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

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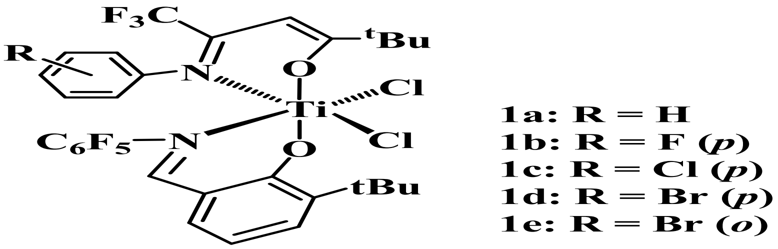
ABSTRACT: A series of sterically encumbered (salicylaldiminato)(β-enaminoketonato)titanium complexes [3-^{t}Bu-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][RN=C(^{t}Bu)CHC(CF$_3$)O]TiCl$_2$ [**1a**: R = Ph, **1b**: R = C$_6$H$_4$F(*p*), **1c**: R = C$_6$H$_4$Cl(*p*), **1d**: R = C$_6$H$_4$Br(*p*), **1e**: R = C$_6$H$_4$Br(*o*)] have been synthesized and tested to be efficient catalysts for syndiospecific polymerization of propylene in the presence of modified methylaluminoxane at room temperature. The introduction of bulky bromine atom *ortho* to the imine nitrogen of β-enaminoketonato ligand not only successfully improved the pentad syndiotacticity (*rrrr*) of the resultant polypropylenes from 88.5% to 97.2% , but also provided better protection of active site from attack of free AlR$_3$ or monomer and thus contributed to living polymerization nature with keeping high catalytic activity. More importantly, compared with the famous pentafluorinated FI-Ti/MAO catalyst system, the sterically congested complex **1e** with bromine atom *ortho* to N-aryl group displayed almost two times higher catalytic activity (14.5 vs 28.0 kg/mol·h), producing polypropylenes with even higher pentad syndiotacticity (*rrrr* = 97.2% *vs* 96.0%) and the similar narrow molecular weight distributions (M_w/M_n = 1.12-1.26). In addition, the polymerization proceeded with a different monomer insertion mode of 1,2-insertion and a similar chain-end control mechanism. Quantitative ^{13}C NMR spectra revealed that polymers with various stereo structure ranging from highly syndiotactic and regioregular to atactic and regio-irregular polymers at different reaction temperatures were achieved, and the probable formation routes were proposed. The percentage of regio-irregularities of the monomer sequence arising from 2,1-insertion and 3,1-enchainment increased with the rise of reaction temperature.

KEYWORDS*:* Ziegler-Natta polymerization; living polymerization; polypropylene

Introduction

Developing catalysts for both living and stereospecific polymerization of α-olefins has attracted great attention in the past three decades. Because it may create a variety of well-defined novel polymers such as monodisperse poly(α-olefin)s, end-functionalized polymers and block copolymers composed of stereoregular poly(α-olefin) segments, which are anticipated to possess unique material properties and thus expanded utilities. Remarkable progress in the rational design of well-defined complexes has led to the introduction of quite a few efficient catalysts for higher α-olefin polymerizations,[1-2] but there are only limited examples for living propylene polymerization.[3-5] Additionally, most of them have to proceed at very low to subambient temperatures to reduce the rate of chain termination and transfer reactions and thus resulted in low activities, such as $V(acac)_3$ (acac=acetylacetonate or its analogues),[3c] Ni-diimine[3d,3e] and $CpZrMe_2$.[3f] Despite the fact that nearly perfect stereo-specific propylene polymerization can be performed with appropriately designed group 4 metallocene catalysts, the examples for highly stereo-specific living propylene polymerization, especially for syndiospecific living polymerization of propylene, still remain scarce.[1a-b] Shiono and his coworkers demonstrated that the titanium complex possessing the fluorenyldimethylsilylamido ligand conducted syndiospecific living polymerization of propylene activated with dried methylaluminoxane (dMAO) or dried modified methylaluminoxane (dMMAO).[6,7] The employment of *tert*-butyl substituents to the fluorenyl ligand not only enhanced the catalytic activity more than 3 times but also improved the syndiospecificity (*rrrr* = 0.86) of the resultant polymer with keeping the living nature.[7a] However, the living polymerization proceeded only when alkyl aluminum-free MAO was used as the cocatalysts. Mitsui group reported that fluorinated Ti-FI catalysts (the titanium complexes with fluorine-containing phenoxy-imine chelate ligands) were effective for syndiospecific living polymerization of propylene *via* chain-end control mechanism, and successfully in production of block polymers with syndiotactic PP by sequential monomer addition.[8,9] Coates et al. described that the syndiospecificity of the resultant polypropylene could be improved up to 96% in pentad syndiotacticity (*rrrr*) by introduction of sterically two bulky substituents *tert*-butyl to the pentafluorinated phenoxyimine ligand.[10] However, the chain propagation rates in these living systems were much lower than those nonliving polymerization system. Therefore, it would be highly desirable to develop more robust living catalyst systems for syndiospecific propylene polymerization with high activity.

Recently, we reported that sterically congested titanium complex **1a** (**Scheme 1**) $[3\text{-}^t\text{Bu-2-OC}_6\text{H}_3\text{CH=N(C}_6\text{F}_5)][\text{PhN=C(CF}_3)\text{CHC(}^t\text{Bu)O]TiCl}_2$ with C_1-symmetric structure could effectively conduct syndiospecific living polymerization of propylene, accompanied by the improvement of catalytic activity, when activated with dMAO in toluene.[11] The bulky substituent *tert*-butyl played a vital role in achieving highly syndiospecific and living polymerization characteristic. The effect of cocatalyst on the catalytic performance was also investigated. In the case of **1a**/MMAO system, irreversible chain transfer reactions occurred due to its relatively less steric protection to the alkyl oxygen from attack of free AlMe_3 in the reaction medium, leading to non-living catalyst system. With the rational that a more electron-withdrawing ligand would generate a more electrophilic titanium center and enhance catalytic activity. Besides, considering sterically more encumbered ligands would be necessary to provide better protection and suppress probable chain transfer reactions, a series of **1a** derivatives **1b-e** were synthesized possessing substituents with electron-withdrawing effect and spacial congestion (**Scheme 1**). As expected, these complexes show more promising ability for highly syndiospecific polymerization of propylene at ambient temperature. Especially, complex **1e** displays a living polymerization nature. Significantly, compared with (bis[*N*-(3,5-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium(IV) dichloride/MAO system (the most famous FI-Ti catalyst system reported for highly syndiotactic living polymerization of propylene),[10a,10f,12] the new **1e**/MMAO system produced polypropylene with even higher pentad syndiotacticity (*rrrr* = 97.2% *vs* 96.0%) and almost two times higher catalytic activity. As far as we know, this is the first non-metallocene system for living propylene polymerization *via* 1,2-insertion of monomer with such high syndiospecificity and catalytic activity. Moreover, the influences of reaction temperature and activator on the microstructure of the resultant polymers were also investigated, where the probable formation routes were proposed. The results discussed herein would enrich the achievement of highly syndiospecific living polymerization of α-olefins and give more insight into the structure-activity-stereospecificity relations of the catalysts.



Scheme 1. Titanium complexes for propylene polymerization.

