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Rheological Behavior of Chain-Straightened Poly(α-olefin)s

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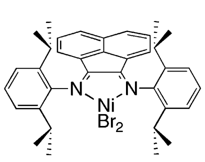
ABSTRACT: A chain-straightened poly(α-olefin) series was prepared via the use of a Ni(II) α-diimine catalyst. The resulting polymers are structurally nearly equivalent to ethylene−propylene copolymers with the exception that methyl groups can be evenly spaced along the polymer main chain. The monomers used ranged from ethylene to 1-decene (excluding 1-heptene and 1-nonene). With the exception of 1-decene, the polyolefins prepared have similar plateau moduli, ∼1.5 MPa at 323 K. This is comparable with values determined over the last 40+ years for copolymers formed using conventional Ziegler−Natta catalysis. Thus, the chain-straightening polymerization systems yield amorphous ethylene−propylene like polymers from single, or mixed, α-olefin monomer feeds. Using this unique type of polymerization allows for the avoidance of ambient temperature gaseous ethylene and propylene while permitting the use of higher molecular weight α-olefins that are both abundant and inexpensive.

Introduction

Chain-Walking Olefin Polymerizations: Nickel α-diimine complexes (see structure **1**) produce poly(olefin)s with unique microstructures due to the ability of the metal center to migrate along the growing polymer chain via a series of *β*-hydride elimination/reinsertion events.[1−5] This process has been dubbed "chain-walking."[3−4] For example, polymerization of 1-hexene with **1**/methylaluminoxane (MAO) produces a highly regioirregular polymer with backbone methylene sequences of varying lengths among the methyl, butyl, and longer side chains that are formed.[3,5] Of note, polymerizations of propylene, 1-hexene, and 1-octadecene with **1**/MAO give polymers with narrow molecular weight distributions.[2] Branched[6] and hyperbranched[7,8] olefin polymers from ethylene have been prepared using palladium α-diimine complexes. The highly branched structures showed[7] quite small values for the entanglement densities. For these polymers, the ethylene pressure was used to control the branching degree where decreasing pressure enhanced branching density.



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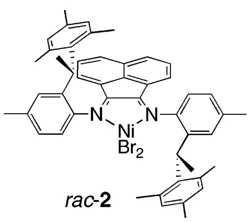
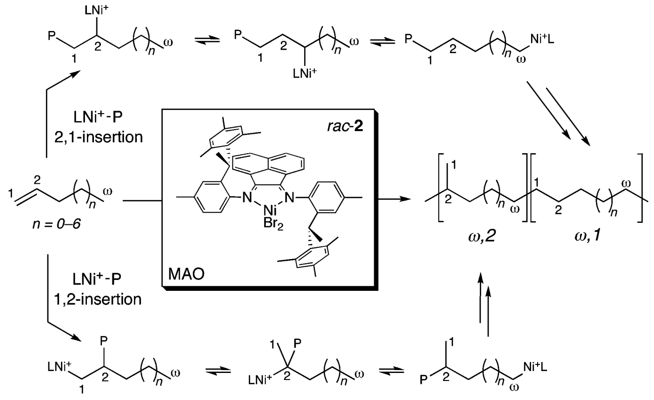


rac-**2**

Scheme 1. Polymerization of α-Olefins with *rac*-2/ Methylaluminoxane (MAO)



Coates and co-workers[9,10] have reported highly regioregular α-olefin polymerization using *rac*-**2**, a chiral, C_2-symmetric Ni(II) α-diimine complex. As depicted in Scheme 1, under optimized conditions, a high selectivity for *ω*,2-enchainment is exhibited resulting in polymers comprised of methylene sequences of precise lengths between methyl branches. This *ω*,2-enchainment results from a 1,2-insertion of the α-olefin into the Ni−polymer bond followed by chain walking to the *ω*-position. As the reaction conditions are changed, a second enchainment mechanism becomes operative; a 2,1-insertion of monomer followed by chain walking to the *ω*-position leads to *ω*,1-enchainment. The result of this is the placement of monomer into the growing polymer chain in a linear fashion. Whether the poly(α-olefin)s are comprised exclusively of *ω*,2-enchainments or contain a mixture of *ω*,2- and *ω*,1-enchainments, they structurally resemble ethylene−propylene (EP) type copolymers and, as will be shown, they mimic the rheological behavior of conventionally prepared EP copolymers. Coupled with living behavior, a system is in place that allows for the synthesis of poly(olefin)s with compositional control, tailored molecular weights, and narrow molecular weight distributions.

We have used *rac*-**2**/MAO to prepare poly(olefin)s using linear α-olefins ranging from ethylene to 1-decene. The rheological loss and storage moduli (reference temperature 323 K) of the polymers were measured and the plateau moduli and entanglement molecular weights determined.

