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New Syndiospecific Catalysts for Styrene Polymerization

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(η^5-Tetramethylcyclopentadienyl)-, (η^5-tetraphenylcyclopentadienyl)-, (η^5-(diphenylphosphino)tetramethylcyclopentadienyl)-, and (η^5-(trimethylsilyl)tetramethylcyclopentadienyl)titanium triisopropoxide have been synthesized and characterized. Their catalytic activities for syndiospecific styrene polymerization have been compared with the reference compound (η^5-cyclopentadienyl)titanium triisopropoxide. (η^5-Tetramethylcyclopentadienyl)titanium triisopropoxide is the best catalyst precursor, giving rise to catalysts having the highest activity to produce polystyrene with the highest syndiotactic yield and molecular weight.

Introduction

Ishihara and co-workers[1] discovered that titanium halides or alkoxides, with or without an η^5-cyclopentadienyl (Cp) ligand, when activated with methylaluminoxane (MAO) formed very active catalysts for the syndiospecific polymerization of styrene above room temperature. Prior to that discovery syndiotactic polystyrene (s-PS) was only obtained at temperatures below −65 °C.[2] Cyclopentadienyltitanium trialkoxides were found to be far more active precursors than tetrabenzyltitanium.[3,4] Styrene is inserted by the secondary mode[4b] and most chains were terminated by β-hydrogen abstraction.[4c] The central purpose of this work has been to develop and evaluate new and better catalysts for the syndiospecific polymerization of styrene.

Experimental Section

All operations were carried out under an argon atmosphere using Schlenk or glovebox techniques except where specified. Argon was deoxygenated with activated BTS catalyst and dried with molecular sieves and P_2O_5. Pentane, hexane, toluene, benzene, diethyl ether, and tetrahydrofuran were distilled under argon from sodium–potassium alloy.

Column chromatography was carried out under argon using Bio-Beads SX-4 which were purchased from Bio-Rad Laboratories. Prior to use, they were swollen in dry diethyl ether.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-300 or an XL-200 spectrometer, respectively. Electron impact mass spectra were obtained at 70 eV on a Varian MAT 311 A mass spectrometer at the Technical University of Berlin, Berlin, Germany. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

Synthesis. The compounds $C_5H_2Me_4$,[5] $(C_5HMe_4)Li$,[5] $C_5HMe_4PPh_2$,[6] $(C_5Me_4PPh_2)Li$,[6] $C_5H_2Ph_4$,[7] and $(C_5HPh_4)K$[7] were prepared by literature procedures. Chlorotitanium triisopropoxide was obtained from Aldrich Chemical Co.

(η^5-Cyclopentadienyl)triisopropoxytitanium (1). Into a 250-mL round bottom Schlenk flask were placed 50 mL of pentane and 2.00 g (30.3 mmol) of freshly distilled cyclopentadiene. The flask was cooled to 0 °C, and *n*-butyllithium in hexane (12.1 mL, 30.3 mmol) was subsequently added via a syringe over a 10-min period. The reaction mixture was stirred for 1 h at 0 °C, allowed to warm to room temperature, and stirred for 12 h. The resulting precipitate was collected on a frit under argon and washed with pentane. Cyclopentadienyllithium prepared in this manner was dissolved in 80 mL of tetrahydrofuran, the flask was cooled to −78 °C, and a solution of 7.10 g (27.2 mmol) chlorotitanium triisopropoxide in 20 mL THF was added dropwise. After the addition was complete, the mixture was allowed to warm to room temperature and stirred for 48 h. The solvent was removed under vacuum and the residue extracted with pentane. The combined extracts were filtered through Celite. The pentane was removed under vaccum to give a red brown liquid. After the crude product was passed several times through a Bio-Beads column, 3.6 g (45%) of (η^5-cyclopentadienyl)triisopropoxytitanium was obtained as a pale yellow liquid. Anal. Calcd for $C_{14}H_{26}O_3Ti$: C, 57.93; H, 9.03. Found: C, 57.29; H, 8.91. ^1H NMR (C_6D_6): δ 1.15 (d, 18H, CH–(C*H*$_3$)$_2$, *J* = 6.1 Hz), 4.53 (h, 3H, C*H*–(CH$_3$)$_2$, *J* = 6.1 Hz), 6.28 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6): δ 27.46 ((CH$_3$)$_2$–CH), 78.84 (CH–(CH$_3$)$_2$), 113.60 (C$_5$). MS (*m/e*, % intensity): 290 (24.1, M$^+$), 275 (47.3, M − CH$_3^+$), 231 (100, M − OCH(CH$_3$)$_2^+$), 224 (33.7, M − CpH$^+$), 181 (34.4, M − CpH − (CH − (CH$_3$)$_2$)$^+$).

