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Communication

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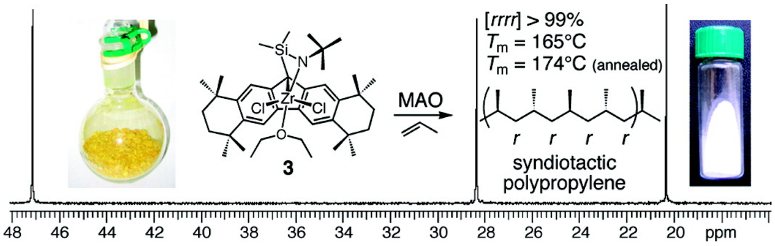

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Unprecedented Syndioselectivity and Syndiotactic Polyolefin Melting Temperature: Polypropylene and Poly(4-methyl-1-pentene) from a Highly Active, Sterically Expanded η^1-Fluorenyl−η^1-Amido Zirconium Complex

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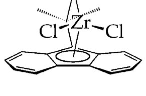
In 1988, Ewen, Razavi, and co-workers first reported the use of a single-site catalyst for the preparation of syndiotactic polypropylene (*s*-PP), a high-melting, crystalline thermoplastic. The *ansa*-zirconocene, $Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{13}H_8)ZrCl_2$ (**1**), upon activation with methylaluminoxane (MAO), produced stereoregular *s*-PP with a T_m (melting temperature) of 138 °C and a stereochemical [*rrrr*] pentad fraction of 86%.[1,2] Since this report, commercial interest in *s*-PP has increased; global production is anticipated to grow to 4×10^8 kg of *s*-PP per year by 2010, approaching 1% of worldwide polypropylene capacity.[3] Despite a number of superior physical properties—such as greater optical clarity, tear resistance, and impact strength—the development of *s*-PP has lagged behind that of isotactic polypropylene (*i*-PP), which can be made with [*mmmm*] > 99% and a T_m as high as 166 °C.[4] Attempts to improve catalyst activity and syndioselectivity have resulted in several second-generation single-site catalysts, including doubly bridged metallocenes,[5] fluorenyl−amido constrained geometry catalysts (CGCs),[6] coordination compounds,[7] and sterically expanded versions of the parent Ewen-type catalyst, such as $Me_2C(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_{29}H_{36})ZrCl_2$ (**2**), which provided markedly improved *s*-PP with [*rrrr*] = 92% and an *unannealed* T_m of 154 °C.[8]



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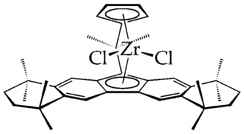

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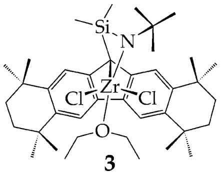

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Our efforts to avoid arduous catalyst syntheses,[5] low catalytic activity,[7] thermal instability, and poor syndioselectivity[6] have culminated in $Me_2Si(\eta^1\text{-}N\text{-}^tBu)(\eta^1\text{-}C_{29}H_{36})ZrCl_2{\cdot}OEt_2$/MAO (**3**/MAO), which we have previously shown to have an inverted reactivity preference toward α-olefins versus ethylene.[9] This sterically expanded constrained geometry catalyst exhibits a novel η^1-C ligation,[10] and it rivals or excels the best attributes of each syndioselective predecessor: (1) ligand and complex syntheses are inexpensive and facile;[11] (2) **3**/MAO is extremely active toward α-olefins—6 times more active in the homopolymerization of propylene than ethylene at 25 °C; (3) **3**/MAO is thermally stable and catalytically active even up to 170 °C; and (4) the obtained polymers have unsurpassed syndiotacticity and unprecedented melting temperatures.

The results of the MAO-cocatalyzed propylene polymerizations with complex **3** are compared with those of syndioselective *ansa*-metallocenes **1** and **2** in Table 1. Aselective MAO-cocatalyzed systems **4** (Cp_2ZrCl_2) and **5** ($Me_2Si(\eta^1\text{-}N\text{-}^tBu)(\eta^5\text{-}C_5Me_4)TiCl_2$)—heralded for its high activity in ethylene/α-olefin copolymerizations—are also included for comparative purposes. The data indicate that **3**/MAO is superior with regard to activity, stereoselectivity, and polymer melting temperature, although lower molecular weights are observed.

