Articles

Sequence and Stereoselectivity of the C_1-Symmetric Metallocene $Me_2Si(1\text{-}(4,7\text{-}Me_2Ind))(9\text{-}Flu)ZrCl_2$

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ABSTRACT: The homo- and copolymerization behaviors of two C_1-symmetric metallocenes $Me_2Si(Ind)$-(9-Flu)$ZrCl_2$ (**2**) and $Me_2Si(1\text{-}(4,7\text{-}Me_2Ind))(9\text{-}Flu)ZrCl_2$ (**3**) in the presence of methylaluminoxane (MAO) are compared. In liquid propylene at 0 °C, metallocene **2** yields a predominantly isotactic polypropylene of low tacticity ([mmmm] = 27%) where metallocene **3** produces syndiotactic polypropylene (74% [rrrr]). The stereoselectivity of metallocene **3** depends on monomer concentration: the percentage of syndiotactic pentads [rrrr] in polymers derived from **3** increases with increasing monomer concentration. Copolymerization of ethylene and propylene with metallocenes **2** and **3** yields highly alternating but atactic ethylene−propylene copolymers.

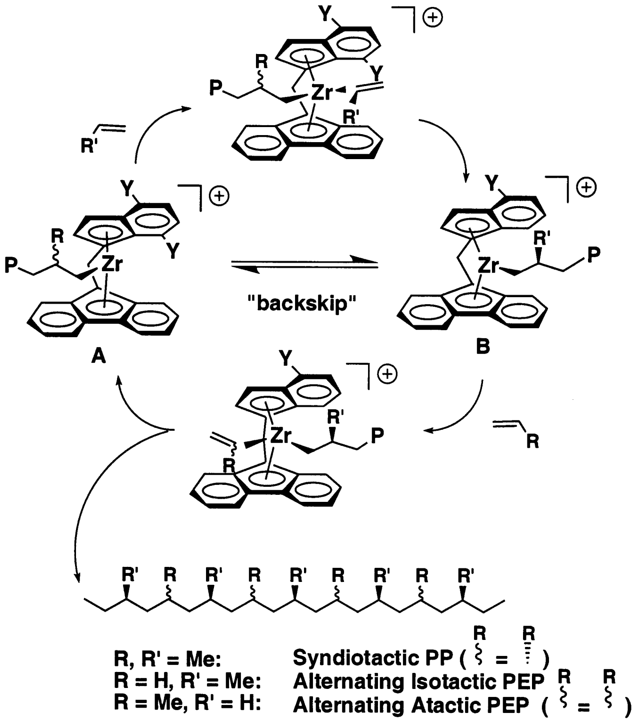
Introduction

The pioneering development by Brintzinger of chiral C_2-symmetric stereorigid bridged metallocenes and the application of these coordination complexes for stereospecific polymerization reactions have stimulated a renaissance in industrial and academic interest in olefin polymerization catalysis.[1−5] Recently, considerable interest has been directed to metallocene catalysts of lower symmetry in an effort to generate new polymer microstructures as well as to test evolving theories on the origin of chemo- and stereospecificity in olefin polymerization reactions. For C_2-symmetric metallocenes, the two reactive coordination sites (occupied typically by chlorides in catalyst precursors) are homotopic and exhibit identical chemo- and stereoselectivity.[1−5] For metallocenes of lower symmetry, the two coordination sites are heterotopic and can exhibit different selectivities for in either homo- or copolymerization. Thus, while metallocenes have been referred to as "single-site" catalysts in the literature, it is clear that even for stereorigid coordination complexes, the different stereoelectronic environments of heterotopic coordination sites can lead to "multisite" behavior.

