Articles

Synthesis of Allyl-Terminated Syndiotactic Polypropylene: Macromonomers for the Synthesis of Branched Polyolefins

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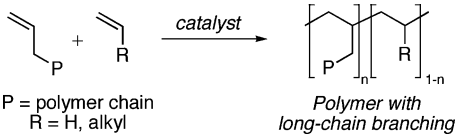
ABSTRACT: Low molecular weight syndiotactic polypropylene (*syndio*-PP) with an olefin end group was synthesized using methylaluminoxane-activated bis(phenoxyimine)titanium dichloride ($(PHI)_2TiCl_2$) catalysts. Propylene enchainment occurs by a 2,1-insertion mechanism, and termination by β-hydride elimination produces low molecular weight *syndio*-PP with allyl end groups. Several new $(PHI)_2TiCl_2$ complexes with various ligand modifications were found to display a wide range of activities (turnover frequency (TOF) = 3−1200 h^{-1}) and syndiospecificities ([*rrrr*] = 0.46−0.93) for propylene polymerization. While the TOF increases with increasing reaction temperature and propylene concentration, the molecular weight of the resulting macromonomer shows little variation. This provides strong support for a chain-transfer mechanism involving one molecule of propylene. The allyl-terminated PPs reported herein can be used to synthesize branched polyolefins or other new polyolefin architectures.

Introduction

Characteristics of polymer architecture such as molecular weight, regiochemistry, stereochemistry, and branching can dramatically influence polymer properties.[1] The pursuit of single-site polymerization catalysts capable of controlling such polymer characteristics has been a major focus of research over the past two decades.[2] Recent advances in the development of single-site metallocene catalysts have led to the production of polymers with high stereoregularity and regioregularity, which can give rise to improved mechanical properties.[3] In addition, numerous non-metallocene catalysts have also been developed that are highly stereoselective for olefin polymerizations.[4−6] The discovery of catalysts capable of living olefin polymerization has made possible the synthesis of block copolymers, which can exhibit greatly improved mechanical properties compared with their homopolymer counterparts.[7−9]

Although drastic improvements in the mechanical properties of polyolefins synthesized with single-site catalysts have been noted (such as impact resistance, toughness at low temperatures, and resistance to stress cracking), the narrow molecular weight distribution (M_w/M_n) of polymers obtained in these single-site polymerizations ($M_w/M_n \leq 2$) often renders them difficult to process in extensional flow processes.[10,11] The addition of even small amounts of long chain branched (LCB) polymers can improve processability in polyolefins.[10,12,13] Branches are typically considered to be long chain branches when the branch length is at least 2.5 times the entanglement molecular weight (M_e; "the molecular weight between adjacent temporary entanglement points", as defined by Eckstein and co-workers[14]) for the given polymer composition,[15−17] resulting in greatly increased melt strength and improved processability.[10,12,18−22]

Scheme 1. Branched Polyolefins via Alkene/ Macromonomer Copolymerization



LCB polymers are typically manufactured using electron-beam irradiation,[23] peroxide decomposition,[20] grafting branches from a polymer backbone,[24−29] addition of a branching agent to a polymerization,[25,30−33] addition of a chain transfer agent to a polymerization,[34−36] or copolymerization of a monomer with a macromonomer.[37−65] Single-site catalysts can be used for the synthesis of LCB polyolefins through the copolymerization of an alkene-terminated macromonomer with a comonomer (Scheme 1).[37−40,42,43,46,48−58,60−74] This method allows for the control of branch length and distribution. In addition, the ability to synthesize LCB polymers with different compositions on the side chains and backbone allows for the precise design of polymer architecture for applications in thermoplastic elastomers[75−79] and compatibilizers.[80] Accessibility to macromonomers with substantial molecular weight and polymerizable end groups is advantageous for the development of LCB polymers.

Isotactic polypropylene (*iso*-PP) is an important commercial polymer, with nearly 18 billion pounds produced in the United States in 2003.[81] *iso*-PP has a high melting point (T_m), tensile strength, and chemical resistance but a low melt strength.[82] Many of the applications for

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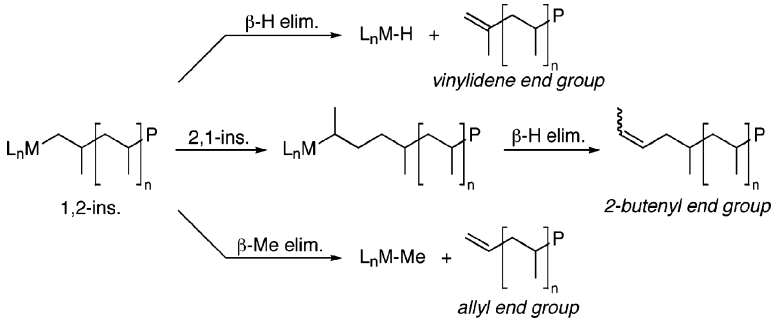
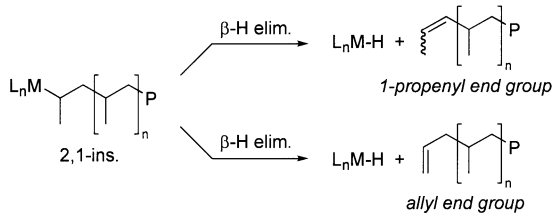
Scheme 2. Chain Termination in Propylene Polymerization with 1,2-Insertions



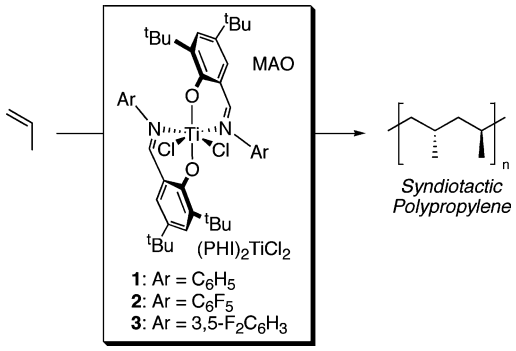
Scheme 3. Chain Termination in Propylene Polymerization with 2,1-Insertions



which *iso*-PP is suitable, such as appliance and automobile parts, require injection-molding and melt-processing methods. The inherent low melt strength of *iso*-PP makes this type of processing difficult; however, the addition of long chain branches to PP has been shown to improve the melt strength greatly.[22] Although LCB−PP has been made using macromonomer incorporation methods,[46,49−51,55−58,62,63,65] it is far less straightforward than the synthesis of LCB polyethylene. The challenge lies in obtaining PP macromonomers with a polymerizable end group and with an M_n that is $>2.5M_e$.[17] Stereoregularity in PP has a significant impact on M_e and the plateau modulus. Isotactic and atactic PP exhibit similar rheological behavior, with M_e determined to be ∼7000 g/mol,[14] while for syndiotactic PP M_e has been reported to be below 3500 g/mol.[14,83] The polymerization of propylene usually occurs through 1,2-insertions; thus, termination by β-hydride (β-H) transfer gives the sterically congested vinylidene end group[84,85] (Scheme 2), which resists subsequent insertion polymerization. Only β-CH_3 elimination yields an allylic end group in this primary insertion mechanism.[86−89] Although most metallocenes exhibit low selectivity for allylic end groups in polypropylene synthesis,[87] $Cp^*_2MCl_2$ (M = Zr, Hf) and bridged bis(fluorenyl)zirconocenes exhibit between 70 and 90% β-CH_3 elimination to give allyl-terminated atactic polypropylene,[87] while select chiral metallocenes exhibit up to 80% β-CH_3 elimination to give allyl-terminated isotactic polypropylene.[87,90,91] Subsequent polymerization steps incorporate propylene as well as allyl-terminated polypropylene chains, leading to the formation of LCB-PP.[46,49−51,55−58,62,63,65]

Another synthetic approach to allyl-terminated PP is the use of catalysts in which propylene 2,1-insertions predominate. As shown in Scheme 3, β-H transfer from a secondary metal alkyl can produce either a 1-propenyl end group or an allyl end group.[84,87] Interestingly, allyl end groups are observed exclusively in propylene polymerizations in which 2,1-insertions predominate.[62,92−95] The resulting metal−hydride can then undergo propylene insertion to generate a new polymer chain. Pyridinediimine−Fe(II) complexes, which polymerize propylene through a 2,1-insertion mechanism, generate

