Living Polymerization of Ethylene and α-Olefins Using a Nickel α-Keto-β-Diimine Initiator

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Supporting Information

General Remarks. All manipulations of air and/or water sensitive compounds were performed under an inert atmosphere using standard glove box and Schlenk-line techniques. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 and 1-hexene from Na/K alloy. Toluene was purchased from Aldrich (anhydrous grade) and used as received. MAO (methylaluminoxane solution, 10 wt. % in toluene) was purchased from Aldrich and dried *in vacuo*, until a free flowing white powder was obtained. Ethylene (99.99%) and propene (99.97%) were purchased from Matheson Trigas and purified by passing through Agilent moisture and oxygen traps. Complex **1** was synthesized as previously reported.[1] Reagents, unless otherwise specified, were purchased from Aldrich and used without further purification. Polymerization activities were calculated from the mass of the product obtained. Polymers were characterized by GPC analysis, relative to polystyrene standards, at 135 °C in *o*-dichlorobenzene (in a Varian Polymer Laboratories, high-temperature chromatograph, PL GPC 220). Polymer melting points (T_m) and glass transition temperatures (T_g) were measured on a TA Instruments differential scanning calorimeter (model Q-20) at a rate of 10 °C/min for three cycles using a temperature range of -70 to 180 °C. NMR spectra were obtained using a 300 MHz Varian Inova spectrometer and chemical shifts were referenced internally to the sequence $-(CH_2)_n-$, at 30.00 ppm. ^{13}C NMR spectra of the polymers were obtained *o*-dichlorobenzene and benzene-d_6 (20% *v/v*) at 90 °C in a 5-mm sample tube. The spectra were taken with a 74° flip angle, an acquisition time of 1.5 s and a delay of 4.0 s.

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Polymerization Reactions:

Polymerization of Ethylene: A 100 mL Parr steel autoclave reactor, equipped with an addition funnel, was loaded inside a glovebox with toluene (40 mL) and solid MAO so that [Al]/[Ni] = 250 (22 mg, 0.375 mmol). A stock solution of **1** was prepared and 1.5 μmol of **1** in approximately 1 mL CH_2Cl_2 was added to the addition funnel. In Table 1 entry 8, 0.75 μmol of **1** in approximately 1 mL CH_2Cl_2 was added to the addition funnel. An [Al]/[Ni] = 250 (11 mg, 0.188 mmol) was maintained in this reaction. The reactor was sealed inside the glovebox and attached to an ethylene line. The addition funnel was pre-pressurized with ethylene at 50 psi above the desired reaction pressure with ethylene. The reactor was pre-pressurized to (P_{C2H4}) with ethylene and cooled to the appropriate reaction temperature (T_{rxn}). The polymerization was initiated via injection of the solution of **1** and ethylene was continually fed into the reactor over the course of the reaction. The reaction temperature (T_{rxn}) was controlled using a dry-ice/acetone bath and found to be ± 2 °C as monitored by an internal thermocouple. Ethylene was vented after a specified amount of time, and methanol was added to quench the polymerization (entries 1-6). The polymer was precipitated with methanol and was collected by filtration and washed with acidified methanol (10% HCl), methanol and acetone sequentially and dried under high vacuum to constant weight. The activity of the polymerization was calculated from the mass of the product obtained. In reactions utilizing triethylsilane (Et_3SiH) as the quenching agent (Table 1, entries 7 & 8 and Table S-1, entries S-7 through S-11), 1 mL Et_3SiH in 2 mL of toluene was added to the addition funnel following introduction of the initiator stock solution. The addition funnel was pre-pressurized with ethylene at 50 psi above the desired reaction pressure (P_{C2H4}) and the solution injected into the rapidly

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stirring reaction mixture at the appropriate time point.