Results and discussion

Synthesis and characterization of catalysts

Heteroligated catalysts **1a-e** were synthesized *via* the procedure of previous literature[13] (**Scheme 1**). Since sterically bulky substituent situated in close proximity to the active site had steric repulsion against the methyl of propylene in reaction and thus leading to stereospecific polymerization,[8b] we tried to introduce various halogen including iodine to β-enaminoketone ligand. However, it is very difficult to obtain the desired titanium complex with sterically demanding iodine atom on the β-enaminoketone ligand. Fortunately, complexes **1b-1e** with sterically less demanding atoms (F, Cl and Br) were well purified and obtained in moderate to good overall yields (50-88%).[13a] Dark red complex **1e** were identified by ^{1}H and ^{13}C NMR spectra as well as elemental analyses. Moreover, over a period of 24 hours no spectra changes were observed in d_1-chloroform solutions of **1e** stored in an inert atmosphere at room temperature, which indicates the complexes were stable.

Propylene polymerization

Propylene polymerizations with complexes **1a-e** were carried out in the presence of MMAO as a cocatalyst under prescribed pressure. The typical results were summarized in **Table 1**. Complexes **1a-e** exhibited the catalytic activity sequence of **1b** > **1a** ≈ **1c** > **1d** > **1e** (60.0 > 48.0 ≈ 46.0 > 40.0 > 28.0 kg/mol$_{\mathrm{Ti}}$·h), which is the result of joint effect of steric congestion and electronic effect of substituents employed (entries 1-5). Compared with catalyst **1a**, complex **1b** with a fluorine *para* to the imine nitrogen displayed the highest catalytic activity for propylene polymerization, due to its strongest electron-withdrawing ability among halogen atoms. Complex **1c** with chlorine atom showed similar catalytic activity to complex **1a** under the same conditions, probably because the increase in catalytic activity benefiting from its relatively strong electron-withdrawing ability was almost offset by the steric congestion. When bromine atom was introduced to the β-enaminoketone ligand, though the steric congestion became competitive, the catalytic activities of complex **1d** and **1e** is still comparable with that of complex **1a**. This trend is different from that of propylene polymerization with ansa-fluorenylamidodimethyltitanium complexes reported by Shiono.[7a] In addition, the comparison in catalytic activity of complex **1d** and **1e** (40.0 *vs* 28.0 kg/mol$_{\text{Ti}}$·h) indicated that the substituent *ortho* to the imine nitrogen had more significant effect upon the catalytic properties of the complexes than those far from the active site (*para* position of the N-aryl ring).

All the resultant polypropylenes possess moderate molecular weights and relatively narrow molecular weight distributions (M_w/M_ns ≤ 1.56). Notably, the polypropylene obtained by the most bulky complex **1e** displayed the narrowest MWD (M_w/M_n = 1.25), indicative of a single active site nature. With the employment of dried MAO or dried MMAO without free $AlMe_3$ as a cocatalyst, polypropylenes with similar narrow MWDs could be achieved by both complex **1a** and **1e** (entries 6-9). In addition, higher catalytic activity for propylene polymerization can be observed with dMMAO as cocatalyst than that with dMAO (entry 6 *vs* entry 8). This difference might stem from the fact that the oligomeric molecules of dried MMAO are bulkier than those of MAO[14a], which could prevent the tight contact of the cocatalyst anion with the titanium and provide more space for propylene insertion. Interestingly, compared with catalyst **1a**, the introduction of bromine atom to N-aryl group (complex **1e**) greatly lowered the polydispersities (PDIs) of the resultant PPs from 1.56 to 1.25 and 1.29 to 1.18, in the presence of MMAO and dried MAO, respectively, as shown in **Figure 1**. These results confirmed that bulky substituents such as bromine atom could indeed provide steric protection to the active site in the reaction medium, and thus inhibit some chain transfer reactions.

It is well known that there are three chain transfer pathways for olefin polymerization, including chain transfer to monomer or AlR_3 or β–H elimination. Chain-end analyses of low molecular weight PPs showed the absence of chains with vinyl or vinylidene double bonds, implying no β-H elimination reaction occurred.[11] The increase of propylene pressure led to enhancement of both polymer yield and MW of the resultant product (entry 10), indicative of no chain transfer to monomer. Besides, the raise in the dosage of dried MMAO had minor influence on the MWs and MWDs of the polymers stemming from catalyst **1a** or **1e** (entries 12-13), similar to the propylene polymerization results by complex **1a**/dMAO system previously reported.[11] However, in the case of MMAO as cocatalyst, increasing Al/Ti molar ratio resulted in the decrease of the MWs and broadening of the MWDs of the PPs obtained by **1a-d** (entries 14-17). In addition, the number of polymer chains almost increased proportionally with the enhancement of the MMAO dosage (entries 1-4 *vs* entries 14-17), suggesting some chain transfer to aluminum reaction occurred and new polymer chains were recreated. Importantly, minor influence on the PPs (entry 5 *vs* entry 18) achieved by **1e**/MMAO catalyst system was observed even with free $AlMe_3$ in the reaction medium, indicative of negligible reaction of chain transfer to aluminum. The number of polymer chains (*N*: 11.4 *vs* 11.1 μmol) is very close the amount of catalysts used (10 μmol). In order to further confirm these results, DFT calculations have been employed as a tool to analyze chain transfer to aluminum (Al) reactions. Previous study showed the free $AlMe_3$ in commercial MMAO solutions played important roles in both decreasing MWs and broadening MWDs of the resultant polymers.[14b-d] Therefore, the calculation model used in our study is chain transfer to $AlMe_3$. Considering the heteroligated titanium complexes favor the 1,2-insertion of propylene (**Figure S1** in Supporting Information), the propylene-1,2-inserted species of **1a** and **1e**[15] were chosen as the representatives and **1a-** and **1e**-$AlMe_3$ were displayed in **Figure S2-3** (see supporting information). The comparison of reaction energy barrier (**1a** *vs.* **1e**, 42.6 *vs.* 58.7 kJ/mol) suggests that the chain transfer reaction of **1a** is more favorable than that of **1e**, in agreement with experiment results (entries 14 and 18).

Reaction temperature is another important effect for the propylene polymerization behavior.[16] Complex **1e** was investigated as the representative herein, because of its unique catalytic properties and the narrowest MWDs of the resultant polymers. Increasing reaction temperature from 10°C to 25°C raised the catalytic activity and the MWs of the resultant polymers (entry 19 and 5) with keeping relatively narrow MWDs. The highest activity of complex **1e** was up to 28 kg/mol·h at the reaction temperature of 25°C, which was *ca*. 2 times of that by the typical FI-Ti catalyst/MAO system (entry 5 *vs* entry 20). The bulky substituents *tert*-butyl and *ortho*-bromine prevent the building of a tight contact ion pair between the catalyst cation and the MMAO anion at a relatively high polymerization temperature and thus result in a better accessability for the monomer to the active center. Meanwhile, the elevated temperature not only sped up chain transfer rate but also the chain propagation rate and thereby increased the M_ns of the resultant PPs. However, further increasing temperature from 25 to 55°C might cause partial catalyst deactivation, and thus reduced the catalytic activity and broadened the MWDs of the resultant PPs (entries 5 and 21-22), forming a more stereoirregular polymer. Instead, performing the polymerizations with **1e** at lower temperature than 0°C had the beneficial impact of both narrowing the MWDs and maintaining relatively high activity (entries 23-24). Notably, the high molecular weight PPs obtained at 0 and -10°C displayed the polydispersities of only 1.19 and 1.18, thereby indicating that the polymerization was most likely living under these conditions.