Scheme 4. Syndiospecific Propylene Polymerization



atactic to partially isotactic ([*mmmm*] ≤ 0.67) PP macromonomers by this method.[62,92−94] These PP macromonomers have been successfully copolymerized with propylene using an isospecific metallocene complex.[46] However, the M_n of these *iso*-PP macromonomers (≤6500 g/mol) is substantially below the $2.5M_e$ that is required for LCB entanglements.[14,17]

Group IV complexes bearing chelating phenoxyimine (PHI) ligands have been studied extensively for alkene polymerization.[96,97] Titanium(IV) complexes **1**−**3**/methylaluminoxane (MAO) give highly syndiotactic PP (*syndio*-PP; Scheme 4) through chain-end control in a 2,1-insertion mechanism.[95,98−102] Furthermore, complexes with ortho fluorination on the *N*-aryl ring (e.g., **2**) produce PP with narrow molecular weight distributions.[103−108] ^1H and ^{13}C NMR spectroscopic end-group analyses of PP synthesized with **3**/MAO showed an equal number of saturated and unsaturated end groups.[95] The only unsaturated end groups observed were allylic, consistent with β-H transfer following a secondary insertion.[95,107,109] Saturated end groups were composed of a 1:1 mixture of *n*-propyl and *n*-butyl chain ends. This composition was proposed to result from a 1,2-insertion of propylene into the Ti−H bond, followed by a 50:50 distribution of 1,2- and 2,1-insertions. A chain-termination mechanism involving direct β-H transfer to monomer has recently been proposed.[107] Given this high selectivity for allyl end groups, we reasoned that catalyst **3**/MAO could be used to make highly syndiotactic macromonomers with substantial molecular weights. These macromonomers could subsequently be used in the synthesis of LCB polymers with crystalline side chains. Herein we describe the synthesis of a variety of new catalysts and the study of different reaction conditions to optimize the polymerization for macromonomer production.

Results and Discussion

Complex Synthesis and Characterization. While numerous isomeric forms of $(PHI)_2TiCl_2$ complexes could

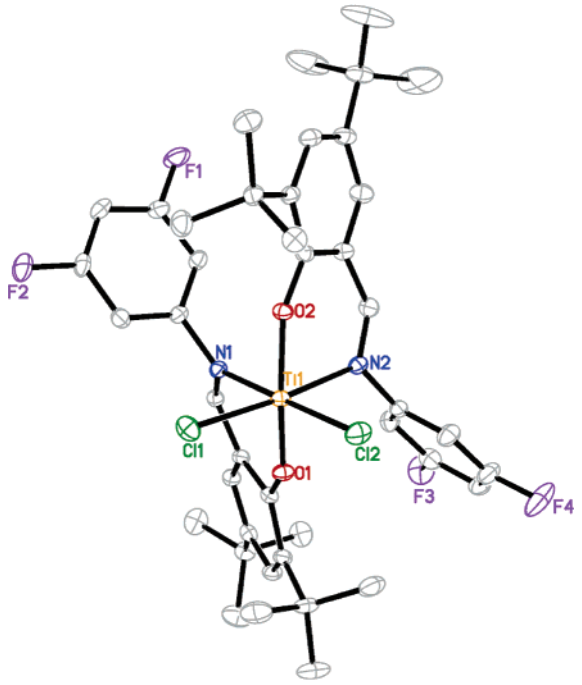


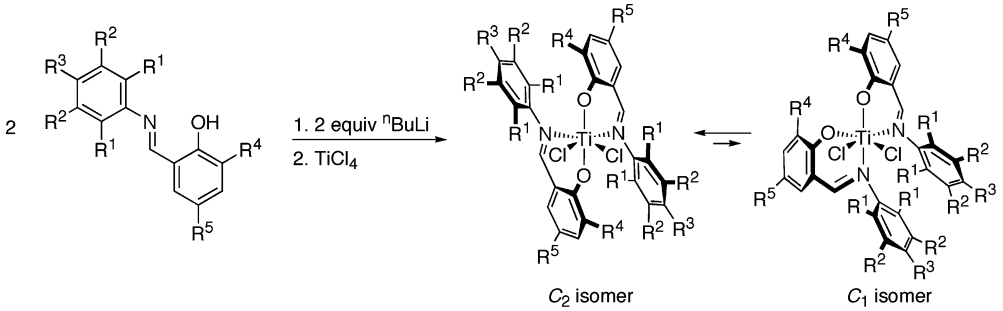
Figure 1. Molecular structure of **3** with thermal ellipsoids at the 40% probability level (hydrogen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ti(1)−O(1) 1.842(1), Ti(1)−O(2) 1.850(1), Ti(1)−N(1) 2.214(2), Ti(1)−N(2) 2.239(2), Ti(1)−Cl(1) 2.285(1), Ti(1)−Cl(2) 2.307(1); O(1)−Ti(1)−O(2) 163.3(1), N(1)−Ti(1)−N(2) 84.2(1), Cl(1)−Ti(1)−Cl(2) 95.8(1).

exist, those complexes exhibiting living polymerization behavior exist as a single C_2-symmetric isomer, both in the solid state and in solution.[103,104] Analysis of a single crystal of **3** using X-ray crystallography shows C_2-symmetric geometry similar to that of our previously reported complexes,[103,104] with oxygen atoms trans and chlorine and nitrogen atoms cis (Figure 1). In solution, however, **3** is determined to be a mixture of C_2-symmetric (73%) and C_1-symmetric (27%) isomers using ^{1}H NMR spetroscopy.[110] Suspecting that the presence of this second isomeric form could be indicative of a nonliving polymerization catalyst, we synthesized several other $(PHI)_2TiCl_2$ complexes to determine the significance of the isomeric forms.

In an effort to find a catalyst that was even more active and stereoselective than is **3**/MAO, systematic steric and electronic modifications to the ligand structure were made. The phenoxyimine ligand synthesis allows for a wide variety of ligands to be prepared from commercially available anilines and readily synthesized salicylaldehydes. Standard synthesis of $(PHI)_2TiCl_2$ complexes involves the deprotonation of the phenoxyimine ligand with *n*-butyllithium, followed by addition of 0.5 equiv of $TiCl_4$ (Scheme 5). Complexes **1**−**8** were synthesized by varying the aniline to study the effect of electron-withdrawing substituents on the *N*-aryl ring (Scheme 5). When $R^1 = R^2 = R^3 = F$ (**2**), the complex exists only as the C_2 isomer with trans oxygen atoms and nitrogen and chlorine atoms oriented in a cis configuration (no C_1 isomer is observed using ^{1}H NMR spectroscopy).[103] When $R^1 = H$ (**1**, **3**−**8**), the complex exists as a mixture of isomers in solution, with 18−29% C_1 isomer. In complexes **9**−**12**, the salicylaldehyde was varied to study the effect of steric bulk in the R^4 substituent. When R^4 is ^{i}Pr or a smaller substituent, only the C_2 isomer is observed using ^{1}H NMR spectroscopy, whereas if R^4 is ^{t}Bu or a larger substituent, the complex is a mixture of C_2 and C_1 isomers. In fact, **11** exists primarily as the C_1 isomer in solution, as determined by ^{1}H NMR spectroscopy, and analysis of a single crystal of **11** using X-ray crystallography (Figure 2) revealed C_1 symmetry, with nitrogen, oxygen, and chlorine atoms cis.

To determine whether the formation of the C_1 isomer was a result of the preparation method, an alternate synthetic route for **3** was investigated. Reaction of 2 equiv of (PHI)H with $Ti(O^iPr)_4$ and subsequent treatment with excess Me_3SiCl gave **3** with C_2- and C_1-symmetric isomers in a 73:27 ratio (Scheme 6). A NOESY NMR experiment indicates rapid exchange between the C_1-symmetric enantiomers of **3**, but no

Scheme 5. Synthesis of $(PHI)_2TiCl_2$ Complexes 1−12



Complex	R^1	R^2	R^3	R^4	R^5	% C_2 isomer[a]
1	H	H	H	^{t}Bu	^{t}Bu	71
2	F	F	F	^{t}Bu	^{t}Bu	100
3	H	F	H	^{t}Bu	^{t}Bu	73
4	H	F	F	^{t}Bu	^{t}Bu	79
5	H	H	F	^{t}Bu	^{t}Bu	75
6	H	Cl	H	^{t}Bu	^{t}Bu	82
7	H	CF_3	H	^{t}Bu	^{t}Bu	81
8	H	H	CF_3	^{t}Bu	^{t}Bu	73
9	H	F	H	Me	Me	100
10	H	F	H	^{i}Pr	H	100
11	H	F	H	CMe_2Ph	CMe_2Ph	9
12	H	F	H	$SiMe_3$	H	80

[a] Determined using ^{1}H NMR spectroscopy (benzene-d_6).

