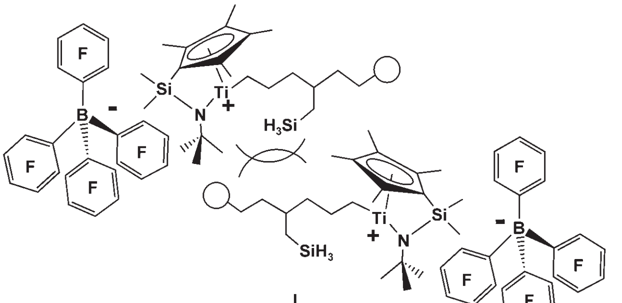
meryl fragment, and the counteranion. Additionally, the ratio of long-chain branches (formally defined as polymeric branches; which lead to materials with advantageous mechanical and processing properties[2]) to total branch content, can be derived from GPC-MALLS data (MALLS = multi-angle laser light scattering), which measures the average radius of macromolecular gyration, and increases in the order:

This long-chain-branching trend is attributed to the kinetic advantage of the longer alkylsilane branches to undergo intermolecular chain transfer to a second growing polymer chain (e.g., **K**). The steric impedance is minimal compared to the transfer of shorter alkylsilane branches (e.g., **L**). These long-chain-branching trends are reflected in dramatic decreases in polymer melting temperature with increased long-chain-branch density. These trends demonstrate that it is possible to control branch density and tune polyolefin microstructure simply by altering the alkenylsilane chain length (Figure 6).

An alternative approach to controlling polyolefin microstructure was investigated by increasing the catalyst nuclearity while holding the structure and concentration of the alkenylsilane chain-transfer agent constant. With unfunctionalized monomers, polynuclear organotitanium catalysts, such as **6** (Figure 1), afford high-molecular-weight polyolefins with dramatically enhanced α-olefin comonomer incorporation selectivities versus mononuclear catalyst analogues.[30] The dicationic bimetallic framework exhibits enhanced monomer-binding affinity (e.g., **M**), resulting in enhanced comonomer enchainment. In these alkenylsilane/ethylene copolymeriza-



K



L

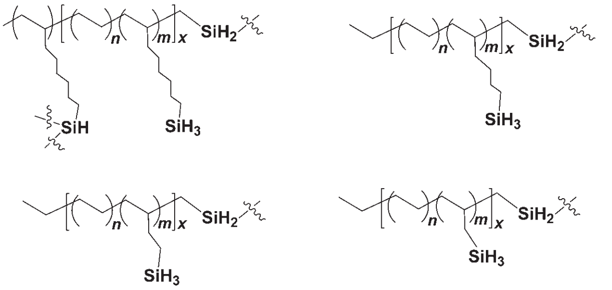
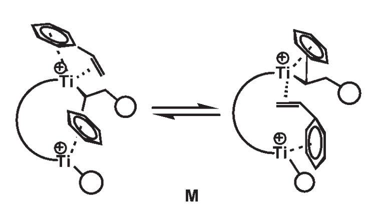


Figure 6. Representative alkenylsilane/ethylene copolymer microstructures produced by organotitanium catalysts.



M

tion systems, the binuclear titanium catalyst **6** consistently produces higher molecular-weight polyolefins compared to the mononuclear analogue **4** (Figure 7). This result is attributable to cooperative enchainment/chain-transfer processes involving the two neighboring active electrophilic centers, which increases the probability of macromonomer re-insertion or chain transfer of the alkylsilane branch. The dicationic bimetallic framework exhibits enhanced α-olefin binding affinity/kinetic detainment (that is, transitory capture; e.g., **M** in the case of styrene) fostering increased selectivity for comonomer enchainment. These bimetallic cooperative effects, resulting in reaction sequences such as shown in Scheme 11, should produce higher molecular-weight polyolefin products having long-chain branches.

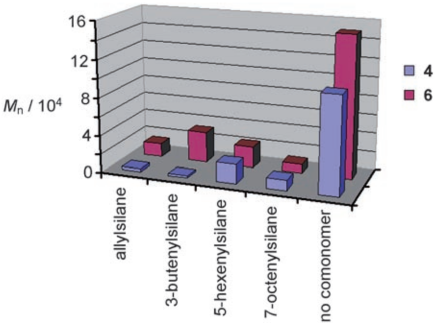


Figure 7. Dependence of copolymer number-average molecular weight on alkenylsilane chain length for the copolymerization of alkenylsilanes with ethylene mediated by catalysts **4** and **6** at a constant alkenylsilane concentration of 100 mм.

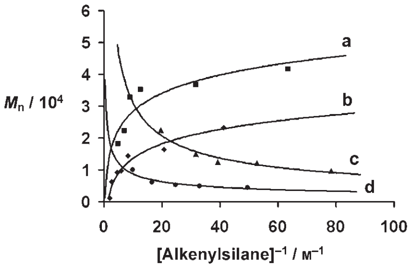
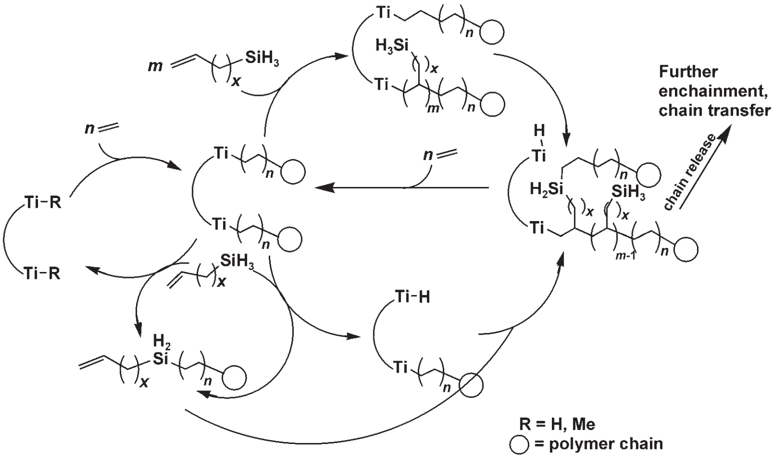


Figure 8. Comparison of ethylene/alkenylsilane copolymer number-average molecular weight (GPC vs. polyethylene standard) relationship to inverse concentrations of: a) 3-butenylsilane, b) allylsilane, c) 5-hexenylsilane, d) 7-octenylsilane at identical fixed **6**/$[Ph_3C]^+[B(C_6F_5)_4]^-$ and ethylene concentrations. Lines through the data points are a guide for the eye.