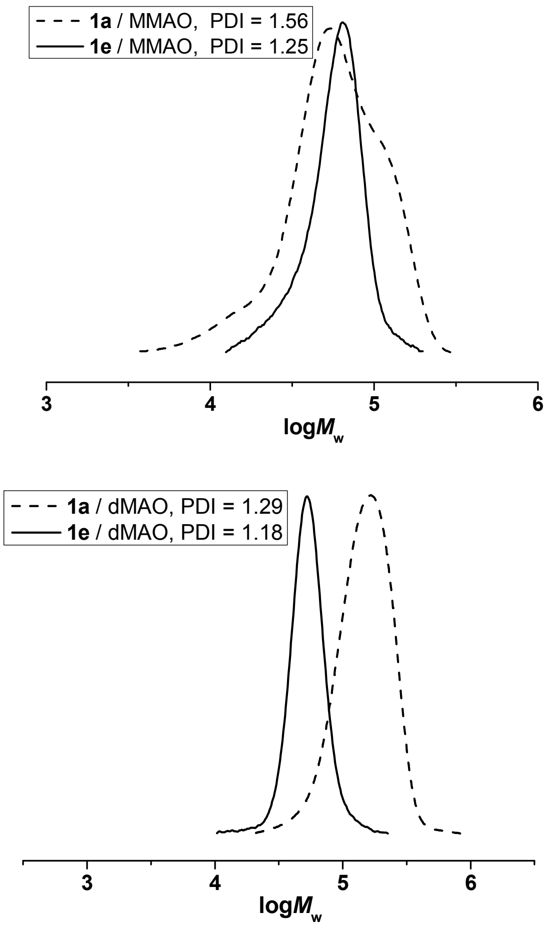


Fig. 1 GPC traces of polypropylenes obtained by complex **1a** and **1e** combined with MMAO or dMAO under the same conditions (10 μmol catalyst, solvent 50 mL toluene, propylene pressure 6 bar, Al/Ti = 500, temperature 25°C).

Additional proof for the living character of **1e**/MMAO catalyst system for propylene polymerization at 0°C was conducted. The M_n and M_w/M_n values were monitored as a function of reaction time (entries 1-4, **Table 2**). Plots of M_n and M_w/M_n *vs* reaction time were shown in **Figure**

2, in which the M_n value increased proportionally with the polymerization time, while the M_w/M_n value retained narrow (M_w/M_n = 1.12-1.26). The GPC peaks of the produced polymers shifted to higher molecular weight region with an increase in reaction time, while the monomodal shape was retained and no shoulder peak or low molecular weight tail was detected (**Figure 3**). In addition, the numbers of polymer chains almost keep constant and were about 75-83% of Titanium used. These results clearly indicated that catalyst **1e** initiated highly controlled propylene polymerization under these conditions.

To investigate the stability of "living" polymer chains, post-polymerization of propylene was performed with **1e** activated by MMAO in toluene at 0°C. The first-step polymerization was conducted for 2 hours, and the second-step polymerization was continued for another 1 hour after the addition of propylene gas feed. The result showed that the number-average molecular weight, the number of polymer chains and molecular weight distributions were almost the same as that of polymerization with the same reaction time (entry 4 *vs* entry 5 of Table 2). The GPC curves of the polymers obtained were illustrated in **Figure 4**, in which the second-step shifted to higher molecular weight region, further indicative of its living nature of **1e**/MMAO system at 0°C.

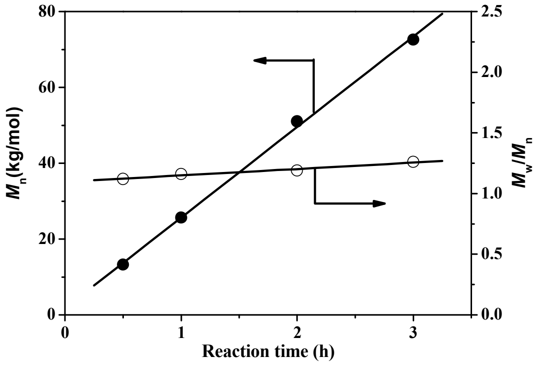


Fig. 2 Plots of M_n and M_w/M_n *vs* polymer yield for propylene polymerization with catalyst **1e** (10 μmol, using MMAO as cocatalyst, Al/Ti = 500, polymerization at 0°C, propylene pressure 6 bar)

Table 1. Propylene polymerization results[a]

Entry	Cat.	Al/Ti	Temp.[b] (°C)	Yield (g)	Activity[c]	M_n (kg/mol)[d]	M_w/M_n[d]	N[e] (μmol)
1	**1a**	500	25	0.96	48.0	50.6	1.56	18.9
2	**1b**	500	25	1.20	60.0	56.1	1.51	21.3
3	**1c**	500	25	0.92	46.0	49.8	1.53	18.5
4	**1d**	500	25	0.80	40.0	44.1	1.55	18.1
5	**1e**	500	25	0.56	28.0	49.0	1.25	11.4
6[f]	**1a**	500	25	1.02	56.0	60.6	1.29	16.8
7[f]	**1e**	500	25	0.60	30.0	51.5	1.18	11.5
8[g]	**1a**	500	25	1.20	60.0	62.2	1.28	19.2
9[g]	**1e**	500	25	0.64	32.0	52.0	1.18	12.2
10[h]	**1e**	500	25	0.64	32.0	50.0	1.27	12.8
11[h]	**1e**	500	0	0.44	22.0	45.4	1.18	9.60
12[g]	**1a**	1000	25	1.28	64.0	62.2	1.29	20.5
13[g]	**1e**	1000	25	0.70	35.0	51.5	1.20	13.5
14	**1a**	1000	25	1.12	50.6	42.3	1.79	26.4
15	**1b**	1000	25	1.30	65.0	41.5	1.76	31.3
16	**1c**	1000	25	0.96	48.0	23.5	2.92	40.8
17	**1d**	1000	25	0.84	42.0	32.0	1.95	26.2
18	**1e**	1000	25	0.55	32.0	49.5	1.26	11.1
19	**1e**	500	10	0.44	22.0	51.0	1.21	8.63
20[i]	**2**	500	25	0.29	14.5	32.7	1.17	8.86
21	**1e**	500	40	0.48	24.0	44.5	1.55	11.0
22	**1e**	500	55	0.36	18.0	41.4	1.74	8.70
23	**1e**	500	-10	0.32	16.0	50.2	1.18	6.40
24	**1e**	500	0	0.40	20.0	51.0	1.19	7.84

[a] Reaction conditions: 10 μmol catalyst, solvent 50 mL toluene, propylene pressure 6 bar; MMAO used as cocatalyst, reaction time 2h. [b] Temperature. [c] Activity (kg/mol$_{Ti}$·h). [d] Determined by GPC data in 1,2,4-trichlorobenzene versus polystyrene standard. [e] Calculated from yield and M_n. [f] Dried MAO used as cocatalyst. [g] Dried MMAO used as cocatalyst. [h] Propylene pressure 8 bar. [i] Catalyst **2** is complex $[3,5\text{-}^t\text{Bu}_2\text{-}2\text{-OC}_6\text{H}_3\text{CH=N(C}_6\text{F}_5)]_2\text{TiCl}_2$. Reaction conditions: 10 μmol catalyst, solvent 50 mL toluene, propylene pressure 6 bar; MAO used as the cocatalyst.