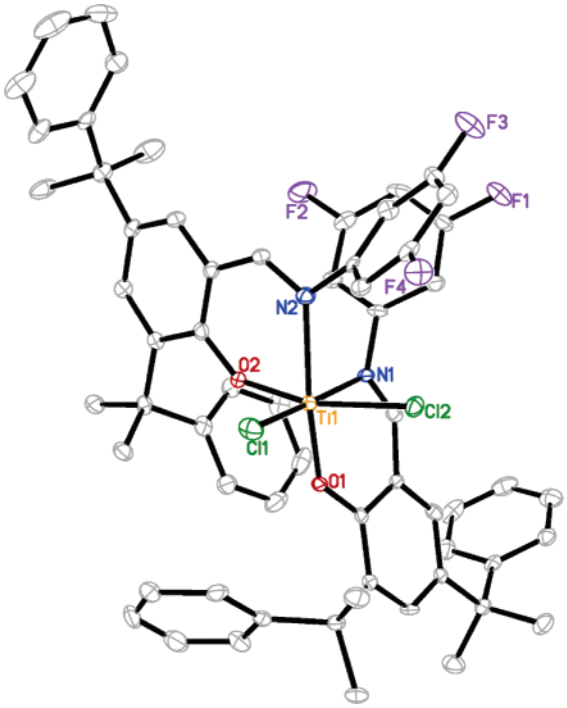
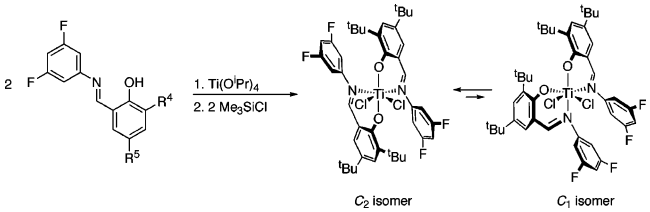


Figure 2. Molecular structure of **11** with thermal ellipsoids at the 40% probability level (hydrogen atoms and a toluene molecule of solvation have been omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ti(1)−O(1) 1.833(2), Ti(1)−O(2) 1.845(2), Ti(1)−N(1) 2.228(3), Ti(1)−N(2) 2.262(3), Ti(1)−Cl(1) 2.299(1), Ti(1)−Cl(2) 2.341(1); O(1)−Ti(1)−O(2) 98.1(1), N(1)−Ti(1)−N(2) 88.2(1), Cl(1)−Ti(1)−Cl(2) 94.8(1).

Scheme 6. Alternate Synthesis of Complex 3



evidence of exchange between the C_2- and C_1-symmetric isomers was observed (see Supporting Information). However, analysis of a single crystal of complex **6** by ^{1}H NMR spectroscopy shows the C_2-symmetric isomer upon initial dissolution, with peaks corresponding to the C_1-symmetric isomer growing in over ≈30 min. Whereas C_1-symmetric (and presumably C_2-symmetric) isomers racemize quickly, interconversion between C_2- and C_1-symmetric isomers occurs much more slowly.

Polymerization Results. Complexes **1**−**12** were studied for the polymerization of propylene to determine which factors influence the polymerization rate, termination rate, tacticity, and M_n of the desired *syndio*-PP macromonomer (Scheme 7).[111] β-H transfer during polymerization leaves an allyl end group that is easily identifiable using ^{1}H NMR spectroscopy, with the vinyl peaks appearing at 5.0 and 5.8 ppm (Figure 3).[3,86,112]

Ligand substitution has a dramatic effect on catalyst activity as well as on the tacticity and M_n of the resulting polymer (Table 1). The presence of electron-withdrawing substituents in the R^2 position (**3**, **6**, and **7**) increases the polymerization rate by almost an order of magnitude (compared to **1**) while leaving M_n essentially unchanged. These effects are most pronounced with R^2 = F (**3**), whereas larger groups, such as Cl (**6**) and CF_3 (**7**), are less active and have lower syndiospecificities. Electron-withdrawing groups in the R^3 position (**5** and **8**) increase the polymerization rate to a small degree, and the resulting polymers are more stereoregular and have higher M_n than those produced by **1**. When these effects are combined, with $R^2 = R^3$ = F (**4**), the polymerization rate is even higher while stereocontrol appears unchanged and the M_n of the polymer is slightly lower than those from complexes **3** or **5**. Fluorination in the R^1 positions (**2**), as already described, decreases activity and leads to a polymer with a very narrow molecular weight distribution and high syndiotacticity.

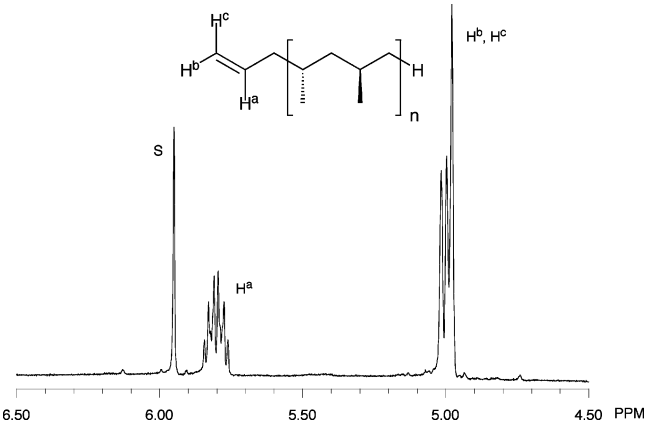
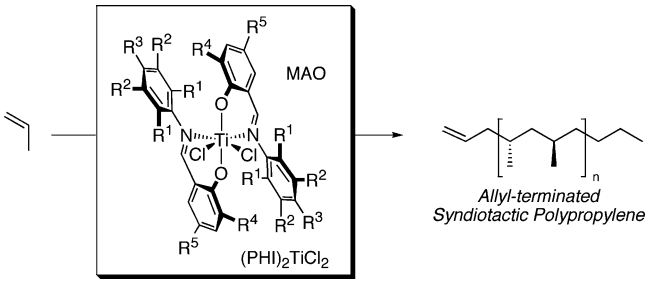


Figure 3. Representative ^{1}H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-d_2, 135 °C) of allyl-terminated syndiotactic polypropylene made using **3**/MAO (S = 1,1,2,2-tetrachloroethane-d_1).

Scheme 7. Synthesis of Allyl-Terminated Syndiotactic Polypropylene Using $(PHI)_2TiCl_2$/MAO



Polymerization behavior is dramatically influenced by the steric bulk of the R^4 substituent on the phenoxy-imine ligand. Decreasing the steric bulk of R^4 from ^{t}Bu (**3**) to Me (**9**) or ^{i}Pr (**10**) greatly increases the catalyst activity. These complexes produce polymer with much lower tacticity than that of **3** (Table 1). Unexpectedly, complexes **9** and **10** produce high molecular weight polymer, show no evidence of β-H transfer, and have narrow polymer molecular weight distributions. To the best of our knowledge, these are the first bis(phenoxy-imine)titanium complexes without ortho fluorination that exhibit living behavior for propylene polymerization, and they will be the subject of future investigation in our lab.

