Secondary Alkene Insertion and Precision Chain-Walking: A New Route to Semicrystalline "Polyethylene" from α-Olefins by Combining Two Rare Catalytic Events

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Ⓢ *Supporting Information*

ABSTRACT: While traditional polymerization of linear α-olefins (LAOs) typically provides amorphous, low T_g polymers, chain-straightening polymerization represents a route to semicrystalline materials. A series of α-diimine nickel catalysts were tested for the polymerization of various LAOs. Although known systems yielded amorphous or low-melting polymers, the "sandwich" α-diimines **3−6** yielded semicrystalline "polyethylene" comprised primarily of unbranched repeat units via a combination of uncommon regioselective 2,1-insertion and precision chain-walking events.

Linear α-olefins (LAOs) are versatile monomers that can be readily sourced from both petrochemical and bioderived feedstocks. Synthetic routes to LAOs include decarbonylative dehydration of fatty acids,[1] ethenolysis of their unsaturated derivatives,[2] and oligomerization of ethylene.[3] The latter generates a distribution of α-olefins of varying chain-length. These olefins have diverse applications: 1-hexene and 1-octene are used as comonomers for the synthesis of linear low density polyethylene (LLDPE), low molecular weight poly(1-decene) is primarily used in synthetic lubricants, and C_{12}−C_{18} olefins are converted into detergents.[3b,4] Homopolymerization of these α-olefins with conventional Group IV heterogeneous and metallocene catalysts results in amorphous polyolefins with *n*-alkyl side-chains (see Scheme 1, 1,2-enchained units) that have important uses as industrial lubricants, but limited use as thermoplastics. We are interested in developing new catalysts that can polymerize α-olefins via unique reaction mechanisms. In particular, we have focused on generating semicrystalline polymers similar to polyethylene from LAOs such as 1-decene. The desired process involves two relatively uncommon mechanistic steps: (1) a regioselective 2,1-olefin insertion and (2) controlled "chain-walking"—a series of sequential β-hydride eliminations, alkene rotations, and reinsertions that relocates the active metal center along the growing polymer chain.[5] Only a handful of olefin polymerization catalysts are known to enchain terminal olefins via a secondary insertion mechanism.[6] Despite the partial chain-straightening ability of known α-diimine complexes of Ni and Pd,[7] competing olefin insertion pathways and nonselective enchainment lead to branched polymers with a low degree of crystallinity. For example, the mode of insertion

with the α-diimine Ni(II) complexes reported by Brookhart and coworkers (e.g., **1**, Scheme 1) is regiorandom,[5a,b] while related catalysts (e.g., **2**) exhibit predominantly 1,2-insertion and precise chain-walking at low temperatures.[7] Osakada and coworkers have also reported controlled chain-walking polymerization of 4-alkyl cyclopentenes[8] and alkyl substituted 1,6-dienes[9] using α-diimine Pd(II) catalysts to afford regioregular polymers.

Scheme 1 outlines the chain-walking polymerization of α-olefins (where ω = the number of carbon atoms in the α-olefin). Provided that the active metal undergoes predominant chain-walking to the ω-carbon following insertion, 1,2-insertion leads to an ω,2-unit while 2,1-insertion installs an ω,1-unit in the polymer backbone.[10] If the metal fails to chain-walk after 1,2-insertion, the final polymer will contain *n*-alkyl branches or 1,2-units found in common poly(α-olefin)s. The amount and type of branching will dictate the properties of chain-straightened polymers, especially the crystallinity. For example, 1,2-units will disrupt the crystallinity more than ω,2-units since methyl branches can pack into the polyethylene crystals, but *n*-alkyl branches cannot.[11] As such, polymers with highly branched microstructures will be amorphous or semicrystalline with low-melting points.