C_1-symmetric catalysts exhibit a rich stereochemistry for α-olefin polymerization and have been observed to produce polypropylenes with a variety of microstructures: isotactic, hemi-isotactic, atactic, or syndiotactic.[1,3,6−19] The stereoselectivity of this family of metallocenes is proposed to depend on the stereospecificity of the two heterotopic sites and the probability and sequence of olefin insertion events at the two heterotopic sites.[20]

Metallocenes with heterotopic coordination sites might be expected to lead to unusual copolymer microstructures if the kinetic selectivity for the two olefins is different at the two coordination sites. Recently, several groups have demonstrated that certain classes of C_1-symmetric metallocenes can generate alternating ethylene/α-olefin polymers.[21−27] While the detailed mechanism to account for this sequence selectivity has yet to be established, one proposed mechanism invokes the alternate insertion of ethylene and the α-olefin at the two different coordination sites (Scheme 1).[27] For example, we have recently reported that metallocenes **1a,b** (Figure 1) generated alternating and isotactic ethylene/propylene copolymers, implicating an alternating site mechanism where one site is chemoselective for ethyl-

Scheme 1. Mechanism for Propylene Homo- and Copolymerization with Metallocenes 2 (Y = H) or 3 (Y = Me)



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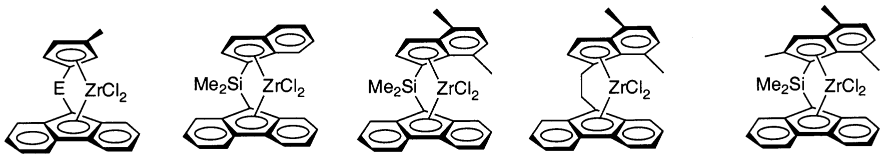

1a, E = Me_2C
1b, E = Me_2Si **2** **3** **4** **5**

Figure 1. C_1-symmetric metallocenes **1**−**5**.

Table 1. Propylene Homopolymerization[a]

metallocene	T_p (°C)	prod[b]	mmmm	mmmr	rmmr	mmrr	mrmm/ rrmr	mrmr	rrrr	rrrm	mrrm	M_n (PDI)
2	0	516	25.3	16.2	4.2	20.0	7.3	2.8	7.8	8.1	8.5	
2	20	6188	27.4	15.7	5.0	19.6	6.9	3.0	7.2	7.7	7.6	4.2 (2.1)
3	0	8442	0	0	2.0	4.3	4.4	0	74.4	15.0	0	318 (2.4)
3	20	11400	0	0	2.0	4.6	9.8	0	66.0	17.7	0	

[a] [Zr] = 1×10^{-5} M, Al:Zr = 2000:1, time = 20 min, liquid propylene. [b] Productivity = kg of PP/(mol of Zr h).

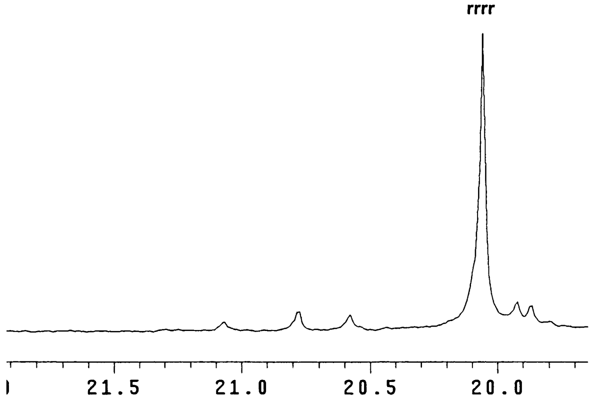

Figure 2. ^{13}C NMR spectra (benzene-d_6 as standard) of polypropylene prepared by **3**/MAO (0 °C, liquid propylene).

ene and the other site is both chemo- and stereoselective for propylene (at the appropriate ratio of monomers in the feed).[23,25]

As part of our ongoing studies to investigate the role of metallocene structure on both the stereoselectivity and chemoselectivity of olefin homo- and copolymerizations, we report a comparison of the homo- and copolymerization behavior of metallocenes **2** and **3** (Figure 1).