Increasing the steric bulk from ^{t}Bu (**3**) to $SiMe_3$ (**12**) has little effect on the catalyst activity, but the M_n of the polymer increased (7100 g/mol) as did the tacticity of the polymer, with [*rrrr*] of 0.94 and T_m of 146 °C. We expected **11**/MAO to perform similarly, but instead very little polymer was formed, and the molecular weight distribution was multimodal. As **11** is 91% C_1 isomer and complexes **1**−**10** and **12** give polymers with a $M_w/M_n \leq 2$—consistent with a single active species—we infer

Table 1. Ligand Effects on Propylene Polymerization (Complexes 1−12)[a]

complex	yield (g)	TOF (h^{-1})[b]	M_n (g/mol)[c]	M_w/M_n [c]	[*rrrr*][d]	T_g [e] (°C)	T_m [e] (°C)
1	0.34	41	2300	1.48	0.76	−15.1	107.7
2	1.28	152	81000	1.08	0.96	−1.8	143.6
3	2.69	320	4300	1.81	0.80	−12.5	113.4
4	3.96	471	3100	1.76	0.80	−16.1	109.4
5	0.43	51	4600	1.82	0.84	−9.3	123.0
6	2.25	268	2200	2.00	0.67	−17.7	87.4
7	0.77	92	4200	1.85	0.54	−12.5	n.d.[f]
8	0.48	57	4900	1.71	0.82	−12.6	122.8
9	9.94	1183	240000	1.13	0.46	−2.1	n.d.[f]
10	7.60	905	212000	1.16	0.48	−3.5	n.d.[f]
11	0.03	3	45000	13.8	0.08	−8.5	n.d.[f]
12	2.97	354	7100	1.54	0.94	−7.4	145.8

[a] A solution of Ti catalyst (50 μmol) in 10 mL of toluene was injected into a glass reactor containing dried MAO (10 mmol Al) and 140 mL of toluene saturated with propylene at 0 °C. Reaction time = 4 h. [b] Turnover frequency (TOF) = mol of propylene/(mol of Ti·h). [c] Molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography at 140 °C in 1,2,4-trichlorobenzene relative to polyethylene standards. [d] Syndiotacticity ([*rrrr*]) was determined using ^{13}C NMR spectroscopy. [e] Glass transition temperature (T_g) and melting point (T_m) were determined by differential scanning calorimetry (second heating run). [f] Not detected.

Table 2. Temperature Effects on Propylene Polymerization Using 3/MAO[a]

entry	temp (°C)	yield (g)	TOF (h^{-1})[b]	M_n (g/mol)[c]	[*rrrr*][d]
1	20	1.08	183	4640	0.77
2	0	1.14	194	5740	0.79
3	−20	0.69	118	6870	0.80

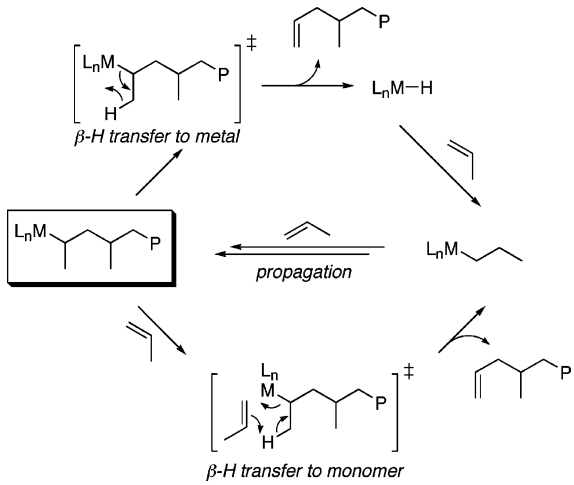
[a] A glass reactor containing dried MAO (7 mmol of Al) and 95 mL of toluene was weighed, equilibrated at the respective temperature, and saturated with propylene (1.65 M). The reactor was then weighed again to determine the mass of propylene (8 g), and the solution volume was marked. A solution of Ti catalyst (35 μmol) in 5 mL of toluene was injected, and the polymerization was run for 4 h. [b] Turnover frequency (TOF) = mol of propylene/(mol of Ti·h). [c] Molecular weight (M_n) was determined by quantitative ^1H NMR spectroscopy in benzene-d_6 at 80 °C. [d] Syndiotacticity ([*rrrr*]) was determined using ^{13}C NMR spectroscopy.

that the C_1 isomer is essentially inactive for propylene polymerization.

Several of the catalysts reported herein show great potential for use in the synthesis of *syndio*-PP macromonomers. Although **4**/MAO has the highest activity of all the catalysts that terminate by β-H transfer, the M_n values are below the ideal $2.5M_e$ necessary for sufficient entanglement as branches of LCB polymers. Even though **8**/MAO produces polymers with sufficient M_n and tacticity, it does not have high enough activity to be viable. Catalyst **12**/MAO is very active and also produces polymer of substantial M_n and high syndiotacticity, but the ligand synthesis is the most complicated of all the complexes, involving four synthetic steps to 2-trimethylsilyl-6-[[(3,5-difluorophenyl)imino]methyl]-phenol. Catalyst **3**/MAO, while not the best performing catalyst in any one area, is the best all-around catalyst and was therefore used to study the effects of reaction conditions on polymerization.

With most Ziegler−Natta catalysts, higher polymerization temperatures lead to lower M_n (the rate of chain termination vs propagation is increased at higher temperatures).[84] Table 2 shows the effects of polymerization temperature on macromonomer M_n and tacticity using **3**/MAO. To keep propylene concentration constant under different reaction conditions, the mass of propylene, rather than pressure, was measured, and polymerizations were run for 4 h to keep conversion under 20%. As expected, decreasing the polymerization temperature increases the syndiotacticity of the resulting polymer, as seen by the increase in [*rrrr*] from 0.77 at 20 °C to 0.80 at −20 °C (Table 2, entries 1 and 3) measured using

Scheme 8. Chain Transfer Mechanisms in Propylene Polymerization



^{13}C NMR spectroscopy. The molecular weights (M_n) of macromonomer products were obtained by relative integration of olefin end groups vs alkyl monomer units. M_n decreases with increasing polymerization temperature, suggesting the rate of chain termination to be highly temperature dependent, following the general trend of most other Ziegler−Natta catalysts.

Detailed Mechanism of β-Hydrogen Elimination. We have extensively studied the mechanism of insertion of propylene polymerization using bis(phenoxyimine)-titanium catalysts and have established that the end groups of the polymers from nonliving catalysts are saturated *n*-propyl and *n*-butyl groups as well as unsaturated allyl groups.[95] This information, in concert with other mechanistic studies,[102,109] is consistent with a mechanism involving 1,2-insertion into a metal hydride (either directly or via β-hydrogen transfer to monomer; Scheme 8) and random 1,2/2,1-insertion into the Ti−^{n}Pr bond. Once a 2,1-insertion occurs, the monomer selectively inserts in a secondary fashion until a β-hydrogen elimination ultimately occurs. Two limiting cases for the β-hydrogen transfer process are (1) a direct, unimolecular hydrogen transfer to the metal and (2) a bimolecular hydrogen transfer to a molecule of propylene (Scheme 8). There are well-documented cases for the unimolecular transfer process, where the degree of polymerization (DP) is directly proportional to monomer concentration (DP = (k_p[monomer][catalyst])/

Table 3. Concentration Effects on Propylene Polymerization Using 3/MAO[a]

entry	propylene concn (M)	yield (g)	TOF (h^{-1})[b]	M_n (g/mol)[c]
1	1.10	0.83	140	5880
2	1.65	1.14	194	5740
3	2.40	1.66	282	5600
4	3.53	2.31	393	5300

[a] A glass reactor containing dried MAO (7 mmol of Al) and 95 mL of toluene was weighed, cooled to 0 °C, and saturated with propylene. The reactor was then weighed again to determine the mass of propylene, and the solution volume was marked. A solution of Ti catalyst (35 μmol) in 5 mL of toluene was injected, and the polymerization was run for 4 h. [b] Turnover frequency (TOF) = mol of propylene/(mol of Ti·h). [c] Molecular weight (M_n) was determined by quantitative ^{1}H NMR spectroscopy in benzene-d_6 at 80 °C.

($k_{\beta-H/metal}$[catalyst])).[87,113] On the other hand, there are cases where β-hydrogen transfer to monomer is the proposed elimination mechanism, as DP is independent of monomer concentration (DP = (k_p[monomer][catalyst])/($k_{\beta-H/monomer}$[monomer][catalyst])).[87,114,115] As discovered by Landis and co-workers, a DP that is independent of monomer concentration is not sufficient evidence to establish a termination mechanism that proceeds by chain transfer to monomer.[113] In the case of hexene polymerization by chiral ethylenebis(indenyl)zirconocene catalysts, the termination process is first order in hexene, not because of chain transfer to monomer, but due to a 2,1-misinsertion that necessitates chain termination. Although the polyhexene DPs are independent of hexene concentration, the exact mechanism of chain transfer cannot be established by these data alone.