Table 2. Effect of reaction time on propylene polymerization results[a]

Entry	Cat.	Time (h)	Yield (mg)	Activity[b]	M_n (kg/mol)[c]	M_w/M_n[c]	T_m (°C)	N (μmol)[d]
1	**1e**	0.5	110	22.0	13.2	1.12	132.3, 112.5	8.33
2	**1e**	1.0	210	21.0	25.6	1.16	142.6, 128.3	8.20
3	**1e**	2.0	400	20.0	51.0	1.19	146.2, 135.8	7.84
4	**1e**	3.0	560	18.7	72.6	1.26	150.9, 138.0	7.71
5[e]	**1e**	3.0	570	19.0	72.3	1.26	150.2, 137.4	7.90
6	**1a**	0.5	220	44.0	18.9	1.35	132.5, 116.3	11.64
7	**1a**	2.0	850	42.5	45.1	1.56	134.5, 117.0	18.84
8	**1a**	3.0	1200	41.7	68.8	1.68	137.6, 126.2	17.44
9	**1b**	0.5	300	60.0	22.9	1.33	133.2, 120.6	13.10
10	**1b**	3.0	1560	52.0	68.8	1.65	139.3, 135.2	22.67
11	**1c**	0.5	200	40.0	16.8	1.35	132.2, 117.5	11.90
12	**1c**	3.0	1000	33.3	64.0	1.67	139.2, 136.0	15.62
13	**1d**	0.5	170	34.0	15.8	1.38	130.6, 115.4	10.44
14	**1d**	3.0	900	30.0	55.2	1.70	140.5, 126.6	16.30

[a] Reaction conditions: 10 μmol catalyst, solvent 50 mL toluene, propylene pressure 6 bar; MMAO was used as cocatalyst, Al/Ti = 500, reaction temperature 0°C. [b] kg PP/mol$_{Ti}$·h. [c] Determined by GPC data in 1,2,4-trichlorobenzene versus polystyrene standard. [d] Calculated from yield and M_n. [e] The first-step polymerization was conducted for 2 hour. After the resultant toluene solution was kept under N_2 for 30 min. The second-step was started later with the adding of the propylene gas, and was continued for another 1 hour.

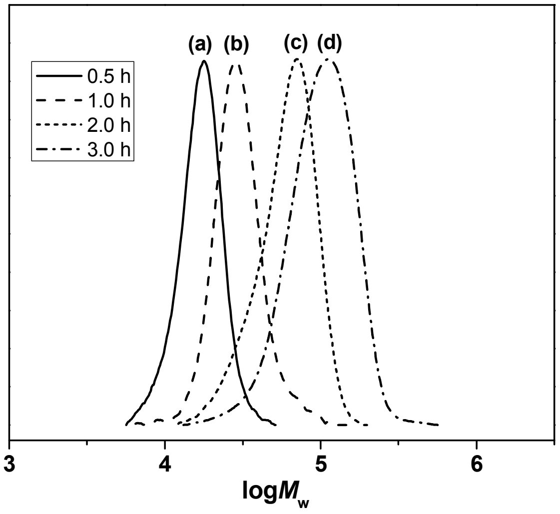


Fig. 3 GPC profile of polypropylenes obtained by catalyst **1e** (10 μmol, using MMAO as cocatalyst, Al/Ti = 500, polymerization at 0°C, propylene pressure 6 bar): (a) 0.5 h, M_n = 13.2 kg/mol, M_w/M_n = 1.12; (b) 1.0 h, M_n = 25.6 kg/mol, M_w/M_n = 1.16; (c) 2.0 h, M_n = 51.0 kg/mol, M_w/M_n = 1.19; (d) 3.0 h, M_n = 72.6 kg/mol, M_w/M_n = 1.26.

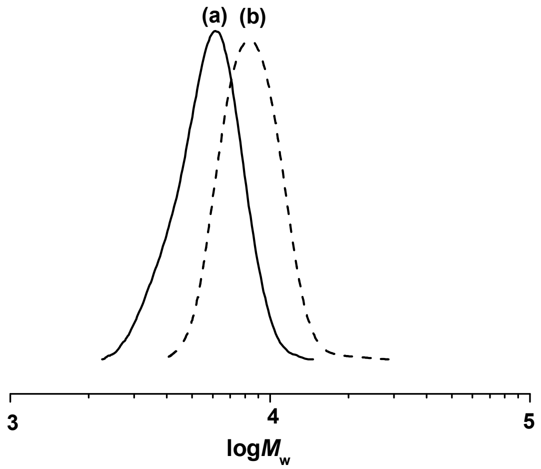


Fig. 4 GPC curves of polypropylenes obtained before (a: M_n = 50.8 kg/mol, M_w/M_n = 1.20) and after (b: M_n = 72.3 kg/mol, M_w/M_n = 1.26) post-polymerization with **1e**/MMAO.

In contrast, under the same conditions, the polymerizations by **1a-d**/MMAO systems proceeded without control of MWs and MWDs of the resultant polymers. The prolonged reaction time decreased the catalytic activity of the complexes and broadened the MWDs of the resultant PPs (entries 6-14, Table 2). In the hypothesis that the calculation way for living polymerization is still suitable for **1a-d**/MMAO systems, the number of polymer chains (*N*) far exceeded the number of the Ti complex employed ($N_{\text{polymer}}/N_{\text{Ti}} > 1$), indicating some irreversible chain transfer reactions occurred and terminated while some new active species were recreated. It seems that chain transfer to Al is indeed the major chain transfer pathway.

As a comparison, the propylene polymerizations by **1b-e**/dMAO systems were also conducted and the typical results were summarized in **Table S1** in supporting information. Without negligible chain transfer to Al reactions, the polymers obtained displayed a little higher MWs and narrower MWDs than those by the parallel catalysts combined with MMAO, consistent with the results of previous report.[11] In addition, with an increase in polymerization time, the linear relationship between average M_n or M_w/M_n and polymerization time as well as narrow MWDs were achieved (**Figure S4**). These results suggest that the propylene polymerization by **1b-e**/dMAO systems were also living without free $AlMe_3$ in solution.

Microstructure of the polypropylenes

The microstructure of the polypropylene was investigated and analyzed by ^{13}C NMR spectroscopy based on the literature data.[17] The ^{13}C NMR spectra of the aliphatic region (15-50 ppm) of selected polypropylene and the peak assignments focusing on the stereo structure were shown in **Figure S5**. The large intensity of the ^{13}C NMR resonance at 20.56 ppm (*rrrr* methyl stereo chemical pentad) from TMS displayed the predominantly syndiotactic arrangement of the monomer units and the detailed results were summarized in **Table 3**. As expected, the introduction of bulky halogen atoms to the β-enaminoketonato ligand greatly increased the syndiotacticity (*rrrr*) of the resultant polypropylenes in the following order: **1a** (88.5%) < **1b** (89.3%) < **1c** (90.8%) < **1d** (91.6%) < **1e** (97.2%), as shown in **Figure 5**. The presence of resonance at 21.08 ppm (*rrmr*/*mrmr* methyl pentad) shows that the PPs only contain isolated *m* stereoerrors.[18] This result indicates, at least in the first approximation, the stereo chemistry of chain propagation is controlled by the (chiral) last unit of the growing chain end under these conditions,[1g] the same chain end control mechanism as that of the pentafluorinated FI-Ti/MAO catalyst system.[10a] In the propylene polymerization with these titanium catalysts herein, migratory insertions occur predominantly from regular alternating sites of the catalysts and thus the system behaves syndiospecifically.[11] However, site epimerization of the polymer chain might occasionally occur to allow repetitive insertions at the same site and stereo-irregularities of isotactic units *m* were produced,[19] similar to that of ^{i}Pr[IndFlu]ZrCl$_2$/MAO system.[16] The site-epimerization (also called chain-back-skip) means a positionally change of the polymer chain without monomer insertion (see **Scheme 3**). Besides, the peak assignments and sequences revealed that the polymer only contain head-to-tail but undetectable other propylene units (e.g. head-to-head, tail-to-tail). There are almost no isolated resonances at 15.4 ppm assignable to primary CH$_3$ carbons and 34.8-35.8 ppm assignable to tertiary CH carbons resulting from 2,1-insertion of propylene. No evidence of 1,3-isomerization have been observed. These results further confirmed that complexes **1a-e** prefer 1,2-insertion of propylene.