We hypothesized that the presence of substantial axial bulk and appropriate functionality on the α-diimine framework might favor the desired 2,1-insertion and permit precise chain-walking to give predominantly ω,1-units in the polymer. Molecular modeling suggests that sterically hindered aryl substituted naphthyl α-diimine catalysts (**3−6**) may influence the regiochemistry of insertion and inhibit associative displacement of the growing polymer chain. Brookhart, Daugulis, and coworkers recently reported a "sandwich" (naphthyl α-diimine)-nickel(II) catalyst (**3**) for ethylene polymerization to generate highly branched polymers.[12] Despite the nonlinear topology of polyethylene generated from **3**, we decided to investigate this class of catalysts for polymerization of LAOs. Herein, we describe the unique polymerization behavior of aryl naphthyl nickel(II) polymerization catalysts (**3−6**) for the conversion of commodity α-olefins to substantially linear, semicrystalline polymers, structurally equivalent to linear low-density polyethylene. At low monomer concentration, these catalysts show predominant 2,1-insertion and precise chain-walking. To the best of our

Scheme 1. Modes of α-Olefin Enchainment and α-Diimine Nickel Catalysts
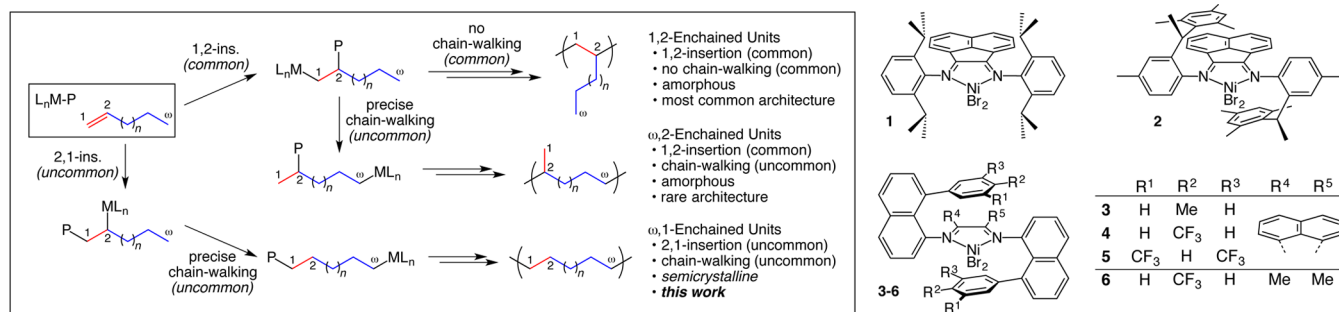
Table 1. Polymerization of 1-Decene by α-Diimine Nickel(II) Complexes[a]

								mole fraction of C_{10} units $(\chi)^d$			
entry	cat.	[1-decene] (M)	toluene (mL)	t_{rxn} (h)	yield (g)	TON[b]	M_n^c (kg/mol)	M_w/M_n^c	linear (χ_L)	methyl-branched (χ_M)	alkyl-branched (χ_A)	$T_m^{\ e}$ (°C)
1	1	3.53	0.0	0.2	1.31	1868	148	1.7	0.32	0.15	0.53	—[f]
2	1	2.07	5.0	0.2	0.51	727	86	1.8	0.43	0.25	0.32	—[f]
3	2	3.53	0.0	1.0	1.06	1517	131	1.5	0.30	0.20	0.50	—[f]
4	2	2.07	5.0	1.0	0.63	903	100	1.8	0.34	0.29	0.37	—[f]
5	3	3.53	0.0	2.0	0.29	415	58	1.1	0.54	0.24	0.22	60[g]
6	3	2.07	5.0	3.0	0.33	472	69	1.1	0.59	0.22	0.19	69[g]
7	3	0.10	37.0	24.0	0.09	128	21	1.4	0.68	0.21	0.11	96[g]
8	4	3.53	0.0	2.0	0.30	431	70	1.1	0.52	0.18	0.30	63[g]
9	4	2.07	5.0	3.0	0.25	361	76	1.1	0.65	0.16	0.19	75[g]
10	4	1.13	15.0	24.0	0.43	612	151	1.1	0.68	0.17	0.15	84[g]
11	4	0.10	37.0	24.0	0.06	86	32	1.2	0.77	0.16	0.07	106
12	4	0.05	38.0	48.0	0.06	81	25	1.3	0.77	0.17	0.06	106
13[h]	5	0.10	37.0	24.0	0.02	8	8	1.2	0.74	—[i]	—[i]	108
14[h]	6	0.10	37.0	24.0	0.05	22	10	1.3	0.76	0.15	0.09	109

[a]Polymerization conditions: Ni = 5 μmol in chlorobenzene (2 mL), [MAO]/[Ni] = 200, T_{rxn} = 22 °C, toluene. [b]TON (turnover number) = (mol 1-decene consumed)/(mol Ni). [c]Determined using gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C vs polyethylene standards. [d]Determined using ^{1}H NMR spectroscopy. [e]Peak melting point (second heat) determined using DSC. [f]No T_m. [g]Broad endotherm. [h]Ni = 17 μmol. [i]$\chi_M + \chi_A$ = 0.26, overlapping NMR signals.

