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A New Catalyst for Highly Syndiospecific Living Olefin Polymerization: Homopolymers and Block Copolymers from Ethylene and Propylene

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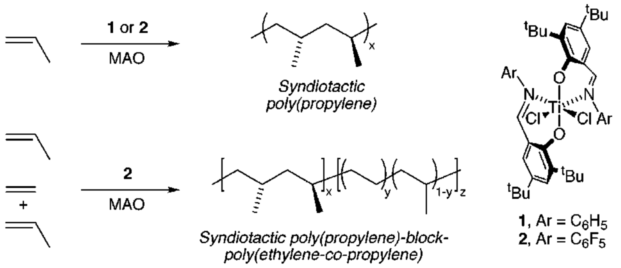
The development of ansa-metallocenes and their application in stereoselective olefin polymerization has stimulated a renaissance in insertion polymerization catalysis.[1−4] Despite prosperity in this field, control of molecular weight in these systems has been met with limited success as most metallocene catalysts are plagued by chain termination and transfer reactions that prohibit the synthesis of block copolymers by sequential monomer addition.[5] However, several ground-breaking reports have appeared in the recent literature concerning living olefin polymerization.[6−12] The importance of these living olefin polymerization catalysts is largely proportional to their ability to form block copolymers with high glass or melting transition blocks from common commercial monomers such as ethylene and propylene, as these materials have applications as compatibilizers and elastomers.[13,14] Although individual living catalyst systems have been reported which achieve some of these goals, the synthesis of block copolymers from ethylene and propylene with crystalline segments remains a challenge.

In an effort to identify new stereoselective catalysts for olefin polymerization, we recently reported a methodology for the rapid screening of polymerization catalyst libraries.[15] This strategy led to the discovery of bis(salicylaldiminato)titanium[16] complex **1**, which formed highly syndiotactic polypropylene when activated by methylaluminoxane (MAO). Microstructural analysis using ^{13}C NMR revealed that the polymerization apparently proceeded by a chain-end control mechanism with a 94% probability of an *r*-dyad placement in the polymer chain. Prior to this communication, this was the highest reported degree of chain-end control in a propylene polymerization. However, the polymerization proceeded without control of molecular weight, producing low molecular weight polymer ($M_n = 9910$, $M_w/M_n = 2.14$). With this lead, we decided to investigate the effects of varying salicylaldimine ligand electronics on these titanium complexes and their polymerization behavior with propylene. Herein, we report the discovery of a new bis(salicylaldiminato)titanium complex that is active for the highly syndiospecific and living polymerization of propylene, as well as the synthesis of ethylene−propylene block copolymers.



With the rationale that a more electron-withdrawing ligand would generate a more electrophilic titanium center and enhance catalytic activity, we decided to target ligands derived from electron-deficient anilines. To this end, we synthesized a pentafluorophenyl version of the parent titanium complex (**2**). X-ray crystallographic analysis of **2** revealed a C_2-symmetric species with a distorted octahedral geometry about the titanium center, analogous to **1**. ^1H and ^{13}C NMR spectroscopy confirmed that the C_2-symmetry was retained in solution.

Upon treatment with MAO, complex **2** was found to be active for the polymerization of propylene. At 0 °C in toluene, this activated species proved to be an exceptional catalyst for the polymerization of propylene relative to **1** with regard to both activity and stereoselectivity. As anticipated, the more electron-deficient titanium center of **2** was approximately an order of magnitude more active than **1** (Table 1). Again, microstructural analysis by ^{13}C NMR revealed that a chain-end control mechanism apparently operates, producing highly syndiotactic polypropylene with an *r*-dyad content of 99% ([*rrrr*] = 0.96). The crystalline polymer exhibits a peak melting temperature of 148 °C, which is

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Table 1. Polymerization of Propylene (P) and Ethylene (E) Using **1** and **2**[a]

complex	reaction time (h)	T_{rxn} (°C)	monomer	polymer yield (g)	activity[b]	M_n[c]	M_w/M_n[c]
1	24	0	P	4.20	1.75	9 910	2.14
2	0.25	0	P	0.49	19.6	11 100	1.09
2	0.50	0	P	0.97	19.4	24 500	1.08
2	1.5	0	P	1.79	11.9	44 700	1.11
2	3.1	0	P	3.84	12.4	75 800	1.08
2	5.2	0	P	5.34	10.3	95 900	1.11
2	66[d]	0	P	14.2	2.15	307 700	1.34
2	24	20	P	7.43	3.09	102 500[e]	1.13[e]
2	2.0/1.0[f]	0	P/E	11.2	NA	38 400/145 100[g]	1.11/1.12[g]

[a] General conditions: **1** or **2** (0.1 mmol) in toluene (6 mL) added to a propylene saturated (40 psi) MAO solution (150 mL toluene; [Al]/[Ti] = 150). [b] kg PP/(mol Ti·h). [c] Determined by GPC in 1,2,4-trichlorobenzene at 140 °C versus polystyrene standards. [d] 0.04 mmol Ti and 6 mmol MAO in 150 mL of toluene. [e] GPC versus PP standards. [f] After reaction with propylene (40 psi) for 2 h, ethylene (40 psi) was added for 1 h. [g] Data for the initial polypropylene block and the final poly(propylene)-*block*-poly(ethylene-*co*-propylene) diblock polymer.

