Neutral, Single-Component Nickel (II) Polyolefin Catalysts That Tolerate Heteroatoms

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More than half of the 170 million metric tons of polymers produced each year are polyolefins. Current technology uses highly active cationic catalysts, which suffer from an inability to tolerate heteroatoms such as oxygen, nitrogen, and sulfur. These systems require scrupulously clean starting materials and activating cocatalysts. A family of catalysts has been developed whose members are tolerant of both heteroatoms and less pure starting materials. These heteroatom-tolerant neutral late transition metal complexes are in fact highly active systems that produce high-molecular-weight polyethylene, polymerize functionalized olefins, and require no cocatalyst.

For years, polyethylene (PE) has been used in food packaging, coatings, countless molded toys, and other household items, and it is finding its way into the market to replace common materials such as glass, metal, paper, and concrete (*1*). The demand for PE is projected to reach 50 million metric tons (1.1×10^{11} pounds) annually by the year 2003 (*2*).

Ziegler and Natta discovered new catalysts for the polymerization of various α-olefins to produce many of the polyolefin products commonly termed "plastics" (*3*). Their original discovery, which led to the dominant technology used industrially, was based on heterogeneous systems that are ill-defined. These systems' mode and mechanism of action still remain a topic of current research.

Shortly after the first reports of metallocenes, these well-defined organometallic species activated with alkylaluminum cocatalysts found use as homogeneous olefin polymerization catalysts (*4–6*). Industrial interest was not sparked, however, until work by Sinn, Kaminsky, Brintzinger, Ewen, Turner, and others demonstrated that metallocenes combined with aluminoxanes led to long-lived catalysts with very high activity (*7–11*). Later it was shown that propene could be polymerized stereospecifically to produce a variety of polymers with novel uses and properties (*9*, *12*). As a result of these findings, the past 15 years have witnessed a new era of worldwide polyolefin catalyst research. The design and application of metallocenes have revolutionized polyolefin chemistry and are only now having an impact on commercially produced materials.

Key to these advancements is the increased understanding of the important factors for stabilizing polymerization-active metal centers and controlling their activity and selectivity (*12*). Most homogeneous catalysts have been based on "early" transition metals (those to the left of the periodic table) (Fig. 1) (*13*). Important to the success of these systems is the formation of a cationic metal center (that is, L_nMR^+, where L is a ligand, M is the transition metal, and R is an alkyl, hydrido, or aryl group), which is both coordinately unsaturated and highly electrophilic (*14*). These sensitive systems require "air-free" handling and rigorous exclusion of moisture, yet the formation of such cationic metal centers remains the single most common design feature for polymerization catalysts (*15*). Several cationic late transition metal systems that have followed this lead have recently been reported (*15*).

Highly active selective catalysts that could tolerate a variety of functional groups would extend these catalysts to work with new monomer combinations to exert ever greater control over the properties of the resultant polymers. Both traditional catalysts for Ziegler-Natta polymerization and cationic metallocenes suffer because heteroatoms (such as O, N, and S) poison the catalysts and cocatalysts [such as modified aluminoxane (MAO)]. In fact, a substantial cost in the production of polyolefins is incurred in the hyperpurification of the monomer feed.

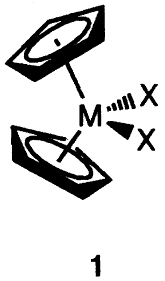
In an attempt to find a catalyst family that could tolerate many functional groups and still produce functionalized linear polyolefin materials from available feedstocks, we chose late transition metal complexes as our starting point. Late transition metals are characteristically less oxophilic than the early metals and are thus more tolerant of functional groups. For example, ruthenium metathesis catalysts maintain high activity in the presence of a wide range of functional groups, including water and acid (*16*).

In addition, the neutral Ni-catalyzed Shell higher olefin process (SHOP) developed by Keim is a prominent industrial method for the synthesis of linear ethylene oligomers in the C_4 to C_{20} range, which are converted to detergents, plasticizers, lubricants, and a variety of fine chemicals (*17*). This complex, **3**, contains a phosphorus-oxygen (P–O) ligand chelate and requires high pressures and temperatures to work productively (Fig. 2). The SHOP process, which is based on insertion-type reactions, has demonstrated an unprecedented tolerance for polar functional groups, so that oligomerizations can be run in solvents such as ethanol or acetone. Under special conditions, it was demonstrated that adding a cocatalyst led to moderate production of linear PE (*18*, *19*). The SHOP catalysts only incorporated functional comonomer when several methylene spacers separated the olefinic bond (C=C) and the functional group (*18*).