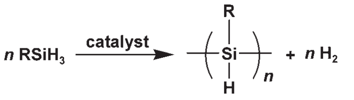
Scheme 11. Catalytic cycle for binuclear organotitanium-mediated alkenylsilane/ethylene copolymerization.

These binuclear-catalyst-mediated copolymerization/chain-transfer processes display a complex, nonlinear dependence of M_n on silane concentration (e.g., Figure 8), which is in contrast to all the previously discussed systems where the silane chain-transfer process is well-behaved with a linear relationship of M_n to 1/[silane] (compare Figures 4, 5, and 8). For shorter C_3 and C_4 alkenylsilanes in the presence of the binuclear catalyst, the standard chain-transfer plot reveals that M_n falls sublinearly with increasing alkenylsilane concentration. One explanation for this nonlinear behavior is that interactions between the neighboring Ti centers and the weakly basic, enchained $-SiH_3$ groups may hinder olefin activation, thus depressing propagation rates versus competing chain-transfer rates. However, longer alkenylsilanes exhibit a superlinear relationship between product M_n and alkenylsilane concentration, which correlates with an increase in selectivity for long-chain branching in the corresponding copolymer microstructures (Figure 7). These binuclear systems are multifaceted and kinetically complex, resulting in non-ideal, nonlinear chain-transfer behavior (Figure 8). These observations demonstrate the flexibility and tunability of polyolefin microstructures by varying the chain length of the alkenylsilane chain-transfer agent and the catalyst nuclearity.

2.4. Supported Ziegler–Natta-Mediated Silanolytic Chain Transfer[5d]

Silanolytic chain termination using supported single-site catalysts was investigated with the goal of developing a heterogeneous catalytic approach to obtaining silane-functionalized polyolefins. Catalyst **3a**, **4**, **7a**, and **8a** were supported on SiO_2/MAO (calcined silica surface area ca. 250 $m^2 g^{-1}$, treated with MAO; MAO = methylalumoxane). The polymerization activities of these supported, single-site Group 4 element catalysts in the presence of silanes are depressed to less than 0.3-times those in the absence of silanes (ca. 3.4 g polymer/(g catalyst × atm ethylene × h)), and the depressed activities may be attributable to the weak Lewis basicity of the silanes. As expected, the product polymer M_n value also decreases upon addition of silanes to the heterogeneous polymerization systems. However, silanolytic chain transfer in these supported systems is not particularly selective, and the resulting polyolefin products are mixtures of silane-capped and uncapped vinyl-terminated polymers or saturated polyolefins devoid of silane-capping. Using silica/MAO supported **7a**, a mixture of approximately 1:1 silane-capped:uncapped polyethylene is produced. Furthermore, the uncapped polyethylene product contains saturated end groups, suggesting that H_2 chain transfer, a likely byproduct of well-documented organo–Group 4 element catalyzed dehydrogenative silane coupling [Eq. (8)],[31] is active as a chain-termination pathway.

Silica/MAO-supported **4** in the presence of $PhSiH_3$ yields a 1:1 mixture of silane-capped:uncapped polyethylenes, while

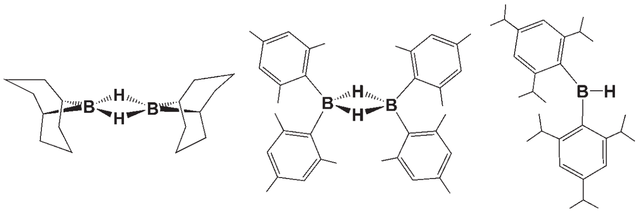


$$n\,RSiH_3 \xrightarrow{\text{catalyst}} \left(\overset{R}{\underset{H}{Si}}\right)_n + n\,H_2 \qquad (8)$$

supported **8a** in the presence of silanes affords only product polypropylenes devoid of silane-capping and having vinylidene chain ends. In addition, SiO_2/MAO supported **4**, **8a**, and [Cp^*TiMe_3] (**3**; $Cp^* = C_5Me_5$) catalyst systems in the presence of *n*-hexyl- and diethylsilane afford polyethylenes devoid of silane-capping. Thus, supported Group 4 metallocenium catalysts exhibit some silanolytic chain-transfer efficiency, albeit with a narrower cope than the homogeneous systems, possibly reflecting the steric constraints imposed by the surface and ancillary ligands around the metal center.