Table S-1. Ethylene Polymerization Reactions:

Entry	**µmoL of 1**	**Time** (min.)	**Pressure** (psi)	**Temp.** (°C)	**TOF** ($x 10^{-3} h^{-1}$)	**Yield** ($x 10^{-3}$ g)	**M_n** (10^{-3} g mol^{-1})	**PDI** (M_w/M_n)	**T_m** (°C)
S-1	1.5	10	300	20	52.9	370	450	1.60	113
S-2	1.5	10	300	10	28.6	200	260	1.35	122
S-3	1.5	10	150	10	21.9	153	216	1.22	115
S-4	1.5	10	150	-10	4.7	33	36	1.09	127
S-5	1.5	20	150	-10	5.6	78	61	1.12	129
S-6	1.5	10	150	-10	5.3	36	33	1.12	126
S-7	1.5	10	50	-10	5.6	39	35	1.09	125
S-8	1.5	20	50	-10	5.4	75	65	1.10	125
S-9	1.5	30	50	-10	5.7	120	88	1.10	124
S-10	0.75	45	50	-10	5.9	94	140	1.08	123
S-11	0.75	60	50	-10	5.9	123	183	1.10	122

Estimation of the number of active sites:

The number of active sites can be estimated as follows: for the polymer in Entry S-11, Entry 8 in Table 1 in the text, the yield of polyethylene was 0.123 grams. Dividing this number by the molecular weight of the polymer (M_n as determined by GPC) gives an estimate for the moles of catalytically active sites,

$$(0.123 \text{ g} / 183 \times 10^{-3} \text{ g mol}^{-1}) = 0.67 \times 10^{-6} \text{ mol}$$

Dividing this number by the amount of initiator used in entry S-11:

$$(0.67 \times 10^{-6} \text{ mol} / 0.75 \times 10^{-6} \text{ mol}) \times 100 = 90\%$$

This number suggests that ~ 90 % of catalytic sites are active. Due to the inherent error associated with the determination of M_n (as determined by GPC) and associated with the collection of the polymer product, we infer that the vast majority of the nickel sites are active and that the polymerization proceeds in a living manner.

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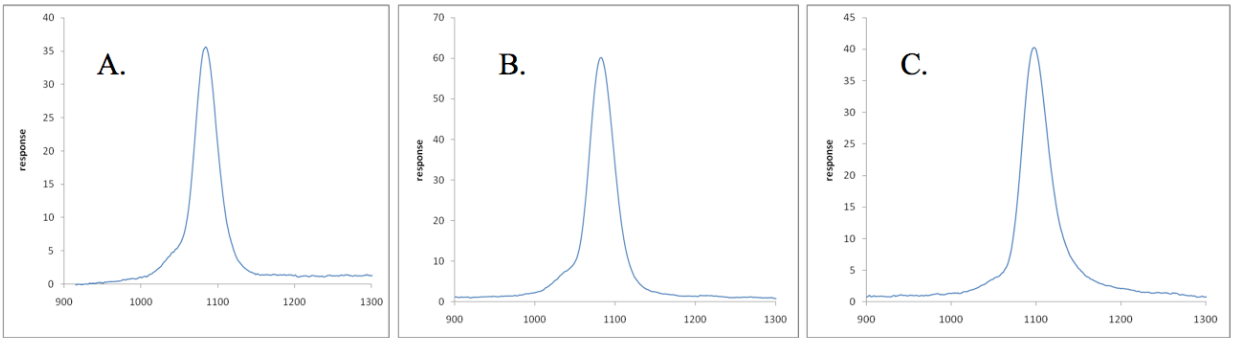

Figure S-1. GPC Traces of Polyethylene Materials; A. P_{C2H4} = 150 psi, MeOH quench (Table 1, entry 4), B. P_{C2H4} = 50 psi, MeOH quench (Table 1, entry 6), C. P_{C2H4} = 50 psi, Et_3SiH quench (Table 1, entry 7).

Living Polymerization of Propene: A 300 mL Parr steel autoclave reactor, equipped with an addition funnel, was loaded inside a glovebox with toluene (100 mL) and solid MAO so that [Al]/[Ni] = 250 (145 mg, 2.50 mmol). A stock solution of **1** was prepared and 10 µmol of **1** in approximately 1 mL CH_2Cl_2 was added to the addition funnel. The reactor was sealed inside the glovebox. The reactor was cooled in a dry-ice/acetone bath and 5 mL propene was transferred into the reactor. The reactor was brought to the appropriate reaction temperature (T_{rxn}) and the polymerization was initiated via injection of the solution of **1** under argon**.** The reaction temperature (T_{rxn}) was controlled by means of a dry-ice/acetone bath and found to be ± 2 °C as monitored by an internal thermocouple. In order to monitor the number average molecular weight (M_n) and polydispersity (PDI) of the product with time; 5.0 mL aliquots of the polymerization solution were taken at 20, 40, 60 and 90 minutes under a flow of argon using a gas-tight syringe. The contents of the syringe were immediately quenched with methanol. Volatiles were removed *in-vacuo* and the residue washed with acidified methanol (10% HCl), methanol and acetone sequentially and dried under high vacuum. The remaining residue

