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Fluorinated Bis(phenoxyketimine)titanium Complexes for the Living, Isoselective Polymerization of Propylene: Multiblock Isotactic Polypropylene Copolymers via Sequential Monomer Addition

Joseph B. Edson,[†] Zhigang Wang,[‡] Edward J. Kramer,[‡] and Geoffrey W. Coates*,[†]

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University,
Ithaca, New York 14853, and Mitsubishi Chemical Center for Advanced Materials and the
Departments of Materials and Chemical Engineering, University of California,
Santa Barbara, California 93106

Received October 9, 2007; E-mail: gc39@cornell.edu

Abstract: A series of bis(phenoxyketimine)titanium dichloride complexes were synthesized and evaluated as catalysts for living, isoselective propylene polymerization upon activation with methylaluminoxane (MAO). Catalysts bearing phenoxyketimine ligands with different substituents at the ortho and para positions of the phenolate ring and substituents at the ketimine carbon were investigated. The identity of the ketimine substituent had the largest effect on the activity and isoselectivity of propylene polymerization. Complex **12**/MAO promoted the living, isoselective polymerization of propylene ($[m^4] = 0.73$, $\alpha = 0.94$). This catalyst system was used for the synthesis of a number of block copolymers featuring isotactic polypropylene semicrystalline blocks and poly(ethylene-*co*-propylene) amorphous blocks. Several triblock samples with varying block lengths, a pentablock, and a heptablock copolymer were synthesized. Mechanical testing has revealed that each is elastomeric with elongations at break between ~790−1000%.

Introduction

One of the ultimate challenges in polymer chemistry is the ability to synthesize polymers and copolymers with well-defined stereochemistry while controlling molecular weight, molecular weight distribution, and sequence. The development of non-metallocene olefin polymerization catalysts has become a rapidly expanding area as new catalyst systems are discovered and improvements upon existing ones are made.[1,2] Homogeneous catalyst systems now exist that enable precise control over polymer stereochemistry through the design of sterically and electronically tunable ancillary ligand frameworks that exert a defined geometry around an active metal center.[3] Until recently, olefin polymerization catalysts have been inferior to other chain-growth polymerization methods (e.g., cationic, anionic, radical) in their ability to promote consecutive enchainment of monomer units without chain transfer or termination, i.e., living polymerization. However, a number of olefin polymerization catalysts that suppress chain termination or transfer events have been developed; these catalysts display living olefin polymerization behavior.[4,5] Living polymerization allows for the synthesis of a wide variety of polymer architectures such as block copolymers, which are most typically prepared via sequential monomer addition. Block copolymers incorporating isotactic polypropylene (iPP) segments are envisioned to provide materials with many potential applications such as compatibilizers and thermoplastic elastomers.[6−8] Therefore, the synthesis of block copolymers containing iPP domains is one of the most highly sought after goals in the field of olefin polymerization.

The living and highly isoselective polymerization of higher α-olefins has been reported. Sita,[9] Kol,[10] Mashima,[11] Sundararajan,[12] and Coates[13] have developed catalyst systems capable of polymerizing 1-hexene in a living manner with moderate to extremely high levels of isoselectivity. However, despite the exquisite stereochemical control manifested in these systems,

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[†] Cornell University.

[‡] University of California.

(1) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447.

(2) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−315.

(3) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252.

(4) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236−2257.

(5) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. S. *Prog. Polym. Sci.* **2007**, *32*, 30−92.

(6) Hotta, A.; Cochran, E.; Ruokolainen, J.; Khanna, V.; Fredrickson, G. H.; Kramer, E. J.; Shin, Y. W.; Shimizu, F.; Cherian, A. E.; Hustad, P. D.; Rose, J. M.; Coates, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15327−15332.

(7) Harney, M. B.; Zhang, Y. H.; Sita, L. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 2400−2404.

(8) Coates, G. W.; Waymouth, R. M. *Science* **1995**, *267*, 217−219.

(9) (a) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959. (b) Zhang, Y. H.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 9062−9069. (c) Zhang, Y. H.; Sita, L. R. *Chem. Commun.* **2003**, 2358−2359. (d) Zhang, Y. H.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 7776−7777. (e) Kissounko, D. A.; Zhang, Y. H.; Harney, M. B.; Sita, L. R. *Adv. Synth. Catal.* **2005**, *347*, 426−432.

(10) (a) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706−10707. (b) Segal, S.; Goldberg, I.; Kol, M. *Organometallics* **2005**, *24*, 200−202.

(11) Yasumoto, T.; Yamagata, T.; Mashima, K. *Organometallics* **2005**, *24*, 3375−3377.

(12) Sudhakar, P.; Sundararajan, G. *Macromol. Rapid Commun.* **2005**, *26*, 1854−1859.

(13) Domski, G. J.; Lobkovsky, E. B.; Coates, G. W. *Macromolecules* **2007**, *40*, 3510−3513.

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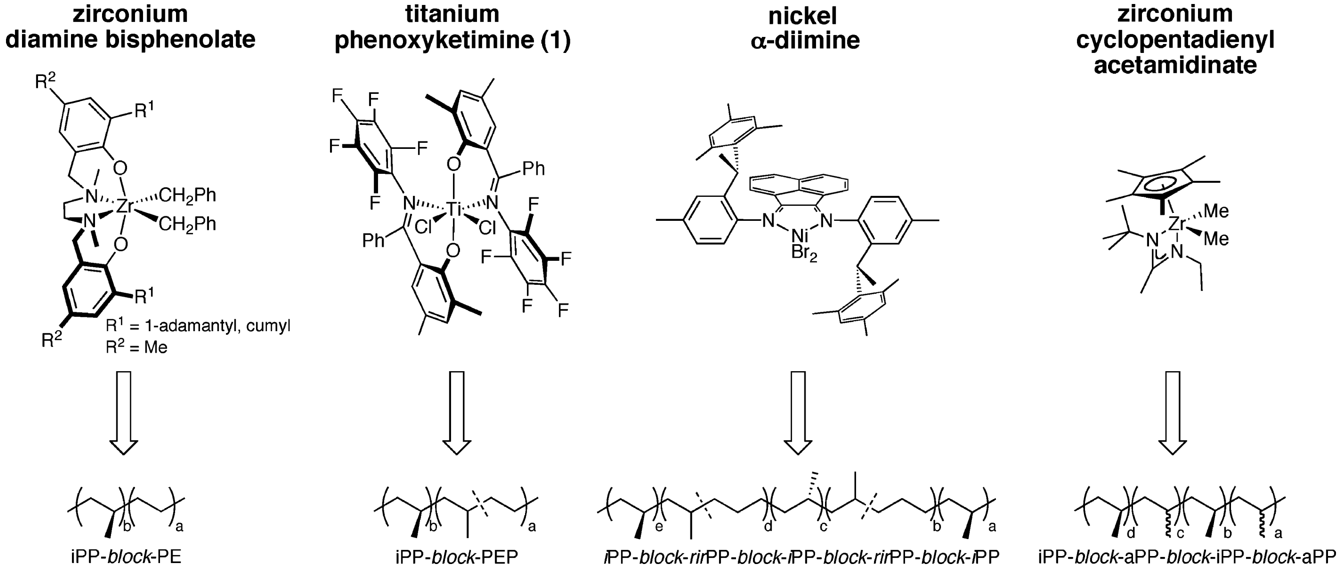

Figure 1. Catalysts used for the synthesis of block copolymers incorporating isotactic polypropylene segments.