We rationalized that replacing the P–O chelate of the neutral SHOP system with a "harder" nitrogen-based ligand containing increased steric demand might lead to higher molecular weight (M_w) products (*20*). This rationale was originally applied to cationic Ni(II) systems by Brookhart *et al.* (*21*). We chose salicylaldimines as the scaffold, because this ligand system allowed manipulation of both the steric and electronic parameters of the metal center. Accordingly, we prepared and reported the Ni(II) complexes **6** through **10** (Fig. 3) (*22*).

Because the SHOP system required cocatalyst activation, we screened these catalysts for the polymerization of ethylene under similar conditions. Complexes using ligands with less bulk than **6** were shown to be inactive in all tests. However, when the steric bulk was increased, PE with M_w ~5000 was obtained (*23*). Unfortunately, this ill-defined mixture had an extremely brief lifetime, possibly due in part to an accelerated decomposition in the presence of the cocatalysts.

Klabunde and co-workers have demon-



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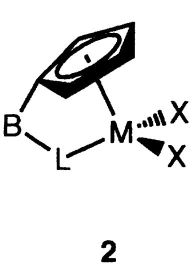

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Fig. 1. Two classes of metallocenes (X, halide): biscyclopentadienyl (**1**) and monopcyclopentadienyl (**2**), with a bridging unit (B) and a donating ligand (L).

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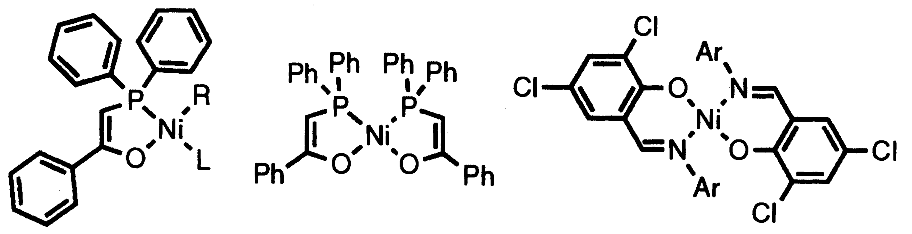
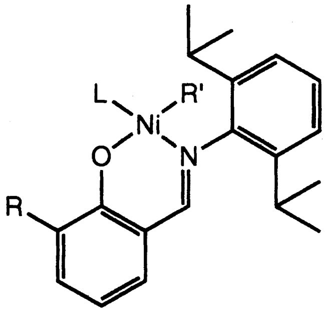


3 **4** **5**

Fig. 2. **3**, Classical SHOP complex. **4**, deactivated SHOP complex or bis ligand complex. **5**, bis ligand analog of salicylaldimine systems, which is inactive for ethylene polymerization under standard conditions.

strated that the mode of inactivation for the SHOP complexes was by formation of the bis ligand complex, **4** (Fig. 2) (*18*, *19*, *24*). We prepared and tested complex **5**, an analogous bis ligand salicylaldimine complex. Similar to the SHOP system, compound **5** was inactive for ethylene polymerization under our standard conditions (*25*). No bis ligand species was observed when a ligand with sufficient ortho bulk was used. For example, catalysts **7** and **8** not only produced PE with M_w in excess of 20,000 but also demonstrated a threefold increase in catalytic lifetime.

By using sufficient bulk in the ortho position of the salicylaldimine ligand to aid phosphine dissociation and to prevent disproportionation of the ligand, we were able to isolate and characterize a new family of neutral, single-component catalysts, **8** through **10**. These catalysts can produce PE with M_w > 250,000 and with fewer than 10 branches per 1000 carbon units (Table 1). In the absence of cocatalysts, these catalysts have an indefinite lifetime and are capable of producing turnover frequencies (TOFs) from 0.5 × 10^6 to 3.0 × 10^6 g of PE per mole of catalyst per hour at low temperatures and pressures. Under our conditions, this relatively linear, low-branched PE contrasts with the highly branched materials obtained with the recently disclosed cationic Ni(II) and Pd(II) systems (*21*).



6 - 13

	R	R'	L
6	H	Ph	Ph_3P
7	^tBu	Ph	Ph_3P
8	Ph	Ph	Ph_3P
9	Phen	Ph	Ph_3P
10	Anth	Ph	Ph_3P
11	Anth	CH_3	CH_3CN
12	Trityl	CH_3	CH_3CN
13	TPhen	CH_3	CH_3CN

Fig. 3. Ni(II) salicylaldimine complexes. Compounds **6** and **7** require cocatalyst activation. Compounds **8** through **13** are neutral, single-component polymerization catalysts. Abbreviations: ^{t}Bu, tert-butyl; Ph, phenyl; Phen, 9-phenanthroline; Anth, 9-anthracene; Trityl, triphenylmethyl; TPhen, *meta*-terphenyl.