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was dissolved in approximately 5 grams of *o*-dichlorobenzene by heating the contents to 135 °C with agitation. Gel permeation chromatography (GPC) of this solution was used to obtain the M_n and PDI of each polymer sample, as shown in Table S-2. M_n values calculated on the basis of TOF are lower than those shown and indicate that the use of polystyrene standards substantially overestimates the M_n.[2] The reaction at a time of 120 minutes was quenched by loading the addition funnel with methanol (5 mL) and injecting the methanol, under argon, directly into the stirring reaction mixture. The polymer was precipitated with methanol, collected by filtration and washed with acidified methanol (10% HCl), methanol and acetone sequentially and dried under high vacuum to a constant weight of 0.340 grams.

Table S-2. GPC Results of Aliquots of the Polymerization Solution

Aliquot	**Time** (minutes)	**M_n** ($g\ mol^{-1}$)	**PDI**
1	20	16000	1.06
2	40	30000	1.06
3	60	44000	1.06
4	90	62000	1.06
5	120	79000	1.05

Living Polymerization of 1-hexene: A 300 mL Parr steel autoclave reactor, equipped with an addition funnel, was loaded inside a glovebox with toluene (125 mL), 1-hexene (15 mL, 120.0 mmol) and solid MAO so that [Al]/[Ni] = 250 (181.3 mg, 3.13 mmol). A stock solution of **1** was prepared and 12.5 µmol of **1** in approximately 1 mL CH_2Cl_2 was added to the addition funnel. The reactor was sealed inside the glovebox and cooled in a dry-ice/acetone bath to the appropriate reaction temperature (T_{rxn}). The

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polymerization was initiated via injection of the solution of **1** under argon**.** The reaction temperature (T_{rxn}) was controlled by means of a dry-ice/acetone bath and found to be ± 2 °C as monitored by an internal thermocouple. In order to monitor the number average molecular weight (M_n) and polydispersity (PDI) of the product with time; 5.0 mL aliquots of the polymerization solution were taken at 20, 40, 60 and 90 minutes under a flow of argon using a gas-tight syringe. The contents of the syringe were immediately quenched with methanol. Volatiles were removed *in-vacuo* and the residue washed with acidified methanol (10% HCl), methanol and acetone sequentially and dried under high vacuum. The remaining residue was dissolved in approximately 5 grams of *o*-dichlorobenzene by heating the contents to 135 °C with agitation. Gel permeation chromatography (GPC) of this solution was used to obtain the M_n and PDI of each polymer sample as shown in Table S-3. M_n values calculated on the basis of TOF are lower than those shown and indicate that the use of polystyrene standards substantially overestimates the M_n.[2] The reaction at a time of 120 minutes was quenched by loading the addition funnel with methanol (5 mL) and injecting the methanol, under argon, directly into the stirring reaction mixture. The polymer was precipitated with methanol, collected by filtration and washed with acidified methanol (10% HCl), methanol and acetone sequentially and dried under high vacuum to a constant weight of 0.603 grams.

Table S-3. GPC Results of Aliquots of the Polymerization Solution

Aliquot	**Time** (minutes)	**M_n** (g mol^{-1})	**PDI**
1	20	19000	1.05
2	40	40000	1.06
3	60	65000	1.05

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4	90	91000	1.06
5	120	120000	1.05

^{13}C NMR Characterization of the Polymer Products:

^{13}C NMR spectroscopy was used to determine the microstructure of the polymers. The main assignments and calculations used to estimate the sequence distributions were made according to the previous literature.[3]

Polyethylene: (Table 1, entry 8):

The only type of branching detected for this polyethylene are methyl branches, 16 methyl branches per 100 carbon atoms (3.1 mol %). The PE resembles a copolymer (ethylene-*co*-propylene) with isolated methyl branches.

Polypropylene (Table 1, entry 9):

This polypropylene (PP) resembles a propylene-ethylene copolymer, with only methyl branches present. The amount of propylene units correspond to 87.4 mol% and ethylene units 12.6 mol%. The amount of triads is given in the Table S-5 below. As can be seen there are a high amount of propylene sequences (PPP= 72.2 mol%) and these sequences are mainly isotactic (77.4 mol%).