poly(1-hexene), regardless of its tacticity, is amorphous and thus not suitable for applications requiring the strength, durability and/or crystallinity of a material such as iPP. While there are numerous catalysts capable of highly isoselective propylene polymerization[3,14] and a growing number of catalysts capable of living olefin polymerization,[4,5] highly active catalysts for both the living and highly isoselective polymerization of propylene remain elusive.[15] This is despite significant research efforts since Natta's first synthesis of iPP more than half a century ago.[16] For example, in 2003 Busico and co-workers reported that various diamine bisphenolate zirconium catalysts exhibit "quasi-living" propylene polymerization behavior producing highly isotactic polypropylene. However, chain lifetimes are relatively short.[17] In 2004, Coates and co-workers reported that fluorinated bis(phenoxyketimine)titanium catalysts are living but only moderately isoselective for propylene polymerization producing polypropylene with 53% of five consecutive monomer sequences possessing the same stereoconfiguration ($[m^4] = 0.53$).[18] The following year, Coates and co-workers reported a C_2-symmetric α-diimine Ni(II) catalyst that is living and highly isoselective for propylene polymerization at low temperatures, however, catalyst activities were extremely low and molecular weight distributions broaden under these conditions.[19] Sita reported in 2006 that monocyclopentadienylzirconium acetamidinate catalysts polymerize propylene in a living manner, albeit with moderate isoselectivity ($[m^4] = 0.71$).[7] While each of these systems can be considered deficient in some regard (e.g., living behavior, isoselectivity, or activity), each has been utilized to synthesize block copolymers incorporating iPP segments. These catalysts and the block copolymers produced are depicted in Figure 1.

For example, Busico and co-workers were able to prepare iPP-*block*-PE (PE = polyethylene) copolymers using the aforementioned diamine bisphenolate zirconium catalysts.[17] Coates and co-workers reported the synthesis of an iPP-*block*-PEP (PEP = poly(ethylene-*co*-propylene)) diblock copolymer employing **1**/methylaluminoxane (MAO).[18] With their C_2-symmetric α-diimine Ni(II) catalyst, Coates and co-workers were able to prepare an iPP-*block*-rirPP-*block*-iPP (rirPP = regioirregular polypropylene) triblock copolymer and an iPP-*block*-rirPP-*block*-iPP-*block*-rirPP-*block*-iPP pentablock copolymer by adjusting the temperature throughout the course of the polymerization to effect changes in the microstructure of each block.[6] Sita and co-workers utilized a degenerative-transfer living polymerization process with a monocyclopentadienylzirconium acetamidinate catalyst system to generate a number of isotactic-atactic stereoblock polypropylene copolymers.[7] Despite these efforts, the synthesis of block copolymers containing two or more iPP segments via sequential monomer addition has yet been achieved. While the ability to use a single monomer to make block copolymers, as shown by Coates,[6] Sita,[7] and Waymouth,[8] is advantageous from both a synthetic and an industrial standpoint, a larger variety of architectures are accessible if more than one monomer is used. For example, thermoplastic elastomers employing PEP for amorphous blocks should exhibit utility over a broader temperature range than those employing atactic polypropylene (aPP) amorphous blocks. This is due to the fact that PEP exhibits a much lower glass transitions temperature (T_g) than aPP (−50 °C vs 0 °C).

Our group[20] and researchers at Mitsui Chemicals[21−23] have independently explored the use of bis(phenoxyimine)titanium dichloride olefin polymerization catalysts for propylene polymerization. Complexes in which the phenoxyimine ligands (PHI, see Figure 2) contain an *ortho*-fluorinated *N*-aryl group and a bulky ortho substituent on the phenolate ring, produce highly

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(14) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253−1345.

(15) We define highly isoselective polymerization of propylene as one with > 95% selectivity at the pentad level of analysis.

(16) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708−1710.

(17) (a) Busico, V.; Cipullo, R.; Friederichs, N.; Ronca, S.; Togrou, M. *Macromolecules* **2003**, *36*, 3806−3808. (b) Busico, V.; Cipullo, R.; Friederichs, N.; Ronca, S.; Talarico, G.; Togrou, M.; Wang, B. *Macromolecules* **2004**, *37*, 8201−8203.

(18) Mason, A. F.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 16326−16327.

(19) Cherian, A. E.; Rose, J. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 13770−13771.

(20) Tian, J.; Coates, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3626−3629.

(21) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576−577.

(22) Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477−493.

(23) Mitani, M.; Fujita, T. In *Beyond Metallocenes: Next-Generation Polymerization Catalysts*; Patil, H. O., Hlatky, G. G., Eds.; American Chemical Society: Washington, D. C., 2003; Vol. 857, pp 26−45.

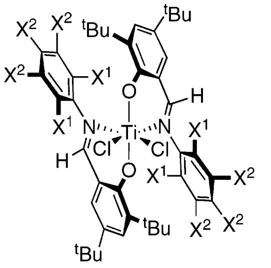

Figure 2. Phenoxyimine polymerization catalysts.

syndiotactic polypropylene (sPP) in a living manner when activated with MAO.[21,24] The syndioselectivity is a result of chain-end control. These catalysts are C_2-symmetric in the solid state and in solution, and are therefore expected to provide isotactic polymer via a site-control mechanism. However, a proposed catalyst isomerization event that occurs between each successive monomer insertion overrides the expected site control and leads to the unexpected syndioselectivity that is observed.[20,25,26] As the ortho substituent on the phenolate moiety decreases in size, the syndioselectivity of propylene polymerization decreases.[27] Using zirconium or hafnium PHI complexes, Fujita and co-workers were able to generate iPP when ^{i}Bu$_3$Al/[Ph$_3$C][B(C$_6$F$_5$)$_4$] was employed as the activator.[28] Under these conditions, the PHI ligands react with the aluminum cocatalyst in situ to generate a new phenoxyamido complex. Activation with MAO[22] results in the formation of regioirregular, atactic polypropylene. Our group has reported a series of phenoxyketimine (PKI) titanium complexes bearing bulky ^{t}Bu groups at the ortho position of the phenolate ring, which are living for ethylene polymerization when activated with MAO.[29] These catalysts were sparingly active for propylene polymerization. However, decreasing the steric demand at the ortho position of the phenolate ring and employing the *N*-pentafluorophenyl moiety leads to living and moderately isoselective propylene polymerization.[18]

We have extensively explored the PKI ligand design space in search of a catalyst capable of polymerizing propylene in a living and highly isoselective manner. In the course of our exploration, we found that **12**/MAO (Scheme 1) was the most isoselective PKI catalyst reported to date. Employing this catalyst, we prepared a number of unique block copolymers including an iPP-*block*-PEP-*block*-iPP triblock copolymer, iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP pentablock copolymer, and iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP-*block*-PEP-*block*-iPP heptablock copolymer. Mechanical testing revealed that each of these polymers displayed good elastomeric properties.

