New Pd(II)- and Ni(II)-Based Catalysts for Polymerization of Ethylene and α-Olefins

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There has been intense recent interest in the use of soluble early transition metal d⁰- and lanthanide d⁰fⁿ-based catalysts for polymerization of ethylene and α-olefins.[1] These well-defined initiators serve as mechanistic models for traditional Ziegler−Natta catalysts, and, in addition, structural variations in these homogeneous catalysts allow control of polymer microstructures and molecular weights.[1] In contrast to early metal systems, late metal catalysts most often dimerize or oligomerize olefins due to competing β-hydride elimination.[2] There are late metal systems which polymerize ethylene to high molecular weights[2c,3] but no systems which convert α-olefins to polymer with high molar mass.[2d] We report here new Pd(II)- and Ni(II)-based catalysts which convert ethylene *and* α-olefins to high molar mass polymers with unique microstructures.

The Pd(II) and Ni(II) initiators are cationic methyl complexes [(ArN=C(R)C(R)=NAr)M(CH₃)(OEt₂)]⁺BAr′₄⁻ (M = Pd, **1**; Ni, **2**; Ar′ = 3,5-C₆H₃(CF₃)₂) which incorporate bulky diimine ligands.[4] Protonation of the palladium **3** and nickel **4** dimethyl precursors with H(OEt₂)₂⁺BAr′₄⁻ results in loss of methane and formation of the diethyl ether adducts **1** and **2** (Scheme 1).[5] Results of polymerization reactions are summarized in Table 1. Exposure of the palladium ether adducts **1** to ethylene, propylene, or 1-hexene results in formation of high molecular weight polymers which were isolated as amorphous materials. The complex ¹³C NMR spectrum of the polyethylene produced indicates extensive branching along the main chain, with branches randomly distributed and of variable length.[6] The degree of branching can be estimated from ¹H NMR integration of the methyl, methylene, and methine groups (see Table 1). For example, initiator **1b** yields polyethylene with 103 branches/1000 carbon atoms. The amorphous polyethylene produced by these catalysts constitutes a new class of polyethylene, as it is far more highly branched than low-density polyethylene.[7]

The isolable nickel diethyl ether adducts **2** also catalyze the polymerization of ethylene and α-olefins and are more conve-

Scheme 1
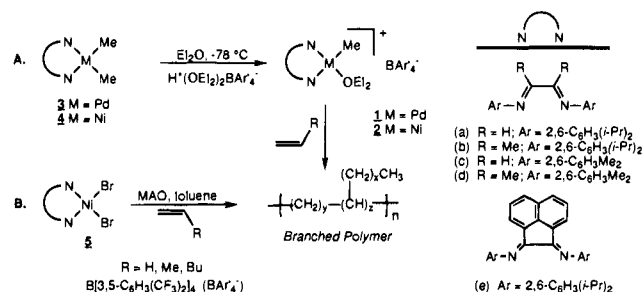
niently generated *in situ* by methylaluminoxane (MAO)[8] activation (1000 equiv, toluene) of the diimine nickel dibromide complexes, **5**, in the presence of olefins (Scheme 1, Table 1, entries 6−16). The polyethylenes produced by these Ni(II) catalysts range from highly linear to moderately branched, with methyl branches predominating. The extent of branching is a function of temperature, ethylene pressure, and catalyst structure. Increased branching occurs with increasing temperature, which results in lower melting temperatures of the semicrystalline polymers (compare entry 6 with 7, 9 with 10, and 13 with 14). At higher ethylene pressures, decreased branching is observed, but polymer yields and molecular weight values are similar (compare entry 9 with 11).[9] Reducing the steric bulk of the diimine ligand by substituting of *o*-methyl groups for *o*-isopropyl groups results in a less branched, more linear polymer with *decreased* molecular weight (compare entry 13 with 8).

The nickel catalysts exhibit extremely high activities which are comparable to those of metallocene catalysts.[1] For example, **5a** + MAO (entry 7) exhibits an apparent turnover frequency of 3.9 × 10⁵/h (11 000 kg of PE mol⁻¹ of Ni h⁻¹). Such high activities require highly dilute catalyst solutions to prevent mass transfer-limited rates. In addition to ethylene, α-olefins are also polymerized by these diimine nickel catalysts to produce high molecular weight polymers. For example, propylene is polymerized by **5e** + MAO at 0 °C in toluene to produce amorphous polypropylene (126 kg of PP mol⁻¹ Ni h⁻¹, 3000 TO/h), while 1-hexene (**5a** + MAO at 0 °C, toluene) produces amorphous poly-1-hexene (176 kg mol⁻¹ of Ni h⁻¹, 2000 TO/h).