We recognized that bis(phenoxyimine)titanium catalysts might provide the ideal basis to examine β-hydrogen transfer mechanisms in more detail. The 2,1-insertion mechanism eliminates the potential for "misinserted" species that mask the kinetics of the elimination process. During our investigation, several studies were reported that suggested chain transfer to monomer mechanisms using these and related catalyst systems. Talarico and co-workers reported an unexpectedly low dependence of M_n on monomer concentration in the propylene polymerization with **1**/MAO (1.1 mol % terminal allyls at [C_3H_6] = 0.7 M, 1.4 mol % terminal allyls at [C_3H_6] = 5.6 M), consistent with chain transfer to monomer.[107] In addition, theoretical studies of a structurally similar bis(pyrroleimine)−Ti(IV) system predicted a chain transfer to monomer mechanism.[116]

We determined the effect of propylene concentration on M_n using **3**/MAO (Table 3). The mass of propylene was determined by weighing the reactor before and after propylene addition, and volume was measured using graduated markings on the glass reactor. With this method, it was possible to measure the molar concentration of the propylene monomer for each reaction. As propylene concentration increased, TOF also increased linearly, as expected on the basis of a propagation rate law that is first order in monomer. Within propylene concentrations ranging from 1.1 to 3.5 M, no significant changes in M_n were observed, suggesting that the rate of chain termination is also dependent on propylene concentration. We determined molecular weights using ^{1}H NMR spectroscopy and were concerned that incorporation of the macromonomers might cause errors in determination of M_n. In a control experiment, the polymerization of propylene and 4-methyl-1-pentene (a model for the allyl-terminated polypropylene) gave polypropylene with no incorporation of the 4-methyl-1-pentene. Moreover, gel permeation chromatography confirmed the lack of dependence of M_n on propylene concentration. Together, these experiments strongly support a termination mechanism involving direct β-H transfer to monomer.

With few exceptions, bis(phenoxyimine)titanium(IV) complexes generally fall into one of two categories with respect to their propylene polymerization behavior: (1) living polymerization catalysts bearing ortho fluorines and (2) non-ortho-fluorinated catalysts that produce allyl-terminated polymers. (Complexes **9** and **10** are examples of exceptions to this trend, where neither complex contains ortho fluorines on the *N*-aryl ring; however, they display living propylene polymerization behavior.) This effect has been proposed to result from an attractive interaction of the ortho fluorine with the β-H of the growing polymer chain, thus stabilizing it against termination.[105,106,108] An alternative proposal is that the effect of the ortho fluorines is primarily steric in nature.[107] Whereas the four-center monomer insertion transition state spans a ~90° angle, the six-center chain transfer to monomer transition state spans a ~130° angle. Sterically demanding ligand sets (including those phenoxyimine ligands with ortho fluorination) inhibit the larger chain-transfer transition state.[117] Our experimental evidence appears to support the second proposal, in which β-H transfer to monomer is the main termination mechanism and is suppressed in systems with ortho-fluorinated ligands. We are currently working to determine the detailed nature of the active sites of these systems to better understand their catalytic behavior.

Conclusion

Some $(PHI)_2TiCl_2$ complexes, while not displaying living polymerization behavior, are excellent catalysts for the synthesis of allyl-terminated *syndio*-PP macromonomers. Several new $(PHI)_2TiCl_2$ precatalysts show an interesting trend between complex solution structure and catalyst activity. When the complex is completely C_2-symmetric, as determined using ^{1}H NMR spectroscopy, no chain termination is observed in the resulting polymerization. When the complex exists as a mixture of C_1 and C_2 isomers, however, significant chain termination in the form of β-H transfer is observed. A new complex (**12**) produces *syndio*-PP macromonomers with a higher M_n (7100 g/mol) and higher syndiotacticity ([*rrrr*] = 0.94, T_m = 145.8 °C) than that observed in other catalysts. Polymerization temperature dramatically influences catalyst activity, with only a moderate effect on M_n. Propylene concentration, however, has a significant impact on catalyst activity but practically no effect on polymer M_n. These catalysts undergo β-H transfer to monomer from a secondary metal alkyl species to leave a polymer with an allyl end group. The origins of chain termination appear to be related to the presence of a C_1 isomer in the catalyst precursor. These new crystalline, allyl-terminated polypropylenes offer an exciting opportunity to make new LCB polymers as well as other polymer architectures with syndiotactic polypropylene segments.

Experimental Section

General Methods. All manipulations of air- and/or water-sensitive compounds were carried out under dry nitrogen using a Braun UniLab drybox or standard Schlenk line techniques. ^{1}H NMR spectra of ligands and complexes were recorded on a

Varian Mercury (300 MHz) or a Varian Inova (400 MHz) spectrometer and referenced vs residual nondeuterated solvent shifts. ^{1}H NMR spectra of polymers and ^{13}C NMR spectra of the complexes and polymers were recorded on a Varian Inova (500 MHz) spectrometer equipped with a ^{1}H/BB switchable with *Z*-pulse field gradient probe and referenced vs residual nondeuterated solvent shifts. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 in a 5 mm o.d. tube, and spectra were collected at 135 °C. Macromonomer M_ns were determined by relative integration of the vinyl vs alkyl peaks in the ^{1}H NMR spectrum or by gel permeation chromatography (GPC) performed with a Waters Alliance GPCV 2000 GPC equipped with a Waters DRI detector and viscometer. The column set (four Waters HT 6E and one Waters HT 2) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt % di-*tert*-butylhydroxytoluene (BHT) at 1.0 mL/min at 140 °C. Data were calibrated using monomodal polyethylene standards (from Polymer Standards Service). Polymer solutions were usually placed in a 140 °C oven for 24 h prior to molecular weight measurements. Syndiotacticity ([*rrrr*]) was measured by Gaussian deconvolution of the methyl region of the ^{13}C NMR spectrum. Differential scanning calorimetric analyses were performed in crimped aluminum pans under nitrogen using a TA Instruments Q1000 calorimeter equipped with an automated sampler. Data were collected from the second heating run at a heating rate of 10 °C/min from −50 to 200 °C and were processed with the TA Q series software package.

Materials. Toluene and hexanes were purified over columns of alumina and copper (Q5). Methylene chloride and tetrahydrofuran were purified over an alumina column and degassed by three freeze−pump−thaw cycles before use. Benzene-d_6 was vacuum-transferred from sodium benzophenone ketyl under nitrogen. Propylene (Matheson, polymer grade) was purified over columns of molecular sieves and copper (Q5). Methylaluminoxane (PMAO-IP, 12.9 wt % Al in toluene, Akzo Nobel) was concentrated in vacuo to remove residual trimethylaluminum, providing a solid white powder. 3,5-Dimethylsalicylaldehyde and 3-trimethylsilylsalicylaldehyde,[106,118] as well as complexes **1**,[98] **2**,[103] **3**,[95] **4**, **5**, **7**, and **8**, were synthesized according to previous reports.[104] All other chemicals were purchased from commercial sources and used as received.

General Procedure for Synthesis of Salicylaldehydes.[118] To a solution of MeMgBr (3.0 M in ether, 10 mL, 30 mmol) and 20 mL of THF at 0 °C was added a solution of the desired phenol (27.3 mmol) in 15 mL of THF dropwise over 20 min. The solution was warmed to room temperature and stirred for an additional 45 min. Toluene (100 mL) was then added, followed by triethylamine (5.3 mL, 40.9 mmol) and solid paraformaldehyde (2.05 g, 68.2 mmol). The solution was heated to 80 °C for 4 h. After cooling to room temperature the mixture was poured into 250 mL of 2 M HCl, extracted with ether, dried over $MgSO_4$, filtered, and purified as described below.