As anticipated, catalyst **1e** with the most bulky substituents close to the active center displayed the highest syndiospecificity among these titanium complexes, consistent with the trends of FI-Ti complexes[10] and ansa-fluorenylamidodimethyltitanium complexes[7a] for syndiotactic polymerization of propylene. The *rrrr*-pentad value of the resultant polypropylenes were up to 97.2% and 98.0% at low polymerization temperatures of 0°C and -10°C, respectively. To our knowledge, this syndiotacticity value [*rrrr*] was closely approximate to that of PP by the most syndiospecific metallocene catalyst.[1f] Bercaw reported a Ph_2C_2 bridged zirconium complex with bulky substituted fluorenyl as a ligand, which can produce PP with the highest syndiotacticity reported ([*rrrr*] > 99%) up to date.[1f] However, increasing temperature led to the formation of more stereoirregular polymers as shown in **Figure 6b-e**. The *rrrr*-pentad of the resultant polypropylene was reduced to 94.5% (**Figure 6b**), 89.0 % (**Figure 6c**), 58.5% (**Figure 6d**) and 21.8% (**Figure 6e**) at 10, 25, 40 and 55°C, respectively. The detailed analysis of pentad distributions measured for these polypropylenes further illustrates that the corresponding data fits well with [*rrmr*] = [*rrrm*] of the chain-end control mode, especially for these obtained at temperatures lower than 25°C (**Figure S6** of supporting information). However, the raise of the reaction temperature results in a slight increase of the stereo-errors of the produced polymers (**Figure S7** of supporting information). Meanwhile, the peaks assignable to the pentad of *rrmr* and *mmrm* overlapped in the ^{13}C NMR spectra, and thus it was not so convincing to confirm the mechanism at these temperatures in the same way. The value of *mm*-triad of 3.7% at 25°C and 17.8% at 55°C were observed for complex **1e**/MMAO system (entries 10-12, **Table 3**), where site epimerization might play a vital role in raising the isotacticity.[20] Differential scanning calorimetry (DSC) indicates that the polymer obtained at temperature lower than 25°C displays two high melting temperatures (T_ms >132°C), while those produced at temperature higher than 25°C resemble amorphous polymer. Typical DSC thermograms were shown in **Figure S8**.

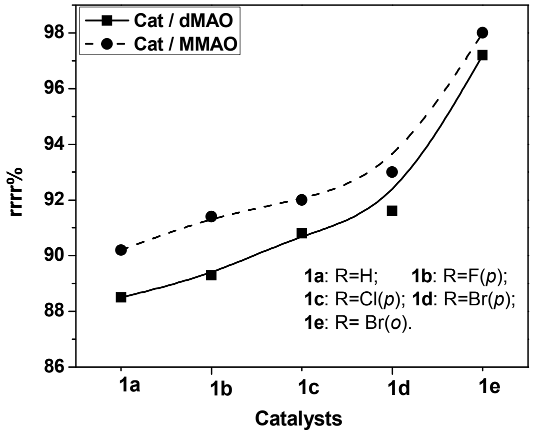
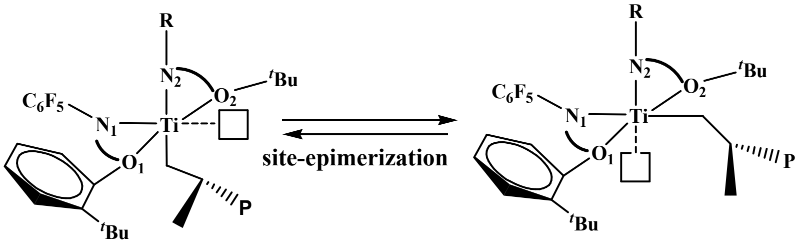


Fig. 5 Plots of syndiotacticity (rrrr%) of polypropylenes obtained by catalysts **1a-e** with MMAO or dMAO as cocatalysts at 0°C.



Scheme 2 The scheme illustrating site epimerization during propylene polymerization (R= Ar).

Table 3. Pentad distribution of the polypropylenes produced with catalysts **1a-1e** at different temperatures[a]

entry	Cat.	Temp	Pentad distribution (%)[b]									T_m[c]
		(°C)	mmmm	mmmr	rmmr	mmrr	rrmr+mmrm	rmrm	rrrr	rrrm	mrrm	(°C)
1	**1a**	0	0	0	0	0	5.8	0	88.5	5.7	0	134.5, 117.0
2	**1b**	0	0	0	0	0	5.4	0	89.3	5.3	0	139.3, 135.2
3	**1c**	0	0	0	0	0	4.6	0	90.8	4.6	0	139.0, 135.5
4	**1d**	0	0	0	0	0	4.2	0	91.6	4.2	0	139.5, 126.8
5	**1a**	40	1.4	2.7	0.7	3.0	11.9	9.4	54.8	11.4	4.7	88.2, 65.0
6	**1a**	55	5.8	8.7	6.4	10.7	17.8	11.3	23.5	10.8	5.0	n.d.[d]
7	**1e**	-10	0	0	0	0	1.0	0	98.0	1.0	0	146.7, 135.8
8	**1e**	0	0	0	0	0	1.4	0	97.2	1.4	0	146.2, 135.8
9	**1e**	10	1.2	0	0	0	1.7	0	94.5	1.6	0	136.2, 133.2
10	**1e**	25	1.4	0.6	1.7	1.8	5.9	2.2	77.0	5.4	4.0	103.8, 92.9
11	**1e**	40	3.2	1.1	1.9	3.8	14.3	2.9	58.5	10.9	3.4	89.6, 65.7
12	**1e**	55	6.6	6.9	4.3	7.2	18.5	10.3	21.8	18.1	6.3	n.d.

[a] Polymerization conditions: 10 μmol catalyst, solvent 50 mL toluene, propylene pressure 6 bar; MMAO was used as co-catalyst, Al/Ti = 500, reaction time 2h. [b] Pentad distribution of the polypropylenes were determined by ^{13}C NMR spectroscopy. [c] Determined by DSC with a heating rate of 10°C/min from -50 –180°C. [d] Not determined.

It is interesting to note that the monomer insertion sequence in the polymer was also greatly dependent upon the reaction temperature as shown in **Figure 6**. For the assignments P designates a primary carbon, S a secondary carbon, and T a tertiary carbon followed by Greek subscripts indicating the position relative to the nearest tertiary carbons in both directions along the polymer chain. The main structure feature in ^{13}C NMR spectra is the normal 1,2-propylene insertion at