Table 1. MAO-Activated Propylene Polymerization Results for **1**−**5**[a]

catalyst (μmol)	T_p (°C)	yield (g)	activity[b]	T_m[c] (°C)	[*rrrr*][d] (%)	M_w[e]	PDI[e]
1 (1.62)	0	0.32	2400	151	91	209200	2.47
1 (1.62)	25	0.31	11480	142	89	179700	2.37
1 (1.62)[f]	90	1.16	42700	116	71	57400	2.16
2 (1.53)	0	0.23	1830	157	96	495400	2.56
2 (1.53)	25	0.45	17730	151	92	362700	2.86
2 (1.53)[f]	90	1.58	61800	am.	64	116800	2.31
3 (1.66)	−15	1.08	1310	165	>99	58600	2.25
3 (1.66)	0	0.54	3890	164	98	46200	1.98
3 (1.66)	25	1.07	38670	157	96	35700	2.17
3 (1.66)[f]	90	1.14	41100	128	82	14400	1.93
4 (1.66)	0	0.04	290	am.			
4 (1.66)	25	0.04	1450	am.			
5 (1.66)	0	0.29	2100	am.	22		
5 (1.66)	25	0.34	12140	am.			

[a] Polymerization conditions: neat propylene (30 mL); 1000 equiv of MAO; 30 min run at $T_p = -15$ °C; 5 min runs at $T_p = 0$ °C; 1 min runs at $T_p = 25$ °C. [b] In kg PP/(mol M·h). [c] Unannealed, determined by DSC; am. = amorphous. [d] The [*rrrr*]% determined by ^{13}C NMR. [e] Average of two injections versus PP. [f] Polymerization conditions: 30 mL of *n*-heptane; 1000 equiv of MAO; 120 psi propylene; 10 min pre-run equilibration; 1 min run.

At $T_p = 25$ °C **3**/MAO is nearly 4 times as active as **1**/MAO, twice as active as **2**/MAO, but only 15% as active as Bercaw's best doubly bridged metallocene system.[5] The data in Table 1 also demonstrate that increasing the temperature from 0 to 25 °C for MAO-cocatalyzed propylene polymerizations with **1**, **4**, and **5** results in a 5-fold increase in activity; however, there is a 10-fold increase in activity for **2**/MAO and **3**/MAO, both of which contain the bulky octamethyloctahydrodibenzofluorenyl ($C_{29}H_{36}$) moiety. Such high activities are reportedly due to a decreased ability of the counteranion to approach a more sterically shrouded cationic metal center.[8] Even at $T_p = 90$ °C and low propylene concentration (120 psi in *n*-heptane), **3**/MAO prevails with the highest T_m (128 °C) and [*rrrr*] (82%) recorded under these conditions—even surpassing the doubly bridged catalyst in neat propylene at $T_p = 70$ °C ($T_m = 119$ °C, [*rrrr*] = 79.5%).[5]

At $T_p = 0$ °C, **3**/MAO produces *s*-PP with a melting point of 164 °C, which is 13 °C higher than that of **1**/MAO, and at least 7 °C higher than the *s*-PP from the most syndioselective catalyst systems reported to date.[7,8,12] Annealing this sample at 160 °C for 3 h results in a melting point of 174 °C—only 8 °C below the theoretical maximum melting temperature of perfectly syndiotactic polypropylene (182 °C).[13] Even polymer fractionation has not afforded samples of *s*-PP that approach these T_m values.[14]

In an effort to maximize stereoselectivity, propylene was polymerized with **3**/MAO at −15 °C, yielding *s*-PP with a T_m of

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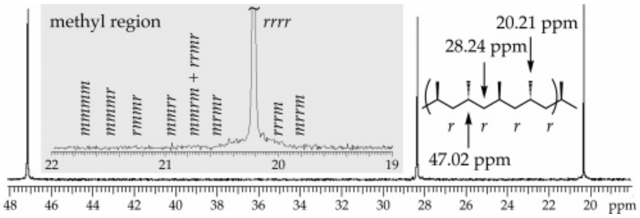

Figure 1. ^{13}C NMR spectrum (20,000 transients) of *s*-PP produced by **3**/MAO at $T_p = -15$ °C; [*rrrr*] > 99%; $T_m = 165$ °C. The methyl region (inset) lacks visible stereoerrors.

