New Phenoxyketimine Titanium Complexes: Combining Isotacticity and Living Behavior in Propylene Polymerization

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Research focusing on homogeneous olefin polymerization catalysis has proliferated in recent years. In addition to metallocene-type catalysts, transition metal active sites are now supported by ancillary ligand frameworks incorporating a wide variety of structural motifs.[1] Homogeneous catalyst systems offer both the option to use ligand geometry for precise control of polymer stereochemistry and the potential to use living catalysts to synthesize block copolymers. Many catalysts can generate highly isotactic polypropylene (iPP),[2] and there are a number of living catalysts for propylene polymerization.[3] Despite 50 years of intense research since Natta's synthesis of iPP,[4] living isospecific propylene polymerization catalysts remain unreported. Such catalysts could be used to synthesize iPP block copolymers that have valuable applications as compatibilizers and thermoplastic elastomers. Sita[5] and Kol[6] have developed catalysts for the living, highly isospecific polymerization of 1-hexene. Busico has reported that Kol-type catalysts are controlled for propylene polymerization and have been used to generate iPP-*block*-PE (PE = polyethylene) copolymers.[7]

Bis(phenoxyimine)titanium catalysts were originally reported for the polymerization of ethylene,[8a] but later studies showed that they had promise for syndiospecific propylene polymerization behavior.[8b–e] If the phenoxyimine (PHI) ligands contain *ortho*-fluorinated *N*-aryl groups and bulky *ortho*-phenol substituents (R^1, see Scheme 1), then the resulting catalysts are active for living, highly syndiospecific propylene polymerization despite being C_2-symmetric both in solution and in the solid state.[8d,e] Ligand isomerization between monomer insertions to give enantiomeric sites is believed to cause this unusual stereocontrol, which is dictated by the chain end of the polymer.[8c,9] As the size of R^1 is reduced for this class of aldimine (R^3 = H) PHI catalysts, syndiotacticity decreases.[8e] Fujita and coworkers have been able to generate iPP using zirconium and hafnium PHI complexes with alkylaluminum/borate activators.[10] The PHI ligands react with the aluminum co-catalyst under these conditions; activation of the same complexes with methylaluminoxane (MAO) yields atactic, regioirregular polypropylene. We have previously reported a series of titanium phenoxyketimine ($R^3 \neq$ H) catalysts with bulky ortho substituents ($R^1 = {}^tBu$) for the living polymerization of ethylene.[11] In this communication, we report a living titanium catalyst that produces crystalline, predominantly isotactic PP.

Although ketimine catalysts with $R^1 = {}^tBu$ (**1**) are active for living ethylene polymerization, they are sparingly active and generally not well behaved for propylene polymerization. We reasoned that smaller ortho substituents might reduce steric congestion around the active metal center and result in active catalysts for the formation of stereoregular polypropylene. Complexes **1–6** contain ligands with *N*-pentafluorophenyl groups and were synthesized using previously reported procedures.[8d,11] Ketimine complexes **1–5** have R^3 = Ph and have *ortho*-phenol substituents that decrease in size from $R^1 = {}^tBu$ to $R^1 =$ H. Phenoxyaldimine (R^3