knowledge, this is the first example of polymerization of LAOs such as 1-decene to semicrystalline polyethylene-type materials with melting temperatures (T_m) >100 °C.[5a,b,7b,13]

We initially screened six different methylaluminoxane (MAO) activated α-diimine Ni(II) catalysts at varying 1-decene concentration (Table 1). Polymers were analyzed by quantitative NMR spectroscopy to obtain mole fractions of the three major C_{10} units: linear (χ_L), methyl-branched (χ_M), and alkyl-branched (χ_A) (see SI for details).[14] Polymerization using the prototypical Brookhart catalyst (**1**) at two different concentrations (3.53 and 2.07 M) leads to amorphous polymers (no T_m observed) with relatively broad molecular weight distributions (entries 1−2). While the mole fraction of linear enchainment (χ_L) increases from 0.32 to 0.43, the polymer remains amorphous. A more sterically encumbered Ni(II) α-diimine, **2**, which is known for preferential 1,2-insertion, is also ineffective at producing crystalline material (entries 3−4). To probe the behavior of sandwich α-diimines, complex **3** (R^1 = R^3 = H, R^2 = Me) was tested. The use of the **3** results in a considerable decline in χ_A and χ_M, while χ_L increases to 0.54 (entry 5). In addition to the effect observed by the use of the sandwich ligand, a reduction in 1-

decene concentration leads to a significant increase in the T_m and χ_L of the resulting polymer with a considerable decline in χ_A (entries 5−7). With [1-decene] = 0.10 M, χ_L rises to 0.68, generating semicrystalline polymer with T_m = 96 °C (entry 7). The observed trend suggests that lowering the concentration of 1-decene results in fewer long-chain branches in the final polymer.

To probe the substituent effects of the naphthyl sandwich framework on polymer properties, catalyst **4** (R^1 = R^3 = H, R^2 = CF$_3$; see Figure 1 for X-ray structure) was screened under a parallel set of reaction conditions (entries 8−12). DSC analysis of polymers produced by **3** and **4** revealed broad endotherms for both polymers at high monomer concentration (3.53 M). However, a closer analysis of the DSC traces indicated that **4** generates polymer with higher melting points in comparison to **3** (see SI). In addition, there is a remarkable correlation between the concentration of 1-decene and the T_m of the resulting polymer from **4** (Figure 2). As monomer concentration is decreased, the melting endotherms begin to resemble that of semicrystalline polyethylene. In-depth analysis of the polymer architecture using quantitative ^{13}C NMR spectroscopy revealed
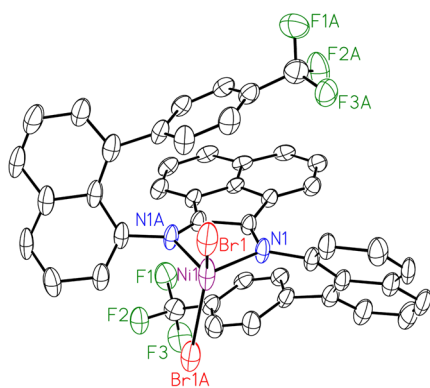
Figure 1. X-ray crystal structure for **4**. Hydrogen atoms are omitted for clarity. Atoms drawn at 40% probability level.
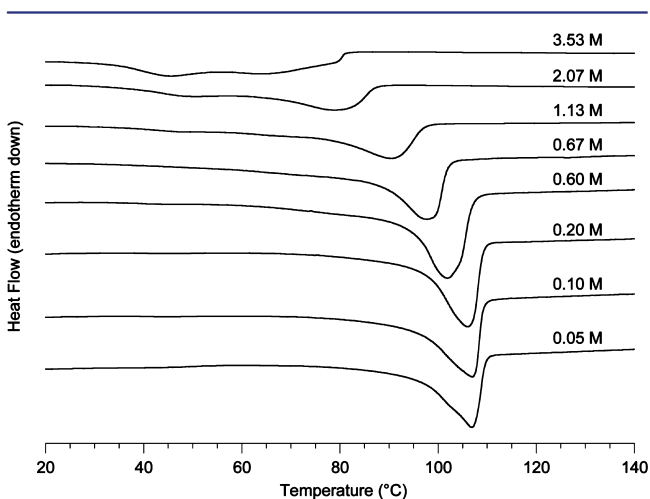