Results and Discussion

The synthesis of **2** and **3** was carried out following slightly modified literature procedures.[18,26] The homopolymerization of propylene was conducted using MAO-activated metallocenes **2** and **3** at 0 and 20 °C in liquid propylene. The productivity and pentad distributions are summarized in Table 1. A surprising observation is that the 4,7-disubstituted metallocene **3**, upon activation with MAO, yielded syndiotactic polypropylene ([rrrr] = 74% at 0 °C, Table 1, Figure 2) under conditions where the unsubstituted metallocene **2** yields a poorly isotactic polypropylene ([mmmm] = 27%). For metallocene **2**, the ratio of [mmmr]:[mmrr]:[mrrm] pentads is approximately 2:2:1, consistent with a predominance of rr stereoerrors. The stereoselectivity of metallocene **2** in liquid propylene is similar at 0 and 20 °C (Table 1); previous studies show that the stereoselectivity decreases modestly with increasing monomer concentration at 20 °C.[26,28] These results for **2** are consistent with previously discussed enantiomorphic site control mechanism depicted in Scheme 1, where one of the coordination sites is stereoselective and the other is nonstereoselective. Insertion of propylene at the stereoselective site, followed by "site epimerization" (or backskip) from the nonstereoselective site prior to monomer insertion, leads to multiple insertions at the stereoselective site and a predominance of isotactic stereosequences.[8,9,11−13,29] This mechanism can account for a variety of predominantly isotactic microstructures depending on the relative rate of propylene insertion into the stereoselective and nonstereoselective site relative to the rate of isomerization of the site in competition with monomer insertion (interconversion of A and B, Scheme 1).[20]

In the context of this mechanism, the observation that metallocene **3** yields syndiotactic polypropylene is unusual. Chien had previously reported that at 30 psig of propylene and 20 °C, the analogous ethylene-bridged metallocene **4** polymerized propylene to an oily waxy material with a slight syndiotactic bias ([rrrr] = 28.5%).[12,13] At higher temperature, this syndiotactic bias disappeared to give an atactic polypropylene.[13] In contrast, the closely analogous 2,4,7-trimethyl-substituted indenylmetallocene **5**[12,13] was reported to yield isotactic polypropylenes of intermediate to high tacticity ([mmmm] = 39−48%).

The high syndiospecificity of metallocene **3** could be ascribed to either an enantiomorphic site control mechanism (Scheme 1) where the monomer inserts alternately at the two heterotopic coordination sites[1] or a chain-end control mechanism, where the stereochemistry of the last inserted monomer unit controls the stereochemistry of insertion. For an enantiomorphic site control mechanism, the high syndiotacticities of the polypropylenes obtained from **3** would require that *both* heterotopic coordination sites of this metallocene are stereoselective. In view of the symmetry of metallocene **3**, it is unusual that both heterotopic coordination sites of metallocene **3** should be stereoselective for opposite faces of propylene, given that, for the analogous metallocene **5**, only one of the sites was proposed to be stereoselective.[12,13] Our current hypothesis is that two stereodifferentiation mechanisms are at work for this catalyst. At one of the sites, orientation of the polymer chain by the ligands is responsible for directing the appropriate insertion enantioface (A to B, Scheme 1).[3] At the other site, we propose that the 4-methyl substituent on the indenyl ligand interacts directly with the methyl group of the inserting polypropylene (B to A, Scheme 1), resulting in a stereoselective placement.

Table 2. Polypropylenes[a] from 3/MAO at Different Monomer Concentrations at 20 °C

[prop] (M)	mmmm	mmmr	rmmr	mmrr	mrmm/ rrmr	mrmr	rrrr	rrrm	mrrm	M_n (PDI)
1.90	0.0	1.5	2.5	5.5	17.0	4.1	43.2	21.5	4.7	204 (2.2)
3.28	0.0	0.6	1.7	4.8	14.4	2.6	51.7	20.8	3.3	268 (2.2)
4.87	0.0	0.3	1.1	3.4	9.6	1.2	62.0	20.0	2.0	278 (2.3)
11.11	0.0	0.5	2.0	4.6	9.6	0.0	66.0	17.7	0.0	

[a] Determined by ^{13}C NMR.