Scheme 1. Olefin Polymerization Using Phenoxyketimine Catalysts
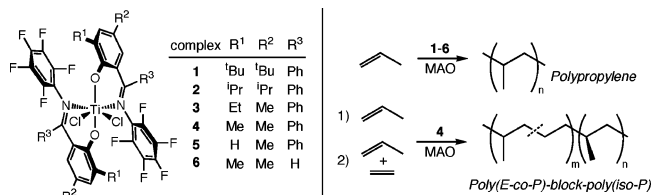
= H) complex **6** can be compared to complex **4**. When activated with MAO, **1–6** are active catalysts for propylene polymerization (Table 1). Catalysts **2–4** produce PPs that are substantially isotactic. All catalysts except for **1** form PP with narrow molecular weight distributions indicative of living behavior ($M_w/M_n \leq 1.17$). As with aldimine catalysts, activity increases as the size of R^1 decreases. The stereoerrors present in the PP ^{13}C NMR spectra (*mmmr*, *mmrr*, and *mrrm* pentads, 2:2:1 ratio; Figure 1) are consistent with an enantiomorphic site-control enchainment mechanism. This contrasts previously reported syndiospecific PHI catalysts, which govern polymer stereochemistry by chain-end control.[8c] Polypropylenes produced by catalysts **2–4** are not completely regioregular: the NMR spectra contain small peaks arising from head-to-head and tail-to-tail mis-insertions (<5%). There are no olefin peaks in the NMR spectra, suggesting that β-H and β-alkyl elimination reactions do not occur during the polymerization.

Of the catalysts tested, **4** produces PP with the highest isotacticity and was used to further investigate catalyst behavior. To demonstrate the living behavior of **4**, we carried out propylene polymerizations from 1 to 10 h at 0 °C (Figure 2). The molecular weight increased linearly with polymer yield, and M_w/M_n values were consistently narrow for all polymerizations. Another requirement for living catalysts is the ability to synthesize monodisperse block copolymers via sequential monomer addition. To demonstrate this ability, we synthesized an iPP-*block*-E/P (E/P = ethylene/propylene copolymer) diblock copolymer using **4**. Narrow molecular weight distributions (both $M_w/M_n = 1.10$) were measured for both the initial iPP block (M_n = 28.1 kg/mol) and the final diblock product (M_n = 62.0 kg/mol).

The effect of temperature on polymerization behavior was also investigated (Table 1). Activity and molecular weight both increased with increasing temperature, and molecular weight distributions remained narrow. At low temperatures, isotacticity increased but catalyst activity was greatly reduced. Preliminary α,ω-diene cyclopolymerization experiments with **4**/MAO support a 2,1-insertion mechanism, as with other PHI catalysts.[12]

Catalysts **1–5** display polymerization behavior significantly different than that of previously reported PHI catalyst systems. The addition of a seemingly remote R^3 substituent shifts polymer stereochemistry from slightly syndiotactic to isotactic. We propose that the R^3 group is bulky enough to prevent catalyst racemization,

Table 1. Propylene Polymerization Data for Catalysts **1**−**6**/Methylaluminoxane[a]

catalyst	method[b]	T_{rxn} (°C)	yield (g)	TOF (h^{-1})[c]	M_n (g/mol)[d]	M_w/M_n[d]	Tacticity[e] [m[4]]	[r[4]]	α[f]	T_g (°C)[g]	T_m (°C)[g]
1[h]	A	0	0.16	9	bimodal	broad	0.07	0.26	NA[k]	−8.6	ND[l]
2	A	0	0.13	35	2710	1.12	0.46	<0.01	0.85	−18.4	ND[l]
3	A	0	0.40	105	7290	1.17	0.45	<0.01	0.85	−14.1	ND[l]
4	A	0	1.11	293	27940	1.11	0.53	<0.01	0.89	−12.5	69.5
5	A	0	1.22	323	35440	1.12	0.08	0.13	NA[k]	−5.5	ND[l]
6[i]	A	0	2.05	1690	123100	1.13	<0.01	0.22	NA[k]	−2.9	ND[l]
4[j]	B	−20	0.44	41	33700	1.15	0.61	<0.01	0.91	−12.9	96.4
4	B	0	0.17	138	13580	1.16	0.54	<0.01	0.89	−13.8	70.1
4	B	20	0.32	267	16760	1.13	0.48	<0.01	0.85	−12.0	ND[l]
4	B	50	1.23	967	59370	1.10	0.27	0.02	0.77	−9.2	ND[l]

