Supporting information

Living Syndiospecific Polymerization of Propylene with Sterically Encumbered Titanium Complexes activated by MMAO

Ying-Yun Long,[a] Yong-Xia Wang,[a] Bai-Xiang Li,[a] Yan-Guo Li,[a] Yue-Sheng Li*[ab]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China, E-mail: ysli@ciac.jl.cn

[b] School of Material Science and Engineering, Tianjin University, Tianjin 300072, China

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by **1e** at -10°C (a), 10°C (b), 25°C (c) combined with MMAO at 0 °C, respectively.

(8) **Figure S7** ^{13}C NMR spectra of the methyl region for syndiotactic poly(propylene) obtained by **1e** at 40°C (d), 55°C (e) and **1a** at 40°C (f) and 55°C (g) combined with MMAO at 0 °C, respectively.

(9) **Figure S8** DSC curves of syndiotactic PPs at a heating rate of 10ºC/min: (a) **1b**/MMAO catalyst system, T_m = 139.3 ºC, 135.2 ºC; (b) **1d**/MMAO catalyst system, T_m = 136.5 ºC, 122.6 ºC; (c) **1e**/MMAO catalyst system, T_m = 150.9 ºC, 138.0 ºC.

Table S1 Propylene polymerization results[a]

Entry	Cat.	Time (h)	Yield (g)	Activity[b]	M_w[c]	M_w/M_n[c]	N(μmol)[d]	T_m[e](°C)
1	**1a**	2.0	0.92	46.0	158.9	1.22	7.06	146.2, 133.4
2	**1b**	2.0	1.10	55.0	170.2	1.23	7.93	137.3, 126.2
3	**1c**	2.0	0.88	44.0	138.5	1.25	7.94	137.2, 119.0
4	**1d**	2.0	0.80	40.0	137.0	1.23	7.18	138.5, 120.6
5	**1b**	0.5	0.29	58.0	45.5	1.19	7.58	135.9, 128.0
7	**1b**	1.0	0.55	55.0	90.2	1.20	7.32	136.3, 128.5
8	**1b**	3.0	1.36	52.0	240.5	1.29	7.29	138.4, 130.8
9	**1c**	0.5	0.23	46.0	43.0	1.20	6.48	136.8, 115.5
10	**1c**	3.0	1.14	38.0	245.3	1.27	5.92	138.3, 131.8
13	**1d**	0.5	0.20	40.0	38.5	1.18	6.12	134.3, 112.3
14	**1d**	3.0	1.11	37.0	235.0	1.25	5.90	137.0, 120.0

[a] Polymerization conditions: 10 μmol catalyst, solvent 50 mL toluene, propylene pressure 6 bar; dMAO used as a cocatalyst, polymerization temperature 0°C. [b] Activity (kg/mol·h). [c] Determined by GPC data in 1,2,4-trichlorobenzene versus polystyrene standard. The unit of molecular weight is kg/mol. [d] Calculated from yield and M_n. [e]Determined by DSC at a heating rate of 10°C/min.

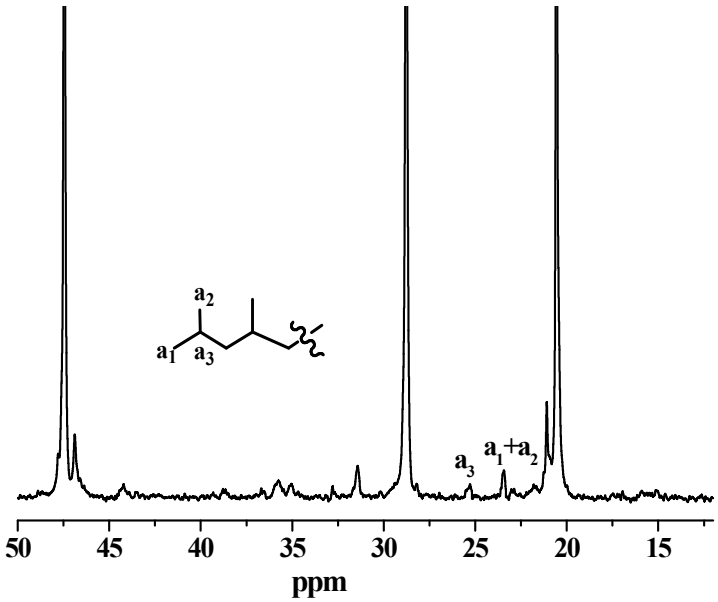
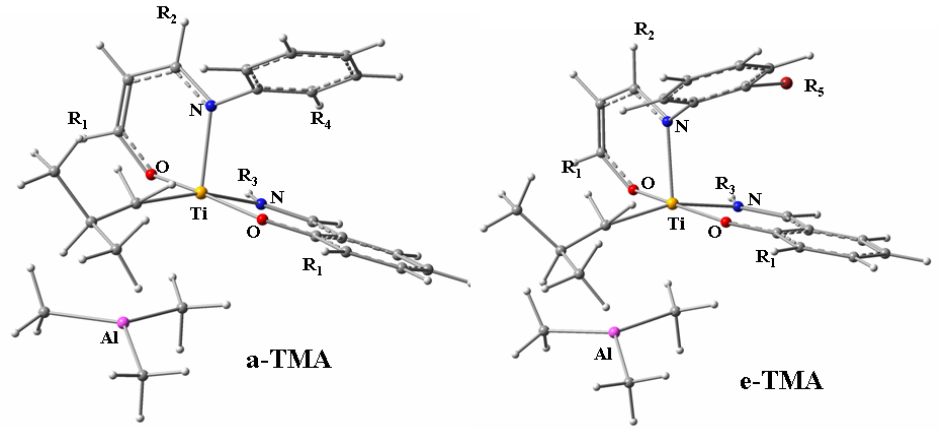