Results and Discussion

Phenoxyimine Polymerization Catalysts. Because of their close structural relationship to PKI catalysts, a brief discussion of the polymerization behavior of PHI catalysts would be beneficial. Bis(phenoxyimine)titanium dichloride complexes were originally explored for the polymerization of ethylene.[30] When activated with MAO, these catalysts displayed high ethylene polymerization activities which prompted a more detailed investigation of this class of catalyst. In our laboratory, a pooled, combinatorial approach was used to develop a library of related complexes and from this was identified a catalyst capable of syndioselective propylene polymerization.[20] Further elaboration of the ligand framework showed that incorporation of *ortho*-fluorine substituents on the *N*-aryl moiety resulted in living and highly syndioselective propylene polymerization.[21,24] Catalysts bearing *meta*- and *para*-fluorine substituents on the *N*-aryl moiety exhibited high activity, but were not living for propylene[31] or ethylene polymerization.[22] Although isoselective polymerization of propylene would be expected from a C_2-symmetric catalyst precursor,[3] the polypropylene produced by the PHI catalysts is actually syndiotactic. The highly syndioselective polymerization of propylene via chain-end control proceeds with prevailing secondary (2,1) monomer insertion.[20,32−35] It is this highly unusual secondary insertion mode that causes fluxional isomerization of the octahedral sites between successive monomer insertions.[20,25,26] Quantum mechanical/molecular mechanical calculations performed on these catalysts predict high isoselectivity for propylene polymerization if the insertion rate is much faster than catalyst isomerization.[25] Complexes with ligand structures that could possibly prevent catalyst isomerization have been developed. For example, zirconium dichloride complexes bearing binaphthyl-bridged Schiff-base PHI ligands were prepared by Pellecchia and co-workers.[36] When activated with ^{i}Bu$_3$Al/MAO or with ^{i}Bu$_3$Al//[Ph$_3$C][B(C$_6$F$_5$)$_4$], these catalysts yielded high molecular weight, atactic polypropylene. In the absence of triisobutylaluminum, low olefin polymerization activity was observed. Interestingly, isotactic polymers were obtained under similar conditions from the polymerization of 1-butene, 1-pentene, and 1-hexene. Analogous titanium catalysts yielded mostly aPP with small fractions (ca. 10 wt %) of iPP ([*mm*] = 95%), while complexes bearing a methyl group adjacent to the imine functionality on the phenolate ring resulted in the formation of moderately isotactic PP ([*mm*] = 75%).[37] In all cases, it appears that reaction between the ligand and the alkylaluminum present in the activation cocktail results in the in situ reduction of the imine functionality, leading to multiple active species and broad molecular weight distributions. This

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(24) Tian, J.; Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134−5135.

(25) Milano, G.; Cavallo, L.; Guerra, G. *J. Am. Chem. Soc.* **2002**, *124*, 13368−13369.

(26) Corradini, P.; Guerra, G.; Cavallo, L. *Acc. Chem. Res.* **2004**, *37*, 231−241.

(27) Mitani, M.; Furuyama, R.; Mohri, J.; Saito, J.; Ishii, S.; Terao, H.; Nakano, T.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2003**, *125*, 4293−4305.

(28) (a) Saito, J.; Onda, M.; Matsui, S.; Mitani, M.; Furuyama, R.; Tanaka, H.; Fujita, T. *Macromol. Rapid Commun.* **2002**, *23*, 1118−1123. (b) Prasad, A. V.; Makio, H.; Saito, J.; Onda, M.; Fujita, T. *Chem. Lett.* **2004**, *33*, 250−251.

(29) Reinartz, S.; Mason, A. F.; Lobkovsky, E. B.; Coates, G. W. *Organometallics* **2003**, *22*, 2542−2544.

(30) Matsui, S.; Tohi, Y.; Mitani, M.; Saito, J.; Makio, H.; Tanaka, H.; Nitabaru, M.; Nakano, T.; Fujita, T. *Chem. Lett.* **1999**, 1065−1066.

(31) Mason, A. F.; Tian, J.; Hustad, P. D.; Lobkovsky, E. B.; Coates, G. W. *Isr. J. Chem.* **2002**, *42*, 301−306.

(32) Saito, J.; Mitani, M.; Onda, M.; Mohri, J. I.; Ishi, J. I.; Yoshida, Y.; Nakano, T.; Tanaka, H.; Matsugi, T.; Kojoh, S. I.; Kashiwa, N.; Fujita, T. *Macromol. Rapid Commun.* **2001**, *22*, 1072−1075.

(33) Hustad, P. D.; Tian, J.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 3614−3621.

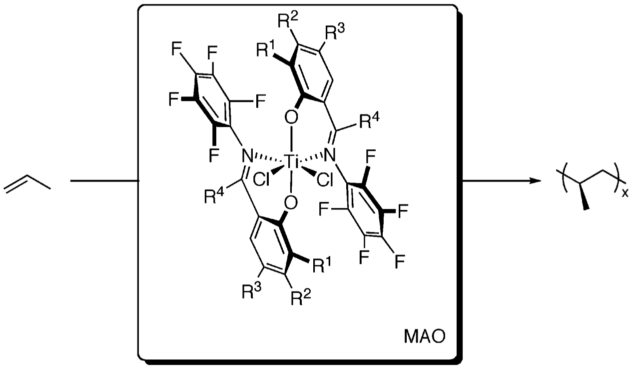
(34) Lamberti, M.; Pappalardo, D.; Zambelli, A.; Pellecchia, C. *Macromolecules* **2002**, *35*, 658−663.

(35) Talarico, G.; Busico, V.; Cavallo, L. *J. Am. Chem. Soc.* **2003**, *125*, 7172−7173.

(36) Lamberti, M.; Consolmagno, M.; Mazzeo, M.; Pellecchia, C. *Macromol. Rapid Commun.* **2005**, *26*, 1866−1871.

(37) Strianese, M.; Lamberti, M.; Mazzeo, M.; Tedesco, C.; Pellecchia, C. *J. Mol. Catal. A: Chem.* **2006**, *258*, 284−291.

Scheme 1. Titanium Phenoxyketimine Compounds



Complex	R^1	R^2	R^3	R^4
1	Me	H	Me	Ph
2	Cl	H	Me	Ph
3	Br	H	Me	Ph
4	Ph	H	Me	Ph
5	Bn	H	Me	Ph
6	$-(CH_2)_4-$		H	Ph
7	Me	H	Cl	Ph
8	Me	H	F	Ph
9	Me	H	OMe	Ph
10	Me	H	Me	Me
11	Me	H	Me	^{i}Pr
12	Me	H	Me	Cy
13	Me	H	Me	Cycloheptyl
14	Me	H	Me	CF_3
15	Me	H	Me	2-Naphthyl
16	Me	H	Me	1-Naphthyl
17	Me	H	Me	4-Methoxyphenyl
18	Me	H	Me	Mesityl
19	Me	H	Me	C_6F_5

in situ ligand modification may also be the source of the observed isoselectivity.

We reasoned that placing substituents on the carbon atom of the imine moiety would inhibit the fluxional behavior for this class of catalysts, thereby enforcing the C_2-symmetry of the active species. Titanium complexes bearing these PKI ligands with *N*-pentafluorophenyl groups resulted in the living and moderately isoselective polymerization of propylene.[18] The microstructure of the iPP was consistent with an enantiomorphic site-control mechanism. Zirconium dichloride complexes bearing PKI ligands have been prepared by Hu and co-workers.[38] When activated with MAO, these catalysts yielded high molecular weight polyethylenes with broadened molecular weight distributions ($M_w/M_n \geq 1.7$).

Synthesis of Phenoxyketimine Complexes. The PKI catalysts were synthesized as previously described.[29] Reaction of the appropriately substituted phenol with the desired imidoyl chloride and $AlCl_3$ in 1,2-dichloroethane gave the corresponding PKI ligands in 4−77% yield, with the major impurity being the *O*-imidoylated product. Deprotonation of the PKI ligand was effected with *n*-BuLi, and the resulting ligand salt was transferred to a tetrahydrofuran (THF) solution of $TiCl_4$ to give the bis-ligated complex. Recrystallization of the compounds from CH_2Cl_2/pentane or toluene/pentane provided the complexes as dark brown to red crystals in 27−61% yield. For all complexes, ^1H, ^{13}C, and ^{19}F NMR spectra showed the presence of a single C_2-symmetric isomer in both benzene-d_6 and chloroform-d at room temperature.