Table 3. Ethylene/Propylene Copolymerizations[a]

entry	Met	E:P	E%[b]	prod[c]	$\chi(r_1r_2)$[d]	r_1	r_2	$M_n \times 10^3$ (M_w/M_n)[e]	ref
1	**2**	0.02	48	24 795	0.009	2.67	0.003		26
2	**2**	0.033	49	20 535	0.011	2.77	0.004	12 (2.0)	26
3	**2**	0.095	56	80 000	0.009	3.36	0.003	14 (2.0)	26
4	**3**	0.02	46	20 000	0.005	2.22	0.002	293 (3.1)	this work
5	**3**	0.046	49.5	66 000	0.006	2.45	0.003	364 (2.3)	this work
6	**3**	0.076	52.2	150 000	0.010	2.80	0.004	347 (2.8)	this work

[a] MAO as cocatalyst, 0 °C, ethylene is fed through constant pressure over liquid propylene. [b] Calculated by Kakugo's method.[32] [c] Productivity = kg of EP/(mol of Zr h). [d] χ = ([EE][PP])/([EP]/2)^2 (ref 35). [e] Measured by high-temperature GPC.

For metallocene **3**, analysis of the pentad distribution reveals both rmrr and rmmr stereoerrors. Both the temperature and the monomer concentration significantly influenced the microstructure of the resultant polypropylene. For this metallocene, the percentage of syndiotactic [rrrr] pentads decreased from 74% at 0 °C to 66% at 20 °C and increased with increasing monomer pressure. As shown in Table 2, as the propylene concentration increased from 1.90 M (in toluene) to 11.1 M, the percentage of syndiotactic pentads increased from 43% to 66%; this increase was largely at the expense of the [xrmx] and [mmmr] pentads; pentads containing consecutive mm sequences ([rmmr], [mmrr]) were not strongly influenced by monomer concentration. These observations are consistent with competitive site isomerization of the metallocene since the relative probability of site isomerization (or "backskip") should decrease with increasing monomer concentration (Scheme 1).

Ethylene−Propylene Copolymerization. In an effort to further characterize the polymerization behavior of these metallocenes, we have also investigated the copolymerization behavior. Ethylene/propylene copolymerizations were conducted at 0 °C in liquid propylene with a constant overpressure of ethylene and kept to less than 5% conversion in propylene. Ethylene/propylene feed ratios were calculated from tabulated fugacities and the partial pressures of ethylene and propylene, as previously described.[30,31] The copolymerization results for metallocenes **2**[26] and **3** are summarized in Table 3. Productivities for the two metallocenes are comparable, but the molecular weights obtained from metallocene **3** are an order of magnitude higher than those from **2** under these conditions (Table 3).

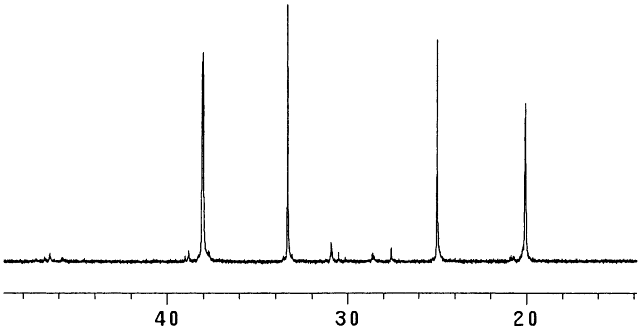

Figure 3. ^{13}C NMR spectra (benzene-d_6 as standard) of ethylene−propylene copolymer (containing 50% E) prepared by **3**/MAO.

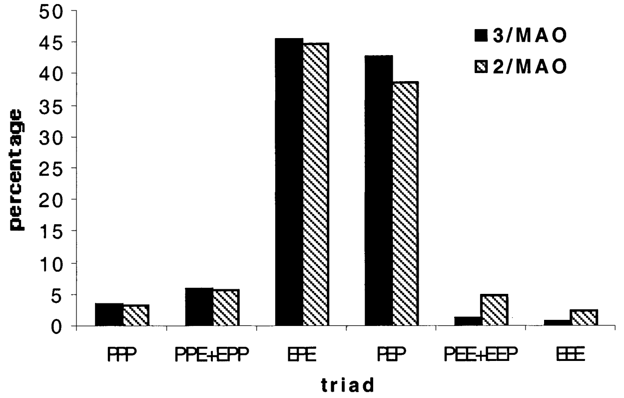

Figure 4. Triad distribution of ethylene−propylene copolymers prepared by **2**/MAO (49%E) and **3**/MAO (48.1% E).