Table 2. MAO-Activated 4-Methyl-1-pentene Polymerization Results for **1**−**3**[a]

catalyst (μmol)	T_p (°C)	yield (g)	activity[b]	T_m[c] (°C)	[*rrrr*][d] (%)
1 (1.62)	0	0.61	500	210	94
1 (1.62)	25	0.17	420	206	93
2 (1.53)	0	0.00	0		
2 (1.53)	25	0.03	80	am.	
3 (1.66)	0	0.47	380	215	97
3 (1.66)	25	2.14	5160	202	89

[a] Polymerization conditions: neat 4-methyl-1-pentene (25 mL); 1000 equiv of MAO; 45 min runs at $T_p = 0$ °C; 15 min runs at $T_p = 25$ °C.[b] In kg P4M1P/(mol M•h). [c] Unannealed, determined by DSC; am. = amorphous. [d] The [*rrrr*]% determined by ^{13}C NMR.

165 °C and an activity of 1310 kg PP/(mol Zr•h). This is clearly the highest known melting temperature for *s*-PP and nearly matches the highest reported T_m (166 °C) for an unfractionated, unannealed *isotactic* polypropylene.[4] Thus, our *s*-PP melts at 96.3% (438 K/455 K) of the theoretical maximum T_m for *s*-PP (182 °C),[13] while the best *i*-PP melts at only 95.6% (439 K/459 K) of the theoretical maximum T_m for *i*-PP (186 °C).[15]

Figure 1 shows the ^{13}C NMR spectrum of the *s*-PP prepared by **3**/MAO at −15 °C. Not surprisingly, close inspection of the methyl region shows that the polymer is virtually devoid of stereoerrors. This high stereoregularity is largely responsible for the unparalleled melting temperature and physical form of the polymer, which, unlike samples from **1**/MAO, is a fine, free-flowing powder that crystallizes from hot tetrachloroethane-d_2. With low monomer concentration (3.6 M) and a higher T_p (45 °C), the stereoerrors[2] observed by ^{13}C NMR ([*rrmr*]/[*mmrr*] = 8) implicate site epimerization as the dominant stereochemical mistake. Enantiofacial selectivity remains nearly perfect at 99.7% ([*mmrr*] = 0.6%).

The syndioselective aptitude of **3**/MAO is further exemplified in the homopolymerization of 4-methyl-1-pentene, as recounted in Table 2. At 25 °C, the activity of **3**/MAO is *12 times* that of **1**/MAO. Polymerization by **3**/MAO at 0 °C apparently yields the highest melting and most stereoregular sample of syndiotactic poly(4-methyl-1-pentene) yet prepared. The few reports of this polymer in the literature (from **1**/MAO) list a maximum T_m of 210 °C and a [*rrrr*] pentad fraction of 95%,[16] both of which have been surpassed by **3**/MAO (T_m = 215 °C, [*rrrr*] = 97%). Note that sterically expanded **2**/MAO suffers from poor activity, providing a minuscule amount of amorphous polymer, but **3**/MAO, with a similar steric environment, is not likewise inhibited.

In summary, we have demonstrated that a structurally unique, sterically expanded η^1-fluorenyl−η^1-amido catalyst system (**3**/MAO) is strikingly active and syndioselective, affording syndiotactic polypropylene with unsurpassed stereoregularity ([*rrrr*] > 99%) and polymer melting temperature (T_m up to 165 or 174 °C upon annealing). Interestingly, **3**/MAO is the only syndioselective catalyst capable of producing polypropylene with stereochemical fidelity and polymer melting temperature equaling that of the most highly engineered isoselective single-site olefin polymerization catalysts. The high activity and syndioselectivity of **3**/MAO is further demonstrated in the polymerization of 4-methyl-1-pentene, resulting in the production of the highest melting and most syndiotactic sample of poly(4-methyl-1-pentene). Future work will focus on the preparation of crystalline copolymers with novel architectures via exploitation of both the extreme stereoselectivity and increased activity toward α-olefins demonstrated by this new structural subclass of single-site catalysts.

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Supporting Information Available: Polymerization procedures and ^{13}C NMR spectra of the syndiotactic polymer samples reported in Tables 1 and 2, as well as DSC thermograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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