Insight into the polymerization mechanism was gained through NMR studies, which established alkyl olefin complexes as the catalyst resting states. Reaction of the palladium ether adducts **1a,b** with ethylene at −80 °C resulted in the formation of ethylene adducts **6a,b** (eq 1).[5] The rate of exchange of bound

$$(2)$$
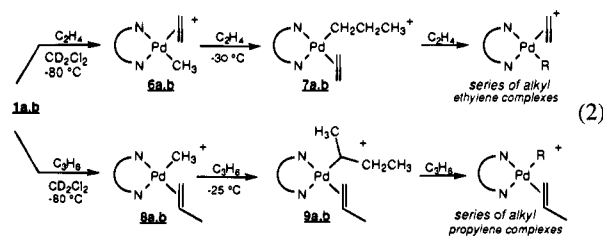
ethylene with free ethylene in **6a,b** was dependent on ethylene concentration (implying associative exchange) and was faster in **6a** than in **6b**.[10] Upon warming, chain growth, which was zero order in ethylene, was monitored by ¹H and ¹³C NMR spectroscopy as a series of new alkyl olefin complexes appeared.

(1) As leading references, see: (a) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219. (b) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (c) Coughlin, E. B.; Bercaw, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 7606−7607. (d) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455−1457. (e) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507−508. (f) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355−6364.

(2) (a) Rix, F.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137−1138. (b) Peuckert, M.; Keim, W. *Organometallics* **1983**, *2*, 594−597. (c) Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 185−206. (d) Certain Ni(II) catalysts convert α-olefins to oligomers with degrees of polymerization of ~4−20: Möhring, V. M.; Fink, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1001−1003.

(3) (a) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443−1444. (b) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvath, I. T.; Millar, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634−5636. (c) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466−467. (d) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123−134.

(4) Van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151−239.

(5) Complete details are given in the supplementary material.

(6) (a) The ¹³C APT NMR spectrum shows multiple methine, methylene, and methyl signals. (b) McCord, E.; McLain, S., unpublished results.

(7) Branching in LDPE: Axelson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, *12*, 41−52.

(8) Kaminsky, W.; Miri, M.; Sinn, H.; Woldt, R. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 417.

(9) The change in microstructure with monomer concentration (pressure) has seen precedent in the early metal systems. Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329−9330.

(10) Associative second-order rate constants for ethylene exchange in CD₂Cl₂ at −85 °C were measured by ¹H NMR line shape analysis: **6a**, *k* = 8100 L mol⁻¹ s⁻¹; **6b**, *k* = 45 L mol⁻¹ s⁻¹.

Table 1. Summary of Olefin Polymerization Data

entry	catalyst	moles of catalyst ($\times 10^6$)	conditions	monomer[a]	yield (g)	M_n[b] ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	branches per 1000 carbons	thermal analysis (°C)[c]
1	**1a**	100	50 mL of CH_2Cl_2, 25 °C, 24 h	ethylene	9.7	0.06	0.18	3.0	116	−85 (T_g)
2	**1b**	100	100 mL of CH_2Cl_2, 25 °C, 17 h	ethylene	45.3	2.9	11.2	3.9	103	−68 (T_g)
3	**1b**	50	50 mL of CH_2Cl_2, 25 °C, 16 h	propylene	19.5	1.5	6.6	4.3	213	−43 (T_g)
4	**1b**	100	50 mL of CH_2Cl_2, 25 °C, 2 h	1-hexene	10.9	3.1	7.7	2.5	88	−42 (T_g)
5	**2a**	0.83	75 mL of toluene, 0 °C, 30 min	ethylene	1.5	9.2	28	3.0	6.0	129 (T_m)
6	**5a**/MAO	1.7	100 mL of toluene, 0 °C, 15 min	ethylene	2.6	11	28	2.7	7.0	129 (T_m)
7	**5a**/MAO	1.7	100 mL of toluene, 25 °C, 15 min	ethylene	4.6	3.1	7.6	2.5	38	95 (T_m)
8	**5e**/MAO	17	100 mL of toluene, 0 °C, 30 min	ethylene	7.0	17	39	2.3	74	97 (T_m)
9	**5e**/MAO	0.83	100 mL of toluene, 30 min	ethylene	2.2	65	160	2.4	24	112 (T_m)
10	**5e**/MAO	0.83	100 mL of toluene, 25 °C, 30 min	ethylene	1.8	19	41	2.2	71	39 (T_m), −46 (T_g)
11	**5e**/MAO	0.83	200 mL of toluene, 0 °C, 30 min	ethylene[d]	2.1	61	140	2.3	5.0	122 (T_m)
12	**5b**/MAO	1.6	100 mL of toluene, 0 °C, 15 min	ethylene	1.2	52	81	1.6	48	109 (T_m)
13	**5c**/MAO	17	100 mL of toluene, 0 °C, 30 min	ethylene	3.4	4.3	11	2.5	1.2	132 (T_m)
14	**5c**/MAO	17	100 mL of toluene, 25 °C, 30 min	ethylene	7.2	1.4	4.0	2.9	29	112 (T_m)
15	**5d**/MAO	17	100 mL of toluene, 0 °C, 10 min	ethylene	5.1	17	44	2.6	20	115 (T_m)
16	**5e**/MAO	17	50 mL of toluene, 0 °C, 2 h	propylene	4.3	15	24	1.6	300	−20, −78 (T_g)
17	**5e**/Et_2AlCl[e]	17	50 mL of toluene, 0 °C, 2 h	1-hexene	2.1	14	31	2.2	100	−57 (T_g), −20 (T_m)

[a] Ethylene polymerizations run at 1 atm pressure unless otherwise indicated. [b] Molecular weight data reported against polystyrene standards. [c] T_m and T_g were determined by differential scanning calorimetry. [d] Polymerization run at 4 atm ethylene pressure. [e] Al:Ni ratio of 10:1.