The copolymer microstructure was investigated by quantitative ^{13}C NMR as described by Randall,[32,33] while the sequence distribution at the triad level can be conveniently analyzed by the method of Kakugo.[34] A relatively narrow range of E:P feed ratios (0.02−0.09) was investigated to yield copolymers with compositions close to 50% ethylene. A representative spectrum of a copolymer with 50% ethylene incorporation (**3**/MAO, 0 °C) is shown in Figure 3. Four primary resonances can be observed at 20.11, 24.99, 33.35, and 38.05 ppm, which correspond to the four unique carbon atoms of an alternating copolymer, the remaining resonances are due to the resonances of all carbons of all possible sequence errors. Figure 4 shows the representative triad distributions of the 50/50 copolymers made by **2**−**3**/MAO. As seen from Figure 4 and Table 3, metallocene **3**/MAO produces copolymers with a degree of alternation similar to that of the unsubstituted metallocene **2**/MAO. The copolymer sequence distribution can be described by parameter χ = EE[PP/(PE/2)^2].[35] This parameter is a measure of the deviation from a random sequence distribution, where values of $\chi < 1$ are indicative of an alternating sequence distribution and values of $\chi > 1$ are indicative of a blocky distribution.[36] As shown in Table 2, the low values of χ = 0.005−0.010 for **3**/MAO are indicative of a high degree of sequence alternation. The corresponding values for the unsubstituted **2** are comparable with χ ranging from 0.006 to

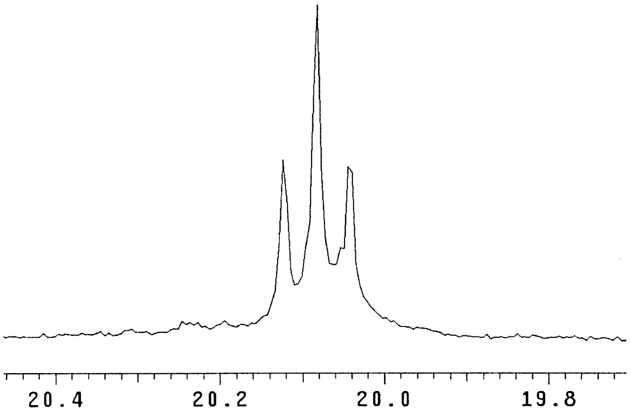

Figure 5. ^{13}C NMR chemical shift (benzene-d_6 as standard) of the methyl peak in PE*P*EP sequence (the italicized propylene unit) in ethylene–propylene copolymer (containing 50% E) prepared by **3**/MAO.

0.011,[26] indicating the similar sequence selectivities of **2** and **3** in ethylene–propylene copolymerization.

Because of its highly alternating structure, the stereochemistry of the EP copolymer can be conveniently analyzed from the ^{13}C NMR spectra.[37] The tacticity of the PE*P*EP sequences can be deduced from the multiplicity of resonances for the $S_{\alpha\gamma}$ and $P_{\delta\delta}$ carbon atoms. As shown in Figure 5, the ratio of P^mEP^mEP, P^mEP^rEP, and P^rEP^rEP resonances for the copolymer prepared from **3**/MAO (approximately 50% E incorporation) is 1:2:1, identical to that from **2**/MAO, indicative of a stereorandom microstructure (Figure 5). Thus, while the polypropylene microstructures from metallocenes **2** and **3** are very different (poorly isotactic or syndiotactic respectively), the microstructures of the ethylene/propylene copolymers are very similar, being both highly alternating and atactic.[21–24,26,38–40]