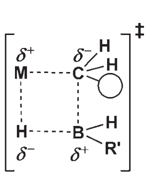
3. Borane Chain-Transfer Processes

Another group of electron-deficient/neutral chain-transfer agents that have been successfully combined with single-site-catalyzed olefin polymerizations are organoboranes. Thus, Chung and co-workers used 9-bora-bicyclononane (9-BBN) and other organoborane hydrides (Figure 9) to selectively and catalytically functionalize polyolefin chain ends. Using [$Cp^*_2ZrMe_2$]/$B(C_6F_5)_3$ or [$Cp^*_2ZrMe_2$]/$[Ph_3C]^+[B(C_6F_5)_4]^-$ to effect ethylene polymerization in the presence of 9-BBN, it was found that boranes function similarly to silanes during olefin polymerization (Scheme 2, transition state **II**). The turnover-limiting step in this catalytic cycle is again the σ-bond metathesis-type B–H/M–C transposition, resulting in the selective, efficient catalytic introduction of a boron functional group at the polyolefin terminus. This four-center[28] B–H/M–C transposition reaction has extensive precedent in catalytic hydroboration pathways.[21] In the presence of boranes, zirconocene systems **7b** and **9** (Figure 1) yield polyolefins with high activities (up to 10^6 g polymer/(mol Zr×atm ethylene × h)), and the borane chain-transfer kinetic behavior is linear and kinetically well-behaved (Figure 10). At constant catalyst and ethylene concentration, the product polymer M_n value decreases linearly with increasing borane concentration, indicating that borane chain transfer is the dominant chain-termination pathway (Figure 10). Note that these borane-functionalized polyolefins can be subsequently oxidized to produce hydroxy-terminated polyolefins or radical-terminated polyolefins which can then initiate a second polymerization (Scheme 12). Chung and co-workers expanded this work to use catalysts **3** and **4** with $B(C_6F_5)_3$ to produce 9-BBN-capped poly(ethylene-*co*-styrene), poly(ethylene-*co*-1-octene), and syndiotactic polystyrene.[6b] The scope of borane chain-transfer agents was later expanded to include dimesitylborane [$(HBMes_2)_2$] and 2,4,6-triisopropylphenylborane ($HB(Trip)_2$; Figure 9) to selectively and efficiently produce borane-functionalized polyolefins.[6b]



9-BBN **(HBMes$_2$)$_2$** **(HBTrip)$_2$**

Figure 9. Borane chain-transfer agents effective in metallocene-mediated olefin polymerization.



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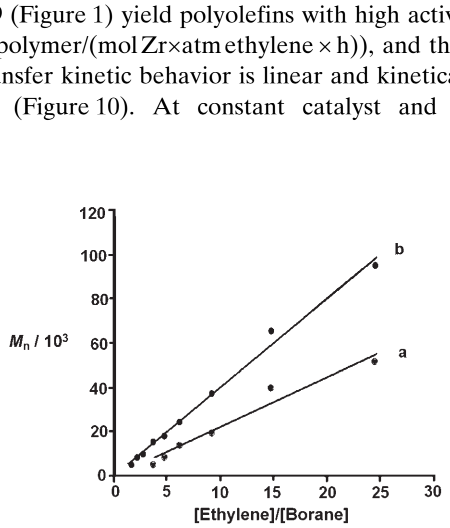
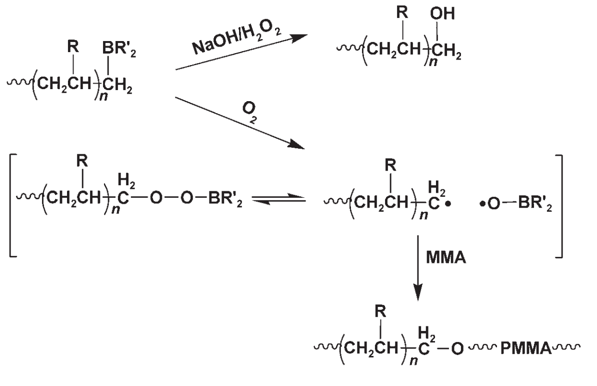


Figure 10. Plots of number-average molecular weight of borane-terminated polyethylenes vs. the mole ratio of: a) [ethylene]/[9-BBN] and b) [ethylene]/[H-B(Mes)$_2$] in single-site-mediated boranolytic chain-transfer processes for ethylene polymerization. Reproduced from reference [6b].

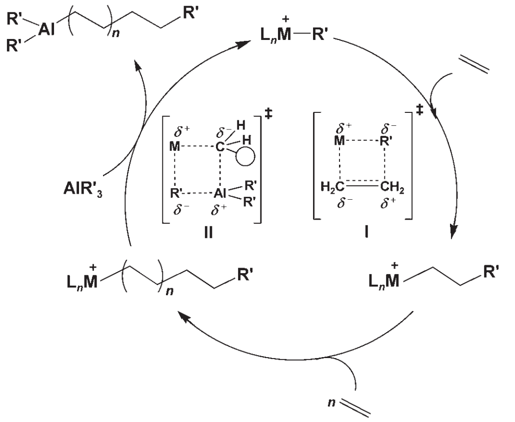


Scheme 12. Pathways for further functionalization of borane-terminated polyolefins. MMA = methyl methacrylate.

4. Alane Chain Transfer (Chain Transfer to Aluminum)[7–12]

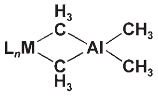
4.1. Metallocene-Mediated Chain Transfer to Aluminum

There are numerous reports of olefin-polymerization systems that undergo chain transfer to aluminum, referred to herein as alane chain transfer.[7–12] Herein we limit the discussion to examples where chain transfer to aluminum is the dominant chain-termination pathway. The overwhelming majority of alane chain-transfer examples are reported for zirconocene-mediated propylene polymerizations in the presence of MAO or AlR$_3$, which exhibit activities as large as 10^7 g polymer/(mol Zr×atm propylene × h)).[8] A diversity of zirconocene catalysts have been shown to mediate alane chain-transfer processes, including Cp-, indenyl-, and fluorenyl-based Group 4 systems (Figure 1, complexes **7**–**15**). The indenyl-based zirconocene catalysts, used to synthesize highly isotactic polypropylene, efficiently mediate alane chain transfer using MAO as both the cocatalyst and the source of the alane chain-transfer agent.[8b,f–h] In these systems, aluminum-terminated isotactic polypropylene is selectively and catalytically synthesized as shown by the distinctive signal for saturated isopropyl end groups in the ^{13}C NMR spectrum. In addition, the product polypropylene M_n value decreases with increasing MAO concentration, indicating that alane chain transfer is the dominant chain-transfer pathway. It was also noted in some systems that alane chain transfer dominates at lower temperature, owing to depressed, competing β-H elimination rates.[8b] Note however that other studies have argued that the residual alkylaluminum compounds (AlR$_3$) typically contained in MAO samples are the species actually responsible for alane chain-transfer processes.[8d,e] Interestingly, these studies indicate that AlMe$_3$ and AlEt$_3$ both behave as efficient chain-transfer agents in zirconocene-catalyzed propylene polymerization systems, producing polymers with saturated isopropyl end groups after acidic work-up, as judged by ^{13}C NMR spectroscopy. The addition of AlMe$_3$ and AlEt$_3$ also results in a dramatic decrease in product polymer M_n values, again implicating alane chain transfer as the dominant chain-termination pathway. In contrast, more encumbered Al*i*Bu$_3$ does not behave as an ideal chain-transfer agent, resulting in polymer molecular weights that are essentially independent of Al*i*Bu$_3$ concentration as well as product polymer microstructures having negligible isopropyl end-group resonances in the NMR spectra. A plausible catalytic cycle for organoaluminum chain transfer combined with single-site olefin polymerization is shown in Scheme 13. Note that the σ-bond metathesis transition state (**II**) typically invokes a formal μ-R′ moiety in this case.