Packing Length. A methodology has been developed[11−13] that relates the entanglement state of polymers to their unperturbed chain dimensions and mass density. This approach (the packing model) works for a diverse body of polymer types

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Table 1. Molecular Characteristics of Chain Straightened Poly(olefin)s

								backbone methylene sequence length distribution (mole fraction)[c]							branch length distribution (mole fraction)[c]			
sample	monomer	theor M_n[a] (kg/mol)	M_n[b] (kg/mol)	M_w/M_n[b]	av no. of CH_2/CH_3[c]	MFE[d]	T_g[e] (°C)	0	1	2	3	4	5	6+	1	2	3	4+
BUT-62	1-butene	75.1	86.0	1.14	4.19	61.5	−64.5			0.58		0.05	0.12	0.25	0.90	0.07		0.03
PRO-63	propylene	82.3	83.0	1.09	4.41	63.0	−56.8	0.08	0.11			0.51		0.30	1.00			
HEX-65	1-hexene	246.0	239.1	1.15	4.66	64.7	−62.3					0.93	0.02	0.05	0.80	0.04	0.09	0.07
BUT-65	1-butene	101.3	98.1	1.16	4.77	65.3	−64.3[f]			0.56		0.07		0.37	0.92	0.08		
BUT-69	1-butene	68.1	83.9	1.16	5.61	69.7	−62.9[f]			0.48		0.06	0.05	0.41	0.84	0.10		0.06
ETH-70	ethylene	88.0	97.7	1.25	5.50	69.2	−65.6[f]			0.35		0.23	0.02	0.40	0.86	0.04	0.03	0.07
PEN-71	1-pentene	88.5	119.0	1.11	5.94	71.2	−61.7[f]				0.62		0.02	0.36	0.85		0.09	0.06
HEX-74	1-hexene	101.5	127.6	1.12	6.70	74.0	−61.6[f]					0.62	0.02	0.36	0.84		0.01	0.15
DEC-79	1-decene	63.2	78.4	1.12	8.65	79.3	−67.2			0.08	0.09	0.04	0.35	0.44	0.55		0.02	0.43
OCT-82	1-octene	100.0	100.6	1.09	9.80	81.5	−59.7[f]			0.05			0.05	0.90	0.75	0.02	0.02	0.21

[a] Theoretical M_n determined by the equation: (kg polymer)/(mol catalyst). [b] Determined by GPC (140 °C, 1,2,4-trichlorobenzene) vs PE standards. [c] Determined using ^{13}C NMR spectroscopy. [d] Mole fraction of ethylene. [e] Determined by differential scanning calorimetry (second heating run). [f] Broad endothermic transition adjacent to T_g present on DSC thermogram.

including statistical hydrocarbon co- and terpolymers.[11−18] Simple expressions emerge that connect the plateau modulus (G_e) with measurable chain parameters:

$$G_e \equiv \frac{kT}{P_e^{\,2} p^3} = \frac{kT}{a^2 p} = \frac{kT}{V_e} = \rho_e kT \qquad (1)$$

where k is the Boltzmann constant, T the absolute temperature, p the packing length, V_e the entanglement volume, ρ_e the chain entanglement density, and a the tube diameter. Graessley[19] has dubbed this expression the Lin−Fetters equation.[11,20]

P_e is defined[14,20] as the number of entanglement strands that share a volume equal to the cube of the tube diameter (eq 2).

$$P_e \equiv a/p = a^3/V_e = [kT/p^3 G_e]^{0.5} = 20.8 \qquad (2)$$

The material independent packing length parameter (p) was defined by Witten et al.[21] as the ratio of the occupied volume of a chain ($M/\rho N_{Av}$) and the mean-square end-to-end distance ($\langle R^2\rangle_0$) of the chain:

$$p \equiv [M/\langle R^2\rangle_0 \rho N_{Av}] = \pi d^2/4b_k = [\upsilon_b/b_k]^{0.5} = P_e^{\,-0.667}$$
$$[G_e/kT]^{-0.333} = 0.132\rho_e^{\,-0.333} \qquad (3)$$

where υ_b is the average volume per backbone bond, N_{Av} is the Avogadro number, M is the chain molecular weight, ρ the material density, b_k the Kuhn step length ($b_k \equiv \langle R^2\rangle_0/R_{max} = \ell_0 C_\infty$) and d the effective chain diameter: $d^2 = [4\upsilon_b/\pi\ell_0]$. Since $\langle R^2\rangle_0$ is proportional to M, the packing length p is independent of molecular weight and thus is characteristic of the chemical structure of the polymer.

The plateau modulus G_e defines the entanglement spacing of a polymer melt and the entanglement molar mass M_e (eq 4).

$$M_e \equiv \frac{\rho kT N_{Av}}{G_e} = V_e \rho N_{Av} = P_e^{\,2} p^3 \rho N_{Av} \qquad (4)$$

The entanglement density is defined as $\rho_e \equiv \rho N_{Av}/M_e = G_e/kT = 1/V_e$. This parameter allows a direct and unbiased comparison of the entanglement characteristics of all polymers since chain density is accounted for.

Experimental Section

Polymer Synthesis. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk techniques. Toluene was purified over columns of alumina and copper (Q5). Methylene chloride was purified over an alumina column and degassed by three freeze−pump−thaw cycles before use. Heptane and chlorobenzene (anhydrous, Aldrich) were used as received. Propylene (Matheson, polymer grade) was purified over columns of molecular sieves and copper (Q5). Ethylene (Matheson, polymer grade) was purified by passing it through an Oxiclear model DGP-250-R2 purification column. 1-Octene (98%, Aldrich) was stirred over CaH_2 for several days, degassed by three freeze−pump−thaw cycles, vacuum distilled, and stored under nitrogen prior to use. 1-Pentene (99%, Aldrich) and 1-hexene (99+%, Aldrich) were used as received. 1-Decene (94%, Aldrich) was degassed by three freeze−pump−thaw cycles and stored under nitrogen prior to use. 1-Butene (99+%, Aldrich) was used as received. MMAO-3A (7 wt % Al in heptane, Akzo Nobel) and MMAO-7 (7.1 wt % Al in Isopar E, Akzo Nobel) were used as received. PMAO-IP (13 wt % Al in toluene, Akzo Nobel) was dried *in vacuo* to remove residual trimethylaluminum and used as a solid white powder.