3-Isopropylsalicylaldehyde. 2-Isopropylphenol (3.67 mL, 27.3 mmol) was reacted as described above, and the product was isolated as an orange oil (4.12 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.37 (s, 1H, OH), 9.88 (s, 1H, HC=O), 7.47 (dd, 1H, J_{HH} = 1.7, 7.7 Hz, Ar), 7.40 (dd, 1H, J_{HH} = 1.7, 7.7 Hz, Ar), 6.99 (t, 1H, J_{HH} = 7.7 Hz, Ar), 3.38 (s, 1H, J_{HH} = 6.9 Hz, C*H*$(CH_3)_2$), 1.25 (d, 6H, J_{HH} = 6.9 Hz, CH(C*H*$_3)_2$).

3,5-Bis(α,α′-dimethylbenzyl)salicylaldehyde. 2,4-Bis-(α,α′-dimethylbenzyl)phenol (6.01 g, 18.2 mmol) was reacted as described above and the product crystallized from MeOH, giving a light yellow solid (2.89 g, 44% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.26 (s, 1H, OH), 9.77 (s, 1H, HC=O), 7.1−7.5 (m, 12 H, Ar), 1.73 (s, 6H, C(C*H*$_3)_2$), 1.64 (s, 6H, C(C*H*$_3)_2$).

General Procedure for Synthesis of Phenoxyimine Ligands.[106] The desired salicylaldehyde (1 equiv) and aniline (1.5 equiv) were combined in toluene with a small amount of *p*-toluenesulfonic acid. The solution was heated to 110 °C for 5 h. After cooling to room temperature the mixture was dried over $NaSO_4$, filtered, solvent removed in vacuo, and purified as described below.

2,4-Di-*tert*-butyl-6-[[(3,5-dichlorophenyl)imino]methyl]phenol. 3,5-Di-*tert*-butylsalicylaldehyde (2.92 g, 12.4 mmol) and 3,5-dichloroaniline (3.02 g, 18.6 mmol) were reacted as described above and crystallized from CH_2Cl_2/MeOH, giving orange blocks (3.45 g, 73% yield). ^{1}H NMR (300 MHz, benzene-d_6): δ 13.36 (s, 1H, OH), 7.61 (d, 1H, J_{HH} = 2.5 Hz, Ar), 7.58 (s, 1H, HC=N), 6.94 (t, 1H, J_{HH} = 1.9 Hz, Ar_{Cl}), 6.88 (d, 1H, J_{HH} = 2.5 Hz, Ar), 6.57 (d, 2H, J_{HH} = 1.9 Hz, Ar_{Cl}), 1.63 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu).

2,4-Dimethyl-6-[[(3,5-difluorophenyl)imino]methyl]phenol. 3,5-Dimethylsalicylaldehyde (1.39 g, 9.27 mmol) and 3,5-difluoroaniline (1.80 g, 13.9 mmol) were reacted as described above and crystallized from MeOH, giving orange blocks (1.08 g, 45% yield). ^{1}H NMR (300 MHz, benzene-d_6): δ 12.79 (s, 1H, OH), 7.70 (s, 1H, HC=N), 6.81 (s, 1H, Ar), 6.55 (s, 1H, Ar), 6.30 (tt, 1H, J_{HH} = 2.2 Hz, J_{HF} = 8.8 Hz, Ar_F), 6.23 (m, 2H, Ar_F), 2.32 (s, 3H, CH_3), 2.07 (s, 3H, CH_3).

2-Isopropyl-6-[[(3,5-difluorophenyl)imino]methyl]phenol. 3-Isopropylsalicylaldehyde (1.77 g, 10.8 mmol) and 3,5-difluoroaniline (2.09 g, 16.2 mmol) were reacted as described above, and the product was purified using column chromatography with 95/5 hexanes/EtOAc as eluant, giving an orange oil (1.11 g, 37% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.01 (s, 1H, OH), 8.58 (s, 1H, HC=N), 7.39 (dd, 1H, J_{HH} = 7.7, 1.2 Hz, Ar), 7.25 (dd, 1H, J_{HH} = 7.7, 1.2 Hz, Ar), 6.94 (t, 1H, J = 7.7 Hz, Ar), 6.81 (m, 2H, Ar_F), 6.74 (tt, 1H, J_{HH} = 2.2 Hz, J_{HF} = 8.8 Hz, Ar_F), 3.43 [s, 1H, J = 6.9 Hz, C*H*$(CH_3)_2$], 1.28 [d, 6H, J = 6.9 Hz, CH(C*H*$_3)_2$].

2,4-Bis(α,α′-dimethylbenzyl)-6-[[(3,5-difluorophenyl)-imino]methyl]phenol. 3,5-Bis(α,α′-dimethyl-benzyl)salicylaldehyde (1.28 g, 3.6 mmol) and 3,5-difluoroaniline (0.69 g, 5.4 mmol) were reacted as described above, and the product was purified using column chromatography with 95/5 hexanes/EtOAc as eluant, giving an orange oil (1.41 g, 84% yield). ^{1}H NMR (300 MHz, benzene-d_6): δ 12.99 (s, 1H, OH), 7.65 (d, 1H, J = 2.5 Hz, Ar), 7.41 (s, 1H, HC=N), 7.00−7.38 (m, 10H, Ar), 6.87 (d, 1H, J = 2.5 Hz, Ar), 6.25 (tt, 2H, J_{HH} = 2.0 Hz, J_{HF} = 8.9 Hz, Ar_F), 5.89 (m, 2H, Ar_F), 1.77 (s, 6H, CH_3), 1.66 (s, 6H, CH_3).

2-Trimethylsilyl-6-[[(3,5-difluorophenyl)imino]methyl]-phenol. 3-Trimethylsilylsalicylaldehyde (1.05 g, 5.4 mmol) and 3,5-difluoroaniline (1.05 g, 8.1 mmol) were reacted as described above, and the product was purified by column chromatography with 95/5 hexanes/EtOAc as eluant, giving orange solid (1.37 g, 83% yield). ^{1}H NMR (300 MHz, benzene-d_6): δ 13.10 (s, 1H, OH), 7.61 (s, 1H, HC=N), 7.47 (dd, 1H, J_{HH} = 1.8, 7.0 Hz, Ar), 6.89 (dd, 1H, J_{HH} = 1.8, 7.0 Hz, Ar), 6.77 (t, 1H, J_{HH} = 7.6 Hz, Ar), 6.29 (tt, 1H, J_{HH} = 2.0 Hz, J_{HF} = 8.8 Hz, Ar_F), 6.14 (m, 2H, Ar_F), 0.46 (s, 9H, $SiCH_3$).

Synthesis of Bis[2,4-di-*tert*-butyl-6-[[(3,5-difluorophenyl)imino]methyl]phenolato]titanium Dichloride (3). A solution of 2,4-di-*tert*-butyl-6-[[(3,5-difluorophenyl)imino]-methyl]phenol (1.08 g, 3.13 mmol) in THF (10 mL) was added dropwise to a solution of Ti(O^{i}Pr)$_4$ (0.47 mL, 1.57 mmol) in THF (7 mL) at room temperature. The solution was heated to 60 °C for 2 h and cooled, and the solvent was removed in vacuo. ^{1}H NMR (300 MHz, benzene-d_6, isomeric mixture in solution, 70% C_2 isomer): δ 7.56 (d, 2H, J_{HH} = 2.5 Hz, Ar), 7.45 (s, 2H, HC=N), 6.86 (d, 2H, J_{HH} = 2.5 Hz, Ar), 6.44 (m, 4H, Ar_F), 6.19 (tt, 2H, J_{HH} = 2.5 Hz, J_{HF} = 8.8 Hz, Ar_F), 5.84 [s, J_{HH} = 6.0 Hz, C*H*$(CH_3)_2$], 1.47 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu), 1.14 (d, 6H, J_{HH} = 6.0 Hz, CH(C*H*$_3)_2$), 1.07 (d, 6H, J_{HH} = 6.0 Hz, CH-(C*H*$_3)_2$). (C_1 isomer): δ 7.70 (d, 1H, J_{HH} = 2.5 Hz, Ar), 7.60 (d, 1H, J_{HH} = 2.5 Hz, Ar), 7.36 (s, 1H, HC=N), 7.35 (s, 1H, HC=N), 6.62 (d, 1H, J_{HH} = 2.5 Hz, Ar), 6.47 (d, 1H, J_{HH} = 2.5 Hz, Ar), 5.32 (s, 1H, J_{HH} = 6.0 Hz, C*H*$(CH_3)_2$), 4.26 (s, 1H, J_{HH} = 6.0 Hz, C*H*$(CH_3)_2$), 1.78 (s, 9H, ^{t}Bu), 1.37 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.23 (s, 9H, ^{t}Bu), 1.0−1.4 [m, 12H, CH(C*H*$_3)_2$]. The dark yellow residue was dissolved in CH_2Cl_2 (10 mL), and chlorotrimethylsilane (1.0 mL, 7.8 mmol) was added by syringe. The red solution was stirred overnight, and volatiles were removed in vacuo. The crude product was purified by crystallization from CH_2Cl_2/pentane to give dark red crystals (0.80 g, 63% yield). ^{1}H NMR (300 MHz, benzene-d_6, isomeric mixture in solution, 73% C_2 isomer): δ 7.59 (d, 2H, J_{HH} = 2.5 Hz, Ar), 7.16 (s, 2H, HC=N), 6.76 (d, 2H, J_{HH} = 2.5 Hz, Ar), 6.35 (m, 4H, Ar_F), 6.09 (tt, 2H, J_{HH} = 2.5 Hz, J_{HF} = 8.8 Hz,