Effect of the Ortho Substituent on the Phenolate Ring. Recently, Pellecchia and co-workers have shown that titanium complexes bearing PHI ligands with halide substituents at the ortho position of the phenolate ring and *N*-pentafluorophenyl groups quite unexpectedly promoted moderately isoselective polymerization of propylene ($R^1 = R^3 = I$, $R^4 = H$; $[mm] = 0.73$, $\alpha = 0.90$; see Scheme 1).[39] A related PKI complex ($R^1 = R^3 = Br$, $R^4 = Ph$) produced aPP. This lies in stark contrast to the observed isoselectivity of PKI titanium complexes bearing alkyl substituents.[18] In all cases, molecular weight distributions were broad ($M_w/M_n \geq 1.6$) indicative of a non-living polymerization system.

We have previously investigated titanium complexes supported by PKI ligands bearing different alkyl substituents at the ortho position of the phenolate moiety (R^1).[18] As this substituent decreases in size, polymerization activity and the isotacticity of the resultant polypropylene increases. The highest isotacticity was observed with complexes bearing *ortho*-methyl substituents on the phenolate rings of the ligand. Due to the interesting behavior reported by Pellecchia for halogenated PHI catalysts,[39] we reasoned that complexes bearing halogens at the ortho position of the phenolate ring could be worth investigating.

A series of PKI complexes with pentafluorophenyl *N*-aryl groups, a phenyl ketimine (R^4) substituent and various ortho substituents on the phenolate ring (R^1) were investigated to optimize facial selectivity (Scheme 1, complexes **1**−**6**). In this series, the ortho substituents on the phenolate moiety were chosen on the basis of having pronounced steric and electronic differences. We expected that the propylene polymerization catalyzed by **1**−**6**/MAO would follow the trends observed for previously reported PKI catalysts, where decreasing the size of the R substituent leads to higher activities and stereoselectivities.[18] From this initial report, it was shown that a methyl group at the ortho position of the phenolate ring was optimally sized to provide good facial selectivity for propylene polymerization.

Table 1 provides the propylene polymerization data for complexes **1**−**6**. When activated with MAO, all complexes were active with the exception of **4**, and produced isoenriched polypropylene with [m^4]-values ranging from 0.30 to 0.57. All active catalysts formed polymers with very narrow molecular weight distributions ($M_w/M_n \leq 1.12$), which suggests living behavior. Compared to **1**, the halogenated complexes (**2** and **3**) showed much higher activity. This could be attributed to both the increase in electronegativity of

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(38) Chen, S. T.; Zhang, X. F.; Ma, H. W.; Lu, Y. Y.; Zhang, Z. C.; Li, H. Y.; Lu, Z. X.; Cui, N. N.; Hu, Y. L. *J. Organomet. Chem.* **2005**, *690*, 4184−4191.

(39) Mazzeo, M.; Strianese, M.; Lamberti, M.; Santoriello, I.; Pellecchia, C. *Macromolecules* **2006**, *39*, 7812−7820.

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

cplx	T (h)	yield (g)	TOF (h^{-1})[b]	M_n^{theo} (g/mol)	M_n (g/mol)[c]	M_w/M_n[c]	[$mmmm$][d]	α[e]	T_g (°C)[f]	T_m (°C)[f]
1	6.0	0.55	230	55 000	43 000	1.10	0.52	0.88	−12.4	n.d.[g]
2	6.0	2.24	890	224 000	148 000	1.09	0.31	0.79	−9.4	n.d.[g]
3	6.0	1.34	530	134 000	93 300	1.08	0.57	0.89	−14.3	73.4
4	6.0	trace[h]								
5	6.0	0.04	20	4000	3000	1.10	0.43	0.84	−23.2	n.d.[g]
6	6.0	0.15	58	15 000	15 000	1.12	0.54	0.89	−13.3	85.1

[a] General conditions: 10 μmol of the complex in toluene (5 mL) was added to a propylene-saturated PMAO-IP solution (100 mL of toluene; [Al]/[Ti] = 150) at 0 °C. [b] Average turnover frequency (TOF): mol propylene/(mol Ti·h). [c] Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 140 °C versus polyethylene standards. [d] Determined by integration of the methyl region of the ^{13}C NMR spectrum. [e] Enantiofacial selectivity parameter, calculated from the ^{13}C NMR spectrum using the equation $[m^4] = \alpha^5 + (1-\alpha)^5$. [f] Determined using differential scanning calorimetry (second heating). [g] None detected. [h] Polymer yield was insufficient for characterization.

Table 2. Propylene Polymerization Data for Catalysts **7**−**9**/MAO[a]

cplx	T (h)	yield (g)	TOF (h^{-1})[b]	M_n^{theo} (g/mol)	M_n (g/mol)[c]	M_w/M_n[c]	[$mmmm$][d]	α[e]	T_g (°C)[f]	T_m (°C)[f]
7	6.0	0.32	130	32 000	70 000	1.13	0.53	0.88	−14.2	n.d.[g]
8	6.0	1.05	420	105 000	77 500	1.07	0.51	0.87	−12.8	n.d.[g]
9	3.0	1.45	1170	146 000	78 200	1.98	0.51	0.87	−8.5	145.8

[a] General conditions: 10 μmol of the complex in toluene (5 mL) was added to a propylene-saturated PMAO-IP solution (100 mL of toluene; [Al]/[Ti] = 150) at 0 °C. [b] Average turnover frequency (TOF): mol propylene/(mol Ti·h). [c] Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 140 °C versus polyethylene standards. [d] Determined by integration of the methyl region of the ^{13}C NMR spectrum. [e] Enantiofacial selectivity parameter, calculated from the ^{13}C NMR spectrum using the equation $[m^4] = \alpha^5 + (1-\alpha)^5$. [f] Determined using differential scanning calorimetry (second heating). [g] None detected.

the halogen substituent as well as a decrease in steric congestion near the active site. Interestingly, **3** (R^1 = Br) was approximately two times more active than **1** for propylene polymerization, and the resultant polymer had an [m^4]-value of 0.57 and a melting temperature (T_m) of 73.4 °C. However, **2** (R^1 = Cl) provided polypropylene with an [m^4]-value of 0.31 and no melting transition, thus illustrating the extreme sensitivity of the relationship between the facial selectivity and the size of the ortho substituent of the phenolate ring. Complex **4** (R^1 = Ph) only produced trace amounts of polymer, while complex **5**, bearing a bulkier benzyl substituent, showed a marginally higher activity. Complex **6**, derived from tetrahydronaphthol, was sparingly active and produced a polymer with an [m^4]-value of 0.54 and T_m of 85.1 °C. The polypropylene produced by **6**/MAO, despite having a similar [m^4]-value, showed a higher T_m than the polypropylene produced by **3**/MAO. This could be attributed to a decrease in the number of regioinversions of the polypropylene produced by **6**/MAO versus **3**/MAO (see Supporting Information).

Effect of the Para Substituent on the Phenolate Ring. Once the role of the ortho substituent on the phenolate ring (R^1) was established, the effect of the para substituent (R^3) was investigated. Scheme 1 (entries **7**−**9**) summarizes the series of complexes that were synthesized and screened for propylene polymerization behavior. We anticipated that electron-withdrawing R^3 groups with greater electronegativities would increase catalyst activity by increasing the electrophilicity of the metal center. We did not expect these changes to effect the facial selectivity of the catalyst due to the remote location of the para substituent relative to the active site.

Table 2 provides the propylene polymerization data for complexes **7**−**9**. When activated with MAO, all catalysts were active and produced polypropylene with [m^4]-values ranging from 0.51 to 0.53. Catalyst activities did not follow the expected trend where more electron-withdrawing substituents give higher activities. For example, **7** (R^3 = Cl) had an activity approximately half that of **1**, whereas **8** (R^3 = F) had an activity approximately twice that of **1**. Both **7** and **8** formed polypropylene with very narrow molecular weight distributions ($M_w/M_n \leq 1.13$). Surprisingly, **9** (R^3 = OMe) had an activity five times higher than that of **1**. The GPC trace for the polypropylene produced by **9** was broad and multimodal, indicative of multiple active species. The resultant polypropylene showed a T_m of 145.8 °C and could be separated into ether-soluble (ca. 24 wt %) and ether-insoluble (ca. 76 wt %) fractions, both giving GPC traces that were again broad and multimodal. One possible explanation for this observation is that the methoxy group on the ancillary ligand reacts with the cocatalyst in situ to generate one or more new active species. We are currently investigating the source of this unusual polymerization behavior.