***rac*-(ArN=C(1,8-naphthalenediyl)C=NAr)NiBr$_2$ (Ar = 4-Methyl-2-(*sec*-(2,4,6-trimethylphenethyl)phenyl) (*rac*-2).** was prepared by a previously reported method.[10]

Note that polymer sample names reflect the monomer used and mole fraction of ethylene (MFE) measured for each sample (i.e., BUT-62 was made from 1-butene and has a MFE equal to 62%).

BUT-62. See Table 1: all subsequent polymerization and characterization data are provided in this table. Toluene (50 mL) and MMAO-3A solution (4.3 mL, 7.5 mmol) were combined in a 6-oz Lab-Crest reaction vessel (Andrews Glass) which was cooled to −78 °C. 1-Butene (15.1 g, 269 mmol) was condensed into the vessel which was then allowed to warm to 0 °C. After 10 min of equilibration, a solution of *rac*-**2** (31 mg, 30 μmol) in CH_2Cl_2 (2 mL) was injected into the reaction mixture. After 2.75 h, the reaction was quenched with MeOH, and the polymer was precipitated with a copious amount of methanol/HCl, filtered, washed with methanol, and dried *in vacuo* at 60 °C to constant weight (2.24 g). This polymer isolation protocol was used for all of the following samples.

PRO-63. Toluene (300 mL) and MMAO-7 solution (13.5 mL, 25.8 mmol) were combined in a 12-oz Lab-Crest reaction vessel (Andrews Glass) which was cooled to 0 °C. Propylene (20 psi) was introduced and a solution of *rac*-**2** (180 mg, 173 μmol) in CH_2Cl_2 (10 mL) was injected into the reaction mixture. After 3.25 h, the reaction was quenched, yielding 14.24 g of polymer.

HEX-65. 1-Hexene (100 mL, 808 mmol) and MMAO-7 solution (7.8 mL, 15 mmol) were combined in a Schlenk flask which was cooled to −20 °C. A solution of *rac*-**2** (156 mg, 150 μmol) in CH_2Cl_2 (10 mL) was injected into the reaction mixture. After 19 h, the reaction was quenched, yielding 36.86 g of polymer.

BUT-65. Toluene (100 mL) and MMAO-3A solution (4.3 mL, 7.5 mmol) were combined in a 6-oz Lab-Crest reaction vessel

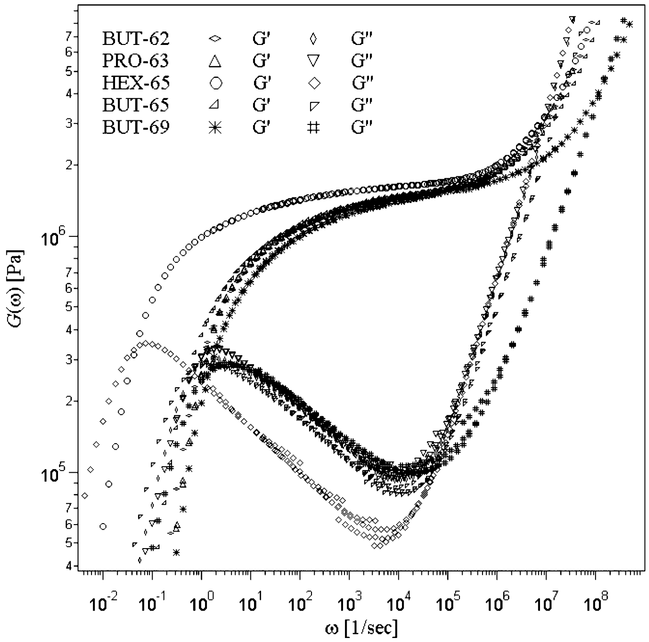


Figure 1. Master curves of the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, at $T_{ref} = 323$ K.

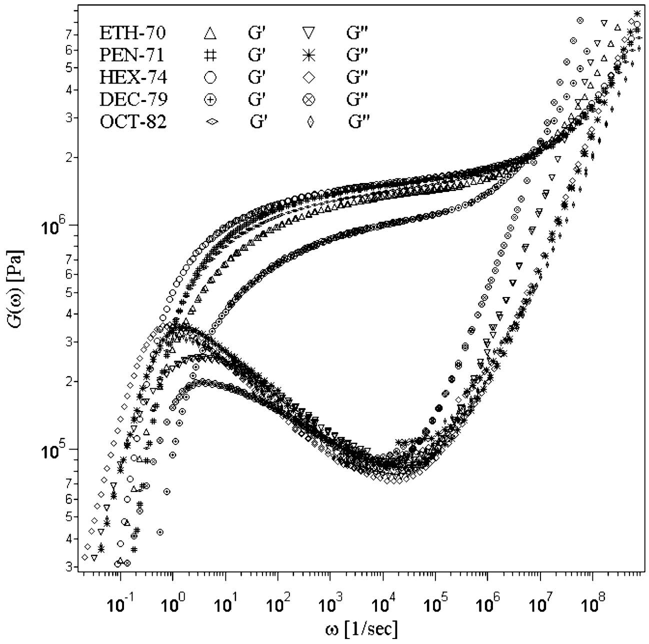


Figure 2. Master curves of the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, at $T_{ref} = 323$ K.

