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A C_2-Symmetric, Living α-Diimine Ni(II) Catalyst: Regioblock Copolymers from Propylene

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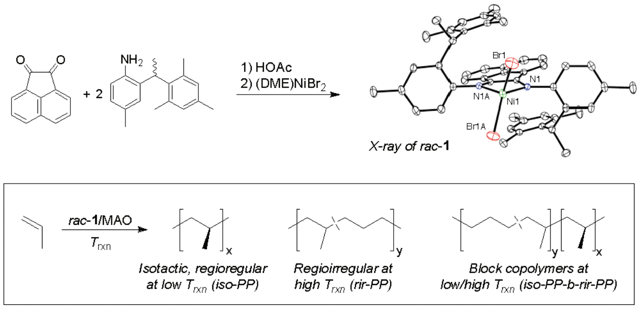
The development of new methods for the synthesis of polyolefins of defined molecular weight, stereochemistry, and comonomer composition continues to be an important frontier in the field of polymer synthesis. Early transition metal catalysts have been developed that give precise control over polymer stereochemistry[1] and are, in some cases, living;[2] however, they are generally inferior at polymerizing functional alkenes. In contrast, late transition metal catalysts are more functional group tolerant and can also show living behavior, but they generally produce amorphous, atactic polymers.[3] Given the promise of Ni(II) and Pd(II) α-diimine catalysts originally reported by Brookhart for living and functional alkene polymerization,[3,4] we began to develop chiral ligands in an attempt to promote isotacticity in these systems.[5] We recognized the challenge in this approach, as these catalysts generally make amorphous polymers due to both poor regioselectivity and chain-end isomerization during polymerization.[6] In fact, at low temperatures, the growing chain end can induce *syndiotactic* enchainment in the case of propylene.[7] We have reported a new class of chiral anilines and their incorporation in α-diimine Ni(II) catalysts that exhibit isoselectivity in *trans*-2-butene polymerization, but no regio- or stereocontrol in propylene polymerization.[8] Herein we report a C_2-symmetric Ni(II) catalyst that exhibits both living behavior and isospecificity in the polymerization of propylene.

Condensation of 2 equivalents of *rac*-4-methyl-2-(1-(2,4,6-trimethylphenyl)ethyl)aniline with acenaphthenequinone yields one isomerically pure C_2-symmetric α-diimine ligand in 78% isolated yield. Interestingly, the reversibility of imine formation and the lower solubility of the racemic ligand isomer give a nonstatistical stereochemical mixture. Metalation with (dimethoxyethane)$NiBr_2$[4] followed by crystallization gave complex *rac*-**1** in 79% yield (Scheme 1). The molecular structure of *rac*-**1** was determined by single-crystal X-ray diffraction (Scheme 1); the complex exhibits crystallographic C_2-symmetry, with the mesityl groups stacked above and below the acenaphthene backbone. This conformation appears to be the sole solution structure of the complex based on ^{1}H NMR spectroscopy. Although *rac*-**1** shows very low activity and stereoselectivity for *trans*-2-butene polymerization in the presence of methylaluminoxane (MAO), it is active for the polymerization of both ethylene and propylene.

The regiochemistry of polypropylene (PP) produced by *rac*-**1**/MAO shows an interesting temperature dependence (Scheme 1). At low temperature (−78 °C), the polymer is regioregular and highly isotactic (*iso*-PP); at room temperature (22 °C), the polymer is completely amorphous and regioirregular (*rir*-PP). We therefore chose to study the effect of the polymerization temperature (T_{rxn}) in more detail. As T_{rxn} decreased from 22 to −78 °C, turnover frequency (TOF) decreased from 966 to 1 h^{-1}. Number average molecular weight (M_n) data corresponded well to theoretical values for a living polymerization. Further support for living polymerization behavior is the narrow M_w/M_n values (≤1.11) at temperatures above −40 °C. We believe the active centers are stable to chain termination below this temperature as well, but M_w/M_n values increase due to polymer precipitation. To demonstrate the living behavior of *rac*-**1** at 0 °C, we carried out propylene polymerizations over a 6 h period (Figure 1). Molecular weights increased linearly with polymer yield, and M_w/M_n values were consistently narrow for all polymerizations.

Scheme 1. Synthesis of *rac*-**1** and Polymerization of Propylene



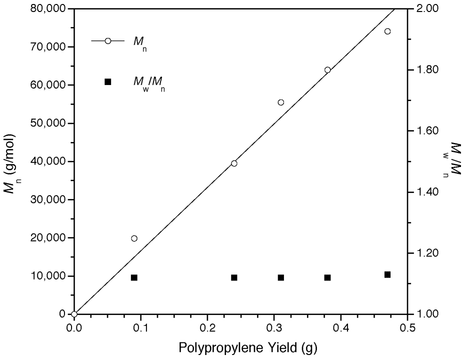


Figure 1. Plot of PP M_n (○) and M_w/M_n (■) versus yield using *rac*-**1**/MAO at 0 °C, determined by gel-permeation chromatography at 140 °C (polyethylene standards).