(η^5-Tetramethylcyclopentadienyl)triisopropoxytitanium (2). Into a 100-mL round bottom Schlenk flask were placed 30 mL of THF and 1.00 g (8.18 mmol) of tetramethylcyclopentadiene. The flask was cooled to 0 °C, and *n*-butyllithium in hexane (3.27 mL, 8.18 mmol) was added via a syringe over a period of 10 min. The white slurry was allowed to warm to room temperature and stirred for 6 h. The flask was cooled to −78 °C, and a solution of 1.92 g (7.37 mmol) of chlorotitanium triisopropoxide in 10 mL of THF was added slowly via a syringe. After completion of the addition, the yellow solution was allowed to warm to room temperature and stirring was continued for 12 h. The solvent was removed under vacuum, the residue was extracted with pentane, and the solution was filtered through Celite. The pentane was removed, and the remaining red brown oil was passed several times through a Bio-Beads column to give 2.3 g (90%) of (η^5-tetramethylcyclopentadienyl)triisopropoxytitanium as a yellow oil. An analytical sample was obtained by distillation at 125–135 °C/10^{-3} torr. Anal. Calcd for $C_{18}H_{34}O_3Ti$: C, 62.42; H, 9.89. Found: C, 62.24; H, 10.12. ^1H NMR (C_6D_6): δ 1.13 (d,

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Table I. Styrene Polymerization Catalyzed by (η^5-C_5H_5)Ti(O-*i*-Pr)$_3$/MAO (1)

run no.	T_p (°C)	[Ti] (mM)	10^{-3}[Al]/[Ti]	PS (g)	$10^{-6}A$ (g of PS/(mol of Ti·mol of S·h))	SY (%)
1.1	25	0.05	1.0	0.162	2.97	90.1
1.2	25	0.1	1.0	0.087^a	0.80	85
1.3	25	0.2	1.0	0.058^a	0.27	78
1.4	25	0.3	1.0	0.039^a	0.12	61
1.5	25	0.05	0.1	0.017^a	0.31	
1.6	25	0.05	0.5	0.022^a	0.40	
1.7	25	0.05	1.0	0.162	2.97	90.1
1.8	25	0.05	2.0	0.176	3.23	92.0
1.9	25	0.05	4.0	0.080^a	1.47	87
1.10	0	0.05	2.0	0.010^a	0.18	
1.11	25	0.05	2.0	0.176	3.23	92.0
1.12	50	0.05	2.0	0.270	4.95	94.2
1.13	75	0.05	2.0	0.335	6.14	96.1
1.14	90	0.05	2.0	0.010^a	0.18	

[a] Reproducibility of about ±10% because of low yield.

Table II. Styrene Polymerization Catalyzed by (η^5-C_5HMe_4)Ti(O-*i*-Pr)$_3$/MAO (2)

run no.	T_p (°C)	[Ti] (mM)	10^{-3}[Al]/[Ti]	PS (g)	$10^{-6}A$ (g of PS/(mol of Ti·mol of S·h))	SY (%)
2.1	25	1.0	0.1	0.25	0.23	80
2.2	25	1.0	0.5	0.81	0.74	96
2.3	25	1.0	1	0.43	0.93	74
2.4	25	0.05	0.5	0.01^a	0.18	
2.5	25	0.10	0.5	0.16	1.46	93.8
2.6	25	0.30	0.5	0.25	0.76	98
2.7	25	0.50	0.5	0.09^a	0.17	94.4
2.8	25	0.10	0.5	0.16	1.46	93.8
2.9	50	0.10	0.5	0.66	6.1	95.5
2.10	75	0.10	0.5	1.43	13.1	99.3
2.11	90	0.10	0.5	0.04^a	0.37	25

[a] Reproducibility of about ±10% because of low yield.