19.5-22.0 ppm correspond to methyl carbons. The main methane and methylene resonances are present at 28.2-28.9 ppm and 46.3-46.9 ppm, respectively. Other resonances can be attributed to regio-irregularities. The probable formation routes of the regio-irregular units of polypropylenes were shown in **Scheme 3**. The signals at 30.5 ppm ($T_{\beta\gamma}$) assignable to tail-to-tail units were observed in the spectra of the polymer obtained at reaction temperature higher than 10°C (**Figure 6b-e**), which likely occurred *via* a 1,2-insertion of propylene and followed by 2,1- and 1,2-insertion (**Scheme 3C**) or successive 2,1-insertion(**Scheme 3D**). Further increase the polymerization temperature to 40 or 55°C led to the presence of more regio-irregularity units as shown in **Figure 6d-e**. For example, the peaks at 15.05 ppm ($P_{\alpha\beta}$) and 35.0 ppm ($T_{\alpha\beta}$) assigned to head-to-head propylene units were detected, which arise from the process of successive 2,1-insertion following 1,2-insertion of propylene (**Scheme 3B**). The resonances at 29.90 ppm ($S_{\delta\delta}$) originated from the process of 1,2-insertion of propylene followed by successive 3,1-enchainment. Regioerrors of 3,1-enchainment occur *via* a 2,1-insertion of propylene, followed by β-H elimination and reinsertion of the resultant unsaturated polymer chain to give a methylene $(-CH_2-)_3$ linkage (**Scheme 3E**). Such a 3,1-enchainment is probably similar to a two-step mechanism proposed by Chien.[21] β-H was first transferred from the methyl group of last (secondary) inserted unit to metal and the coordinated α-olefin end group was rotated from secondary to primary; and then reinserted to the metal-hydrogen bond.[21] This mechanism was in agreement with similar conclusions of many other authors, which is different from the typical chain-walking mechanism prevalent with late transition catalysts with Pd and Ni as metals.[22] Obviously, there are no or minor errors when the polymerization temperature is lower than 25°C. However, the percentage of 3,1- and 2,1-insertions of propylene approximately increase up to 4.8% and 4.3% with the reaction temperature of 55°C, respectively. Similar results were also observed in the ^{13}C NMR spectra of PPs obtained by **1a-d**/MMAO catalyst systems as shown in Figure **6f-g**. The possible explanation was that higher reaction temperature not only provided enough activation energy necessary for the occurrence of 2,1-insertion of propylene, but also sped up the chain transfer reactions such as β-H elimination leading to the formation of polymers with unsaturated chain end as reactants of 3,1-insertion.

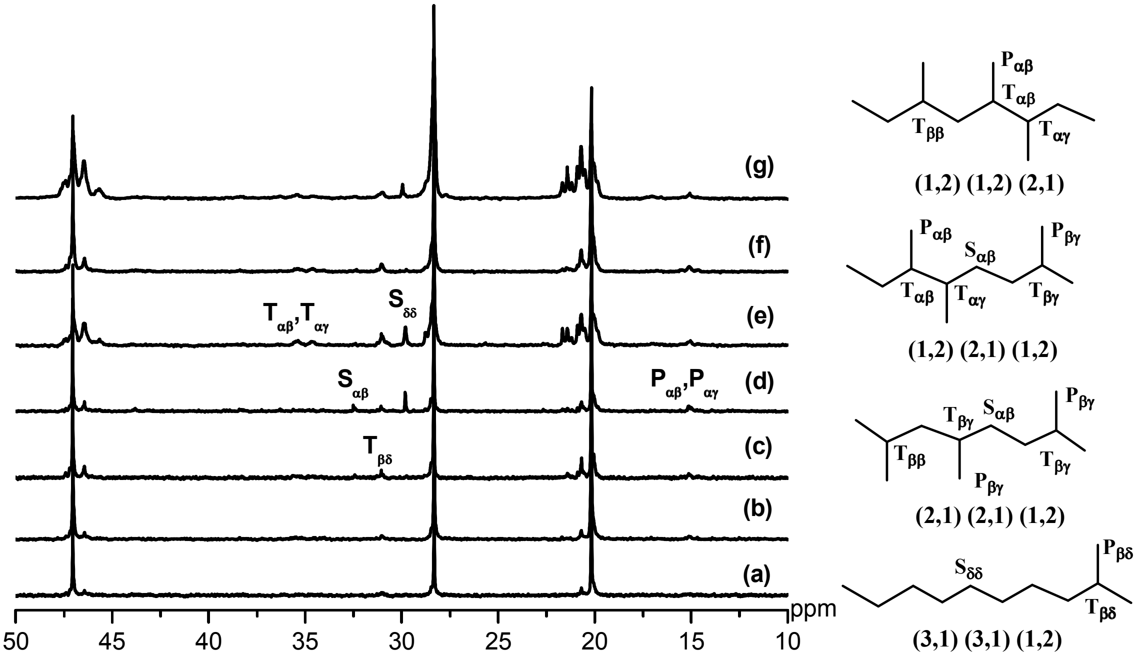
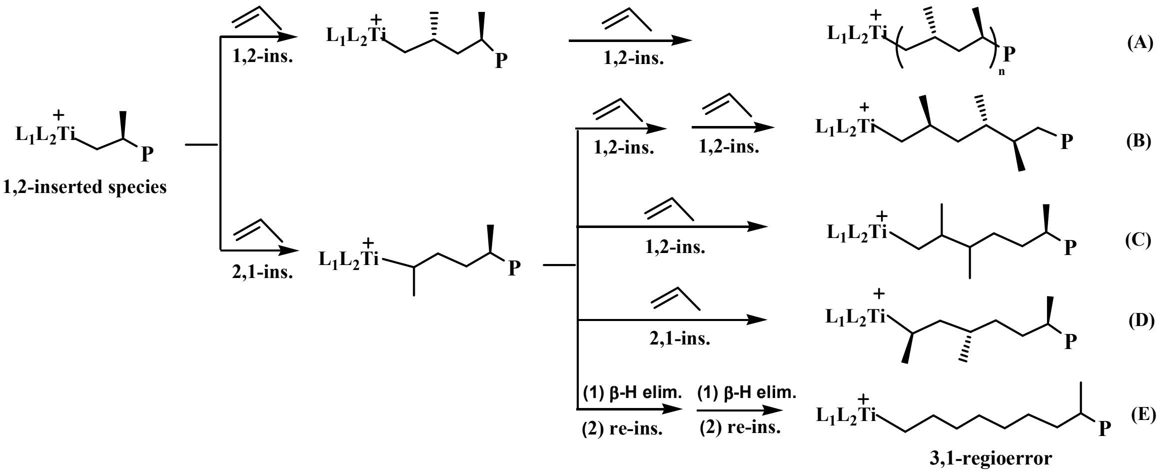


Fig. 6 The aliphatic region of ^{13}C NMR spectra for PPs obtained by **1e**/MMAO catalyst system at -10°C (a), 10°C (b), 25°C (c), 40°C (d), 55°C (e) and PPs obtained by **1a**/MMAO system at 40°C (f) and 55°C (g), respectively. The structures of the regio-irregular sequences in polypropylene and their assignments in ^{13}C NMR spectra were included.



Scheme 3. Formation of syndiotactic PP and region-irregular sequences in PPs.

To understand the role of activators on the stereospecificity of propylene polymerization, the stereospecificity of a given catalyst with the variation of the cocatalysts were investigated. Typical ^{13}C NMR spectra of their resultant PPs were shown in **Figure 7**. It is observed that the rrrr-pentad values of the PPs obtained by catalyst **1a** decreased from 90.2% and 88.5% to 42.5%, when dried MAO or MMAO were replaced by dried MMAO. The strong dependence of the stereoselectivity on the nature of the cocatalysts implies that the nature of the ion pairs formed in the activated complexes has a relatively strong influence on the polymerization behavior of these catalyst systems. The ion-pair might influence (1) the relative population and/or activity of accessible active centers or (2) the relative rate of site epimerization (conformations interconversion) relative to that of polymer chain propagation. Since the productivities are comparable (entry 1, 6, 7 *vs* entry 5, 7, 9) with these three cocatalysts for a given complex, this may imply a relatively lower rate of site epimerization with dMAO or MMAO. Because of their less congested structures, the interaction of the anions $[Me\text{-}AlMe_2]^-$ from MMAO solution or $[Me\text{-}MAO]^-$ with the titanium cation $[R_1R_2TiP]^+$ might be stronger than that of $[Me\text{-}MMAO]^-$ or free $^iBu_3Al$ from dried MMAO (**Scheme 4**). The corresponding coordination site even might possibly be occupied by $AlMe_3$ or $[Me\text{-}MAO]^-$ before the next propylene insertion,[23] which could better inhibit the positionally change of the polymer chain (site epimerization) and thus suppress the production of diads *m*. In addition, the loose contact of the titanium and the dMMAO anions would make the propylene easier to replace the AlR_3 ligands and thus led to slightly higher polymerization activity, consistent with the propylene polymerization results (60.0 *vs* 48.0 kg/mol·h). Similarly, the syndiotacticity of the polymers obtained by complex **1e** also showed a decrease trend from 98.0% and 97.2% to 72.5%, when dried MAO or MMAO were replaced by dried MMAO. Importantly, complex **1e** displayed much higher syndiotacticity (72.5% *vs* 42.5%) than the less congested complex **1a** in the presence of dried MMAO as a cocatalyst (**Figure 6**). It can be attributed to the bulk of the bromine atom of complex **1e**, which far exceeded that of hydrogen atom of complex **1a**. The much congested structure could further suppress the occurrence of site epimerization and formation of stereoerrors. One can conclude that the introduction of bulky substituents to these titanium complexes not only can provide better protection of active site from attack of cocatalyst anion, but also can retard the positionally change of the polymer chain without monomer insertion and thus improve the syndiotacticity of the resultant polypropylenes, irrespective of the cocatalysts employed.

