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# Living Polymerization of α-Olefins with an α-Diimine Ni(II) Catalyst: Formation of Well-Defined Ethylene−Propylene Copolymers through Controlled Chain-Walking

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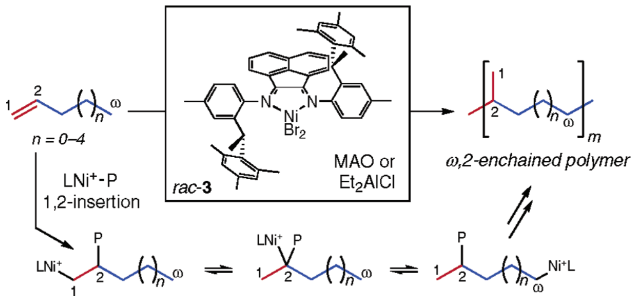
Living olefin polymerization catalysts[1] that control polymer microstructure enable the development of new polymers from inexpensive, readily available monomers. In 1996, Brookhart and co-workers reported the living polymerization of propylene, 1-hexene, and 1-octadecene with nickel α-diimine complexes/methylaluminoxane (MAO) of the general form (ArN═C(1,8-naphthalenediyl)C═NAr)-NiBr$_2$.[2] Polymerizations with complexes **1**/MAO (Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$) and **2**/MAO (Ar = 2-$^t$BuC$_6$H$_4$) provided polymers with narrow molecular weight distributions. In addition, this class of catalysts produces polyolefins with a unique microstructure due to the ability of the metal center to randomly migrate along the growing polymer chain via a series of $\beta$-hydride eliminations/reinsertions—a process referred to as "chain-walking".[3,4] For example, the polymerization of 1-hexene with **1**/MAO produces a highly regioirregular polymer with backbone methylene sequences of varying lengths with methyl, butyl, and longer side chains.[3,5] Herein we report the living and *regioregular* polymerization of α-olefins using *rac*-**3**/MAO (Scheme 1), a $C_2$-symmetric catalyst based on bulky chiral anilines[6] previously reported by us for the synthesis of regioblock copolymers from propylene.[7] Under optimized conditions, a high selectivity for $\omega$,2-enchainment is exhibited, resulting in amorphous ethylene−propylene (EP)-type polymers comprised of methylene sequences of precise lengths between methyl branches. A prior example of such materials has been reported by Fink and co-workers.[8] Using a Ni$^0$ aminobis(imino)phosphorane catalyst, linear C$_5$ and C$_9$ α-olefins were oligomerized primarily by $\omega$,2-enchainment to form oligomers with $M_n \approx 1000$ g/mol. The work described herein demonstrates that controlled chain-walking coupled with living behavior allows for the synthesis of EP copolymers with tailored molecular weight and "ethylene" content.

Scheme 1 depicts the polymerization of α-olefins with *rac*-**3** under optimized conditions whereby 1,2-insertion of the α-olefin into the Ni−polymer bond followed by chain-walking to the $\omega$-position results in $\omega$,2-enchainment. As the reaction conditions are changed, a second enchainment mechanism becomes operative; a 2,1-insertion of monomer followed by chain-walking to the $\omega$-position leads to $\omega$,1-enchainment. The result of this is the placement of monomer into the growing polymer chain in a linear fashion. The predominant regioerror evident in α-olefin polymerizations with *rac*-**3** appears to be monomer insertion into metal secondary alkyl species resulting in nonmethyl branches.

Reaction conditions for 1-hexene polymerization with *rac*-**3** were varied in an attempt to maximize selectivity for 6,2-enchainment (Table 1). Entries 1−3 show that, as the concentration of 1-hexene is increased, the mole fraction of 6,2-enchainments is increased and is offset by a decrease in enchainments arising from 2,1-insertion. This very unusual concentration influence on the mode of monomer insertion has also been observed for 1-hexene polymerization with **1**/MAO[9] and with **2**/MAO.[10] While the cause of this phenomenon is unknown, the role of reaction medium polarity can be ruled out. In addition, entries 5−7 indicate that as $T_{\mathrm{rxn}}$ is decreased the amount of 6,2-enchainments in the polymer is increased. Entries 4 and 9 show that enchainments containing branches of four or more carbons predominate in the poly(1-hexene)s formed by **1**.