Table III. Styrene Polymerization Catalyzed by (η^5-C_5HPh_4)Ti(O-*i*-Pr)$_3$/MAO (3)

run no.	T_p (°C)	[Ti] (mM)	10^{-3}[Al]/[Ti]	PS (g)^a	$10^{-6}A$ (g of PS/(mol of Ti·mol of S·h))	SY (%)
3.1	25	0.050	0.50	0.02	0.37	40
3.2	25	0.10	0.5	0.02	0.18	40
3.3	25	0.50	0.50	0.01	0.0009	
3.4	25	0.050	0.50	0.014	0.26	
3.5	25	0.050	1.0	0.02	0.38	15
3.6	25	0.050	4.0	0.016	0.29	62.5
3.7	0	0.050	4.0	0.023	0.42	4.3
3.8	25	0.050	4.0	0.026	0.48	46
3.9	50	0.050	4.0	0.031	0.57	25
3.10	75	0.050	4.0	0.080	1.47	75
3.11	90	0.050	4.0	0.030	0.55	66

[a] Reproducibility of about ±10% because of low yield.

Table IV. Styrene Polymerization Catalyzed by (η^5-$C_5Me_4(PPh_2)$)Ti(O-*i*-Pr)$_3$ (4)

run no.	T_p (°C)	[Ti] (mM)	10^{-3}[Al]/[Ti]	PS (g)^a	10^{-6} A^a (g of PS/(mol of Ti·mol of S·h))
5.1	25	0.05	1	0.006	0.11
5.2	25	0.1	1	0.014	0.13
5.3	25	0.2	1	0.013	0.06
5.4	25	0.1	0.5	0.013	0.12
5.5	25	0.1	1	0.014	0.13
5.6	25	0.1	2	0.019	0.17
5.7	25	0.1	4	0.013	0.12
5.8	0	0.1	2	0.015	0.14
5.9	25	0.1	2	0.019	0.17
5.10	50	0.1	2	0.001	0.06
5.11	60	0.1	2	0.008	0.07
5.12	75	0.1	2	0.008	0.07
5.13	90	0.1	2	0.006	0.055

[a] Reproducibility of about ±10% because of low yield.

18H, CH(C*H*$_3$)$_2$, *J* = 6.6 Hz), 1.94 (s, 6H, $(CH_3)_2C_5$), 2.00 (s, 6H, $(CH_3)_2C_5$), 4.56 (h, 3H, C*H*(CH$_3$)$_2$, *J* = 6.6 Hz), 5.64 (s, 1H, C_5H). ^{13}C NMR (C_6D_6): δ 11.36 ((*C*H$_3$)$_2$C$_5$), 13.39 ((*C*H$_3$)$_2$C$_5$), 26.66 ((*C*H$_3$)$_2$–CH), 75.64 ((CH$_3$)$_2$–*C*H), 111.10 (C$_5$–*C*H), 121.69, 123.91 (C$_5$). MS (*m*/*e*, % intensity): 346 (18, M$^+$), 287 (55, M – OCH(CH$_3$)$_2$$^+$), 228 (100, M – 2(OCH(CH$_3$)$_2$)$^+$), 121 (10, C$_5$H(CH$_3$)$_4$$^+$).

(η-Tetraphenylcyclopentadienyl)triisopropoxytitanium (3). Tetraphenylcyclopentadienylpotassium (4.25 g, 10.4 mmol) and chlorotitanium triisopropoxide (2.72 g, 10.4 mmol) were added to separate 200-mL round bottom Schlenk flasks in a glovebox. Both solids were dissolved in a minimum amount of THF and then placed in a salt/ice bath for 15 min. The solution of the potassium salt was cannulated into the titanium solution slowly and allowed to react at cold temperatures for 3 h. The reaction was then allowed to warm to room temperature. THF was removed in vacuo, and the resulting oily, orange solid was extracted by stirring with hexane overnight. The hexane solution was filtered over Celite on a Schlenk frit and then placed in a –20 °C freezer overnight. The resulting yellow solid was dried in vacuo to produce 3.9 g of product. Concentration of the mother liquor and cooling of the latter in a freezer resulted in an additional 0.8 g of product, giving 4.7 g (86%) of (η^5-tetraphenylcyclopentadienyl)triisopropoxytitanium. An analytical sample was obtained by slow recrystallization from hexane at 0 °C, mp 133–135 °C. Anal. Calcd for $C_{38}H_{42}O_3Ti$: C, 76.75; H, 7.13. Found: C, 77.25; H, 7.13. ^{1}H NMR (CDCl$_3$): δ 1.22 (d, 18H, CH–(*C*H$_3$)$_2$, *J* = 6.1 Hz), 4.05 (h, 3H, C*H*–(CH$_3$)$_2$, *J* = 6.1 Hz), 6.72 (s, C$_5$H), 6.83–7.45 (m, 20H, Ph H). ^{13}C NMR (CDCl$_3$): δ 27.81 ((*C*H$_3$)$_2$–CH), 58.41 (C$_5$H), 79.11 (*C*H–(CH$_3$)$_2$), 127.21 (*p*-Ph C), 128.10, 128.44 (*o*/*m*-Ph C), 129.16, 129.47 (q, C$_5$–C), 133.51, 133.68 (*o*/*m*-Ph C), 136.10 (q, Ph C). MS (*m*/*e*, % intensity): 594 (5.4, M$^+$), 476 (4.3, M – 2(OCH(CH$_3$)$_2$)$^+$), 370 (100, C$_5$HPh$_4$$^+$).