A dissociated phosphine was not observed in nuclear magnetic resonance (NMR) spectroscopic studies of the polymerization reaction. Proton and phosphorus NMR show only three phosphine species, which we have assigned to be (i) starting material, (ii) an alkyl complex (a growing polymer chain), and (iii) a hydrido complex (a chain-terminated species ready to reenter the catalytic cycle) (Fig. 4). This result suggests that the resting state of these systems is the phosphine complex. However, careful experiments showed that the addition of varying amounts of additional phosphine reduced the catalytic activity of the complexes. For example, when complex **10** was used in a reaction vessel and one equivalent of triphenylphosphine was added, the catalyst's activity was reduced by half and several equivalents completely stopped the polymerization. Furthermore, when one equivalent of tricyclohexylphosphine (a more basic and coordinating ligand) was added, a more than twofold reduction in catalyst activity was observed.

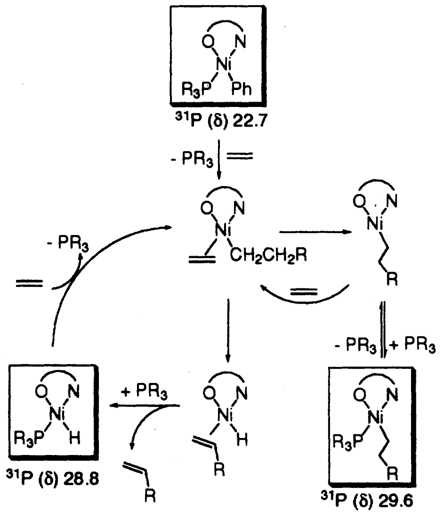


Fig. 4. Possible catalytic cycle based on ^{31}P NMR spectroscopic studies. Boxed structures are tentatively assigned on the basis of observed species.

The phosphine-containing catalysts' activity increased with temperature. However, they are susceptible to deactivation above 80°C under polymerization conditions. The optimal operating temperatures are between 45° and 50°C. At these slightly elevated temperatures, complex **10** exhibits an activity of 3.7 × 10^6g of PE mol^{-1} of Ni $hour^{-1}$. This activity is comparable to that of "classical" metallocenes, such as $(Cp_2ZrMe)^+[B(C_6F_5)_4]^-$ (= 4.5 × 10^6 g of PE mol^{-1} of Zr $hour^{-1}$) and other highly active late metal cationic systems with cocatalysts such as MAO; for example, [(Ar*N* = C(Me)C(Me)=*N*Ar]NiBr$_2$/MAO = 3.0 × 10^6 g of PE mol^{-1} of Ni $hour^{-1}$; Ar = 2,6-$(^iPr)_2C_6H_3$] (*21*, *26*); where Pr = isopropyl and *N* = nitrogen. The rate of β-hydride elimination in our system also increased with temperature, yielding lower M_w and higher branched polymer at elevated temperatures. The detailed mechanistic aspects of polymerizations using these complexes remain to be addressed.

In an attempt to further enhance the activity of the catalyst, we prepared complexes **11** through **13**, which contained acetonitrile, a ligand that is more labile than

Table 1. Polymerization of ethylene with catalysts **6** through **13**. Conditions were as follows: 65 μmol of catalyst, 90 ml of toluene, 100 psig (6.9 × 10^5 Pa) of ethylene, and a 10°C external bath used to control any exotherm. PDI, polydispersity index. The branch content is total methyl, ethyl, propyl, and butyl branches per 1000 carbons. TOFs are in 10^6 g of PE $mol^{-1}$of Ni $hour^{-1}$. For **6** through **8**, 130 μmol of Ni(cyclooctadiene)$_2$ was used as a cocatalyst. Typical reaction times for these trials were 10 min. Typical reaction times for single-component trials were 1 to 2 hours.

Catalyst	M_w (×10^3)	PDI [M_w/M_n]	Branch content	T_m (°C)	TOF
		Cocatalyst activation			
6	3.4	1.5	45	89.4	0.16
7	11.4	1.8	55	95.0	0.29
8	23.5	2.3	40	92.6	0.57
		Single-component catalysts			
8	207.0	2.2	10	132.9	0.10
9	207.0	2.4	8	129.5	0.31
10	236.0	2.2	5	133.2	0.94
10*	347.0	3.0	5	136.1	1.20
11	11.3	3.0	55	105.5	2.10
11*	120.0	3.0	20	128.3	6.40
12	6.1	1.6	50	87.3	0.58
13	532.0	2.1	7	121.6	0.96

*250 psig of ethylene without temperature control.

triphenylphosphine. These complexes were synthesized by reacting the ligand with the previously reported Ni(Me)$_2$TMEDA (TMEDA, tetramethylethylene-diamine) (*27*). This family of catalysts exhibits a two- to threefold increase in catalytic activity as compared with catalysts **8** through **10**, without any observable compromise to the apparent indefinite catalyst lifetime. Activities are in the mid- to upper 10^6 g of PE per mole of catalyst per hour at relatively low temperatures and pressures. These catalysts can produce PE with $M_w > 250{,}000$, branching about 5 to 20 per 1000 carbon atoms. Similar to their phosphine-containing analogs, these catalysts appear to be active at elevated temperatures.