Scheme 13. Catalytic cycle for single-site-mediated olefin polymerization in the presence of aluminum chain-transfer agents. R′ = alkyl, aryl; M = Group 4 metals.

Additionally, there have also been several studies of alane chain transfer in fluorenyl- and Cp-based zirconocene-mediated propylene polymerization systems.[8a,c,d] These studies again indicate that addition of AlMe$_3$ or excess MAO to the polymerization processes results in depressed product polymer M_n values along with polymer microstructures containing saturated isopropyl end groups, suggesting alane chain transfer as the dominant chain-termination pathway. Increasing the AlR$_3$ or MAO concentration in the aforementioned systems generally results in decreased polymerization activity, likely a result of catalyst deactivation by AlMe$_3$. Model compounds have been synthesized to study poisoning processes by AlMe$_3$, and suggest that AlMe$_3$ substantially suppresses olefin polymerization rates compared to other aluminum alkyls through greater coordinative tendencies towards the metal catalytic center (e.g., **N**; M = Group 4 metals).[32] Zirconocene-mediated alane chain transfer coupled to ethylene polymerization has also been studied,[9] albeit to a lesser extent compared to propylene polymerization systems. In these ethylene polymerization systems, AlR$_3$ (R = Me, Et, *i*Bu) compounds all behave as efficient chain-transfer agents, producing aluminum-terminated polyethylenes of molecular weights that decrease linearly with increasing AlR$_3$ concentration at constant catalyst and ethylene concentration. Furthermore, working up the aluminum-terminated product polyethylenes with O$_2$ or H$_2$O$_2$/NaOH affords hydroxy-terminated polyethylenes (readily identified by NMR spectroscopy) and suggests alane chain transfer as the dominant chain-functionalization/termination pathway (Scheme 13).[9c] Interestingly, metallocene-based chromium catalysts also mediate alane chain transfer in ethylene-polymerization systems.[9f,g] In this case, product polymer M_n value weight decreases approximately linearly with increasing AlR$_3$ concentration, suggesting alane chain transfer as the dominant chain-termination pathway. Furthermore, GC-MS analyses of the product oligomers indicate saturated chain ends after protonic work-up, again supporting an alane chain-termination pathway.



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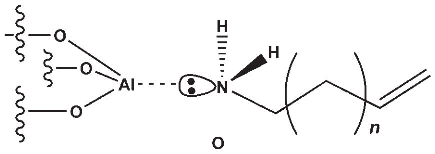
Metallocene-mediated alane chain transfer has also been reported for higher α-olefin polymerization processes, such as those involving 1-hexene,[10a] 1,5-hexadiene,[10d,e] styrene,[10c] and allylbenzene.[10b] In all of the higher α-olefin polymerization systems, aluminum-terminated product polyolefins yield completely saturated end groups on protonic work-up[10a–c] or hydroxy end groups after oxidative work-up.[10d,e] Addition of aluminum alkyls or MAO to these systems, depresses product polymer M_n values, implicating alane chain transfer as the dominant chain-termination mechanism. Metallocene-mediated chain transfer to aluminum is also reported for several copolymerization systems.[11] Thus, zirconocene-mediated alane chain transfer occurs efficiently and selectively for ethylene/propylene copolymerizations.[11a] ^{13}C NMR spectroscopy end-group analyses indicate that after protonic work-up, the majority of end groups are saturated isopropyl groups arising from chain transfer to aluminum. Zirconocene-mediated alane chain transfer also proceeds efficiently in ethylene/allylbenzene copolymerization processes.[11c,d] In this case, aluminum-terminated copolymer products are oxidatively worked-up to afford hydroxy-terminated copolymers, readily identified by NMR spectroscopy. Analysis by ^1H and ^{13}C NMR spectroscopy indicates complete conversion into hydroxy end groups with no detectable vinylic β-H elimination products. Furthermore, product copolymer M_n decreases approximately linearly with increasing MAO or AlR_3 concentration at constant catalyst and monomer concentration, again suggesting alane chain transfer as the kinetically dominant chain-termination pathway. Finally, zirconocene-mediated alane chain transfer has been found to be efficient in ethylene/aminoalkene copolymerizations.[11b] In this case, alane chain transfer is effected during the copolymerization, with activities as high as 10^6 g polymer/(mol Zr×atm ethylene × h). The activities are not depressed despite the presence of Lewis basic amine functional groups; this is probably a result of binding of the amine moieties by the Lewis acidic aluminum alkoxy species (e.g., **O**). NMR spectroscopic analyses of the product copolymers reveal saturated isopropyl end groups and the complete absence of any resonances for vinyl groups, suggesting that competing β-H elimination processes are negligible and that alane chain transfer is the dominant chain-growth termination pathway.



O

Additionally, the aluminum-terminated copolymer products can be converted into hydroxy-terminated copolymers by oxidative work-up, indicating selective transfer of aluminum to the polymer chain termini. Product copolymer M_n decreases approximately linearly with increasing MAO concentration at constant catalyst and monomer concentrations, again suggesting alane chain transfer as the dominant chain-termination mechanism (Scheme 13).