Figure S1. The aliphatic region of ^{13}C NMR spectra for low molecular weight syndiotactic polypropylene obtained by **1e**/MMAO systems (10μmol catalyst, polymerization time 20 min, polymerization temperature 0°C, M_n = 9.0 kg/mol, M_w/M_n = 1.09). The peaks at 23.3-23.6 ppm and 25.6 ppm are assigned to the methyl and methine carbons of isobutyl chain-end groups, respectively. No peaks assignable to other possible chain-end groups, namely ethyl, *n*-propyl, *n*-butyl, isopropyl, *sec*-butyl and isopentyl, were observed in the ^{13}C NMR spectrum. These results confirmed that the polymerization proceeded via 1,2-insertion of monomer.



R_1 = ^{t}Bu, R_2 = CF_3, R_3 = C_6F_5, R_4 = H, R_5 = Br

Figure S2. Calculated structures of propylene 1,2-inserted species of **1a** and **1e** in propylene polymerization activated by MMAO with free TMA. The groups R_1-R_3 are omitted. The red, blue, yellow and pink atoms represent oxygen, nitrogen, titanium and aluminum atoms, respectively.

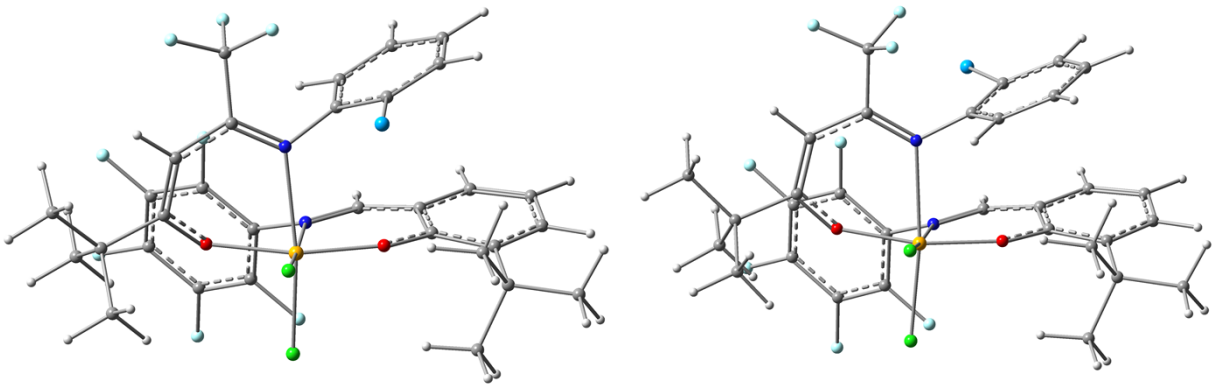


Figure S3. The calculated structures of complex **1e**. The red, navy blue, blue, cambridge blue, green and yellow atoms represent oxygen, nitrogen, bromine, fluorine, chlorine and titanium atoms, respectively.