Figure 2. DSC traces of polymers obtained using **4** at different concentrations of 1-decene at 22 °C (Table 1, entries 8−12 and SI).

the presence of a relatively intense polyethylene (CH$_2$) signal at 29.2 ppm and other low intensity signals from methyl and alkyl branch defects (Figure 3). Similar to the trend observed with DSC measurements, ^{13}C NMR spectra show a drastic reduction
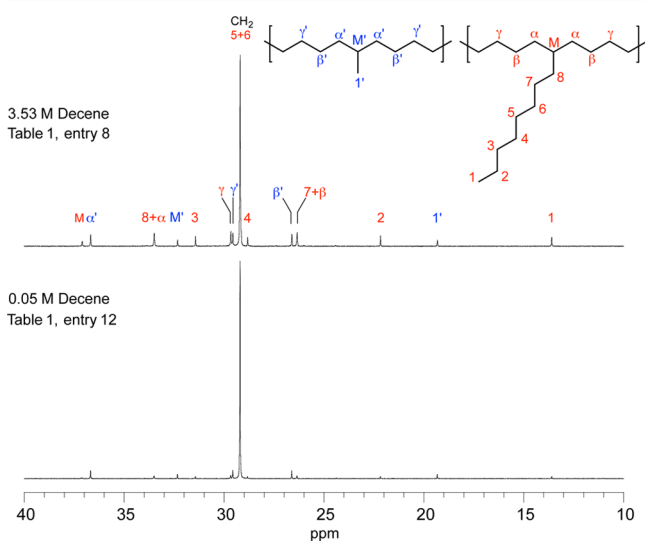

Figure 3. ^{13}C NMR spectra and assignments of polymers obtained using **4** (Table 1, entries 8 and 12).

in the amount of branching with decreasing 1-decene concentration. In sharp contrast to the results observed for **1**−**3**, at 0.10 M of 1-decene, the observed T_m of the polymer produced by **4** is 106 °C with $\chi_L = 0.77$ (entry 11). Lowering the 1-decene concentration below 0.10 M does not further enhance the polymer crystallinity (entry 12). Surprisingly, decreasing the concentration of 1-decene has a profound effect on χ_L, while χ_M remains relatively constant. It is possible that monomer concentration determines the microstructure either by influencing the regiochemistry of olefin insertion or by diminishing partial chain-walking.[14]

To further investigate the effect of naphthyl substituents on the chain straightening polymerization, complexes **5** and **6** were tested. It is worth noting that **5** (R^1 = R^3 = CF$_3$, R^2 = H) creates polymer of higher T_m (108 °C) but shows lower activity than **4** (entry 13). Altering the backbone diimine from acenaphthene to dimethyl (**6**, R^1 = R^3 = H, R^2 = CF$_3$) results in a polymer with T_m of 109 °C (entry 14). While both **4** and **6** produce semicrystalline material, a closer analysis of the DSC traces reveals that the polymer from **4** has a relatively sharp melting transition compared to **6**. In light of overall performance and polymer properties, **4** was selected for further investigation.

Optimization of 1-decene polymerization with respect to catalyst concentration, various types and amounts of activators, 1-decene concentration, and solvents led to the following observations: (a) the catalyst concentration has no significant effect on the T_m, (b) dried MAO is the optimal cocatalyst for **4**, and (c) chlorobenzene is an effective solvent compared to less polar solvents. Reaction temperatures above 22 °C reduce the efficacy of **4** in terms of M_n, M_w/M_n, and T_m (see SI). Catalyst **4** provides the best combination of activity and polymer crystallinity, although it should be noted that these materials are more similar to linear low-density PE rather than high-density PE on the basis of their melting points. In addition, polymers produced by **4** at 22 °C have a very narrow molecular weight distribution (<1.3), consistent with living polymerization behavior. At 0 °C, **4** generates semicrystalline polyethylene with a T_m of 107 °C, χ_L of 0.80 and enthalpy of fusion ($-\Delta H_m^f$) of 112 J/g. A further reduction in temperature does not result in an increase in T_m, and catalyst activity decreases substantially.