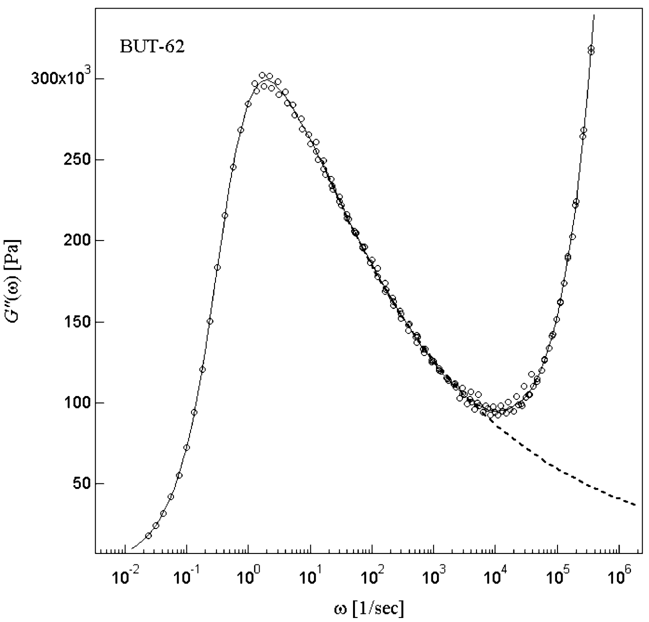


Figure 3. Loss moduli, $G''(\omega)$, for BUT-62.

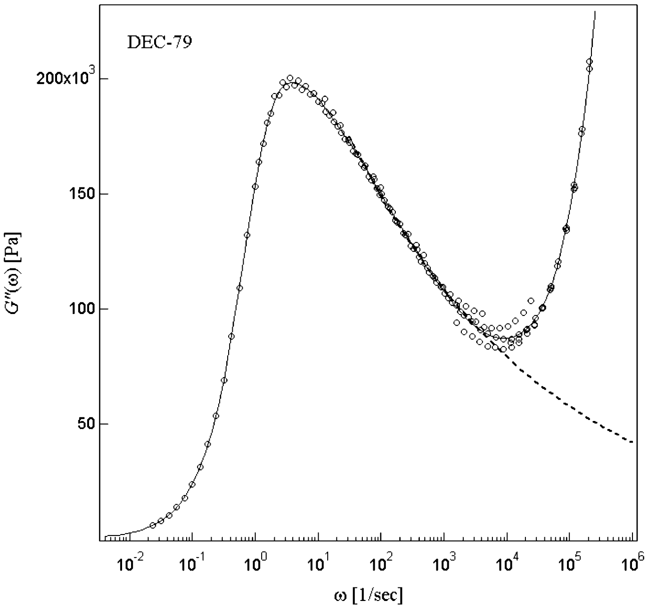


Figure 4. Loss moduli, $G''(\omega)$, for DEC-79.

(Andrews Glass) which was cooled to −78 °C. 1-Butene (15.1 g, 269 mmol) was condensed into the vessel which was then allowed to warm to 0 °C. After 10 min of equilibration, a solution of *rac*-**2** (31 mg, 30 μmol) in CH_2Cl_2 (2 mL) was injected into the reaction mixture. The reaction was quenched after 5 h, yielding 3.04 g of polymer.

BUT-69. Toluene (125 mL) and MMAO-3A solution (4.3 mL, 7.5 mmol) were combined in a 6-oz Lab-Crest reaction vessel (Andrews Glass) which was cooled to −40 °C. 1-Butene (9.3 g, 170 mmol) was condensed into the vessel which was then allowed to warm to 0 °C. After 10 min of equilibration, a solution of *rac*-**2** (32 mg, 31 μmol) in CH_2Cl_2 (2 mL) was injected into the reaction mixture. The reaction was quenched after 6 h, yielding 2.11 g of polymer.

ETH-70. Toluene (200 mL) and PMAO−IP (516 mg, 8.90 mmol) were combined in a 12-oz Lab-Crest reaction vessel (Andrews Glass), which was allowed to stir under ethylene (6 psi) for 8 min. A solution of *rac*-**2** (36 mg, 35 μmol) in CH_2Cl_2 (4 mL) was injected into the reaction mixture. The reaction was quenched 30 min later, yielding 3.08 g of polymer.

PEN-71. 1-Pentene (43.8 mL, 400 mmol), toluene (137 mL), and MMAO-7 solution (8.9 mL, 17 mmol) were combined in a Schlenk flask which was cooled to 0 °C. A solution of *rac*-**2** (177 mg, 170 μmol) in CH_2Cl_2 (10 mL) was injected into the reaction mixture. The reaction was quenched after 3.5 h, yielding 15.05 g of polymer.