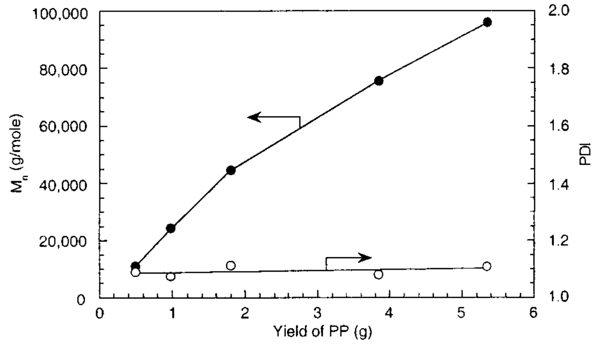

Figure 1. Plot of *syn*-PP M_n (●) and polydispersity index (○) as a function of yield using **2**/MAO at 0 °C, determined using GPC.

among the highest reported for syndiotactic polypropylene.[17,18] To our surprise, the polymer also exhibited a narrow molecular weight distribution ($M_w/M_n \sim 1.1$) and a lack of olefinic endgroups in both the ^{1}H and ^{13}C NMR spectra, indicating the living nature of the polymerization. Not only was this process devoid of chain termination through β-hydride and β-methyl elimination, but it also proceeded without chain transfer to the aluminum cocatalyst. The living nature of the polymerization was demonstrated by a plot of the number-average molecular weight, M_n, of the polypropylene produced versus the mass of polymer collected, which provided a linear relationship to molecular weights approaching 50 000 g/mol (Figure 1, Table 1). At longer reaction times the polymer molecular weight continues to grow, and although there is a slight deviation from the initial linear relationship of M_n and yield, the molecular weight distribution remains narrow ($M_w/M_n \leq 1.11$) to $M_n = 100\,000$ g/mol. Furthermore, the molecular weight of the polymer was close to that calculated from the monomer/initiator ratio obtained from the mass of the polymer produced, indicating that each molecule of catalyst makes one polymer chain during the course of the polymerization. Remarkably, polymers with $M_n > 300\,000$ g/mol can be synthesized with fairly narrow molecular weight distributions ($M_w/M_n = 1.34$). Notably, the reactions are also living at room temperature (Table 1).

Although the synthesis of monodisperse stereoregular α-olefin homopolymers is attractive, the real value of a living polymerization catalyst lies in its ability to synthesize block copolymers. To further demonstrate the utility of this living catalyst system, we decided to synthesize block copolymers from propylene and ethylene. When catalyst **2** was added to a solution of MAO and propylene (6.4 M) in toluene at 0 °C, syndiotactic polypropylene was formed after 2 h ($M_n = 38\,400$, $M_w/M_n = 1.11$). Then, addition of a slight overpressure of ethylene to the reactor for 1 h rapidly produced a higher molecular weight polymer ($M_n = 145\,100$, $M_w/M_n = 1.12$), resulting in the first synthesis of a *syndio*-poly(propylene)-*block*-poly(ethylene-*co*-propylene) diblock copolymer. The T_m of this polymer is 131 °C, while the T_g of the ethylene−propylene block (33 mol % ethylene) is −45 °C. This unique and powerful strategy for block polymer formation is currently being applied to the synthesis of ethylene and propylene copolymers with new architectures.

In summary, we report the first example of a catalyst system for the highly syndiospecific and living polymerization of propylene. Unlike previously reported systems that require the use of boron-based activators to carry out the living polymerization of higher α-olefins, **2** performs the living polymerization of propylene when activated by impurity-scavenging MAO under mild reaction conditions. The catalyst proceeds without appreciable chain termination or transfer to produce high molecular weight polymers, even after reaction times on the order of days. The living nature of the catalyst allows the synthesis of block copolymers previously unavailable from Ziegler−Natta catalysts. This represents the first example of the synthesis of monodisperse ethylene and propylene block copolymers with stereoregular, crystalline domains. Additional new materials, as well as work describing the mechanistic details of **1** and **2**, will be reported shortly.

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Supporting Information Available: Synthesis and characterization (NMR, and X-ray data) of **2**, details of polymer synthesis, and polymer analysis data (NMR, GPC, DSC) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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