These results prompted us to evaluate the scope of this polymerization with other LAOs at 0.1 M (Table 2). Each LAO leads to semicrystalline polyethylene with primarily ω,1 enchainment units with χ_L ranging from 0.63 to 0.77 (entries 1−4). An increase in the monomer chain length shows a corresponding increase in T_m. With 1-octadecene as the monomer, the T_m of the polymer rises to 113 °C (entry 4). Complex **4** is successful at generating semicrystalline polymers from different monomers; qualitatively, the polymers exhibit very similar ^{13}C NMR spectra, i.e., a distinct polyethylene CH$_2$ signal at 29.2 ppm with minor signals from branching (Figure 3 and SI).

To assess the practicality of the process, an equimolar mixture of multiple LAOs (C$_6$, C$_8$, C$_{10}$, and C$_{18}$) was polymerized by **4**/MAO. For comparison purposes, the total olefin concentration was maintained at 0.1 M (0.025 M each). Remarkably, the polymerization led to semicrystalline polyethylene with a melting point of 103 °C (Figure 4). This result suggests that semicrystalline polyethylene can be prepared from mixed α-olefin feeds, reducing the need for tedious separation processes.

In conclusion, we report that bulky "sandwich" α-diimine Ni(II) catalysts convert α-olefins into semicrystalline polymers with T_m >100 °C. Quantitative NMR analysis of the polymers suggests that the catalysts are highly selective for 2,1-insertion

Table 2. Polymerization of Linear α-Olefins by 4[a]

entry	α-olefin	yield (g)	TON[b]	M_n[c] (kg/mol)	M_w/M_n[c]	mole fraction of units (χ)[d]			$-\Delta H_m$[e] (J/g)	T_m[e] (°C)
						linear (χ_L)	methyl-branched (χ_M)	alkyl-branched (χ_A)		
1	1-hexene	0.08	195	24	1.3	0.76	0.17	0.07	77	95
2	1-octene	0.04	78	18	1.3	0.73	0.17	0.10	79	99
3	1-decene	0.06	86	32	1.2	0.77	0.16	0.07	76	106
4	1-octadecene	0.06	45	25	1.3	0.63	0.14	0.23	97	113

[a]Polymerization conditions: [α-olefin] = 0.1 M, catalyst 4 = 5 μmol in 2 mL chlorobenzene, [MAO]/[4] = 200, T_{rxn} = 22 °C, t_{rxn} = 24 h, toluene (37 mL). [b]TON = (mol α-olefin consumed)/(mol Ni). [c]Determined using GPC in 1,2,4-trichlorobenzene at 150 °C vs polyethylene standards. [d]Determined using ^{1}H NMR spectroscopy, see SI for detailed calculations. [e]Enthalpy and peak melting point (second heat) determined using DSC.
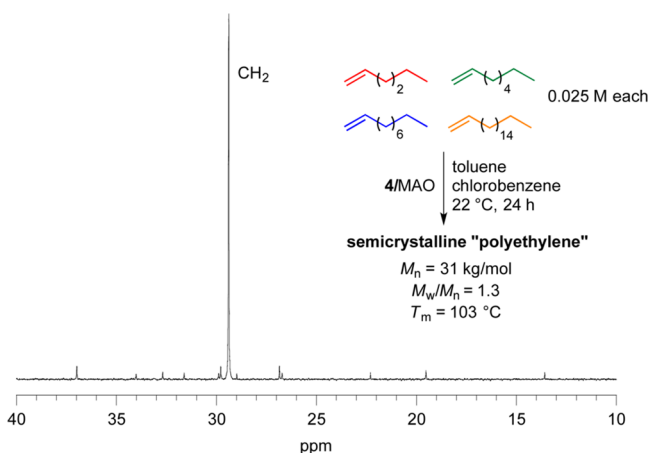

Figure 4. Single-pot polymerization of a mixture of linear α-olefins using catalyst 4 (see Figure 3 for assignment of defect peaks).

followed by precise chain-walking. A mixture of α-olefins may be used to generate substantially linear material. We are currently investigating the polymerization mechanism in more detail to facilitate the development of catalysts with better control of regiochemistry as well as employ these catalysts for the polymerization of other α-olefins.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) Although methyl- and alkyl-branched units likely result from 1,2-insertion with and without chain-walking, respectively, we cannot rule out other mechanisms, including incomplete chain-walking.