HEX-74. 1-Hexene (50 mL, 400 mmol), toluene (100 mL), heptane (30 mL), and MMAO-7 solution (8.9 mL, 17 mmol) were combined in a Schlenk flask which was cooled to 0 °C. A solution of *rac*-**2** (177 mg, 170 μmol) in CH_2Cl_2 (10 mL) was injected into the reaction mixture. The reaction was quenched after 4 h, yielding 17.25 g of polymer.

DEC-79. 1-Decene (15.0 mL, 79.1 mmol) and MMAO-3A solution (2.9 mL, 5.1 mmol) were combined in a Schlenk flask which was cooled to 0 °C. A solution of *rac*-**2** (26 mg, 25 μmol) in CH_2Cl_2 (2 mL) was injected into the reaction mixture. The reaction was quenched after 2 h, yielding 1.58 g of polymer.

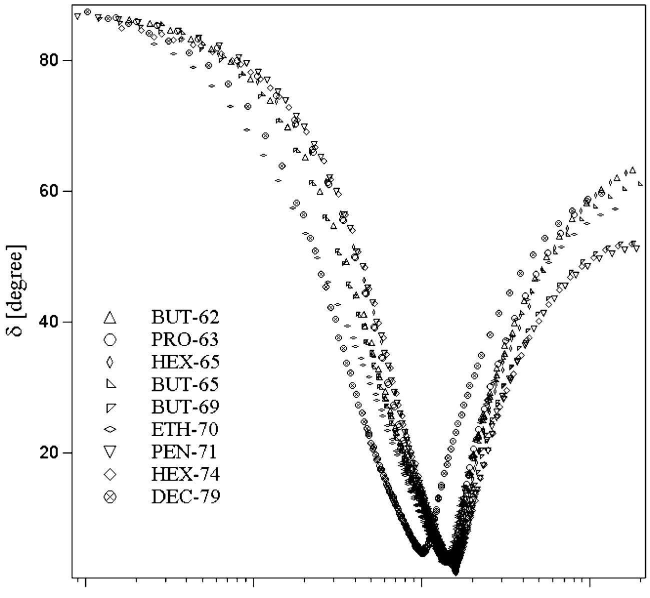
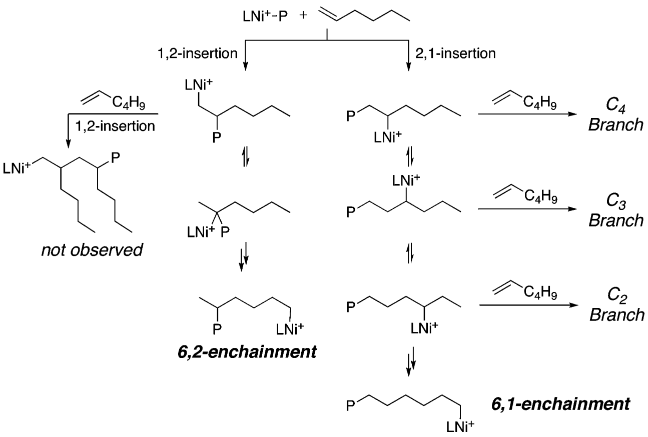
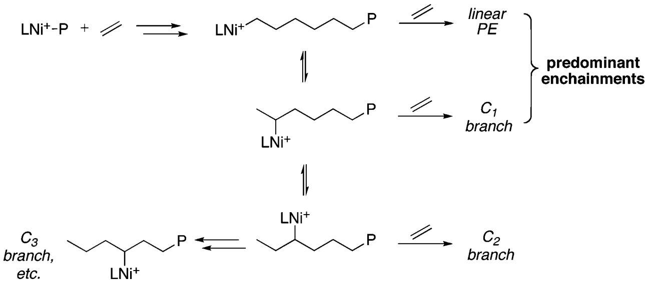


Figure 5. Van Gurp−Palman plots for chain walking poly(olefin)s.

Scheme 2. Proposed Mechanism for the Polymerization of 1-Hexene with *rac*-2/MAO



Scheme 3. Proposed Mechanism for the Polymerization of Ethylene with *rac*-2/MAO



OCT-82. 1-Octene (62 mL, 400 mmol), toluene (119 mL), and MMAO-7 solution (8.9 mL, 17 mmol) were combined in a Schlenk flask which was cooled to 0 °C. A solution of *rac*-**2** (178 mg, 171 μmol) in chlorobenzene (10 mL) was injected into the reaction mixture. The reaction was quenched after 3 h, yielding 16.92 g of polymer.

Polymer Characterization. ^{13}C NMR spectra of the polymers were recorded on a Varian Inova (500 MHz) spectrometer equipped with a ^{1}H/BB switchable with Z-pulse field gradient probe and referenced vs residual non-deuterated solvent shifts. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 in a 5 mm O.D. tube, and spectra were collected at 135 °C. Molecular weights (M_n and M_w) and polydispersities (M_w/M_n) were determined by high-temperature gel permeation chromatography (GPC), using a Waters Alliance GPCV 2000 GPC equipped with a Waters DRI detector and viscometer. The column set (four Waters HT 6E and one Waters HT 2) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt % di-*tert*-butyl-hydroxytoluene (BHT) at 1.0 mL/min at 140 °C. Data were calibrated using monomodal polyethylene standards (from Polymer Standards Service). Polymers were placed in a 140 °C oven for 24 h prior to molecular weight measurements.