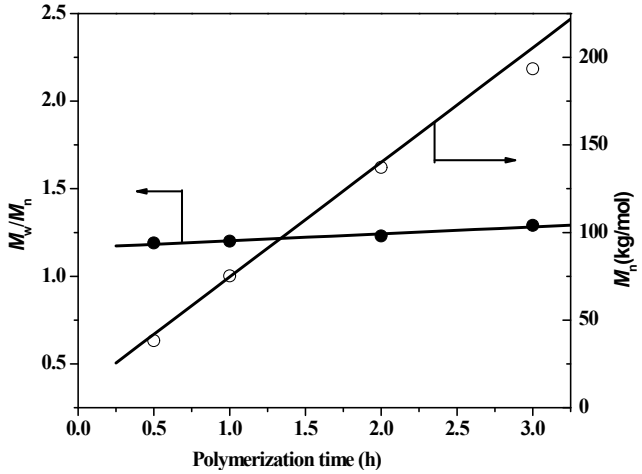


Figure S4. Plots of M_n and M_w/M_n *vs* reaction time for propylene polymerization with catalyst **1b** (20 μmol, using dried MAO as co-catalyst, Al/Ti = 500, polymerization at 0°C, propylene pressure 6 bar).

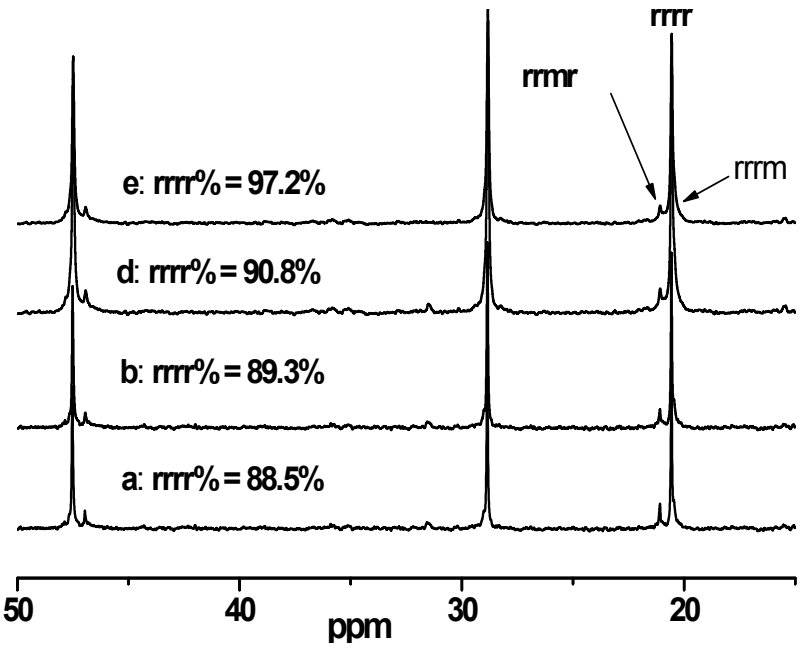


Figure S5. The aliphatic region of ^{13}C NMR spectra for syndiotactic poly(propylene) obtained by **1a** (entry 6, **Table 2**), **1b** (entry 9), **1d** (entry 13) and **1e** (entry 3) combined with MMAO at 0 °C, respectively.