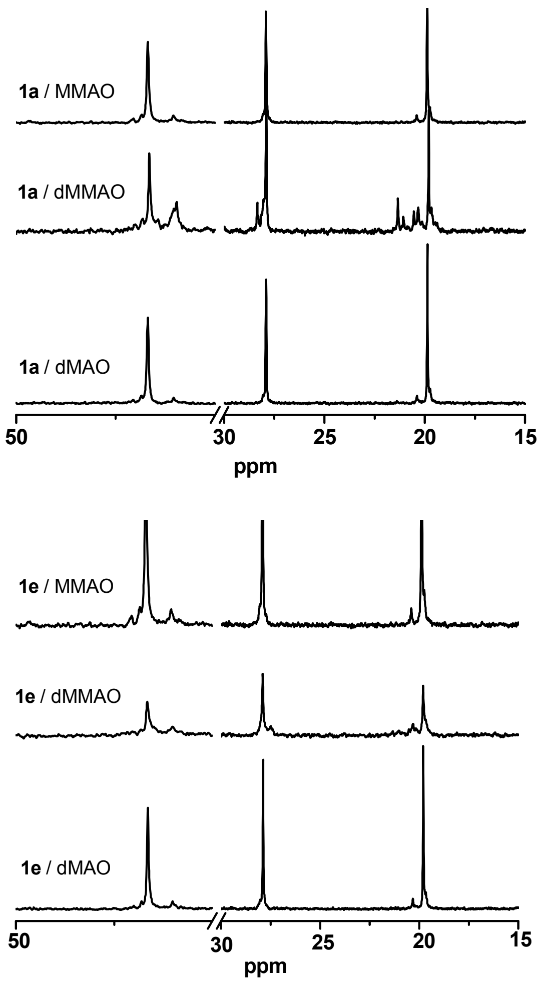
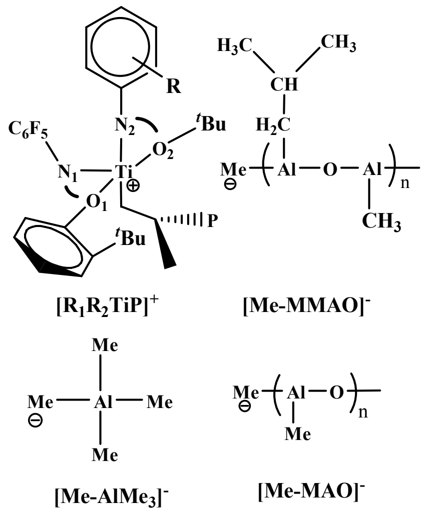


Fig. 7 The aliphatic region of ^{13}C NMR spectra for polypropylene catalyzed by complex **1a** and 1**e** with different cocatalysts at 0°C and the same Al/Ti mole ratio of 500.



Scheme 4 The possible interaction between active species and the anions formed by dried MMAO (top right), free $AlMe_3$ in the MMAO (bottom left), dried MAO (bottom right) before the next propylene insertion.

Conclusions

A series of sterically encumbered C_1-symmetric (salicylaldiminato)(β-enaminoketonato)titanium complexes were synthesized and used as the catalysts for propylene polymerization in combination with MMAO, producing highly syndiotactic polymers (*rrrr* ≥ 88.5%) with high molecular weights and narrow molecular weight distributions at room temperature. The introduction of bulky substituents to N-aryl group of β-enaminoketonato ligand not only can greatly improve the syndiospecificity, but also can better suppress chain termination and chain transfer reactions. Notably, the most sterically congested complex **1e** with bromine atom ortho N-aryl group was able to initiate living polymerization, affording polypropylenes with the pentad syndiotacticity (*rrrr*) up to 98.0%. ^{13}C NMR characterization of the polymer provides the evidence that the stereoselectivity in the propagation sequence arise as a result of end chain control, predominantly *via* 1,2-insertion of propylene. In addition, polymer ranging from highly syndiotactic and regio-regular to atactic and regio-irregular at different reaction temperatures could be achieved. As far as we know, this is the first non-metallocene system with such high syndiospecificity and catalytic activity for living propylene polymerization *via* 1,2-insertion of monomer. This highly active living polymerization system offers the opportunities for design of various polyolefin architectures. Furthermore, this example gives a deeper understanding of the correlation between ligand structure, reaction temperature, activators and polymer microstructure. Further studies on developing more robust living α-olefin polymerization system for production of polymers without regio- and stereo-irregularities especially at high reaction temperature would be desirable.

Experimental part

Materials

The $TiCl_4$ and Me_3SiCl were purchased from Aldrich. Patassium hydride KH (40% mineral oil suspension) was purchased from Aldrich and washed with light petroleum. Modified methylaluminoxane (MMAO, 7 wt% aluminum in heptane solution with about 20 mol% of free $AlMe_3$ and 3.3 mol% of free $^{i}Bu_3Al$) and methylaluminoxane (MAO, 8 wt% aluminum in toluene solution with about 21 mol% of free $AlMe_3$) were purchased from Akzo Nobel Chemical Inc. Dried MAO was prepared from its toluene solution according to the following procedure. Me_3Al was removed from the toluene solution of pure MAO by evaporating the solvent and volatile Me_3Al

under vacuum for 4 hours. The remaining Me_3Al was removed by means of washing with hexane for 3 times, and the solid part was dried under vacuum to obtain a white powder called dried MAO without free Me_3Al. Me_3Al and $^iBu_3Al$ were removed from the toluene solution of MMAO according to the following procedure. The toluene solution of MMAO (150 ml) was dried under vacuum for 6 h at room temperature to evaporate solvent, Me_3Al and $^iBu_3Al$. The solid residue was dissolved in heptane (200 ml) and then was evaporated under vacuum again. This procedure was repeated 5 times to give a white powder (called dried MMAO) with about 0.5 mol% free $^iBu_3Al$ remained after these purification procedures. Commercial propylene was directly used for polymerization without further purification. The other reagents and solvents were commercially available. All manipulation of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from MBraun solvent purification system (SPS).