4.2. Non-Metallocene-Mediated Chain Transfer to Aluminum[12]

Alane chain transfer is operative, not only in metallocene-catalyzed olefin polymerizations, but also in non-metallocene single-site systems, demonstrating the pronounced versatility of alane chain-transfer agents. The majority of examples of alane chain transfer mediated by non-metallocene polymerization catalysts are for ethylene-polymerization processes.[12a,b,d–k] In these cases, early-transition-metal-based catalyst systems, including bis(phenoxyimine)-[12b] (**16**) and tris(pyrazolyl)borate-based[12e,g,h] (complexes **17**–**19**) catalysts undergo extremely efficient alane chain-transfer processes in conjunction with polymerization. In these examples, product polyethylene M_n values decrease approximately linearly with increasing MAO or $AlMe_3$ concentration at constant catalyst and ethylene concentration, consistent with alane chain transfer being the dominant operative chain-termination pathway. In addition, analysis by ^1H and ^{13}C NMR spectroscopy reveal saturated end groups and the absence of vinyl groups, again indicating that β-H elimination processes are negligible and that alane chain transfer dominates the chain-termination pathways. Chelating diamide-based titanium complexes **20** have also been employed to successfully mediate alane chain transfer in 1-hexene polymerizations.[12l] Again in these systems, the product poly(1-hexene) M_n decreases linearly with increasing MAO concentration at constant catalyst and 1-hexene concentration, thus indicating that alane chain transfer is the dominant chain-termination mechanism. ^1H and ^{13}C NMR spectroscopy reveals the presence of saturated end groups and the absence of vinyl groups, suggesting that β-H elimination processes are negligible compared to alane chain transfer. Similar results are obtained with an organoyttrium-mediated (**21**) ethylene-polymerization system in the presence of AlR_3-type ($R = C_1$–C_5 alkyl substituents) alkylaluminum compounds.[12a]

Late-transition-metal catalyst (**22**–**24**) mediated alane chain transfer is also reported to be efficient in ethylene-polymerization systems.[12d,f,i–k] These late-transition-metal systems produce polyethylenes with saturated end groups in the presence of aluminum alkyls (AlR_3) ($R = C_1$–C_5 alkyl substituents) or MAO, they have activities as high as 10^6 g polymer/(mol metal × atm ethylene × h). Furthermore, ^1H and ^{13}C NMR spectroscopy reveals the absence of vinyl end groups, indicating that β-H elimination is not an important chain-termination pathway in these processes. Finally, late-transition-metal-mediated alane chain transfer has been reported for single-site acrylate-polymerization systems, and the aforementioned criteria for efficient alane chain-transfer processes apply to these systems as well.[12c]

4.3. Organozinc Chain Transfer[33]

Organozinc compounds (ZnR_2, R = Et, Me, *i*Pr, CH_2Ph) have been explored as chain-transfer agents in single-site olefin-polymerization systems, albeit to a lesser extent than the aforementioned chain-transfer agents.[33] Diethylzinc has been used in bis(phenoxyimine)–Group 4 element mediated ethylene-polymerization systems to efficiently produce zinc-terminated polyethylenes with controlled molecular weight.[33a,c] These types of catalytic systems, in addition to systems based on hafnium pyridylamide, have also implemented organozinc compounds as efficient, selective chain-shuttling agents (molecules that efficiently convey polymer chains between catalytic sites) during olefin polymerization.[33a] In these cases, addition of diethylzinc to olefin-polymerization systems produces zinc-terminated polyolefins as well as transferring polyolefin chains to other catalyst sites to efficiently and selectively create unique block copolymers. The aforementioned dialkylzinc compounds have also been successfully implemented into bis(imino)pyridine iron mediated ethylene-polymerization systems to afford zinc-terminated polyethylenes of controlled molecular weight, with activities up to 140×10^4 g polymer/(mol × atm ethylene × h).[33b] Finally, analogous polymerization systems employing GaR_3 (R = Et, *n*Bu, Me) chain-transfer agents also efficiently produce gallium-terminated, low-molecular-weight polyethylenes.[33b]

4.4. Organomagnesium Chain Transfer[34]

Another group of lesser-explored chain-transfer agents encompasses organomagnesium compounds. Organolanthanide-mediated synthesis of polyolefins in the presence of dialkylmagnesium reagents (MgRR′, R,R′ = Et, *n*Bu, *s*Bu, *n*-hexyl, Me_3SiCH_2) affords magnesium-terminated polyolefins with controlled molecular weight. These systems efficiently and selectively produce magnesium-terminated syndiotactic polystyrene,[34a] polyethylene,[34b,d] and ethylene–methyl methacrylate (MMA) block copolymers.[34c] In this case, the absence of vinyl resonances in the product polymer ^{1}H NMR spectra suggest chain transfer to magnesium as the dominant chain-transfer pathway. Additionally, these magnesium-terminated polyolefins can undergo further reaction sequences to produce a variety of microstructures, such as star-shaped polymers and block copolymers.

5. Electron-Rich Chain-Transfer Agents

5.1. Metallocene-Mediated Phosphine Chain Transfer[15]

In the preceding Sections, we have discussed catalytic processes where addition of electron-deficient/neutral chain-transfer agents to single-site olefin-polymerization systems results in selective and catalytic chain termination and polyolefin functionalization. The heteroatom–carbon bond-formation step involves a four-center σ-bond metathesis process which cleaves the metal–polymeryl linkage (Schemes 2, 8–11). Now we shall discuss the much less explored scope and mechanism of complementary electron-rich chain-transfer agents in metallocene-mediated olefin polymerization (Scheme 3). In the first example, alkyl- and aryl- as well as dialkyl- and diarylphosphines (Figure 11) were used to efficiently functionalize and terminate polyethylene chains in organolanthanide catalytic systems.[15] In these {Cp^*_2LnR}-mediated (R = alkyl or polymeryl group) ethylene polymerizations, activities as high as 10^7 g polymer/(mol Ln × atm ethylene × h) are observed in the presence of a variety of primary and secondary phosphine chain-transfer agents. The phosphine-capped product polyethylenes give characteristic ^{1}H NMR spectra with resonances at $\delta = 2.3$ ppm for -CH_2PR_2 end groups in 1:1 proportion to the signals for -CH_3 end groups. Additionally, the ^{31}P NMR spectra reveal a single resonance corresponding to tertiary phosphine end groups. ^{1}H and ^{13}C NMR spectra of product functionalized polyethylenes demonstrate the absence of vinyl groups, indicating that β-H elimination is not an important chain-growth termination pathway (Figure 12).