Differential scanning calorimetry (DSC) was performed using a TA Instruments Q1000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from −100 to +200 °C, and processed with the TA Q series software.

Rheology. The storage $G'(\omega)$ and loss $G''(\omega)$ moduli were quantified using small amplitude oscillatory shear measurements. A Rheometric Scientific Inc. (RSI) ARES rheometer with 6 and 4 mm diameter parallel-plate fixtures was used for measurements at temperatures ranging from −50 to +50 °C. The master curves shown, Figures 1 and 2, were derived by using the RSI Orchestrator software at the reference temperature (T_{ref} = 323 K) with a two-dimensional residual minimization technique.

The G_e data were evaluated via three different methods.

(i) Integration of the $G''(\omega)$ Dispersion.[22] This protocol involves the integration of the loss moduli in the terminal zone where

$$G_e = \left(\frac{2}{\pi}\right) \int_{-\infty bu > \infty} G''(\omega)\, d(\ln(\omega)) \qquad (5)$$

with units in MPa. The data were treated via the procedure given by Colby et al.[23] Examples are given in Figures 3 and 4.

(ii) van Gurp—Palmen Analyses.[24] This procedure involves the plotting of the phase angle (δ) against the complex modulus $|G^*(\omega)|$. The specimen phase angle can be identified with the ratio of its viscous and elastic components as its value follows the complex modulus. The minimum in the plot (see Figure 5) defines G_e. The plot minimum is an unambiguous measure of the plateau modulus as other evaluations[25,26] have shown.

(iii) Minimum Method. In this evaluation the value of G_e was taken as the average value of the storage modulus, $G'(\omega)$, at which the minimum of the loss modulus, $G''(\omega)$, is observed.

The values of G_e are shown in Table 2. The values evaluated by the van Gurp−Palmen approach and the minimum method protocol are in excellent agreement. The integration procedure yields plateau moduli values that are marginally higher than those derived by the two previous procedures. The mean G_e values from all three analytical procedures are summarized in Table 3.

Discussion

Polymerization Mechanisms. Polypropylene and Higher Poly(α-olefin)s. The poly(α-olefin)s used for this study (Table 1) were formed under reaction conditions that would provide EP-like materials with "ethylene" contents greater than 50 mol % (see Table 1). The average lengths of methylene sequences are insufficiently long to allow for the onset of ambient temperature crystallinity.

Because *rac*-**2** can polymerize α-olefins in a living fashion, excellent molecular weight control and narrow polydispersity indices were obtained. Like traditional ethylene−propylene copolymers,[27−31] the chain straightened polyolefins have a T_g of ∼ 213 K (see Table 1). Some of the polymers with higher CH_2/CH_3 ratios exhibit, as noted, broad endothermic transitions from ∼223 to 250 K, consistent with the β-transitions observed in low-density polyethylene and highly branched polyethylene produced by other α-diimine Ni(II) catalysts.[6] Through variation of reaction temperature and olefin concentration the ratio of ω,2-enchainments (those that contain a methyl branch) to ω,1-enchainments (those that contain no branch) can be controlled.[9]

Table 2. Plateau Moduli and Entanglement Molecular Weights

		G_e (MPa)			M_e (kg/mol)		
sample	m_b	van Gurp	integral	$G'_{(min)}$	van Gurp	integral	$G'_{(min)}$
BUT-62	~16.7	1.49(±0.02)	1.74(±0.03)	1.46(±0.01)	1.46	1.25	1.40
PRO-63	16.6	1.48(±0.02)	1.76(±0.03)	1.48(±0.01)	1.47	1.24	1.47
HEX-65	~16.6	1.60(±0.01)	1.77(±0.01)	1.59(±0.01)	1.36	1.23	1.37
BUT-65	16.4	1.49(±0.02)	1.70(±0.03)	1.46(±0.01)	1.46	1.28	1.49
BUT-69	~16.1	1.42(±0.04)	1.66(±0.07)	1.40(±0.04)	1.53	1.31	1.55
ETH-70	~16.1	1.48(±0.02)	1.70(±0.03)	1.53(±0.11)	1.47	1.28	1.42
PEN-71	~16.0	1.56(±0.02)	1.69(±0.02)	1.54(±0.01)	1.39	1.29	1.41
HEX-74	~15.8	1.55(±0.02)	1.69(±0.01)	1.55(±0.01)	1.40	1.29	1.40
DEC-79	~15.5	1.01(±0.02)	1.29(±0.04)	1.02(±0.03)	2.15	1.69	2.13
OCT-82	~15.3	1.44(±0.04)	1.60(±0.02)	1.47(±0.07)	1.51	1.36	1.48

Since placement of these enchainments into the polymer is random, branches will be separated by varying numbers of methylene (CH_2) units. By using ^{13}C NMR spectroscopy, the global composition of these poly(olefin)s can be quantified in terms of the mole fractions of the different length methylene sequences present between branch points along the polymer backbone. In addition, the ratio of methylene to methyl groups present in the polymer (average no. of CH_2/CH_3) can be determined (Table 1). In order to compare these polymers to traditional ethylene−propylene copolymers, which are typically characterized by the mol % (or weight %) ethylene content, the average no. of CH_2/CH_3 value can be used to calculate the mol % ethylene.