Effect of Alkyl Substituents on the Ketimine Carbon. PKI catalysts previously studied for propylene polymerization contained a phenyl ketimine substituent (R^4). Although remote from the active center, we reasoned that by investigating other substituents off of the ketimine carbon that improved isoselectivity for propylene polymerization could be achieved. To probe the difference between a phenyl and alkyl groups at this position, complexes bearing various alkyl ketimine substituents (R^4) incorporating the 2,4-dimethylphenol moiety were synthesized and screened for propylene polymerization behavior (Scheme 1, entries **10**−**14**).

Table 3 provides the propylene polymerization data for complexes **10**−**14**. When activated with MAO, all catalysts were active and produced polypropylene with [m^4]-values ranging from 0.61 to 0.73. In all cases, catalysts bearing alkyl substituents on the ketimine carbon were more isoselective for propylene polymerization than **1** (R^4 = Ph). Catalyst **10** (R^4 = Me) furnished a polymer with [m^4] = 0.61 and T_m = 90.3 °C, but the activity was approximately an order of magnitude lower than **1**. Increasing the steric demand of the R^4 substituent led to improved tacticity. For example, catalyst **11** (R^4 = ^{i}Pr) polymerized propylene with an activity comparable to **10** and furnished a polymer with [m^4] = 0.67 and T_m = 114.5 °C. A further gain in tacticity was achieved upon replacing the ^{i}Pr ketimine substituent with cyclohexyl as catalyst **12** exhibited similar activity to **10** and **11** but provided polymer with [m^4] =

Table 3. Propylene Polymerization Data for Catalysts **10**−**14**/MAO[a]

cplx	T (h)	yield (g)	TOF (h^{-1})[b]	M_n^{theo} (g/mol)	M_n (g/mol)[c]	M_w/M_n[c]	[*mmmm*][d]	α[e]	T_g (°C)[f]	T_m (°C)[f]
10	6.0	0.08	30	8000	8000	1.14	0.61	0.91	−14.4	90.3
11	6.0	0.10	41	10 000	8500	1.25	0.67	0.92	−11.4	114.5
12	6.0	0.07	30	7000	8000	1.22	0.73	0.94	−12.9	116.8
13	6.0	0.09	30	9000	8000	1.23	0.69	0.93	−11.5	111.9
14	6.0	1.53	604	153 000	364 000	1.33	0.68	0.93	−11.3	93.8
14[g]	4.0	0.29	340	58 000	76 000	1.09	0.67	0.92	−13.0	93.3

[a] General conditions: 10 μmol of the complex in toluene (5 mL) was added to a propylene-saturated PMAO-IP solution (100 mL of toluene; [Al]/[Ti] = 150) at 0 °C. [b] Average turnover frequency (TOF): mol propylene/(mol Ti•h). [c] Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 140 °C versus polyethylene standards. [d] Determined by integration of the methyl region of the ^{13}C NMR spectrum. [e] Enantiofacial selectivity parameter, calculated from the ^{13}C NMR spectrum using the equation $[m^4] = \alpha^5 + (1-\alpha)^5$. [f] Determined using differential scanning calorimetry (second heating). [g] A 5-μmol portion of the complex in toluene (5 mL) was added to a propylene-saturated PMAO-IP solution (100 mL of toluene; [Al]/[Ti] = 150) at −40 °C.

Table 4. Propylene Polymerization Data for Catalysts **15**−**19**/MAO[a]

cplx	T (h)	yield (g)	TOF (h^{-1})[b]	M_n^{theo} (g/mol)	M_n (g/mol)[c]	M_w/M_n[c]	[*mmmm*][d]	α[e]	T_g (°C)[f]	T_m (°C)[f]
15	6.0	0.65	250	65 000	45 000	1.08	0.52	0.88	−12.0	n.d.[g]
16	6.0	0.12	49	12 000	12 000	1.19	0.66	0.92	−12.4	105.2
17	2.0	0.41	490	41 000	87 000	3.19	0.53	0.88	−7.1	144.1
18	6.0	0.76	310	76 000	83 000	1.28	0.32	0.80	−6.5	n.d.[g]
19	6.0	1.33	538	133 000	170 000	1.11	0.58	0.89	−15.1	68.8

[a] General conditions: 10 μmol of the complex in toluene (5 mL) was added to a propylene-saturated PMAO-IP solution (100 mL of toluene; [Al]/[Ti] = 150) at 0 °C. [b] Average turnover frequency (TOF): mol propylene/(mol Ti•h). [c] Determined using gel permeation chromatography in 1,2,4-$C_6H_3Cl_3$ at 140 °C versus polyethylene standards. [d] Determined by integration of the methyl region of the ^{13}C NMR spectrum. [e] Enantiofacial selectivity parameter, calculated from the ^{13}C NMR spectrum using the equation $[m^4] = \alpha^5 + (1-\alpha)^5$. [f] Determined using differential scanning calorimetry (second heating). [g] None detected.

0.73 and T_m = 116.8 °C. Despite incorporating the bulkier cycloheptyl ketimine substituent, catalyst **13** resulted in a polymer with $[m^4]$ = 0.69 and T_m = 111.9 °C, although the activity was comparable to that observed with **12**. Catalysts **10**−**13** formed polypropylene with narrow molecular weight distributions ($M_w/M_n \leq 1.25$) and with good agreement between the number average molecular weight (M_n) and that expected based on the assumption of one chain per metal center (M_n^{theo}). To investigate the difference between alkyl and fluorinated alkyl substituents, catalyst **14**, which bears a trifluoromethyl ketimine substituent (R^4 = CF_3), was synthesized. Polymerization of propylene with **14**/MAO proceeded with an activity approximately 20 times that of **10** and provided a polymer with $[m^4]$ = 0.68 and T_m = 93.8 °C. The resultant molecular weight distribution (M_w/M_n = 1.33) was slightly broadened upon replacing the methyl ketimine substitution for CF_3, and there was a discrepancy between M_n and M_n^{theo}. Cooling the reaction to −40 °C led to a more controlled polymerization where the disparity between M_n and M_n^{theo} was smaller and the resultant polypropylene showed a much narrower molecular weight distribution (M_w/M_n = 1.09). However, lower reaction temperature did not have a pronounced effect on the activity of the polymerization and furnished polypropylene with similar tacticity; $[m^4]$ = 0.67 and T_m = 93.3 °C.

Effect of Aryl Substituents on the Ketimine Carbon. To investigate the effect of the aryl ketimine substituents (R^4), catalysts incorporating the 2,4-dimethylphenol moiety were synthesized and screened for propylene polymerization (Scheme 1, entries **15**−**19**). In light of the trends observed with PKI catalysts bearing different alkyl substituents, we reasoned that bulkier aryl substituents would give increased isoselectivity for propylene polymerization.