***Scheme 1.*** Polymerization of α-Olefins with *rac*-**3**



A series of poly(α-olefins) formed under optimized conditions is presented in Table 2. As the length of the α-olefin increases, the amount of $\omega$,2-enchainments decreases in favor of enchainments containing branches longer than methyl. Because the barrier of insertion into a metal secondary alkyl decreases with increased distance from a branch point, the likelihood of migration to the methyl carbon of the inserted monomer decreases for longer α-olefins. Figure 1 provides $^{13}$C NMR spectra for some of the polymers given in Table 2. The fine structure in the spectrum of poly(1-butene) is indicative of moderate isotacticity.[11b]

Other routes to the polymers given in Table 2 have been reported. For example, the poly(1-butene) described here is isostructural with poly(*trans*-2-butene) made using various Ni α-diimine complexes.[11] The poly(1-pentene) described here can be prepared by the alternating copolymerization of ethylene and propylene,[12] or by hydrogenation of polyisoprene or 1,4-poly(1,3-pentadiene).[13] In addition, the ring-opening metathesis polymerization (ROMP)/hydrogenation of cyclic alkenes and dienes can produce some of the polymers described here.[14] A more general route to these EP-type polymers is through acyclic diene metathesis (ADMET) polymerization of symmetrical methyl-substituted α,$\omega$-dienes, which can furnish polymers with precise methylene sequences (ranging in length from 6 to 20) between methyl branches.[15] However, the route described here is the only one that allows for the formation of EP-type polymers of variable structure in a living fashion without the need for laborious monomer synthesis or post-polymerization hydrogenation.

The living behavior of *rac*-**3** enables the formation of interesting block polymers synthesized from a single α-olefin. For example, variation of monomer concentration and reaction temperature during the polymerization of 1-decene with *rac*-**3** produced an elastomeric triblock copolymer with semicrystalline endblocks ($T_m$ = 81 °C) and an amorphous midblock ($T_g$ = −65 °C).

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***Table 1.*** Optimization of 1-Hexene Polymerization Using *rac*-**3**

| | | | | | | | | | | | Enchainment Type (mole fraction) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | complex ($\mu$mol) | [1-hexene] (M) | activator ([Al]/[Ni]) | $T_{rxn}$ (°C) | $t_{rxn}$ (h) | yield (g) | TOF[a] ($h^{-1}$) | $M_n$[b] (g/mol) | $M_n$ theor. (g/mol) | $M_w/M_n$[b] | 6,2[c] | 6,1[d] | $C_2$ branch[c] | $C_3$ branch[c] | $C_{\geq 4}$ branch[c] |
| 1 | *rac*-**3** (4.3) | 0.43 | MMAO (260) | −20 | 24 | 0.22 | 25 | 65 100 | 51 000 | 1.10 | 0.51 | 0.38 | 0.00 | 0.02 | 0.09 |
| 2 | *rac*-**3** (4.3) | 1.9 | MMAO (260) | −20 | 24 | 0.23 | 26 | 60 500 | 53 000 | 1.17 | 0.75 | 0.10 | 0.03 | 0.05 | 0.07 |
| 3 | *rac*-**3** (4.3) | 6.4 | MMAO (260) | −20 | 24 | 0.61 | 70 | 130 000 | 140 000 | 1.13 | 0.82 | 0.01 | 0.03 | 0.08 | 0.06 |
| 4 | **1** (17) | 0.92 | MMAO (260) | 0 | 1 | 0.88 | 620 | 71 500 | 52 000 | 1.08 | 0.13 | 0.24 | 0.00 | 0.00 | 0.63 |
| 5 | *rac*-**3** (17) | 0.92 | MMAO (260) | 0 | 2 | 0.46 | 160 | 41 900 | 27 000 | 1.09 | 0.51 | 0.41 | 0.00 | 0.00 | 0.08 |
| 6 | *rac*-**3** (17) | 0.92 | MMAO (260) | −30 | 24 | 0.38 | 11 | 33 600 | 22 000 | 1.15 | 0.77 | 0.13 | 0.01 | 0.03 | 0.06 |
| 7 | *rac*-**3** (17) | 0.92 | MMAO (260) | −40 | 24 | 0.16 | 5 | 16 200 | 9 400 | 1.21 | 0.84 | 0.05 | 0.02 | 0.04 | 0.05 |
| 8 | *rac*-**3** (10) | 3.2 | $Et_2AlCl$ (100) | −40 | 24 | 0.38 | 19 | 31 000 | 38 000 | 1.14 | 0.84 | 0.05 | 0.02 | 0.04 | 0.05 |
| 9 | **1** (10) | 3.2 | $Et_2AlCl$ (100) | −40 | 3 | 0.27 | 110 | 20 700 | 27 000 | 1.15 | 0.42 | 0.05 | 0.00 | 0.00 | 0.53 |

[a] TOF (turnover frequency): mol 1-hexene/(mol Ni·h). [b] Determined using gel-permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 140 °C versus polyethylene standards. [c] Determined by $^{13}C$ NMR spectroscopy. [d] Determined by the equation $\chi_{6,1} = [(1-4R)/(1+2R)]$, where $R = [CH_3]/[CH_2]$, determined by $^1H$ NMR spectroscopy.