Scheme 2

chain migration chain growth
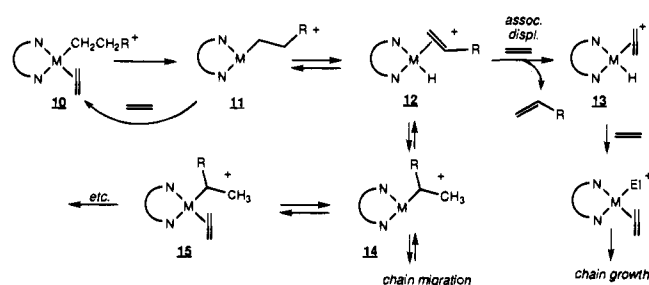
The first-order rate constants for the first insertions were obtained from the rates of disappearance of **6a,b** at −30 °C: $k_{6a} = 1.9 \times 10^{-3}$ s^{-1}, $\Delta G^{\ddagger} = 17.2$ kcal/mol; $k_{6b} = 1.7 \times 10^{-3}$ s^{-1}, $\Delta G^{\ddagger} = 17.3$ kcal/mol.[5] The rates of subsequent insertions were modeled by the zero-order rate of ethylene disappearance: $k'_{6a} = 8.8 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger} = 17.6$ kcal/mol; $k'_{6b} = 3.4 \times 10^{-3}$ s^{-1}, $\Delta G^{\ddagger} = 16.9$ kcal/mol. Treatment of **1a,b** with propylene at −30 °C resulted in formation of the propylene methyl complexes **8a,b**.[5] Chain growth could again be monitored at −30 °C; the first-order rate constant for migratory insertion of **8b** is 5.4×10^{-4} s^{-1}, $\Delta G^{\ddagger} = 17.8$ kcal/mol.[5] Significantly, the first insertion of propylene enables observation of propylene alkyl complex **9a**, which suggests a 2,1 regiochemistry for insertion.

A mechanistic rationale for the observations described here is outlined in Scheme 2 (R = polymer chain). The catalyst resting states are alkyl olefin complexes indicated by structure **10**. Migratory insertion results in **11**, which can be rapidly trapped by ethylene to reform to an alkyl ethylene species **10**. Alternatively, **11** can also β-hydride eliminate to yield an olefin hydride **12**. Complex **12** can undergo reinsertion with opposite regiochemistry, which introduces a branched alkyl group in **14**. Trapping and insertion of **14** produces a methyl branch, while further chain migration via β-hydride elimination and readdition processes produces longer branches.[11] In a chain transfer

process, complex **12** can release olefin to yield **13**, which can initiate a new chain. However, in these M(II) square planar complexes, conversion of **12** to **13** must be an associative process, as observed for ethylene exchange in the analogous methyl complexes **6a,b**. The rates of associative displacement and chain transfer (**12** to **13**) are greatly retarded by the extreme steric bulk of the diimine ligands. The aryl rings lie roughly perpendicular to the square plane, and the ortho substituents block axial approach of olefins. This feature results in rates of chain propagation which are much greater than chain transfer rates and thus permits formation of high polymers.[12,13]

In summary, these Ni and Pd diimine olefin polymerization catalysts are unique late metal systems capable of converting α-olefins to high polymers and are the first systems in which olefin alkyl complexes have been demonstrated to be the catalyst resting states. In addition, this is the first reported catalyst system where simple variation of pressure, temperature, and ligand substituents allows access to an ethylene homopolymer whose structure varies from a highly branched, completely amorphous material to a linear, semicrystalline, high-density material. Successful copolymerization of ethylene with functionalized comonomers will be reported shortly.

Supplementary Material Available: Details of catalyst and polymer synthesis and characterization (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

(11) 2,1-insertions of α-olefins followed by chain migration (see Scheme 2) to the terminal carbon can result in *fewer* branches than observed in polymers where chain growth occurs by 1,2-insertions (see Table 1, entries 3 and 4).

(12) Consistent with this postulate, **6a** yields polyethylene of lower molecular weight than **6b**. (Phenanthroline) Pd (Et)(H_2C=CH_2)$^+$ BAr'$_4^-$ only *dimerizes* ethylene,[3a] and associative exchange with ethylene is too fast to measure at −100 °C.

(13) This mechanistic scheme is consistent with lower branching at higher ethylene pressures (shorter lifetimes of **11** ⇌ **12**) and higher branching under mass transfer-limited conditions (longer lifetimes of **11** ⇌ **12**).