Table 4 provides the propylene polymerization data for complexes **15**−**19**. When activated with MAO, all catalysts were active and produced polypropylene with $[m^4]$-values ranging from 0.32 to 0.66. Catalyst **15**/MAO bearing a 2-naphthyl ketimine substituent behaved almost identically to catalyst **1**, giving approximately the same molecular weight, activity, and level of isoselectivity. Upon changing the connectivity (**16**, R^4 = 1-naphthyl), the activity decreases 5-fold from **15** and furnishes PP with an $[m^4]$ = 0.66 and T_m = 105.2 °C. Catalyst **17** (R^4 = 4-methoxyphenyl) provided polypropylene with a high T_m (144.1 °C) but behaved similarly to **9** in that a multimodal GPC trace was obtained. Because this behavior is only observed with ligands featuring methoxy groups, we believe an interaction between the aluminum cocatalyst and the methoxy group could be causing this unusual behavior. Catalyst **18**, which contains a mesityl ketimine (R^4) substituent, exhibits an activity that is slightly higher than **1** and produces PP with $[m^4]$ = 0.32. Employing a perfluorophenyl ketimine substituent, **19**/MAO exhibited an activity twice that of **1** and produced PP with $[m^4]$ = 0.58 and T_m = 68.8 °C. In all cases, the PP produced from **15**−**19**/MAO displayed narrow molecular weight distributions ($M_w/M_n \leq 1.28$).

Microstructural Analysis of Polypropylenes by ^{13}C NMR Spectroscopy. Figure 3 provides the ^{13}C NMR spectrum of iPP obtained from **12**/MAO at 0 °C. The major stereoerrors present correspond to *mmmr*, *mmrr*, and *mrrm* pentads. These three pentads are present in a 2:2:1 ratio, which is indicative of an enantiomorphic site-control enchainment mechanism. The ^{13}C NMR spectra of iPPs obtained from **1**−**11** and **13**−**19**/MAO were similar in appearance to that obtained from **12**/MAO (see Supporting Information) and show varying degrees of stereocontrol with the major stereoerrors present corresponding to *mmmr*, *mmrr*, and *mrrm* pentads in a 2:2:1 ratio. This is consistent with previously reported PKI catalysts,[18] but is quite different from the previously reported syndioselective PHI catalysts which have stereoerrors resulting from a chain-end control mechanism.[20]

While the polymer obtained from **12**/MAO is very regioregular, resonances corresponding to head-to-head and tail-to-tail misinsertions can be detected in the δ 14−16 and δ 31−46 ppm regions of the ^{13}C NMR spectrum.[14] The occurrence of regioerrors varied in polypropylenes produced using **1**−**19**/

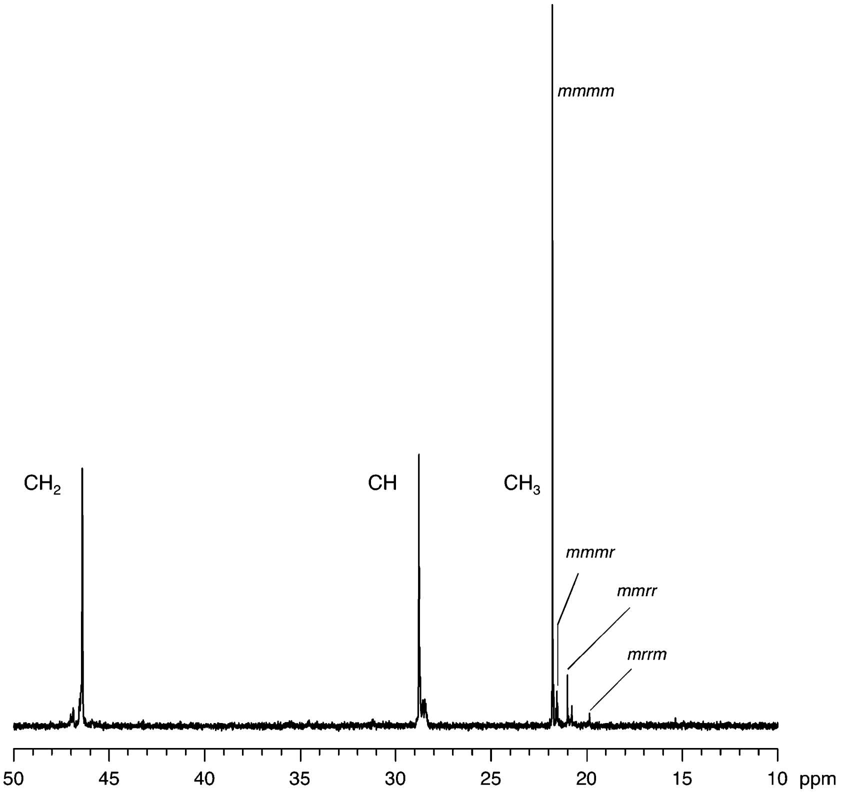

Figure 3. ^{13}C NMR spectrum (1,1,2,2$-$C$_2$D$_2$Cl$_4$, 125 MHz, 135 °C) of isotactic polypropylene formed by **12**/MAO at 0 °C. The presence of the unmarked peak in the methyl region is due to regioinversions.

MAO. The PP produced by **18**/MAO displayed the lowest occurrence of regioerrors (see Supporting Information). Despite being more isoselective than **1**, the PP produced by **19**/MAO displayed the highest occurrence of regioerrors of the catalysts studied (see Supporting Information).

Living Behavior of Bis(phenoxyketimine)titanium Complexes. The narrow molecular weight distribution of the iPP produced by **12**/MAO, coupled with the observed good agreement between M_n and M_n^{theo}, indicate that propylene polymerization catalyzed by **12**/MAO is living. The living behavior of **12**/MAO is further exemplified by the observation that M_n increases linearly with polypropylene yield (Figure 4). The molecular weight distribution for shorter reaction times is somewhat broadened ($t = 6$ h; $M_w/M_n = 1.30$), but narrows for longer reaction times ($t = 48$ h; $M_w/M_n = 1.15$). This is presumably due to slow initiation.

Block Copolymers from Propylene and Ethylene. While one drawback of a living polymerization system is that only one polymer chain per metal center is produced, the real utility of these systems lies in the ability to synthesize well-defined block copolymers and identify new polymer architectures with promising physical, mechanical, and chemical properties. There are few examples of block copolymers incorporating iPP segments in the literature,[5−8,17,18] which is due in large part to the fact that few catalyst systems have been reported that are capable of polymerizing propylene in a living manner with high isoselectivity and activity. Block copolymers incorporating sPP, however, have been synthesized with much greater ease.

In 1988, Doi and co-workers synthesized an *s*PP-*block*-PEP-*block*-*s*PP triblock copolymer with a narrow molecular weight distribution ($M_w/M_n = 1.24$) and a high molecular weight ($M_n = 94$ kg/mol) utilizing a catalyst system composed of V(acac)$_3$/Et$_2$AlCl/anisole.[40] Bis(phenoxyimine)titanium complexes employing the *N*-pentafluoroaniline moiety and bulky *tert*-butyl ortho phenolate groups have been used to synthesize an *s*PP-*block*-PEP diblock[24,41] and an *s*PP-*block*-PEP-*block*-*s*PP triblock copolymer.[6] This class of catalysts has also been used to produce a PE-*block*-*s*PP diblock copolymer and a PE-*block*-PEP-*block*-*s*PP triblock copolymer.[42] A sPP-*block*-poly(propylene-*co*-MCP-*co*-3-VTM) (MCP = methylene-1,3-cyclopentane; 3-VTM = 3-vinyl tetramethylene) diblock copolymer has also been produced via sequential monomer addition using propylene and 1,5-hexadiene with this class of catalysts.[43]

Owing to the living behavior and the relatively high isoselectivity of **12**/MAO for propylene polymerization, we reasoned that it would make an ideal catalyst for the synthesis of block copolymers incorporating iPP segments (Scheme 2). Living polymerization of propylene at 0 °C resulted in the formation of iPP ($[m^4] = 0.73$). Once a block of the desired length was formed (typically after 15 h), a slight overpressure of ethylene was added and copolymerized with the unreacted propylene to produce a PEP block. The molecular weight of the PEP block was adjusted by varying the duration of polymerization (Table 5, entries 1−3). Triblock iPP-*block*-PEP-*block*-iPP copolymers were synthesized by the removal of ethylene and by reestablishing the propylene feed for the specified time. To our knowledge, this is the first synthesis of an iPP-*block*-PEP-*block*-iPP triblock copolymer via sequential monomer addition. A pentablock

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(40) Doi, Y.; Ueki, S.; Keii, T. *Makromol. Chem. Rapid Commun.* **1982**, *3*, 225−229.