Table S-4. Amount of ethylene ([E]) and propylene ([P]) sequences as calculated by ^{13}C spectroscopy.

Sequences	Amount of sequences per 100 ethylene units (mol%)	Amount of branches per 1000 C atoms
[PPP]	72.2	361
[EPP+PPE]	13.9	69

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[EPE]	0.5	2.5
[EEE]	1.3	
[PEP]	0.4	
[PEE+EEP]	4.7	
[PP*P]	0.7	3.5
[EP*PE]	0.1	0.5
[EP*EPE]	6.2	
[P]	**87.4**	**437**
[E]	**12.6**	

Table S-5. Polypropylene tacticity

Sequence	**(%)**
mm	67.4
mr	20.1
rr	12.5
m	**77.4**
r	**22.6**

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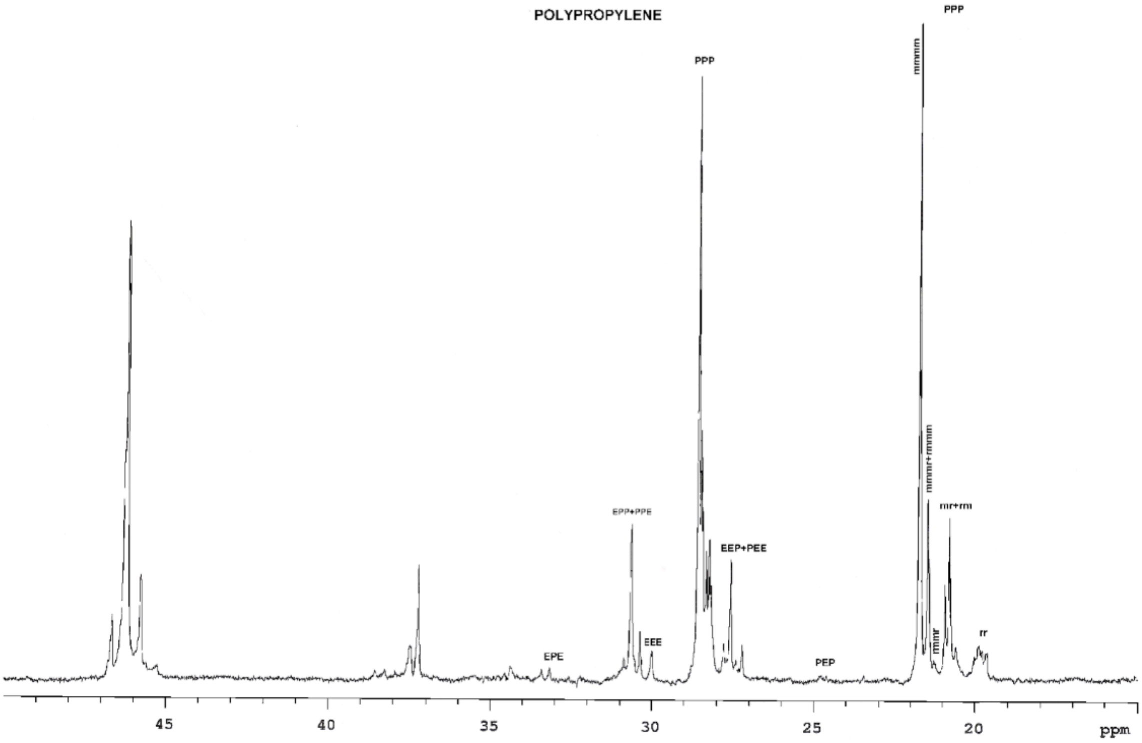

Figure S-2. ^{13}C NMR spectrum of the polypropylene obtained in Table 1, entry 9.

Poly (1-hexene) (Table 1, entry 10):

Table S-6. Type and amount of branches given as a percentage of the total branches or per 100 ethylene units.

Branch Type	Poly(1-hexene) (mol%)
Methyl	16.5
Ethyl	1.4
Propyl	1.9
Butyl	75.7
Long	4.5
Total	100.0

Table S-7. Type and amount of branches in number of branches per 1000 carbon atoms

Branch Type	Poly(1-hexene)
Methyl	77
Ethyl	7
Propyl	9

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Butyl	350
Long	21

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