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Substituent Effects on Silicon of Bridged Tetramethylcyclopentadienyl−Phenoxy Titanium Complexes for Controlling the Regiochemistry and Molecular Weight in 1-Olefin Polymerization

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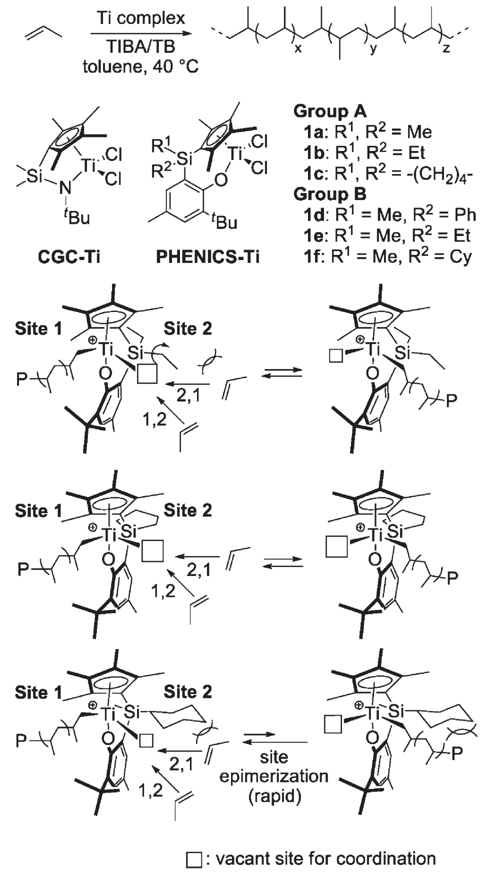
Single-site polymerization catalysts have attracted great interest in terms of their highly controllable polymerization performance based on precise design of catalyst architecture and their industrial applications.[1] Among them, CGC (constrained geometry catalyst)[2,3] and PHENICS (phenoxy-induced complex of Sumitomo),[4] which are half-metallocene catalysts with an anionic armed-pendant, have been well developed for industrial production of copolymers of ethylene and 1-olefins. Modification at the cyclopentadienyl ring system has been mainly tuned to finely control polymerization behaviors such as activity, molecular weight, and regiochemistry.[5] In general, minimizing 2,1-insertion is essential to obtain high molecular weight polyolefins; otherwise, facile β-elimination occurs, leading to termination of chain growth. Thus, the largely open coordination sites of half-metallocene catalyst systems possess an indispensable problem of irregularity in propagation. Through tuning bulkiness of substituents on the bridged-silicon unit of PHENICS−Ti, we demonstrated that 2,1-insertion of propylene was controlled by the bridging substituents to produce high molecular weight polypropylene (PP), and additionally found reasonable correlation between M_w and 2,1-content of PP.

To begin our studies, a series of PHENICS−Ti bearing various bridging groups $R^1R^2Si(\eta^5\text{-}C_5Me_4)(3\text{-}^tBu\text{-}5\text{-}Me\text{-}2\text{-}C_6H_2O)TiCl_2$ (Scheme 1: **1b**−**f**) were prepared, following a similar procedure previously described for **1a**.[4c] To investigate the influence of the bridging silylene group of PHENICS−Ti, polymerization of propylene was conducted because regio- and stereochemistry of propylene polymerization reaction could be easily estimated based on information of the resulting PP microstructure.[6,7] The results of polymerization catalyzed by **1a**−**f** and $Me_2Si(\eta^5\text{-}C_5Me_4)(^tBuN)TiCl_2$ (CGC−Ti: **2**) activated with $^iBu_3Al/Ph_3C[B(C_6F_5)_4]$ (TIBA/TB) are summarized in Table 1. All PHENICS−Ti similarly exhibited high polymerization activities, and generally afforded high molecular weight PP. It is obvious that bridging substituents have strong influence on the polymer M_w values, as there is no difference except for the bridging moiety in the ligand structure of **1a**−**f**. These PHENICS−Ti can be divided into two groups by their substituted pattern on bridging silylene moieties: one group consisting of symmetrically substituted silylene complexes (Group A: **1a**−**c**), and the other of unsymmetrically substituted ones (Group B: **1d**−**f**). In group A, Et_2Si-bridged complex (**1b**) was found as the best complex to afford the highest M_w value (entry 2), whereas introduction of cyclic structure into the bridging moiety causes a significant drop in the M_w value (entry 3). Among the MeR^2Si-bridged complexes (group B and **1a**), **1f** gave the highest molecular weight PP (entry 6), and the value of M_w is decreased with the size of R^2 (Cy ≫ Et > Ph > Me).