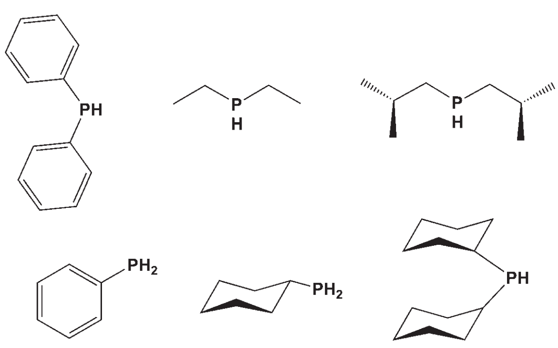


Figure 11. Phosphine chain-transfer agents used in lanthanocene-mediated olefin polymerization.

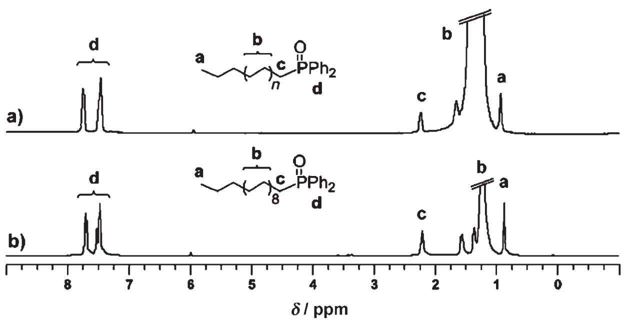


Figure 12. ^{1}H NMR spectra (500 MHz, $C_2D_2Cl_4$) of a) diphenylphosphine oxide terminated polyethylene synthesized by in situ generated [$Cp^*_2YPPh_2$] and b) 1-eicosyldiphenylphosphine oxide model for the product.

The chain-transfer efficiency trends for various phosphines parallel those of the rates for the protonolysis of [$Cp^*_2Ln\text{-}CH(SiMe_3)_2$] (**1b**) by the same phosphines:

$$H_2PPh \gg H_2PCy > HPPh_2 > HPEt_2 \approx HP\mathit{i}Bu_2 > HPCy_2$$

The product polyethylene M_n values in these experiments decreases linearly with increasing HPR_2 concentration at constant catalyst and ethylene concentration, indicating phosphine chain transfer to be the dominant chain-transfer process in these systems (Figure 13). Furthermore, primary phosphines are found to be extremely efficient chain-transfer agents, producing only low-molecular-weight oligomers, whereas the rates of protonolyses for secondary-phosphine chain-transfer agents are somewhat slower, affording higher-molecular-weight polyolefins under the same reaction conditions. Interestingly, theoretical DFT/B3LYP-level studies of organolanthanide-mediated small-molecule hydrophosphination suggest that protonolysis of the Ln–C bond by incoming phosphine substrate (step C, Scheme 6) is turnover limiting.[24] This result stands in contrast to theoretical results for hydroamination, where olefin insertion into the Ln–N bond

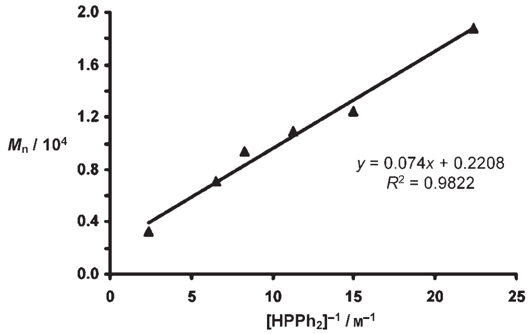
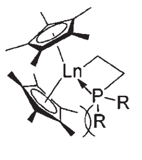
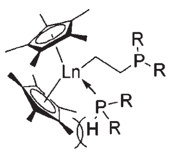


Figure 13. Relationship of diphenylphosphine-capped-polyethylene number-average molecular weight (GPC vs. polyethylene standard) to inverse diphenylphosphine concentration at constant {Cp^*_2Ln} catalyst and ethylene concentrations.

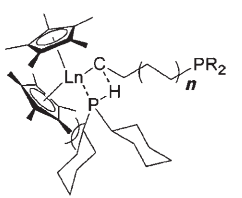
(step C, Scheme 7) is found to be turnover limiting.[26] The higher-molecular-weight polymers produced with secondary phosphines are likely a consequence of the increased steric repulsions between the catalyst ancillary ligands and the polymeryl fragment (e.g., **P** and **Q**) resulting in less-favorable coordination of the phosphine to the Ln center, promoting more rapid propagation (**P**) and depressing the rate of chain-terminating protonolysis (**Q**). Note that $HPCy_2$ (Cy = cyclohexyl) is not an efficient chain-transfer agent under these conditions for organolanthanide-mediated ethylene polymerization, presumably a consequence of severe nonbonded repulsions, as illustrated in transition state **R**.