The microstructure of the PP changes significantly with T_{rxn}. At −78 °C, the polymer is both regioregular and highly isotactic. Analysis of the methyl region of the ^{13}C NMR spectra of the *iso*-PPs made below −40 °C shows a predominant *mmmm* peak, with errors which are inconsistent with typical stereoerrors (*mmmr* or *mmrr*), but rather appear to be regioerrors due to 3,1-insertions[1a] (Figure 2). With Ni(II) catalysts, this error occurs by a 2,1-insertion with subsequent chain-walking, yielding $-(CH_2)_3-$ linkages (3,1-insertions) in the polymer backbone. While these are minor errors when T_{rxn} is very low, the percentage of 3,1-insertions increases with increasing T_{rxn} up to 56.2% at $T_{rxn} = 22$ °C. In fact, this polymer with methyl branches more closely resembles poly(ethylene-*co*-propylene) than polypropylene, with $T_g = -59.9$ °C. At $T_{rxn} = -78$ °C, T_g and T_m values are consistent with *iso*-PP. This dramatic change in polymer structure provides a unique

10.1021/ja0540021 CCC: $30.25

Table 1. Propylene Polymerization Data for *rac*-**1**/Methylaluminoxane[a]

entry	T_{rxn} (°C)	propylene (g)	time (h)	yield (mg)	TOF[b] (h^{-1})	M_n[c] (g/mol)	M_w/M_n[c]	$[CH_3]/[CH_2]$[d]	% 3,1[e]	T_g[f] (°C)	T_m[f] (°C)
1	22	5	1.0	690	966	57 100	1.11	0.21	56.2	−59.9	ND[g]
2	0	5	2.0	550	385	48 200	1.08	0.31	43.1	−54.4	ND[g]
3	−20	5	6.0	445	104	31 500	1.09	0.48	26.8	−43.0	ND[g]
4	−40	5	24	280	16	19 400	1.10	0.67	13.9	−27.0	68.8
5	−60	15	48	110	3	9 000	1.34	0.80	7.6	−14.3	129.7
6	−78	15	96	73	1	5 700	1.37	1.00	0.0	−0.5	137.3

[a] Polymerization conditions: toluene = 25 mL, Ni = 17 μmol, [Al]/[Ni] = 270. [b] TOF (turnover frequency): mol propylene/(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 ^{1}H NMR. [e] Determined by the equation: % 3,1-insertions = $[(1 - R)/(1 + 2R)] \times 100$, where $R = [CH_3]/[CH_2]$. [f] Determined by differential scanning calorimetry (second heating). [g] None detected.

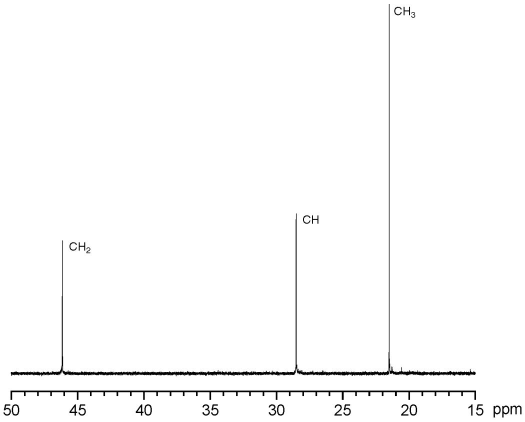


Figure 2. ^{13}C NMR spectrum (1,1,2,2-$C_2D_2Cl_4$, 125 MHz, 135 °C) of *iso*-PP formed by *rac*-**1**/MAO at −78 °C (Table 1, entry 6).

opportunity for the synthesis of propylene homopolymers with blocks of controlled sequence length and composition. Polypropylene block copolymers are primarily made using four techniques. First, catalysts with dynamic active sites can produce isotactic/atactic stereoblock polypropylenes.[9] Second, the sequential polymerization of propylene with other alkenes using living catalysts produces isotactic and syndiotactic polypropylene block copolymers.[2] Third, chain exchange between catalysts of different stereospecificities can be used for block copolymer synthesis.[10] Fourth, changing the solvent during a living propylene polymerization can produce stereoblock polymers.[11] We chose to investigate the simple change of T_{rxn} during chain growth as a straightforward technique to give polymers with blocks that are well-defined in number, size, and composition. Propylene was polymerized at −60 °C for 7 h to give an *iso*-PP block with M_n = 5 400 g/mol, M_w/M_n = 1.24. Warming to 0 °C for 1 h gave a diblock polymer (*iso*-PP-*block*-*rir*-PP) with M_n = 47 400 g/mol, M_w/M_n = 1.12. Thermal analysis of the diblock polymer by DSC showed characteristics of each of the homopolymers, with T_g = −44.5 °C and T_m = 118.6 °C. Polymerization at T_{rxn}= −60, 0, then −60 °C gave a triblock copolymer with elastomeric properties.

In conclusion, we report a new chiral, living Ni(II) complex which produces polypropylenes with microstructures ranging from highly isotactic at low T_{rxn} to regiorandom at high T_{rxn}. By changing T_{rxn} during propylene polymerization, regioblock copolymers can be synthesized. This represents a new strategy for the synthesis of copolymers with multiple blocks of defined size and microstructure from a single alkene. Future work will focus on the application of this system for the synthesis of model *iso*-PP block copolymers, as well as the development of systems with higher activity.

Acknowledgment. G.W.C. gratefully acknowledges support from the Packard and Sloan Foundations, and Mitsubishi Chemicals. This material is based upon work supported in part by the U.S. Army Research Laboratory and the U.S. Army Research Office under Grant No. DAAD19-02-1-0275, Macromolecular Architecture for Performance (MAP) MURI. This research made use of the Cornell Center for Materials Research Shared Experimental Facilities supported through the NSF MRSEC program (DMR-0079992).

Supporting Information Available: Catalyst synthesis and characterization, X-ray data for *rac*-**1**, propylene polymerization data, and polymer characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0540021