The observation that the EP copolymers obtained from both **2** and **3** are atactic implies either that (1) a chain-end control mechanism is responsible for both the sequence[41] and stereoselectivity of metallocenes **2** and **3** or (2) the copolymerization occurs by a two-site mechanism as shown in Scheme 1, but the stereoselectivity of propylene insertion depends on the nature of the last inserted monomer unit. We favor the latter interpretation in light of the concentration dependence of the stereochemistry for propylene polymerization with **3** as well as the fact that, at these temperatures, chain-end control is not generally observed to be strongly stereodifferentiating.[1,42]

With regard to the influence of the previously inserted monomer unit on the stereoselectivity, it is generally established that for most metallocenes the nature of the previously inserted monomer unit is not strongly stereodifferentiating[1,3] and that even following an ethylene insertion the stereoselectivity of propylene insertion is preserved.[38,39,43,44] Nevertheless, several recent reports have provided evidence that the stereoselectivity of propylene insertion following an ethylene insertion can be much lower than that following a propylene insertion.[45,46]

In summary, the homopolymerization of propylene and copolymerization of ethylene and propylene with metallocenes **2** and **3** have revealed additional unusual features of C_1-symmetric metallocenes. The highly alternating copolymer microstructures obtained from **2** and **3** are consistent with a dual-site mechanism where olefin insertion occurs alternately at the two heterotopic coordination sites that have different kinetic selectivities for ethylene and propylene.[21–27,38] The syndiospecificity of metallocene **3** is unusual in that it is not obvious why the heterotopic coordination sites of metallocene **3** should be stereoselective for opposite faces of propylene. Further studies are warranted to establish the origin of this unusual behavior. The observation that propylene homopolymerizations are stereoselective while the copolymerizations are stereorandom implies that the nature of the previous monomer unit can be an important stereodifferentiating element in olefin insertion.

Experimental Section

General Consideration. All manipulation with organometallic compounds was conducted using standard Schlenk and drybox techniques. Metallocenes **1a,b** and **2** were synthesized according to slightly modified literature procedures.[18]

Toluene was passed through two purification columns packed with activated alumina and supported copper catalysts. Polymerization grade ethylene and propylene gases were purchased from Matheson. Liquid propylene was obtained either from Amoco or purchased from Scott Specialty gases. Both monomers were further purified by passage through two columns packed with activated alumina and supported copper catalyst. Methylaluminoxane (MAO), type 3A, purchased from Akzo Nobel, was dried in vacuo prior to use.

Preparation of (9-Fluorenyl)-1-[(4,7-dimethyl)indenyl]-dimethylsilane. 4,7-Dimethylindene[47] (2.52 g, 17.5 mmol) was dissolved in diethyl ether (100 mL) in a Schlenk flask under N_2. After the solution is cooled in ice–water bath, *n*-butyllithium (2.5 M in hexanes, 7 mL, 17.5 mmol) was added dropwise, and the reaction was stirred for 4 h at room temperature. The volatile components were removed under vacuum, and to the resultant 4,7-dimethylindenyllithium salt 9-fluorenyldimethylsilyl chloride[18] (5.16 g, 20 mmol) was added. Under N_2, 80 mL of tetrahydrofuran was added via cannula, and the reaction was stirred at room temperature overnight. The resulting solution was partitioned between water/diethyl ether, and the aqueous phase was extracted with diethyl ether. The combined ether layer was washed with brine and dried with magnesium sulfate. Removal of the ether yielded (9-fluorenyl)-1-[(4,7-dimethyl)indenyl]dimethylsilane, which was purified by column chromatography using silica gel (230–400 mesh, elute with hexanes). Yield: 63% (two steps). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): −0.45 (s, 3H), −0.27 (s, 3H), 2.23 (s, 3H), 2.44 (s, 3H), 3.75 (d, 1H), 4.04 (s, 1H), 6.51 (q, J = 2.0 and 5.4 Hz, 1H), 6.87–6.98 (m, 3H), 7.28–7.42 (m, 7H), 7.64 (d, J = 7.6 Hz, 1H), 7.88 (t, J = 7.3 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: −6.0, −3.0, 18.6, 20.0, 42.8, 42.9, 43.7, 119.8, 120.0, 120.1, 124.2, 124.3, 125.6, 125.6, 126.2, 126.3, 127.7, 129.0, 134.8, 140.6, 143.8, 145.2, 145.2.