Ar_F), 1.56 (s, 18H, ^{t}Bu), 1.26 (s, 18H, ^{t}Bu). (C_1 isomer): δ 7.75 (d, 1H, J_{HH} = 2.5 Hz, Ar), 7.61 (d, 1H, J_{HH} = 2.5 Hz, Ar), 7.33 (s, 1H, HC=N), 7.28 (s, 1H, HC=N), 6.91 (d, 1H, J_{HH} = 2.5 Hz, Ar), 6.70 (d, 1H, J_{HH} = 2.5 Hz, Ar), 6.23 (m, 6H, Ar_F), 1.78 (s, 9H, ^{t}Bu), 1.31 (s, 9H, ^{t}Bu), 1.27 (s, 9H, ^{t}Bu), 1.18 (s, 9H, ^{t}Bu). ^{13}C NMR (125 MHz, benzene-d_6, C_2 isomer): δ 167.69, 162.45 (dd, J_{CF} = 250, 14 Hz), 159.81, 154.21 (t, J_{CF} = 11 Hz), 143.76, 138.75, 132.69, 129.27, 124.27, 107.81 (d, J_{CF} = 24 Hz), 101.89 (t, J_{CF} = 25 Hz), 35.51, 34.35, 31.18, 29.83. (C_1 isomer): δ 169.77, 167.15, 162.50 (dd, J_{CF} = 250, 14 Hz), 162.40 (dd, J_{CF} = 250, 14 Hz), 161.02, 160.28, 157.27 (t, J_{CF} = 11 Hz), 155.22 (t, J_{CF} = 11 Hz), 144.56, 144.54, 138.24, 137.29, 132.10, 131.67, 129.75, 129.64, 124.56, 124.12, 107.80 (d, J_{CF} = 24 Hz), 107.70 (d, J_{CF} = 24 Hz), 102.42 (t, J_{CF} = 25 Hz), 102.22 (t, J_{CF} = 25 Hz), 35.59, 35.23, 34.48, 34.42, 31.21, 31.18, 29.89, 29.55. Anal. Found: C, 62.82; H, 5.72; N, 3.34. Calcd for $TiC_{42}H_{48}N_2O_2F_4Cl_2$: C, 62.46; H, 5.99; N, 3.34.

General Procedure for Synthesis of Bis(phenoxyimine)titanium Dichloride Complexes. *n*-Butyllithium (1.6 M in hexanes, 4.0 mmol) was added dropwise to a solution of phenoxyimine ligand (3.9 mmol) in THF (35 mL) at −78 °C. The solution was warmed to room temperature and stirred for 45 min and then added dropwise via cannula to a solution of $TiCl_4$ (1.0 M in toluene, 1.95 mmol) in THF (35 mL) at −78 °C. The resulting solution was warmed to room temperature and stirred under nitrogen for 12 h. The solvent was removed in vacuo and the solid residue dissolved in methylene chloride and filtered through Celite. The solvent was removed in vacuo and purified as described below.

Bis[2,4-di-*tert*-butyl-6-[[(3,5-dichlorophenyl)imino]methyl]phenolato]titanium Dichloride (6). 2,4-Di-*tert*-butyl-6-[[(3,5-dichlorophenyl)imino]methyl]phenol (1.11 g, 2.9 mmol) was reacted as described above and crystallized from a toluene/hexanes mixture to give deep red crystals (0.28 g, 22% yield). ^{1}H NMR (300 MHz, benzene-d_6, isomeric mixture in solution, 82% C_2 isomer): δ 7.60 (d, 2H, J_{HH} = 2.2 Hz, Ar), 7.12 (s, 2H, HC=N), 6.80 (d, 2H, J_{HH} = 2.2 Hz, Ar), 6.73 (t, 2H, J_{HH} = 1.9 Hz, Ar_{Cl}), 6.63 (br s, 4H, Ar_{Cl}), 1.45 (s, 18H, ^{t}Bu), 1.27 (s, 18H, ^{t}Bu). (C_1 isomer): δ 7.72 (d, 1H, J_{HH} = 2.2 Hz, Ar), 7.62 (d, 1H, J_{HH} = 2.2 Hz, Ar), 7.24 (s, 1H, HC=N), 7.15 (s, 1H, HC=N), 6.99 (t, 1H, Ar_{Cl}), 6.94 (t, 1H, Ar_{Cl}), 6.88 (d, 1H, J_{HH} = 2.2 Hz, Ar), 6.71 (d, 1H, J_{HH} = 2.2 Hz, Ar), 6.63 (br s, 4H, Ar_{Cl}), 1.73 (s, 9H, ^{t}Bu), 1.29 (s, 9H, ^{t}Bu), 1.25 (s, 9H, ^{t}Bu), 1.15 (s, 9H, ^{t}Bu). ^{13}C NMR (125 MHz, benzene-d_6, C_2 isomer): δ 168.09, 159.94, 154.15, 143.72, 138.85, 134.85, 133.06, 129.58, 126.69, 124.16, 122.59, 35.44, 34.43, 31.25, 29.60. (C_1 isomer): δ 170.00, 167.32, 161.07, 160.26, 156.79, 153.14, 144.57, 144.48, 138.15, 137.35, 135.17, 134.44, 132.19, 132.02, 130.21, 129.75, 127.04, 127.02, 124.61, 123.90, 122.60, 122.50, 35.58, 35.26, 34.53, 34.46, 31.28, 31.21, 29.93, 29.58. Anal. Found: C, 59.58; H, 6.07; N, 2.98. Calcd for $TiC_{42}H_{48}N_2O_2Cl_6 \cdot {}^1/_2C_7H_8$: C, 59.43; H, 5.70; N, 3.05.

Bis[2,4-dimethyl-6-[[(3,5-difluorophenyl)imino]methyl]phenolato]titanium Dichloride (9). 2,4-Dimethyl-6-[[(3,5-difluorophenyl)imino]methyl]phenol (0.41 g, 1.6 mmol) was reacted as described above and crystallized from a toluene/hexanes mixture to give dark red/brown crystals (0.09 g, 17% yield). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.10 (s, 2H, HC=N), 6.60 (d, 2H, J_{HH} = 2.2 Hz, Ar), 6.57 (m, 4H, Ar_F), 6.20 (d, 2H, J_{HH} = 2.2 Hz, Ar), 6.05 (tt, 2H, J_{HH} = 2.2 Hz, J_{HF} = 8.8 Hz, Ar_F), 2.05 (s, 6H, CH_3), 1.89 (s, 6H, CH_3). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 167.62 (dd, J_{CF} = 250, 14 Hz), 167.26, 150.23, 139.99, 132.50, 132.01, 126.39, 123.38, 117.45, 107.86 (d, J_{CF} = 25 Hz), 102.21 (t, J_{CF} = 25 Hz), 20.25, 15.26. Anal. Found: C, 55.29; H, 3.21; N, 4.15. Calcd for $TiC_{30}H_{24}N_2O_2F_4Cl_2 \cdot {}^1/_4CH_2Cl_2$: C, 55.01; H, 3.74; N, 4.24.