***Table 2.*** Polymerization of α-Olefins Using *rac*-**3** under Optimized Conditions[a]

| | | | | | | | | | | Enchainment Type (mole fraction) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| entry | α-olefin | [α-olefin] (M) | activator | yield (g) | TOF[b] ($h^{-1}$) | $M_n$[c] (g/mol) | $M_n$ theor. (g/mol) | $M_w/M_n$[c] | $T_g$[d] (°C) | $\omega$,2[e] | $\omega$,1[f] | $C_2$ branch[e] | $C_3$ branch[e] | $C_{\geq 4}$ branch[e] |
| 1 | 1-butene | 9.2 | PMAO | 0.38 | 28 | 66 100 | 38 000 | 1.26 | −56.2 | 0.96 | 0.04 | 0.00 | 0.00 | 0.00 |
| 2 | 1-pentene | 7.6 | PMAO | 0.30 | 18 | 26 700 | 30 000 | 1.21 | −60.0 | 0.92 | 0.00 | 0.04 | 0.04 | 0.00 |
| 3 | 1-hexene | 3.2 | $Et_2AlCl$ | 0.38 | 19 | 31 000 | 38 000 | 1.14 | −62.2 | 0.84 | 0.05 | 0.02 | 0.04 | 0.05 |
| 4 | 1-heptene | 2.8 | $Et_2AlCl$ | 0.22 | 9 | 21 200 | 22 000 | 1.14 | −63.9 | 0.78 | 0.01 | 0.02 | 0.05 | 0.14 |
| 5 | 1-octene | 2.5 | $Et_2AlCl$ | 0.46 | 17 | 33 400 | 46 000 | 1.06 | −66.3 | 0.70 | 0.06 | 0.01 | 0.04 | 0.19 |

[a] Polymerization conditions: Ni = 10 $\mu$mol, [Al]/[Ni] = 100, $T_{rxn}$= −40 °C, $t_{rxn}$ = 24 h. [b] TOF (turnover frequency): mol α-olefin/(mol Ni·h). [c] Determined using gel-permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 140 °C versus polyethylene standards. [d] Determined by differential scanning calorimetry; no $T_m$ detected. [e] Determined by $^{13}C$ NMR spectroscopy. [f] Determined by the equation $\chi_{\omega,1} = [(1 - NR)/(1 + 2R)]$, where $N = (\omega - 2)$; R = $[CH_3]/[CH_2]$, determined by $^1H$ NMR spectroscopy.

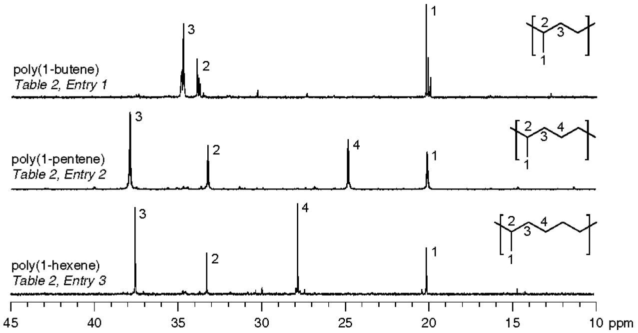

**Figure 1.** $^{13}C$ NMR spectra (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of poly(α-olefin)s formed by *rac*-**3** (Table 2, entries 1−3).

In summary, we have developed a system to polymerize α-olefins in a living fashion to furnish EP-type polymers. Advantages of using *rac*-**3** to produce these materials include the employment of inexpensive, readily available monomers as well as the ability to control the composition of the polymers not only through choice of monomer but also through reaction conditions. As demonstrated with 1-hexene polymerization, modification of $T_{rxn}$ and monomer concentration can introduce varying amounts of $\omega$,1-enchainment defects into the polymers which increase the average backbone length between methyl branches. This control of polymer structure can allow for the formation of new polymers with desirable properties. Use of higher α-olefins, such as 1-decene, is particularly attractive as oversupplies of linear α-olefins higher than 1-octene are expected to grow in the coming years.[16]

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**Supporting Information Available:** Polymerization procedures, mechanism, plot of $M_n$ versus conversion for 1-octene polymerization using *rac*-**3**, and polymer characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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