Scheme 1



In the ^{13}C NMR spectra of the PP (Figure 1), there are isolated resonances assignable to primary CH_3 carbons ($P_{\alpha\beta}$ and $P_{\alpha\gamma}$) and tertiary CH carbons ($T_{\beta\gamma}$) resulting from 2,1-insertion of propylene. The percentage of 2,1-insertion was calculated from eq 1 depicted in Figure 1.[8] Notably, the values of 2,1-% as well as M_w were controlled by bridging substituent. Among them, highest value of the 2,1-% (17.8%) was obtained using **1c** as a precatalyst (Figure 1a).[9] The 2,1-% was significantly reduced by introducing bulky cyclohexyl (Cy) group at bridged silicon atom (Figure 1c). Although reported values of 2,1-insertion using **2** as a catalyst precursor were low (up to 2.2%),[10] relatively high degree of 2,1-content (9.8%) was observed under our tested polymerization conditions (Figure 1d). Different from directly bridged cyclopentadienyl−phenoxy complex $[2\text{-}(\eta^5\text{-}C_5Me_4)\text{-}4,6\text{-}^tBu_2\text{-}C_6H_2O]TiCl_2$,[11] the ^{13}C NMR spectra obtained by PHENICS−Ti catalysts showed no peaks around 25 ppm and 28 ppm assignable to 1,3-enchainment after 2,1-insertion.[12] The results that the PP samples obtained with PHENICS−Ti catalyst systems are almost completely atactic (Table 1 and Figure S1).[13] Discussion regarding propylene insertion mechanisms based on pentad distributions

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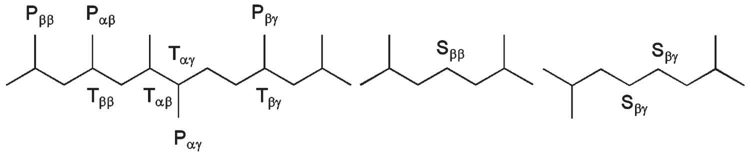
Table 1. Polymerization of Propylene Using 1a−f and 2 Catalyst Systems with TIBA/TB[a]

						triads (%)			pentads (%)								
entry	complex	act[b]	M_w[c] ($\times 10^3$)	M_w/M_n[c]	2,1-%[d]	*mm*	*mr*	*rr*	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*xmrx*	*mrmr*	*rrrr*	*rrrm*	*mrrm*
1	**1a**	554	1 250	1.5	14.3	12.5	49.9	37.5	2.11	4.26	5.43	8.47	24.19	18.03	8.68	16.70	12.14
2	**1b**	914	2 170	1.6	9.6	17.2	51.7	31.0	2.77	6.09	7.25	10.32	24.04	17.23	8.13	15.41	8.77
3	**1c**	1 510	645	1.6	17.8	11.7	48.5	39.7	1.67	3.64	5.08	10.40	19.19	19.67	9.05	16.78	14.51
4	**1d**	638	1 300	1.5	11.5	13.4	51.1	35.5	2.05	5.54	5.87	9.07	24.46	16.66	7.74	15.97	12.64
5	**1e**	1 390	1 340	1.6	9.9	14.9	51.6	33.5	1.58	5.96	6.29	10.46	23.50	18.01	7.53	15.41	11.27
6	**1f**	482	2 340	1.5	4.1	14.0	49.2	36.8	2.22	5.18	5.92	9.72	25.24	14.72	12.23	16.14	8.63
7	**2**	120	797	1.5	9.8	13.9	47.9	38.2	2.11	6.49	5.84	10.03	20.52	18.37	8.59	16.33	11.73