Preparation of Dimethylsilane–(9-Fluorenyl)-1-[(4,7-dimethyl)indenyl]zirconium Dichloride (3). Under N_2, (9-fluorenyl)-1-[(4,7-dimethyl)indenyl]dimethylsilane (2.96 g, 8.09 mmol) was dissolved in 60 mL of diethyl ether in a Schlenk flask, and the flask was cooled in ice–water bath. *n*-Butyllithium (2.05 equiv, 6.63 mL, 2.5 M in hexanes) was added dropwise, and the mixture was stirred at room temperature for 6 h before it was cooled to 0 °C and a suspension of $ZrCl_4$ (1.88 g, 8.10 mmol) in 40 mL of diethyl ether was added via cannula. The reaction solution turned to red instantly with formation of a red precipitate and was stirred overnight. Evacuation of the solvent yielded a red residue which was extracted with methylene chloride (3 × 80 mL). Pure **3** was obtained by recrystallization in methylene chloride. Yield: 35%. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): −1.29 (s, 3H), 1.42 (s, 3H), 2.31 (s, 3H), 2.54 (s, 3H), 6.35 (d, J = 3.56 Hz, 1H), 6.72–6.82 (m, 3 H), 7.21–7.31 (m, 2H), 7.44 (t, 1H), 7.61 (t, 1H), 7.61–7.74 (m, 2H), 7.97 (d, J = 8.28 Hz, 1H), 8.05 (d, J = 8.30 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 2.5, 3.7, 18.8, 23.1, 115.5, 119.1, 120.0, 123.1, 123.9, 124.3, 124.3, 125.3, 126.2, 125.6, 125.7, 125.9, 126.0, 126.2, 126.3, 128.4, 129.0, 131.2, 131.4, 133.2, 136.6, 140.7. Anal. Calcd for $C_{26}H_{24}Cl_2SiZr$: C, 59.32; H, 4.56. Found: C, 59.00; H, 4.74.

Propylene Homopolymerization. A 300 mL stainless steel reactor (Parr) equipped with a mechanical stirrer was evacuated, purged three times with argon and three times with gaseous propylene by pressurizing and venting, and charged with 100 mL of liquid propylene. Propylene was cooled to the 0 °C, and polymerization was started by injection under a nitrogen pressure of a toluene solution of zirconocene and MAO that had been prepared in a stainless steel injection tube in the drybox. Polymerization was carried out for 20 min. The reaction was quenched by injection of 5 mL methanol solution, and the reactor was slowly vented and opened. The polymer was stirred in 300 mL of methanol (5% HCl), washed with methanol, and dried in vacuo at 40 °C overnight.

Ethylene–Propylene Copolymerization. A 300 mL stainless steel Parr reactor equipped with a mechanical stirrer was evacuated, purged three times with Ar and three times with gaseous propylene by pressurizing and venting, and charged with 100 mL of liquid propylene. Propylene was cooled to the reaction temperature and overpressurized with ethylene to the desired total pressure. After 30 min equilibration, polymerization was started by injection of zirconocene/MAO solution and proceeded for 20 min. Temperature control was necessary due to the exothermic nature of the reaction. The reaction was quenched by injection of 5 mL of methanol, and the reactor was slowly vented and opened. The polymer was stirred in 300 mL of methanol (5% HCl), washed with methanol, and dried in vacuo at 40 °C overnight.

Polymer Characterization. Polymer molecular weights and molecular weight distributions were determined by high-temperature gel permeation chromatography.

^{13}C NMR measurements was carried out on a Varian UI300 spectrometer. 150–200 mg of each polypropylene or copolymer sample was dissolved in 2.5 mL of *o*-dichlorobenzene/10 vol % benzene-d_6 in a 10 mm diameter tube. The spectra was taken at 100 °C using acquisition times of 0 s (polypropylene) and 5 s for copolymers (2–3 mg of $Cr(acac)_3$ was added to each copolymer sample to shorten the acquisition time).

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