One structural complication for olefins higher than propylene arises from the fact that insertion of monomer into a metal−secondary alkyl species can occur. As shown with 1-hexene in Scheme 2, complete chain walking to the end of an inserted monomer to form a metal-primary alkyl species can be disallowed if insertion occurs partway through the chain-walking event. This error results in the formation of a branch in the polymer longer than methyl, and its frequency is dependent on the length and concentration of the α-olefin employed, with longer α-olefins and higher initial olefin concentration favoring non-methyl branch formation.

Polyethylene. While the ethylene-based sample (ETH-70, Table 1) is structurally very similar to the poly(α-olefin)s produced, the mechanism for its formation is quite different. Since insertion of ethylene does not result in branch formation, the presence of branching in the sample results not from chain walking down the length of the inserted monomer but rather from chain walking back through the growing polymer chain itself[6] (Scheme 3). Insertion of subsequent ethylene into the metal−secondary alkyl species results in branch formation, the length of which being equal to the number of times the metal center chain walked.

Table 3. Rheological, Chain Dimension, and Characteristic Ratio Values

sample	G_e (MPa)	M_e (kg/mol)	ρ_e (nm^{-3})	$\langle R^2\rangle_0/M$ (Å^2 mol/g)[a]
		323 K		
BUT-62	1.56	1.37	0.35	1.09 (7.8)[b]
PRO-63	1.57	1.39	0.35	1.10 (7.8)
HEX-65	1.65	1.32	0.37	1.11 (7.9)
BUT-65	1.55	1.41	0.35	1.09 (7.6)
BUT-69	1.49	1.46	0.33	1.08 (7.4)
ETH-70	1.57	1.39	0.35	1.10 (7.5)
PEN-71	1.60	1.36	0.36	1.10 (7.5)
HEX-74	1.60	1.36	0.36	1.10 (7.4)
DEC-79	1.11	1.99	0.25	0.931 (6.2)
OCT-82	1.50	1.45	0.34	1.08 (7.1)298K
		298 K		
alt-PEP[28]	1.45[c]	1.45	0.35	1.04 (7.8)
EP: Ferry[29]	1.26[d]	1.67	0.31	0.996 (7.3)
EP: Ver Strate[30]	1.60[e]	1.32	0.39	1.08 (--)
EP: BGRS[31]	1.20[f]	1.75	0.29	0.980 (7.2)

[a] $\langle R^2\rangle_0/M = P_e^{0.667}[G_e/kT]^{0.333}[\rho N_{av}]^{-1}$. [b] Flory's dimensionless characteristic ratio. [c] MFE = 0.50. [d] MFE = 0.56. [e] The ethylene content of this sample (JBG-11) was not reported. The presence[28] of a T_m of 255 K for this fraction is indicative of a high ethylene content. [f] MFE = 0.56.

Rheological Behavior. The mechanistic characteristics described above limit the length of the ethylene segments so as to exclude, at ambient temperature, the formation of crystallites.

The G_e data for the chain straightened poly(olefin)s are given in Figure 3. With the exception of 1-decene, the poly(olefin)s prepared were found to have similar plateau moduli, 1.57 (±0.11) MPa at 323 K. This indicates, in terms of the packing model, that the compositions and chain dimensions were nearly equivalent in spite of the diverse structural range of the monomers. The values of G_e, M_e, and the characteristic ratios for the chain-straightened poly(olefin)s are similar to those recorded for conventional EP copolymers (Table 3). Examples come from Gotro and Graessley,[28] Ferry,[29] Ver Strate,[30] and Scholtens.[31] While the polymers formed by *rac*-**2**/MAO from a variety of higher α-olefins structurally resemble EP copolymers, other Ni α-diimine catalysts such as **1**/MAO typically produce poly(α-olefin)s that predominantly exhibit branches longer than methyl.[1,3,5,9] This difference in polymer structure correlates, expectedly, to a difference in plateau modulus. For example, a poly(1-hexene) sample with predominantly methyl branching formed using *rac*-**2**/MAO (HEX-65, Table 3) exhibits a plateau modulus of ~ 1.6 MPa, while Ye and co-workers[32] have reported that a poly(1-hexene) sample with predominantly butyl branching formed using **1**/MAO exhibits a plateau modulus of 0.74 MPa.

While ^{13}C NMR spectroscopy provides a great deal of structural information about these branched polymers, sensitivity limits the ability to distinguish branch length in branches longer than three carbons. In all of the polymer samples in Table 1, methyl branches predominate and are typically present in a mole fraction greater than ~0.8. A notable exception is the poly(1-decene) sample that has only 55 mol % methyl branches. Conversely, this sample has the highest concentration (43 mol %) of the 4+ carbon side groups. The large amount of non-methyl branching, however, was anticipated due to the relatively long length of 1-decene and to the high monomer concentration used in the polymerization.