P

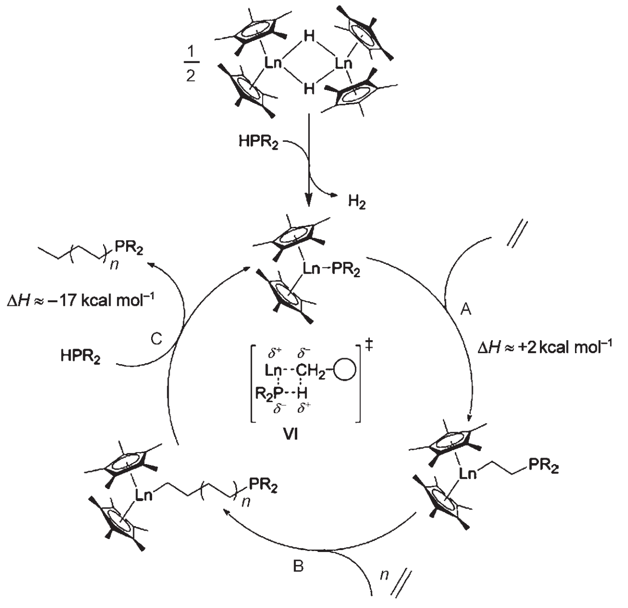


Q

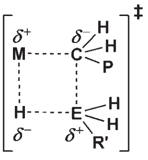


R

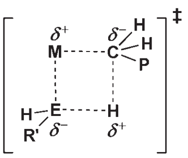
The effect of the metal ionic radius on the polymerization activity for phosphine-capped-polyethylene synthesis parallel that observed for intramolecular hydrophosphination/cyclization (Scheme 6), where protonolysis of the Ln–C bond by incoming phosphine substrate may be turnover limiting: Y > Lu, Sm > La. The proposed catalytic cycle for the synthesis of phosphine-capped polyethylenes follows the sequence: A) C=C insertion into the lanthanide–phosphido bond, B) multiple C=C insertions into the Ln–alkyl bond, C) chain termination by protonolysis of the polymer chain and regeneration of the lanthanide–phosphido active species (Scheme 14). Theoretical studies on key reaction sequences support experimental evidence for the phosphine chain-transfer processes outlined above.[23] Note that the electronic structure of transition state **II** (Scheme 2) for electron-deficient chain-transfer agents is significantly different from transition state **IV** (Scheme 3) for electron-rich chain-transfer agents, where heteroatom delivery to carbon occurs at the beginning of the polymerization cycle.[28]



Scheme 14. Catalytic cycle for organolanthanide-catalyzed synthesis of phosphine-terminated polyethylenes.



II



IV

5.2. Metallocene-Mediated Amine Chain Transfer[16]

Amines also have the potential to be effective chain-transfer agents in metallocene-mediated olefin polymerizations. However, the catalytic introduction of amines into such polymerization processes requires careful attention to steric and electronic factors because Ln–C protonolyses by amines are approximately 10^4-times more rapid than for the corresponding phosphines.[22] Thus, the amine reagent must not be so sterically encumbered as to hinder efficient olefin enchainment yet must not be so protonolytically reactive as to prematurely terminate chain propagation.

Catalytic and selective amine chain-transfer processes in ethylene polymerizations mediated by **1b** were recently reported.[16] In these systems, dicyclohexylamine and diisopropylamine are found to exhibit the optimum balance of desired ethylene propagation rate versus amine-originated chain-termination rate. Thus, the ^1H and ^{13}C NMR spectra of the product dicyclohexylamine-capped polyethylenes reveal characteristic -CH_2NR_2 resonances ($\delta = 2.4$ ppm and $\delta = 61$ ppm, respectively) with an approximately 1:1 CH_2NR_2:CH_3 chain-end-resonance ratio, indicative of a single amine functionality at the terminus of each polyethylene chain (Figure 14). Furthermore, at constant catalyst and ethylene concentration, product polyethylene M_n decreases linearly with increasing dicyclohexylamine concentration,

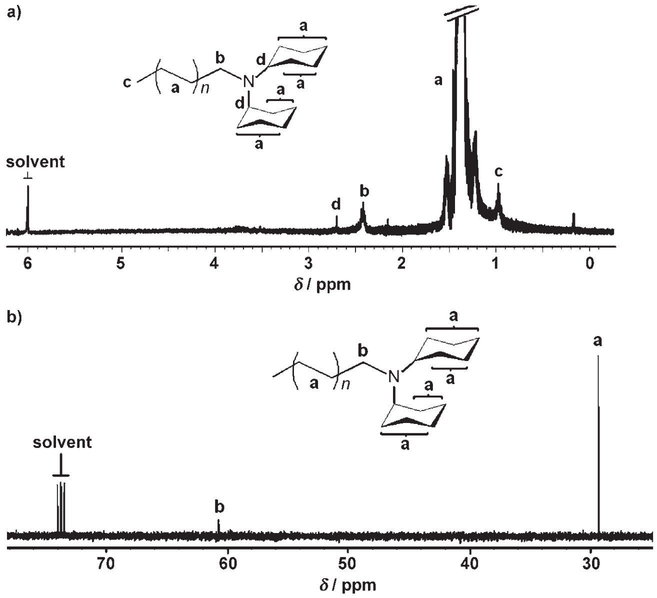


Figure 14. a) ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) spectrum and b) ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) spectrum of a dicyclohexylamine-capped polyethylene ($M_n = 131\,600$) produced by polymerization mediated by **1b**.

arguing that amine chain transfer is the dominant chain termination mechanism in these organolanthanide systems (Figure 15).