[a] Conditions: toluene 150 mL, propylene 0.2 MPa, complex 0.05 μmol, TIBA 60 μmol, TB 0.5 μmol, initial polymerization temperature 40 °C, and polymerization time 5 min. [b] In kg of PP/(mmol of Ti·h). [c] Determined by GPC with polystyrene standards. [d] Percentage of 2,1-insertion determined by ^{13}C NMR.



$$\text{2,1-content (\%)} = \frac{[T_{\beta\gamma}]}{[T_{\beta\beta}] + [T_{\beta\gamma}] + [T_{\alpha\beta}] + [T_{\alpha\gamma}]} \times 100 \qquad (1)$$

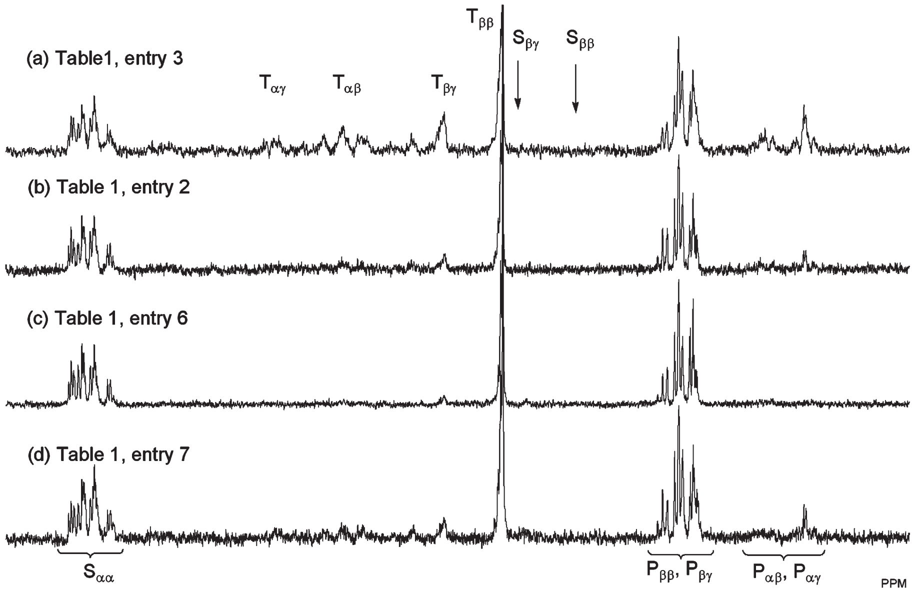


Figure 1. ^{13}C NMR spectra of polypropylene samples obtained by (a) **1c** (2,1-content = 17.8%), (b) **1b** (2,1-content = 9.6%), (c) **1f** (2,1-content = 4.1%), and (d) **2** (2,1-content = 9.8%).

are difficult because of considerably high ratio of regioirregular insertions. In the ^{1}H NMR spectra of the PP, there are resonances at δ 4.74 and δ 4.67, attributed to vinylidene end-group arising from β-hydride elimination after a 1,2-insertion, and around δ 5.30, attributed to 2-butenyl end group arising from that after a 2,1-insertion (Figure S2).[9] It was difficult to determine end-group by ^{1}H NMR analysis of the PP because these intensities are too weak due to high molecular weight.

It is generally accepted that once 2,1-insertion occurs, the rate of insertion of the next monomer is reduced, leading to termination of chain growth.[14,15] Although a relatively high degree of 2,1-insertion was observed in polymerization of **1a−f**, the M_w value of PP is generally high, indicating PHENICS−Ti allows insertion of the monomer even after 2,1-insertion. In light of the results, we found a linear correlation between 2,1-insertion and M_w of PP in groups A and B, respectively (Figure 2). The M_w value of PP increases with decrease in 2,1-content.

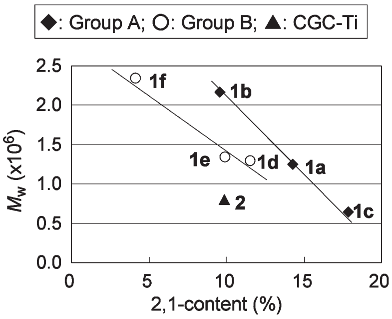


Figure 2. Correlation between 2,1-content and M_w of polypropylenes.