Characterization

The NMR data of the ligands and complexes used were obtained on a Bruker 400 MHz spectrometer (400.1 MHz for ^1H, 100.6 MHz for ^{13}C) at ambient temperature, with $CDCl_3$ as the solvent (dried by MS 4Å). The NMR data of the polypropylene were obtained on a Varian Unity-400 MHz spectrometer at 135 °C, with $o\text{-}C_6D_4Cl_2$ as a solvent. Elemental analyses were recorded on an elemental Vario EL spectrometer. The DSC measurements were performed on a Perkin-Elmer Pyris 1 Differential Scanning Calorimeter at a prescribed rate. The weight-average molecular weight (M_w) and the polydispersity index (PDI) of polymer samples were determined at 135ºC by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

Procedure for propylene polymerization

Propylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. Prescribed amount of toluene and cocatalyst (MMAO, dried MAO or dried MMAO) were charged into the autoclave in sequence in the glovebox. The autoclave was placed under propylene atmosphere (1 bar). After the addition of a toluene solution containing a prescribed amount of catalyst via a syringe, the reactor was sealed and pressurized to the desired level, and then the stirring motor was engaged. After the prescribed reaction time, the stirring motor was stopped and the reactor was ventilated, and the resulted mixture was added to acidic ethanol. The solid polymer was isolated by filtration, washed with ethanol, and dried at 60 °C for 12 h in *vacuo*. The post-polymerization was carried out using the same type of equipment. The first-step polymerization was conducted for 2 hour. Then, the propylene gas feed and the stirring were stopped, while the resultant toluene solution was kept under N_2 for 30 min. The second-step was started later with the adding of the propylene gas, and was continued for another 1 hour. The polymerization was terminated with acidic ethanol. The polymers obtained were adequently washed with methanol and dried under vacuum at 60 °C for 12 h.

Synthesis of titanium catalysts

The titanium complexes **b-e** were synthesized according to the procedures reported previously.[11]

$[3\text{-}^t\text{Bu-2-OC}_6\text{H}_3\text{CH=N(C}_6\text{F}_5)][(o\text{-BrC}_6\text{H}_4)\text{N=C(CF}_3)\text{CHC(}^t\text{Bu)O]TiCl}_2$ (e). To a solution of compound $3\text{-}^t\text{Bu-2-OC}_6\text{H}_3\text{CH=N(C}_6\text{F}_5)$ (0.69 g, 2 mmol) in dried tetrahydrofuran (20 mL) at −78°C was added a 2.5 M n-butyllithium hexane solution (0.8 mL, 2 mmol) dropwise over 5 min. The mixture was allowed to warm to room temperature and stirred for 4 h, affording a yellow solution. Then, at 0°C $(CH_3)_3SiCl$ (4 mmol, 0.5mL) was added dropwise over 3 min and stirred for 18 h, the formed colorless solution was concentrated and added dried toluene 15 mL, then filtered. The colorless filtrate was added dropwise to a toluene solution of $TiCl_4$ (2 mmol) at 0°C, and allowed to warm to room temperature, then evaporated under reduced pressure after stirred for 12 h to afford a solid residue, which was needed to be recrystallized with dichloromethane and hexane to form dark red solid $[3\text{-}^t\text{Bu-2-OC}_6\text{H}_3\text{CH=N(C}_6\text{F}_5)]\text{TiCl}_3\text{(THF)}$. Thereupon, a solution of $[3\text{-}^t\text{Bu-2-OC}_6\text{H}_3\text{CH=N(C}_6\text{F}_5)]\text{TiCl}_3\text{(THF)}$ (0.78 g, 1.4 mmol) in dichloromethane (10 mL) at -78°C was treated with $(o\text{-BrC}_6\text{H}_4)\text{N=C(}^t\text{Bu)CHC(CF}_3)\text{OK}$ (0.55 g, 1.4 mmol). The reaction mixtures were allowed to warm slowly to room temperature and stirred for 20 h, affording a dark red solution. The solution was filtered to remove KCl and the isolated product was concentrated. Purification by precipitation from dichloromethane/hexane at room temperature gives the desired complex a dark red power in 50% yield. ^{1}H NMR ($CDCl_3$, 20 °C): δ 8.30 (d, 1H, CH=N), 7.41-7.49 (d, 1H, Ar), 7.26-7.30 (d, 1H, Ar), 7.13-7.17 (d, 1H, Ar), 6.87-6.95 (m, 1H, Ar), 6.73-6.83 (m, 3H, Ar), 6.16-6.22 (d, 1H, CH), 1.34 (s, 9H, *t*-Bu), 1.18 (s, 9H, *t*-Bu). ^{13}C NMR (100.6 MHZ, $CDCl_3$, 20°C): δ 196.9, 173.2, 168.1, 154.5, 146.3, 141.5, 138.5, 136.7, 134.2, 128.5, 127.1, 126.4, 126.1, 125.6, 122.7, 122.0, 121.3, 117.5, 96.2, 95.5, 73.0, 40.6, 35.2, 30.1, 27.4. Anal. Calc. for $C_{31}H_{27}BrCl_2F_8N_2O_2Ti$: C 45.95, H 3.36, N 3.46. Found: C 45.97, H 3.37, N 3.33. EI-MS: m/z = 823 (M^+).

DFT studies

Density functional theory (DFT) calculations was employed as a tool for analyzing the chain termination mechanism using the Amsterdam Density Functional (ADF) program package.[24] The structures and energies were obtained based on the local density approximation augmented with Becke's nonlocal exchange corrections[25] and Perdew's nonlocal correlation correction.[26] A triple STO basis set was employed for Ti, while all other atoms were described by a double-ζ plus polarization STO basis. The 1s electrons of the C, N, O and F atoms as well as 1s-2p electrons of Ti atom were treated as frozen core. The first-order scalar relativistic corrections were added to the total energy of the system. DFT calculations were combined with molecular mechanics calculations by using the quantum mechanics/molecular mechanics (QM/MM) implementation in the ADF program.[27] The CF_3 and Ph on the β-enaminoketone ligand, as well as with ^{t}Bu and C_6F_5 on salicylaldiminato ligand, were represented by a augmented Sybyl force field[28] which includes van der Waals parameters from the UFF forces field for titanium.[29]

Acknowledgments

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produced polypropylenes with the highest syndiotacticity (96.0%), according to the literatures by Coates (*Angew. Chem. Int. Ed.* 2002, **41**, 2236-2257) and Fujita (*Accounts Chem. Res.* 2009, **42**, 1532-1544). In addition, the same experiment with this catalyst system has been performed under the same conditions, in which similar results have been obtained and shown in entry 20 of Table 2.

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predominantly from regular alternating sites of the catalysts and thus the system behaves syndiospecifically. Whereas, at higher reaction temperatures and lower propylene concentration, the second-order chain propagation process slows and unimolecular site epimerization becomes competitive, thus stereo-irregularities (isotactic units) are produced.

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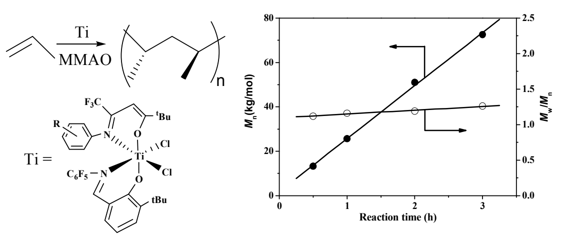
Graphical Abstract (for table of contents use only)

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

Ying-Yun Long, Yong-Xia Wang, Bai-Xiang Li, Yan-Guo Li, Yue-Sheng Li



[*rrrr*] up to 98.0%, PDI = 1.12-1.26, high activity

On activation with MMAO, the newly designed sterically congested titanium complex with bulky substituent *tert*-butyl and bromine atom promotes living polymerization of propylene with high catalytic activity, affording highly syndiotactic (*rrrr* 98.0%) polymers with high molecular weights and narrow molecular weight distributions ($M_w/M_n \leq 1.26$), *via* propagation of 1,2-insertion of monomer and chain-end control mode.