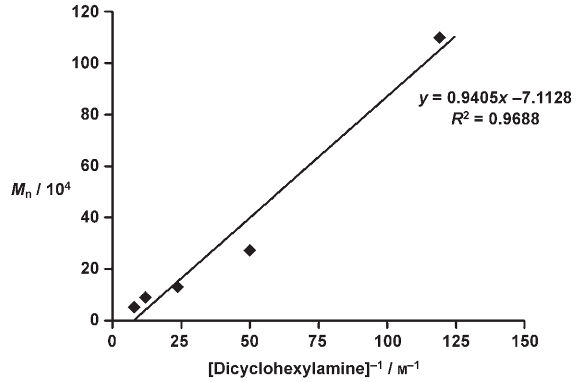
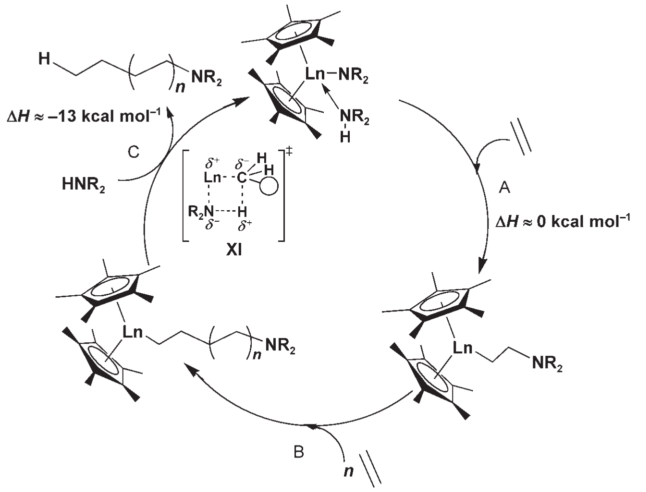


Figure 15. Relationship of polyethylene number average molecular weight (GPC versus polyethylene standard) to inverse $(C_6H_{11})_2NH$ concentration at fixed catalyst and ethylene concentrations for **1b**-catalyzed ethylene polymerization with amine chain transfer.



Scheme 15. Catalytic cycle for organolanthanide-mediated ethylene polymerization in the presence of amine.

The proposed catalytic cycle for amine-capped-polyethylene synthesis proceeds by sequences of well-precedented: A) insertion of C=C unsaturation into the Ln–N bond, B) multiple C=C incorporation into the growing polymer chain, and C) Ln–polymeryl protonolysis with simultaneous regeneration of the lanthanide amido active species to close the cycle (Scheme 15, transition state **XI**). DFT/B3LYP-level computational studies on key reaction sequences in aminoalkene hydroamination/cyclization support this mechanistic scenario.[26] The influence of the Ln^{3+} ionic radius on polymerization activity for amine-capped-polyethylene formation exactly parallels that of organolanthanide-catalyzed small-molecule hydroamination/cyclization,[25] with larger lanthanides exhibiting the greatest polymerization activity and high product molecular weights: La > Sm > Y > Lu. In contrast to the results obtained with dicyclohexylamine, organolanthanide-catalyzed ethylene polymerization in the presence of diisopropylamine only produces diisopropylamine-capped oligoethylenes of the type $H(CH_2CH_2)_nN(i\text{Pr})_2$ ($n = 10$–17) as indicated by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry. Other amine chain-transfer agents that have been studied include $(SiMe_3)_2NH$, $PhNH_2$, $(SiMe_3)(t\text{Bu})NH$, and $HN(sec\text{Bu})_2$, and result in products derived from either 1–8 ethylene insertions or no detectable insertion. Further studies on the scope and mechanism of amine chain transfer in olefin-polymerization systems are underway.

Lastly, it is noteworthy to mention that thiophene chain transfer is also possible in lanthanocene-catalyzed olefin-polymerization processes, invoking a mechanism similar to those seen above for electron-rich chain-transfer agents (Scheme 3) with a thiophene C–H bond effecting the Ln–polymeryl cleavage.[35] Interestingly, in these $\{Cp^*_2Ln\}$ systems, high ethylene pressures ranging from 2.5 to 7.5 bar are required to produce solid, polymeric products. The ^{1}H NMR spectra of the product polymers indicate a 1:1 CH_3:C_4H_3S chain-end ratio. Furthermore, GC-MS analyses of the quenched volatile polymerization mixture reveal an excess of monoethylene insertion products. These systems show that at high ethylene pressures, thienyl moieties can be catalytically introduced into a polyethylene chain end.

6. Summary and Outlook

The outstanding efficiency of heteroatom chain-transfer agents in controlling polyolefin molecular weight while effecting in situ introduction of heteroatom functional groups led to the exploration of electron-deficient/neutral and electron-rich chain-transfer agents in a variety of single-site olefin-polymerization systems. Alkyl-, aryl-, and alkenylsilanes are shown to be efficient in metallocene-mediated olefin homo- and copolymerization systems. These systems exhibit high polymerization activities, selectivities, and control of polymer microstructure in the presence of silanes. Silanes can play the role of either robust macromolecule linking groups or precursors of other functional groups. Metallocene-mediated olefin polymerizations in the presence of boranes are likewise shown to be extremely efficient with high productivities and selectivities, and with the reactive boron groups being versatile synthons. Alane chain-transfer processes span a great range of metallocene- and non-metallocene-mediated olefin-polymerization systems and exhibit good efficiencies with control of polymer molecular weights. Polymer–alane substituents are readily converted into other functional groups. Organozinc and organomagnesium compounds also effect selective, efficient chain-transfer processes to produce chain-end functionalized polyolefin products.

The mechanisms of all of these electron-deficient/neutral reagent chain-transfer processes differ substantially from those of electron-rich reagent chain-transfer processes. The mechanistic sequences differ in heteroatom–carbon atom bond formation at the end (electron-deficient/neutral reagents) versus at the beginning (electron-rich reagents) of the polymer-forming catalytic cycles. In spite of this difference, the electron-rich systems can exhibit high productivities and selectivities. Phosphine chain transfer is found to be extremely efficient and selective for a variety of lanthanocene-mediated polymerization systems, allowing the introduction of electron-rich chain-transfer agents into olefin polymerizations for the first time. Subsequently, amines have also been demonstrated as efficient and selective chain-transfer agents in lanthanocene-mediated olefin-polymerization systems.

The wide scope of elements useful in chain-transfer processes as well as the complementary nature of electron-deficient/neutral and electron-rich chain-transfer agents illustrates the diverse possibilities in this research area. The use of chain-transfer agents in olefin-polymerization systems affords control of functionalization, reactivity, molecular weight, and microstructure of the polyolefin products. Expanding and applying this type of chain-transfer methodology to new elements and new catalytic olefin-polymerization systems will be the next step in the continued effort to understand, control, and elaborate olefin-polymerization processes.

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