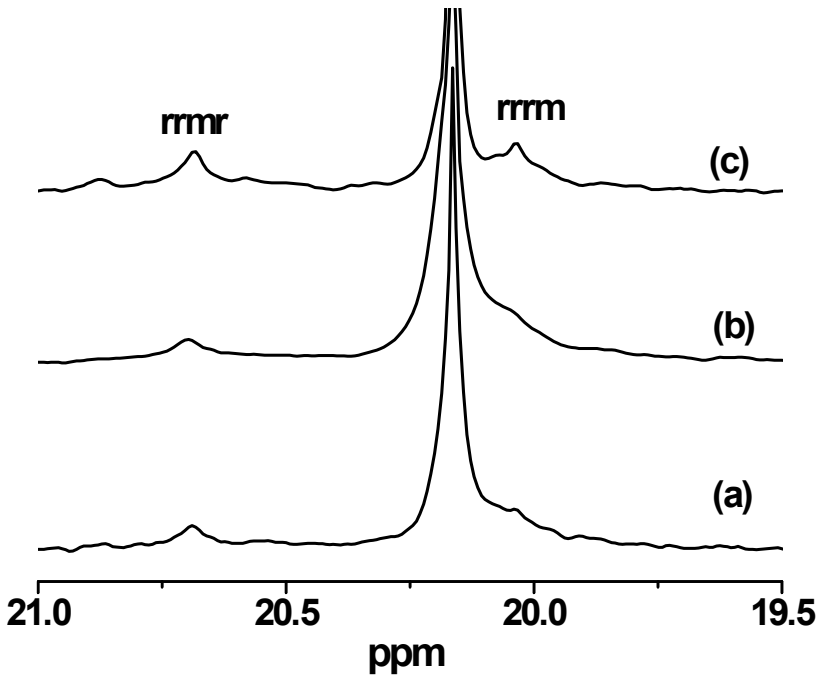


Figure S6 ^{13}C NMR spectra of the methyl region for syndiotactic polypropylenes obtained by **1e** at -10°C (a), 10°C (b), 25°C (c) combined with MMAO at 0 °C, respectively.

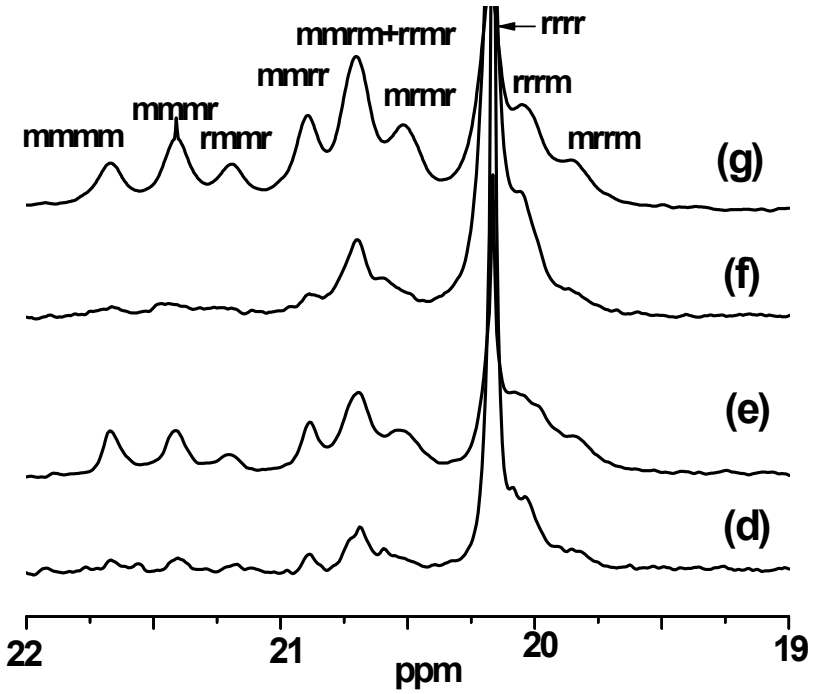


Figure S7 ^{13}C NMR spectra of the methyl region for syndiotactic polypropylenes obtained by **1e** at 40°C (d), 55°C (e) and **1a** at 40°C (f) and 55°C (g) combined with MMAO at 0 °C, respectively.

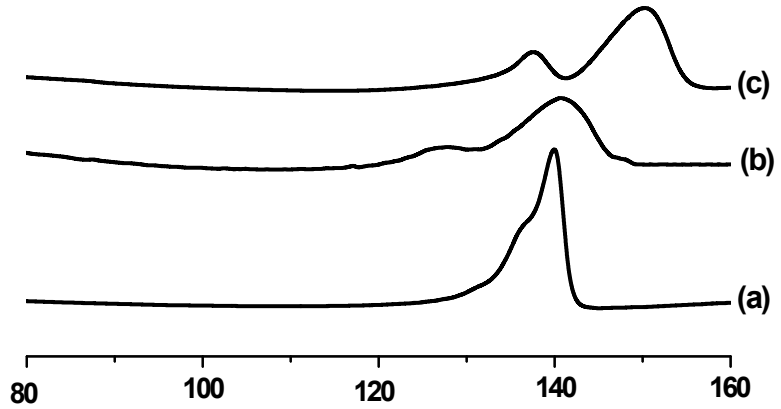


Figure S8. DSC curves of syndiotactic PPs at a heating rate of 10ºC/min: (a) 1**b**/MMAO catalyst system, T_m = 139.3 ºC, 135.2 ºC (entry 8, Table 2); (b) **1d**/MMAO catalyst system, T_m = 140.5 ºC, 126.6 ºC (entry 12, Table 2); (c) **1e**/MMAO catalyst system, T_m = 150.9 ºC, 138.0 ºC (entry 4, Table 2).