(η^5-(Diphenylphosphino)tetramethylcyclopentadienyl)triisopropoxytitanium (4). ((Diphenylphosphino)tetramethylcyclopentadienyl)lithium (2.18 g, 6.98 mmol) was weighed into a 100-mL Schlenk flask. THF (50 mL) was added, and the reaction mixture was cooled to –78 °C. Subsequently, a solution of 1.55 g (5.95 mmol) of chlorotitanium triisopropoxide in 20 mL of THF was added dropwise via a syringe. The yellow solution was allowed to warm to ambient temperature and stirred for 15 h. The solvent was removed under vacuum, and the residue was taken up in pentane. After filtration through Celite the solvent was evaporated under vacuum. The remaining yellow oil was fractionally distilled at 135–145 °C/10^{-3} Torr to give 1.34 g (42.1%) of (η^5-(diphenylphosphino)tetramethylcyclopentadienyl)triisopropoxytitanium as an orange-yellow oil. Anal. Calcd for $C_{30}H_{43}O_3PTi$: C, 67.92; H, 8.17. Found: C, 67.68; H, 7.79. ^{1}H NMR (C_6D_6): δ 1.24 (d, 18H, CH–(C*H*$_3$)$_2$, *J* = 6.3 Hz), 1.96 (s, 6H (CH$_3$)$_2$C$_5$), 2.05 (s, 6H, (CH$_3$)$_2$C$_5$), 4.74 (h, 3H, C*H*(CH$_3$)$_2$, *J* = 6.3 Hz), 7.00–7.25 (m, 6H, Ph H), 7.50–7.65 (m, 4H, Ph H). ^{31}P NMR (C_6D_6): δ –22.41. MS (*m*/*e*, % intensity): 530 (3.8, M$^+$), 472 (46.2, M – OCH(CH$_3$)$_2$$^+$), 412 (100, M – 2(OCH(CH$_3$)$_2$)$^+$), 352 (5.2, M – 3(OCH(CH$_3$)$_2$)$^+$), 305 (8.9, M – 3(OCH(CH$_3$)$_2$) – Ti$^+$), 185 (2.2, PPh$_2$$^+$), 120 (9.2, C$_5Me_4$$^+$).

Tetramethyl(trimethylsilyl)cyclopentadiene. *n*-BuLi (4.19 mL, 10.5 mmol) was added dropwise to a stirred, cold (0 °C) solution of 1.28 g (10.5 mmol) of tetramethylcyclopentadiene in 40 mL of THF. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 12 h. The resulting white suspension was cooled to 0 °C and 1.9 mL (15.0 mmol) of chlorotrimethylsilane was added dropwise. The reaction mixture was allowed to warm to ambient temperature and gently refluxed for 24 h. The solvent was removed under vacuum, and the residue was extracted with pentane. The pentane extracts were passed through a Celite plug. Removal of the solvent gave 1.48 g (72.6%) of tetramethyl(trimethylsilyl)cyclopentadiene which was reasonably pure by ^{1}H NMR and was used without

Table V. Styrene Polymerizations Catalyzed by (η^5-$C_5Me_4(SiMe_3)$)Ti(O-*i*-Pr)$_3$/MAO (5)

run no.	T_p (°C)	[Ti] (mM)	10^{-3}[Al]/[Ti]	PS (g)[a]	$10^{-6}A$[a] (g of PS/(mol of Ti·mol of S·h))	SY[a] (%)
4.1	25	0.050	1	0.010	0.18	60
4.2	25	0.10	1	0.022	0.20	63
4.3	25	0.20	1	0.037	0.17	56
4.4	25	0.10	0.50	0.035	0.32	74
4.5	25	0.10	1	0.022	0.20	63
4.6	25	0.10	2	0.012	0.11	50
4.7	25	0.10	4	0.001	0.009	
4.8	0	0.10	0.5	0.013	0.12	23
4.9	25	0.10	0.5	0.035	0.32	74
4.10	50	0.10	0.5	0.047	0.43	85
4.11	60	0.10	0.5	0.086	0.79	93
4.12	75	0.10	0.5	0.150	1.4	98
4.13	90	0.10	0.5	0.001	0.009	