Following these polymerization studies, the key structures of **1b**, **1c**, and **1f** were determined by X-ray analyses for considering the relationship between the molecular structure of PHENICS−Ti and resulting PP microstructures. The molecular structures, selected bond lengths and angles, and the crystal data and data collection parameters are deposited in Supporting Information. The almost identical bond distances of Ti−Cl(1), Ti−Cl(2), Ti−Cp_{cent}, and Ti−O in **1b**, **1c**, and **1f** represents that these complexes essentially have electronically similar character around titanium.[4e] Interestingly, the dihedral angle (θ) between cyclopentadienyl ring and phenyl ring of **1b** (θ = 58.2°) is significantly smaller than those of the complexes **1a** (θ = 68.2°),[4e] **1c** (θ = 68.5°) and **1f** (θ = 68.4°).[16] The twisted structure of PHENICS−Ti is generated as the result of steric repulsion around the bridging silylene moiety.[17] In the structure of **1f**, the Cy group is positioned at the backside of Cl(2), indicating influence of the bulky Cy on one coordination site of **1f**.

A plausible mechanism of 2,1-insertion restriction for PHENICS−Ti is illustrated in Scheme 1. Two coordination sites of active species of the PHENICS−Ti are differentiated due to the twisted ligand architecture as observed in the crystal structure of the complexes. In the case of **1f** in Group B, the polymer main chain is probably situated on the opposite side of the bulky Cy group (site 1) during the polymerization. Once the polymer main chain is directed to the bulky Cy side (site 2), which generates a large monomer coordination site, rapid site epimerization of the polymer chain from site 2 to site 1 occurs to maintain a small coordination site.[18] When the approach of propylene occurs in site 2, the bulky Cy group hinders 2,1-insertion by steric repulsion. The bulkiness of the Cy group is also important to restrict 2,1-insertion. The relatively higher 2,1-insertion rates observed for **1d** and **1e** result in decrease of M_w. In the case of **1b** in Group A, ethyl substituents on the bridging group play a role in restriction of 2,1-insertion. The large torsion angle around the bridging group and rotation of the Si−C(23) bond contributes to direct the C(24) methyl group to the coordination site. On the contrary, **1c** possesses relatively large monomer coordination sites on both sides, because its bridging substituent is fixed upward by the cyclic structure, allowing more frequent 2,1-insertion and tending to cause decrease of M_w. The correlation between M_w and 2,1-content in group A complexes is attributed to the twisted structure around the bridging group, whereas in group B it is attributed to rapid site epimerization and bulkiness of the substituent on the bridging silicon atom.[19]

The mechanisms described above are also applicable to the copolymerization of ethylene and 1-hexene, where PHENICS ligand hampers 2,1-insertion of 1-hexene to yield high M_w copolymer (Table S3). Thus, the PHENICS−Ti system introduces 1-hexene into copolymer more efficiently than **2** under the same polymerization conditions. The tendency of M_w of the copolymer is in good accordance with that of PP. From observations of the microstructure of PP, **1b**, **1e**, and **1f** should effectively restrict the 2,1-insertion of 1-hexene, resulting in the formation of high molecular weight copolymers.

In conclusion, we found that the 2,1-content of PPs were controlled by the substituted pattern of the bridged-silicon of PHENICS−Ti catalysts to afford high molecular weight polypropylenes. In the case of propylene polymerization catalyzed by complexes with symmetric substituted ligands (group A), the dihedral angle between the cyclopentadienyl ring and the phenyl ring observed in the crystal structure of PHENICS−Ti is an important factor to control 2,1-insertion: smaller angles resulted in decreased 2,1-content, whereas 2,1-content of the PP generated by complexes with unsymmetrically substituted ligands (group B) was mainly controlled by the bulkiness of the substituent on the silicon atom. The proposed mechanisms are also applicable to the copolymerization of ethylene and 1-hexene, where PHENICS ligand hampers 2,1-insertion of 1-hexene to yield high molecular weight copolymer.

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Supporting Information Available: Text giving detailed experimental procedures including spectroscopic and analytical data, a scheme showing the preparation, figures showing NMR spectra of PPs and molecular structures, tables of crystal data for **1b**, **1c**, and **1f**, and results of ethylene/1-hexene copolymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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