To determine whether these neutral systems were tolerant of functional groups, a number of polar species were added in large excess relative to catalyst **10** during polymerization reactions (Table 2). The catalyst maintained high activity in the presence of ethers, ketones, and esters. The addition of water had little impact on the polymerization. In the presence of 1500 equivalents of H_2O, PE could still be produced at a rate of 5.4×10^4 g of PE mol^{-1} of Ni $hour^{-1}$. There was, however, a marked decrease in both lifetime and activity upon addition of excess coordinating protic solvents such as alcohols and amines. The addition of acids deactivated the complex under polymerization conditions, and no polymers were produced. Proton NMR studies reveal that catalyst **10** decomposes by protonation and decomplexation of the salicylaldimine ligand from the metal center.

Preliminary experiments showed that **10** and **11** not only tolerate polar monomers such as substituted norbornenes, carbon monoxide, and α-ω functional olefins but can incorporate them into the polymer chain (Fig. 5).

The family of neutral, single-component, late transition metal olefin polymerization catalysts we have synthesized show that a cationic metal center is not required to achieve high polymerization activity. These catalysts exhibit activities that are comparable to those of the early metallocenes. The promise of these catalysts is realized in their ability to polymerize ethylene in the presence of functional additives such as ethers, ketones, esters, alcohols, amines, and water, and in their incorporation of polar monomers into the polymer backbone in variable quantities.

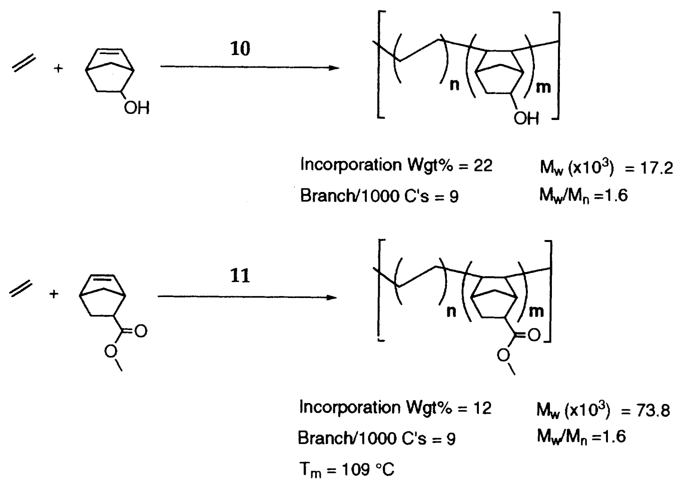
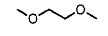
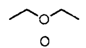
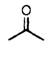
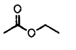
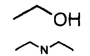
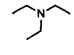


Fig. 5. Copolymerization of ethylene and functionalized olefins with catalysts **10** and **11**. Conditions were as follows: 65 μmol of catalyst, 90 ml of toluene, 100 psig (6.9×10^5 Pa) of ethylene, ~225 equivalents of functionalized olefin, and 10°C external bath used to control any exotherm. M_n, number average molar mass; T_m, melting temperature.

Table 2. Ethylene polymerization with **10** in the presence of functional additives. Conditions were as follows: 65 μmol of catalyst, 90 ml of toluene, 10 ml of additive (~1500+ equivalents), 100 psig (6.9×10^5 Pa) of ethylene, and a 10°C external bath used to control any exotherm. Typical reaction time was 3 hours. The branch content is total methyl, ethyl, propyl, and butyl branches per 1000 carbons. TOFs are in 10^6 g of PE mol^{-1} of Ni $hour^{-1}$.

Additive		M_w (x10^3)	PDI [M_w/M_n]	Branch content	T_m (°C)	TOF
Dimethoxyethane		270.0	2.4	3	135.5	0.49
Diethylether		241.0	2.0	3	135.2	0.31
Acetone		131.0	3.7	13	127.8	0.08
Ethylacetate		188.0	2.0	3	136.6	0.07
Water	H_2O	90.1	2.0	4	129.6	0.05
Ethyl alcohol		40.6	3.0	17	129.2	0.02
Triethyl amine		28.2	2.6	22	129.3	0.01

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