Bis[2-isopropyl-6-[[(3,5-difluorophenyl)imino]methyl]phenolato]titanium Dichloride (10). 2-Isopropyl-6-[[(3,5-difluorophenyl)imino]methyl]phenol (0.480 g, 2.9 mmol) was reacted as described above, producing dark red/brown crystals (0.25 g, 26% yield). ^{1}H NMR (300 MHz, benzene-d_6): δ 7.12 (s, 2H, HC=N), 6.99 (t, 2H, J_{HH} = 8.9 Hz, Ar), 6.51 (m, 4H, Ar), 6.49 (m, 4H, Ar_F), 6.04 (tt, 2H, J_{HH} = 2.2 Hz, J_{HF} = 8.9 Hz, Ar_F), 3.37 [s, 2H, J_{HH} = 6.7 Hz, C*H*(CH_3)$_2$], 1.30 [d, 6H, J_{HH} = 6.7 Hz, CH(C*H*$_3$)$_2$], 1.12 [d, 6H, J_{HH} = 6.7 Hz, CH(C*H*$_3$)$_2$]. ^{13}C NMR (125 MHz, benzene-d_6): δ 166.71, 162.22 (dd, J_{CF} = 250, 14 Hz), 159.80, 154.49 (t, J_{CF} = 11 Hz), 137.77, 133.87, 132.16, 123.37, 121.53, 107.76 (d, J_{CF} = 25 Hz), 101.85 (t, J_{CF} = 25 Hz), 27.95, 23.84. Anal. Found: C, 57.38; H, 4.09; N, 3.95. Calcd for $TiC_{32}H_{28}N_2O_2F_4Cl_2$: C, 57.59; H, 4.23; N, 4.20.

Bis[2,4-bis(α,α′-dimethylbenzyl)-6-[[(3,5-difluorophenyl)imino]methyl]phenolato]titanium Dichloride (11). 2,4-Bis(α,α′-dimethylbenzyl)-6-[[(3,5-difluorophenyl)imino]methyl]-phenol (1.27 g, 2.7 mmol) was reacted as described above, producing deep red crystals (0.99 g, 69% yield). ^{1}H NMR (300 MHz, benzene-d_6, isomeric mixture in solution, 9% C_2 isomer): δ 6.37−7.79 (m, 24H, Ar), 2.10 (s, 6H, CH_3), 2.04 (s, 6H, CH_3), 1.71 (s, 6H, CH_3), 1.49 (s, 6H, CH_3). (C_1 isomer): δ 7.17 (s, 2H, HC=N), 6.62 (s, 2H, HC=N), 6.32 (tt, 2H, J_{HH} = 2.2 Hz, J_{HF} = 8.8 Hz, Ar_F), 6.22 (br d, 4H, Ar_F), 6.14 (tt, 2H, J_{HH} = 2.2 Hz, J_{HF} = 8.8 Hz, Ar_F), 5.72 (br d, 4H, Ar_F), 2.39 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.20 (s, 3H, CH_3). ^{13}C NMR (125 MHz, benzene-d_6, C_2 isomer): δ 167.48, 162.42 (dd, J_{CF} = 250, 13 Hz), 159.44, 157.17, 154.20 (t, J_{CF} = 12 Hz), 150.02, 149.23, 143.31, 138.89, 136.33, 131.42, 128.52, 128.45, 126.88, 126.29, 125.98, 124.22, 107.70, 101.86, 43.22, 42.63, 30.65, 30.61, 29.86, 27.56. (C_1 isomer): δ 169.14, 165.64, 162.25 (dd, J_{CF} = 249, 13 Hz), 162.11 (dd, J_{CF} = 249, 13 Hz), 161.12, 159.98, 157.17 (t, J_{CF} = 12 Hz), 152.67 (t, J_{CF} = 12 Hz), 150.30, 150.18, 149.14, 149.00, 144.38, 144.11, 137.43, 137.27, 133.34, 133.13, 132.13, 131.46, 128.63, 128.62, 128.59, 128.58, 126.97, 126.93, 126.89, 126.48, 126.44, 126.35, 126.11, 126.09, 124.78, 123.64, 107.68 (d, J_{CF} = 24 Hz), 107.72 (d, J_{CF} = 24 Hz), 102.01 (t, J_{CF} = 25 Hz), 101.95 (t, J_{CF} = 25 Hz), 42.96, 42.84, 42.82, 41.86, 32.57, 32.33, 30.99, 30.82, 30.72, 30.70, 26.96, 26.44. Anal. Found: C, 70.17; H, 5.00; N, 2.45. Calcd for $TiC_{62}H_{56}N_2O_2F_4Cl_2$: C, 70.52; H, 5.35; N, 2.65.

Bis[2-trimethylsilyl-6-[[(3,5-difluorophenyl)imino]methyl]phenolato]titanium Dichloride (12). 2-Trimethylsilyl-6-[[(3,5-difluorophenyl)imino]methyl]phenol (1.19 g, 3.9 mmol) was reacted as described above, producing dark red crystals (0.62 g, 44% yield). ^{1}H NMR (300 MHz, benzene-d_6, isomeric mixture in solution, 80% C_2 isomer): δ 7.40 (dd, 1H, J_{HH} = 2.2, 7.6 Hz, Ar), 7.12 (s, 2H, HC=N), 6.71 (dd, 2H, J_{HH} = 2.2, 7.6 Hz, Ar), 6.60 (t, 2H, J_{HH} = 7.6 Hz, Ar), 6.34 (m, 4H, Ar_F), 6.07 (tt, 2H, J_{HH} = 2.2 Hz, J_{HF} = 8.9 Hz, Ar_F), 0.50 (s, 18H, $SiCH_3$). (C_1 isomer): δ 7.54 (dd, 1H, J_{HH} = 2.2, 7.6 Hz, Ar), 7.39 (dd, 1H, J_{HH} = 2.2, 7.6 Hz, Ar), 7.27 (s, 1H, HC=N), 7.19 (s, 1H, HC=N), 6.86 (dd, 2H, J_{HH} = 2.2, 7.6 Hz, Ar), 6.60−6.80 (m, 6H, Ar), 6.20 (m, 2H, Ar), 6.17 (m, 6H, Ar_F), 0.62 (s, 9H, $SiCH_3$,), 0.18 (s, 9H, $SiCH_3$,). ^{13}C NMR (125 MHz, benzene-d_6, C_2 isomer): δ 167.28, 166.98, 162.44 (dd, J_{CF} = 250, 14 Hz), 154.01 (t, J_{CF} = 11 Hz), 144.00, 136.12, 129.89, 122.84, 121.41, 107.78 (d, J_{CF} = 25 Hz), 102.17 (t, J_{CF} = 12 Hz), −0.99. (C_1 isomer): δ 169.12, 168.29, 167.63, 166.45, 162.39 (dd, J_{CF} = 250, 14 Hz), 157.14 (t, J_{CF} = 11 Hz), 153.18 (t, J_{CF} = 11 Hz), 143.15, 142.92, 136.50, 136.20, 129.21, 128.44, 123.51, 122.54, 122.45, 122.03, 107.82 (d, J_{CF} = 25 Hz), 107.80 (d, J_{CF} = 25 Hz), 102.27 (t, J_{CF} = 12 Hz), 102.25 (t, J_{CF} = 12 Hz), −0.92, −1.14. Anal. Found: C, 52.83; H, 4.17; N, 3.67. Calcd for $TiC_{32}H_{30}Si_2N_2O_2F_4Cl_2$: C, 52.97; H, 4.17; N, 3.86.

Polymerization Procedure. A 6 oz Lab-Crest reaction vessel (Andrews Glass) was filled with dried PMAO (0.58 g, 10 mmol) and toluene (140 mL). The reactor was purged with propylene gas three times and equilibrated at the desired temperature and pressure for 15 min. The desired Ti precatalyst (50 μmol, [Al]/[Ti] = 200) was dissolved in toluene (10 mL). The catalyst solution was added to the reactor via gastight syringe. After 4 h the reactor was vented and quenched with MeOH, and the polymer was precipitated in copious methanol/HCl, filtered, and dried in vacuo.

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Supporting Information Available: NOESY and variable-temperature ^{1}H NMR spectra of **3**, full crystallographic data for complexes **3** and **11**, ^{1}H and ^{13}C NMR and differential scanning calorimetry of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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