[a] Reproducibility of about ±10% because of low yield.

further purification. ^{1}H NMR ($CDCl_3$): δ 0.10 (s, 9H, $(CH_3)_3Si$), 1.85 (s, 6H, $(CH_3)_2C_5$), 1.96 (s, 6H, $(CH_3)_2C_5$), 2.89 (s, broad, 1H, C_5H).

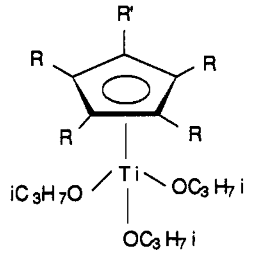
(η^5-Tetramethyl(trimethylsilyl)cyclopentadienyl)triisopropoxytitanium (5). A solution of tetramethyl(trimethylsilyl)cyclopentadiene (1.48 g, 7.61 mmol) in 50 mL of THF, prepared in an argon-flushed Schlenk flask, was cooled to −78 °C. To the flask was added dropwise via a syringe a solution of *n*-BuLi (3.04 mL, 7.61 mmol) in hexane. The solution was stirred for 30 min at −78 °C and allowed to warm to room temperature, and stirring was continued for 15 h. The solvents were removed under vacuum and the remaining pale yellow solid residue washed with pentane, affording (tetramethyl(trimethylsilyl)cyclopentadienyl)lithium as a white powder which was dissolved again in 50 mL of THF. The deep yellow solution was cooled to −78 °C, and a solution of 1.50 g (5.76 mmol) of chlorotitanium triisopropoxide in 20 mL of THF was added slowly via a syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 18 h. Removal of the solvent under vacuum yielded a brown-yellow oil. This oil was extracted with pentane, the pentane layer was filtered through Celite and the solvent was removed under vacuum, leaving a viscous deep yellow oil. Fractional distillation at 125–135 °C/10^{-3} Torr yielded 0.90 g (37%) of (η^5-tetramethyl(trimethylsilyl)cyclopentadienyl)triisopropoxytitanium as a bright yellow viscous oil. Anal. Calcd for $C_{21}H_{42}O_3SiTi$: C, 60.26; H, 10.11. Found: C, 59.71; H, 9.98. ^{1}H NMR (C_6D_6): δ 0.32 (s, 9H, $(CH_3)_3Si$), 1.13 (d, 18H, CH–$(CH_3)_2$, J = 6.0 Hz), 1.98 (s, 6H, $(CH_3)_2C_5$) 2.12 (s, 6H, $(CH_3)_2C_5$), 4.61 (h, 3H, $(CH_3)_2$–C*H*, J = 6.0 Hz). ^{13}C NMR (C_6D_6): δ 3.35 ($(CH_3)_3$-Si), 12.81 ((CH$_3$)$_2$C$_5$), 16.13 ((CH$_3$)$_2$C$_5$), 28.09 ((CH$_3$)$_2$–CH), 76.68 (CH–(CH$_3$)$_2$), 119.06 (C_5–SiMe$_3$), 126.97 and 131.94 (C_5).

Polymerization Studies. Styrene polymerizations were carried out in 250-mL pressure bottles with magnetic stirring and using toluene as the solvent. Toluene was distilled from sodium under argon just before use. Styrene was distilled from calcium hydride and stored at −25 °C under argon in darkness. Toluene (50 mL) was introduced into a metal crimp-capped crown bottle fitted with rubber liners under 1 atm of argon. Styrene (5.00 mL, 4.54 g, 43.6 mmol), MAO (1.45 M in toluene from Akzo), and the appropriate catalyst were injected into the reactor. The polymerizations were performed at 0, 25, 50, 75, and 90 °C for 30-min periods. After this time the polymerizations were terminated by the addition of methanol. The polymer was precipitated with 3% HCl in methanol, washed three times each with 50 mL of methanol, and dried in vacuo to a constant weight. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the syndiotactic polystyrene (s-PS) portion of the obtained polymer. The reproducibility of the amount of total polymer and syndiotactic polymer obtained is estimated at ±5% and ±2%, respectively, except as noted in the tables.