(41) Kojoh, S.; Matsugi, T.; Saito, J.; Mitani, M.; Fujita, T.; Kashiwa, N. *Chem. Lett.* **2001**, 822−823.

(42) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327−3336.

(43) Hustad, P. D.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 11578−11579.

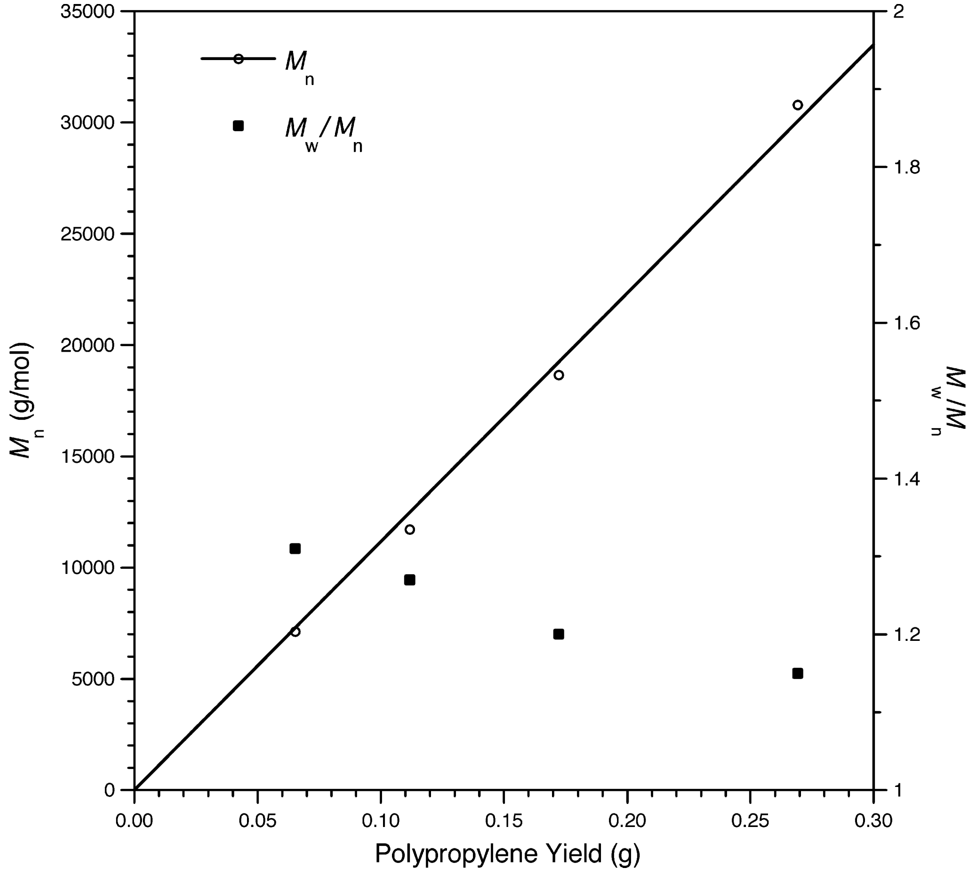

Figure 4. Plot of polypropylene M_n (○) and M_w/M_n (■) vs polypropylene yield using **12**/MAO at 0 °C.

Scheme 2. Synthesis of Block Copolymers from Ethylene and Propylene

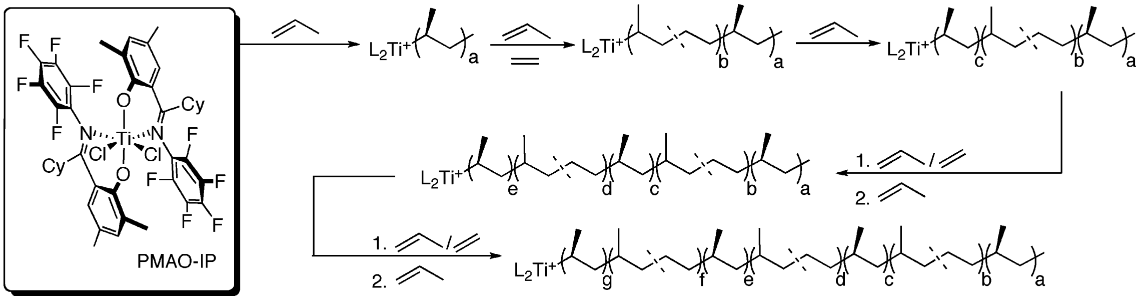

Table 5. Block Copolymer Characterization[a]

sample	$M_{n,tot}$ (kg/ mol)[b]	M_w/M_n[b]	block lengths (kg/ mol)[c]	wt. % of hard blocks[d]	F_e total (mol %)[e]	T_g (°C)[f]	T_m (°C)[f]
*i*PP-*b*-PEP-*b*-*i*PP (*iso***TB-1**)	102	1.13	12−75−15	26	16	−35	115
*i*PP-*b*-PEP-*b*-*i*PP (*iso***TB-2**)	144	1.18	14−117−13	17	17	−33	107
*i*PP-*b*-PEP-*b*-*i*PP (*iso***TB-3**)	235	1.30	14−206−15	12	15	−39	95
*i*PP-*b*-PEP-*b*-*i*PP-*b*-PEP-*b*-*i*PP (*iso***PB**)	195	1.15	14−74−15−78−14	22	20	−40	94
*i*PP-*b*-PEP-*b*-*i*PP-*b*-PEP-*b*-*i*PP-*b*-PEP-*b*-*i*PP (*iso***HB**)	227	1.13	13−74−7−51−32−44 −6	26	18	−33	88

[a] General conditions: 10 μmol of **12** in toluene (5 mL) was added to a propylene-saturated PMAO−IP solution (100 mL of toluene; [Al]/[Ti] = 150) at 0 °C. After the desired time, a C_2H_4 feed was established. The C_2H_4 feed was discontinued and the reactor was vented to 0 psig, 30 psig of propylene reconnected and polymerization allowed to proceed for the desired time. [b] Determined using gel permeation chromatography in 1,2,4−$C_6H_3Cl_3$ at 140 °C versus polyethylene standards. [c] Determined by the difference in M_n of aliquots pulled after the formation of each block. [d] Wt. % of hard blocks = (Σ $M_{n,hard}$)/($M_{n,tot}$). [e] Mole fraction of ethylene (F_e) determined by integration of the ^{13}C NMR spectrum. [f] Determined using differential scanning calorimetry (second heating).

copolymer (*iso***PB**) and heptablock copolymer (*iso***HB**) were made in an analogous manner (Table 5, entries 4 and 5). Due presumably to decreased diffusion efficiency resulting from the high viscosity of the polymerization mixture, a higher overpressure of ethylene was required to install the second and third PEP block of the pentablock and heptablock copolymer, respectively.