This combination of methyl and 4+ branch populations explains the relatively low G_e value of ~1.1 MPa for sample DEC-79. The influence of side group length (in terms of m_b) on the chain dimension (and thus G_e) is seen in the linear plot of Figure 6. It is recognized[14,16−18] that for poly(α-olefin)s, $\langle R^2\rangle_0/M$ (and thus G_e, M_e, V_e and ρ_e) scale with the average molecular weight (m_b) per backbone carbon in a surprisingly regular way. The discontinuity in the chain dimension data can be explained by an increase in the *trans/gauche*(±) ratio once the number of side branch carbons exceeds that of the backbone

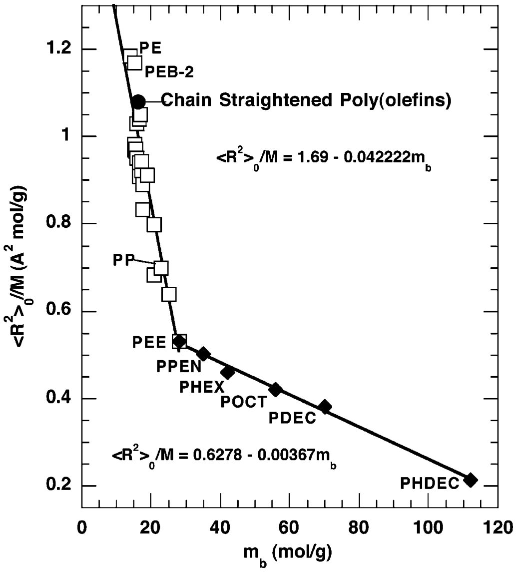


Figure 6. Chain dimensions as a function of m_b for atactic poly(olefin)s.[11−15,33,34] The identities of the polymer acronyms follow; PE = polyethylene; PEB-2 = polyethylene−butene copolymer with two ethyl branches per 100 backbone carbons; PP = polypropylene; PEE = poly(ethyl−ethylene); PPEN = polypentene; PHEX = polyhexene; POCT = polyoctene; PDEC = polydecene; PHDEC = poly(hexadecene). The open symbols are polyolefin samples where the data are given in refs 11−13.

olefin monomer unit. The population enhancement of the more extended *trans* conformer (at the expense of the *gauche*) requires the chain dimension to undergo an increase beyond the level anticipated from the behavior generated by the presence of methyl and ethyl groups.

The melt viscosities of polyethylene and ethylene copolymers containing propylene, 1-butene or 1-hexene yield the following universal[16] expression, $\eta = K(M_w/m_b)^{3.33}$. This behavior will be expected to be universal over the m_b range of 14 to 28. For m_b of 35 to 112 the value of K will change. It has also been suggested[16] that this ratio is connected to the poly(olefin) monomeric friction factors (ξ). Thus, the chain architecture based m_b parameter is directly related to at least some of the basic poly(olefinic) viscoelastic properties.

The chain dimensions of the chain-straightened poly(olefin)s can be estimated from the empirical expression found at the bottom of Table 3. The mean value (discounting the 1-decene based polymer) is 1.08 Å^2 mol/g. This value, taking into account the mild uncertainties in m_b (see below), yields satisfactory agreement with the projected behavior contained in Figure 6. This facet again demonstrates the capacity of the catalyst system to prepare an EP type of polymer from a variety of α-olefin monomers.

The m_b values for most of the chain straightened poly(olefin)s are not precisely known since analysis by ^{13}C NMR spectroscopy cannot distinguish between side units larger than propyl. Thus, the m_b values, listed in Table 2, should be considered to be close approximations. Furthermore, it is expected that the accuracy of this value decreases upon moving to longer α-olefins due to the fact that a greater population of branches of unknown length (longer than butyl) are likely to be present in the resulting polymer according to the proposed mechanism given in Scheme 2. Only two of the samples in Table 1 lack side groups with 4+ carbons. In one case, PRO-63, the side unit is exclusively methyl while for BUT-65 the side units are limited to methyl and a small amount of the ethyl structure. These two samples can be compared with DEC-79 where the 4+ content of side units reaches a mole fraction of 0.43. This balance of side chain structures and backbone methylene unit content serves to explain the G_e disparity between the ethylene to 1-octene based poly(olefin) family and the remaining EP style polymer based upon 1-decene (see Table 3). A foretelling of this behavior is seen in the depressed G_e value of DEC-79. However, as demonstrated by Coates and co-workers with the polymerization of 1-hexene using *rac*-**2**/MAO, significant changes in polymer microstructure are manifested through changes made in reaction conditions.[9] While the population of branches longer than methyl in these polymers is primarily controlled by the length of the monomer employed, the ratio of 6,1 and 6,2 enchainments can easily be controlled through reaction temperature and monomer concentration. Extending what is known of the polymerization of 1-hexene with *rac*-**2**/MAO to higher α-olefins such as 1-decene, the ability to produce poly(1-decene) with a lower occurrence of non-methyl branches and a higher MFE should be possible.

Conclusions

The use of a Ni(II) α-diimine catalyst system permits a useful synthetic maneuver that allows the preparation of ethylene−propylene like materials from a single olefin monomer charge. This chemistry holds for olefins ranging from ethylene to 1-octene. The mole fraction of methyl branches (with the exception of the 1-decene based polymer) ranges from 0.75 to 1. The ethyl and propyl structural concentrations are limited to mole fractions of 0 to 0.10, while the mole fractions of butyl groups, and larger, become >0.20 when 1-octene and 1-decene are used. Minimization of non-methyl side groups, coupled with a high methylene content in the backbone, maintains the high entanglement density in these EP-like polymers. This behavior was experimentally verified by a series of rheological measurements leading to the values of G_e. The results show the control of composition possible by the catalyst system for olefins ranging from ethylene to 1-octene.

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Supporting Information Available: Figure showing selected ^{13}C NMR spectra of the polymer samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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