[a] General conditions: catalyst in toluene (5 mL) was added to a propylene-saturated PMAO−IP solution (100 mL of toluene; [Al]/[Ti] = 150) for 3.0 h. [b] Method A: 0.03 mmol of catalyst, reactor pressure maintained at 30 psi during polymerization. Method B: 0.01 mmol of catalyst, closed reactor to maintain a constant initial [propylene] at different temperatures. [c] Turnover frequency (TOF): mol propylene/(mol Ti·h). [d] Determined using gel permeation chromatography in 1,2,4-C$_6$H$_3$Cl$_3$ at 140 °C versus polyethylene standards. [e] Determined by integration of the methyl region of the ^{13}C NMR spectrum. [f] Enantiofacial selectivity parameter, calculated from the ^{13}C NMR spectrum using the equation [m[4]] = α^5 + (1 − α)^5. [g] Determined using differential scanning calorimetry (2nd heating). [h] t_{rxn} = 15.0 h. [i] 0.01 mmol **6**. [j] t_{rxn} = 24.0 h. [k] Not applicable; data does not fit site control statistics. [l] None detected.
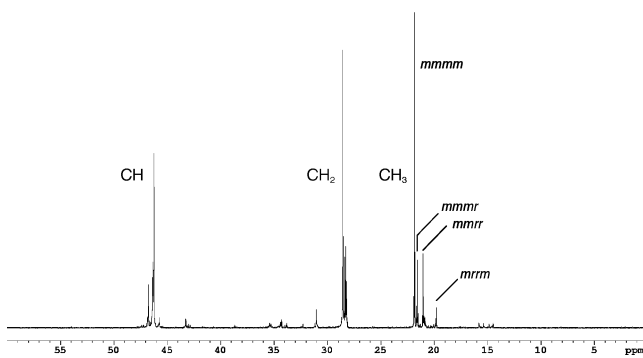
Figure 1. ^{13}C NMR (1,1,2,2-C$_2$D$_2$Cl$_4$, 125 MHz, 100 °C) of isotactic PP formed by **4**/MAO at 0 °C. Unmarked shifts are due to regioinversions.
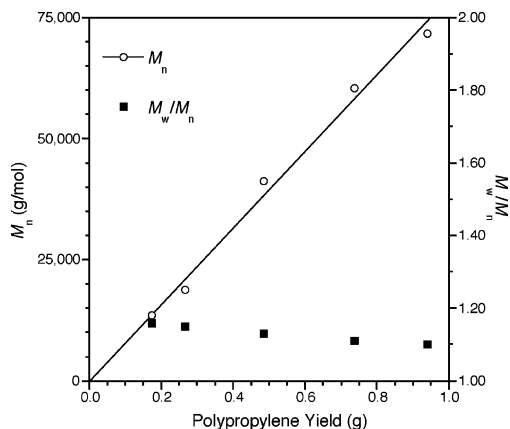
Figure 2. Plot of PP M_n (○) and M_w/M_n (■) versus yield using **4**/MAO at 0 °C, determined by gel permeation chromatography (PE standards).

resulting in the formation of iPP via a site control mechanism. The activity and facial selectivity of a given ketimine catalyst depend on the size of R^1. Presumably, catalyst **1** (R^1 = ^{t}Bu) has the largest steric interaction between R^1 and the incoming monomer, resulting in a high isospecific insertion barrier and making **1** a poor catalyst. Conversely, catalyst **5** (R^1 = H) has the smallest steric interaction between R^1 and the incoming monomer. Although isospecific insertion should be energetically accessible, the small R^1 substituent results in poor enantiofacial selectivity and atactic PP is formed. Catalysts **2**−**4** form iPP owing to their intermediate ligand−monomer interactions combined with appreciable facial selectivity. We are currently using these catalysts to synthesize block copoly-mers and continue to investigate the influence of ligand substituent effects on polymer tacticity.

Supporting Information Available: Catalyst synthesis and characterization, X-ray data for **4**, ethylene polymerization data, and block copolymer characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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