The iPP segments had a melting temperature between 99 and 115 °C, decreasing with increasing overall molecular weight for the triblock copolymer samples (Table 5, entries 1−3). Ethylene fractions (F_e) in the triblock copolymers ranged from 15 to 17 mol %. The melting temperature of the pentablock copolymer was 94 °C and had an F_e of 20 mol %, while the heptablock copolymer had a T_m of 88 °C and an F_e of 18 mol

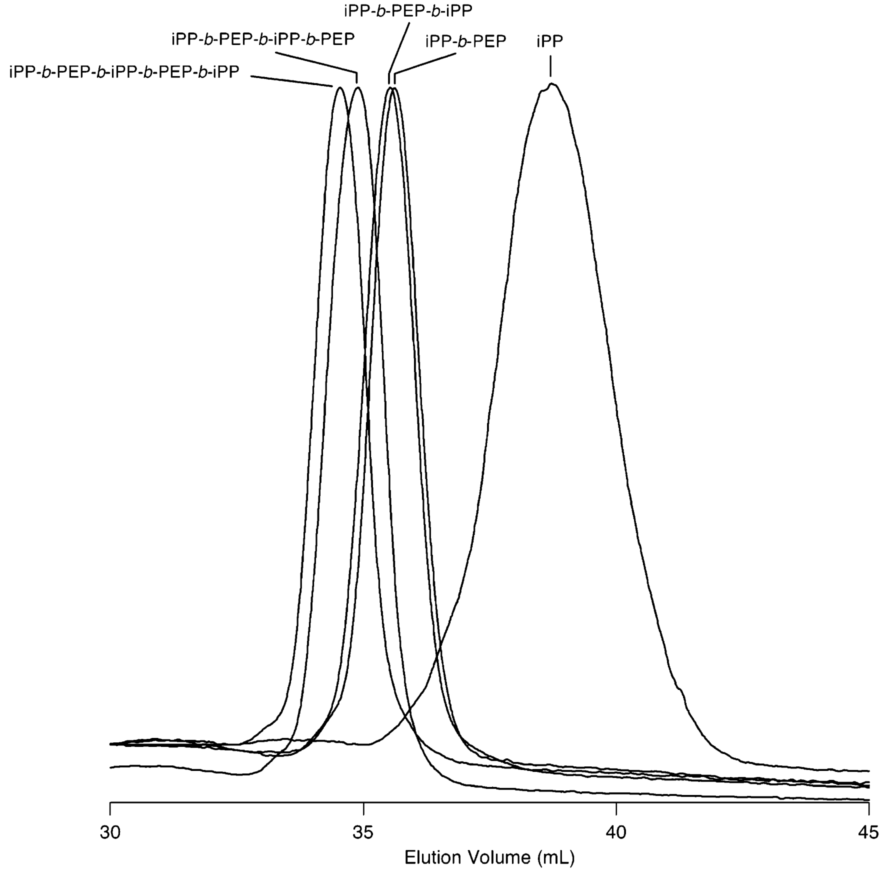

Figure 5. GPC profiles after the formation of each block of the *iso***PB** synthesized using complex **12**/MAO at 0 °C.

%. All block copolymers showed a T_g between −40 and −33 °C. The high melting temperatures and low glass transition temperatures are indicative of block copolymers incorporating iPP and PEP segments. A representative GPC profile of the pentablock copolymer is shown in Figure 5, where aliquots were removed from the polymerization mixture after the formation of each block, and the resultant polymers were analyzed via gel permeation chromatography.

Mechanical Properties of Block Copolymers. The initial Young's modulus is partly determined by the connectivity between crystalline lamellae, which is why it correlates roughly with the melting enthalpy and thus crystallinity. After about a 500% prestrain, the Young's modulus after unloading decreases dramatically to values between 1.2 and 2.5 MPa that are more typical of an elastomer. The prestrain presumably breaks up the network of crystalline lamellae into individual iPP fibrils separated by the rubbery PEP blocks.

The block copolymers all displayed surprisingly similar elastomeric behavior. The triblock copolymer (*iso***TB-1**) displayed an elongation at break of ∼1000% with a tensile true stress of 120 MPa and an 80% recovery up to elongation of 750%. Increasing the midblock PEP segment length of the triblock copolymers led to diminished values for elongation at break and tensile true stress. For example, *iso***TB-2**, exhibited an elongation at break of ∼800% and a tensile true stress of 64 MPa with an 81% recovery up to elongation of 750% while *iso***TB-3** exhibited an elongation at break of ∼950% and a tensile true stress of 112 MPa with a 68% recovery up to elongation of 750%. The pentablock copolymer (*iso***PB**) displayed an elongation at break of ∼790% with a tensile true stress of 84 MPa and a 79% recovery up to elongation of 750%, while the heptablock copolymer showed an elongation at break of ∼830% with a tensile true stress of 100 MPa and an 85% recovery up to elongation of 750%. While the mechanical properties of the block copolymers are similar, it is apparent that incorporation of large PEP segments leads to a decrease in the percent recovery of the materials.

Table 6. Block Copolymer Mechanical Testing Data

sample	Young's Modulus (MPa)[a]	strain at break (%)	true stress at break (MPa)	melting enthalpy (J/g)	elastic recovery (%)[b]
*iso***TB-1**	10.9	∼1000	120	14.3	80
*iso***TB-2**	6.9	∼800	64	11.8	81
*iso***TB-3**	12.0	∼950	112	16.1	68
*iso***PB**	11.7	∼790	84	16.8	79
*iso***HB**	9.0	∼830	100	13.1	85

[a] Measured in tension at strain of 15%. [b] After 750% prestrain.

The triblock copolymer (*iso***TB-1**) displayed the highest ultimate elongation at break (∼1000%) relative to the other copolymers studied herein. This value is lower than the triblock copolymer comprised of iPP-*b*-rirPP-*b*-iPP (∼1700%)[6] and tetrablock copolymer comprised of iPP-*b*-aPP-*b*-iPP-*b*-aPP (∼1200%).[7] The lower elongation at break displayed for *iso***TB-1** could be due to a number of factors such as overall crystallinity, molecular weight, or amorphous segment identity.

Conclusions

Bis(phenoxyketimine)titanium catalyst systems bearing different substituents at the ortho and para positions of the phenolate rings, and ketimine carbon susbstituents featuring an

N-pentafluorophenyl moiety all displayed activity for propylene polymerization. All catalysts were isoselective with [m^4]-values between 0.31 and 0.73 for the resultant polypropylenes. The prevailing mode of stereocontrol was an enatiomorphic site-control mechanism as evidenced by the 2:2:1 ratio of the resonances corresponding to the *mmmr*:*mmrr*:*mrrm* pentads in the ^{13}C NMR spectra of the polypropylenes formed. Complexes bearing *ortho*-halide substituents on the phenolate ring displayed much higher activity than those bearing alkyl substituents with the size of the substituent determining the level of facial selectivity. The identity of the para substituent had a dramatic influence on the activity of the polymerization but had no effect on the selectivity. Varying the substituents at the ketimine carbon of the ancillary ligand had the most pronounced effect on both the activity and the isoselectivity of propylene polymerization. All of the catalyst systems screened showed living behavior except those with methoxy groups on the ancillary ligand. Using **12**/MAO, a number of new block copolymers from propylene and ethylene were synthesized via sequential monomer addition. Specifically an iPP-*b*-PEP-*b*-iPP triblock copolymer, iPP-*b*-PEP-*b*-iPP-*b*-PEP-*b*-iPP pentablock copolymer, and iPP-*b*-PEP-*b*-iPP-*b*-PEP-*b*-iPP-*b*-PEP-*b*-iPP heptablock copolymer were prepared. The block copolymers displayed elastomeric behavior and exhibited excellent mechanical properties.

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Supporting Information Available: Ligand, complex, polymer syntheses, and ^{13}C{^{1}H} NMR spectra of polypropylenes produced from complexes **1**−**19**/MAO. This material is available free of charge via the Internet at http://pubs.acs.org.

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