Polymer Characterization. Differential scanning calorimetry (DSC) measurements wer recorded on a Perkin-Elmer Thermoanalytic System 4. Molecular weight determinations were made by viscosity measurements at different s-PS concentrations. The s-PS was examined by ^{13}C NMR using a Varian XL 300 NMR spectrometer at 120 °C in 1,2,4-trichlorobenzene.

Results and Discussion

A number of titanium alkoxides have been previously evaluated as catalysts for the syndiotactic polymerization of styrene.[1,3,4] For our comparitive study, we have chosen (η^5-cyclopentadienyl)triisopropoxytitanium (1) as the reference compound.



1 R, R' = H

2 R = CH_3; R'-H

3 R = C_6H_5; R' = H

4 R = CH_3; R' = $P(C_6H_5)_2$

5 R = CH_3; R' = $Si(CH_3)_3$

Compound 1 has previously been reported in the literature[8] and was purified by vacuum distillation. Attempts in our laboratory to prepare *pure* 1 by this procedure were unsuccessful. We subsequently were able to synthesize highly pure 1 from a reaction between cyclopentadienyllithium and chlorotitanium triisopropoxide in THF solution, followed by purification several times through a Bio-Beads column. The product was fully characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, and combustion analysis.

In a similar manner, the tetramethyl derivative 2 and the tetraphenyl derivative 3 were obtained in high yields from reactions between chlorotitanium triisopropoxide and tetramethylcyclopentadienyllithium or tetraphenylcyclopentadienylpotassium, respectively. Compound 2 was likewise purified by using Bio-Beads, whereas 3 was purified by crystallization from hexane.

The corresponding diphenylphosphino (4) and trimethylsilyl (5) derivatives were synthesized in moderate yields in an analogous manner from reactions between chlorotitanium triisopropoxide and ((diphenylphosphino)-tetramethylcyclopentadienyl)lithium or ((trimethylsilyl)-tetramethylcyclopentadienyl)lithium in THF solution. Both 4 and 5 could be purified by vacuum distillation, due presumably to higher thermal stability as a result of the more bulky cyclopentadienyl rings.

Styrene polymerizations involving 1–5 and MAO as cocatalyst were performed at various conditions of [Ti], [Al]/[Ti], and T_p (temperature of polymerization). The catalytic activity (A) and wt % of 2-butanone insoluble polystyrene (SY) involving reference compound 1 are given in Table I. The polymerization is most efficient at a low [Ti] of 0.05 mM, at [Al]/[Ti] = 2000, and at T_p = 75 °C. Tables II–V contain the polymerization results for 2/MAO, 3/MAO, 4/MAO, and 5/MAO, respectively.

Table VI summarizes the optimum polymerization behavior for all the catalysts including $\bar{M}_w$ of the polymer as well as its maximum melting transition temperature (T_m).

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Table VI. Comparison of Catalysts at Their Optimum Polymerization Conditions

catalyst	T_p (°C)	[Ti] (mM)	10^{-3}[Al]/[Ti]	$10^{-6}A$ (g of PS/(mol of Ti·mol of S·h))	SY (%)	T_m	$10^{-5}\bar{M}_w$
1	75	0.05	2	6.1	96	256	1.2
2	75	0.05	0.5	13.1	>99	270	3.4
3	75	0.10	4	1.5	75	253	0.99
4	25	0.10	2	0.17			
5	75	0.10	0.5	1.4	98	274	4.0

The catalyst **2**/MAO is twice as active as **1**/MAO and has a higher stereoselectivity. The *s*-PS produced by the former also has almost 3 times the MW as the latter. It appears that small electron-donating substituents are beneficial and increase the rate of propagation without an increase in the rate of chain termination by β-hydrogen abstraction. Both syndioselectivity and catalytic activity for these catalyst systems drop off precipitously at high T_p.

Catalyst **3**/MAO has a very low activity and selectivity. The phenyl substituents probably hinder the approach of monomer for insertion and chain-end control of syndioselection.

The trimethylsilyl group increases both electron density and steric hindrance on the cyclopentadienyl ring in **5**/MAO. The result is low activity but high selectivity and molecular weight.

Addition of a diphenylphosphino group caused a drastic decrease in the catalytic activity. **4**/MAO did not produce a sufficient amount of polymer for characterization.

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