CONTROL OF REGIOSPECIFICITY IN PROPENE POLYMERIZATION WITH SiO$_2$-SUPPORTED Cp*TiMe$_3$ CATALYSTS

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INTRODUCTION

Homogeneous polymerization catalysts composed of transition metals have been highly attractive in the last two decades because of their high activity and high selectivity for synthesis of well-defined polyolefins. Homogeneous catalysts, however, possess some disadvantages in industrial application. Heterogenization of homogeneous metallocene catalysts is required for applying them into recent gas phase polymerization processes. The heterogenization would also bring another privilege that bimolecular aggregation, which is one of the main deactivation processes in homogeneous catalysts, is suppressed. General approaches to the heterogenization of homogeneous catalysts are the following two methods: One is an active species-supported catalyst, and the other is an activator-supported catalyst. The active species-supported catalysts, however, seem to be more effective for the inhibition of bimolecular deactivation process. We have, therefore, directed our attention toward CpTiR$_3$-type complexes as supported species and SiO$_2$ as a supporting carrier, because CpTiR$_3$ easily reacts with surface hydroxyl groups to form CpTiR$_2$O- species accompanied by the elimination of

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alkane. The titanium species on a carrier then can be activated by extracting one of the remaining alkyl ligands with a suitable Lewis acid. In addition, it has already been reported that $CpTiR_3$ complexes gave polyolefins with high activity when combined with $B(C_6F_5)_3$.[1−6]

Control of regio- and stereospecificity of homogeneous and supported metallocene catalysts has been achieved by the improvement of ligand structure.[7, 8] Control of the catalytic specificities by supporting carrier are rarely reported. In this paper, an attempt was made to prepare supported catalysts for propene polymerization based on $Cp*TiMe_3$ ($Cp* = \eta^5$-C_5Me_5) and SiO_2, and surface modification of SiO_2 with dialkyldichlorosilanes were found to be effective to control the regiospecificity of the catalyst. This paper reports the preliminary results of propene polymerization with these SiO_2-supported $Cp*TiMe_3$ catalysts.

EXPERIMENTAL

Materials

Trioctylaluminum (Oct$_3$Al) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) were provided by Tosoh-Akzo Co., Ltd. and Asahi Glass Co., Ltd., respectively, and used without further purification. Research grade propene (98%) (Takachiho Chemicals) was purified by passing through columns of NaOH, P_2O_5, and molecular sieves 3A, followed by bubbling through a $NaAlH_2Et_2$/1,2,3,4-tetrahydronaphthalene solution. Toluene and heptane were dried with sodium/benzophenone under nitrogen atmosphere. SiO_2 (donated from Fuji Silysia Co., Ltd., P-10, 36.0 μm of diameter, 281 m^2/g of surface area) was calcinated at 300°C for 6 hours before use.

Pentamethylcyclopentadienyltrimethyltitanium ($Cp*TiMe_3$) was synthesized according to the literature.[6]

Preparation of SiO₂-Supported Cp*TiMe₃ Catalysts

To a suspension of SiO_2 (4.57 g) in toluene (50 mL) was added Me$_2$-SiCl$_2$ (0.6 mL, 4.9 mmol) in 50 mL of toluene, and the reaction mixture was refluxed for 6 hours. The resulting SiO_2 was separated by filtration and washed 3 times with 50 mL of toluene. Then, to the SiO_2 in 50 mL of toluene was added an aqueous solution of sodium hydrogencarbonate (1.0 N, 0.14 mL), and the mixture was kept stirring at room temperature for 6 h. The solid part was separated by filtration and washed 3 times with 50 mL of toluene, followed by drying under vacuum at 120°C to obtain modified SiO_2.[10] Ph$_2$SiCl$_2$-modified SiO_2 was prepared using the same method.

To a suspension of the unmodified or modified SiO_2 (1.30 g) in 10 mL of toluene was added a toluene solution of $Cp*TiMe_3$ (1.3 M, 1.0 mL) at

room temperature, and stirred for 1 hour. The solid part was separated by filtration, washed 4 times with 10 mL of toluene, followed by drying under vacuum at room temperature to obtain the SiO_2-supported catalyst.

The titanium content of the SiO_2-supported catalysts was 0.61 mmol/g-catalyst in the unmodified SiO_2-supported catalyst, 0.50 mmol/g-catalyst in the Me_2SiCl_2-modified SiO_2-supported catalyst, and 0.54 mmol/g-catalyst in the Ph_2SiCl_2-modified SiO_2-supported catalyst, respectively.

Polymerization Procedures

Polymerization was conducted in a 100-mL glass reactor equipped with a magnetic stirrer. After a measured amount of solvent was placed in the reactor, the solvent was saturated with an atmospheric pressure of propene. Oct_3Al and toluene suspension of supported catalyst were introduced into the reactor. Polymerization was started by introduction of $B(C_6F_5)_3$ as cocatalyst, and the temperature was kept at $-20°C$ during the polymerization. Polymerization was quenched by addition of HCl/MeOH. The polymer was washed several times with methanol and dried under vacuum at $60°C$ for 6 hours.

Analytical Procedures

The content of titanium in the supported catalysts was determined by colorimetry with a JASCO V-550 UV-vis spectrometer. A sample solution was prepared according to the literature.[11] Molecular weight and molecular weight distribution of polymers obtained were determined by gel permeation chromatography with a Waters 150CV at $140°C$ using o-dichlorobenzene as a solvent. $K = 7.36 \times 10^{-5}$, $\alpha = 0.75$ (for PS standard), and $K = 1.03 \times 10^{-4}$, $\alpha = 0.78$ (for PP samples) were employed as parameters for universal calibration. ^{13}C NMR spectra of polymers were recorded at $120°C$ on a JEOL GX-500 spectrometer operated at 125.65 MHz in pulse Fourier-Transform mode. The pulse angle was $45°$, and about 10,000 scans were accumulated in pulse repetitions of 5.0 s. Sample solutions were made with 1,1,2,2-tetrachloroethane-d_2 up to 10 wt%. The central peak of 1,1,2,2-tetracholoroethane (74.47 ppm) was used as an internal reference. Differential scanning calorimetry measurements were made on a Seiko DSC-220. Polymer samples (*ca.* 5 mg) were encapsulated in aluminium pans, preheated at $200°C$ for 5 minutes, cooled to $-50°C$ at $10°C$/min. The glass transition temperatures were determined at the midpoint of DSC curves.

RESULTS AND DISCUSSION

It was reported that homogeneous $Cp*TiMe_3/B(C_6F_5)_3$ catalyst produced polypropene in a living nature for a short time at $-45°C$.[3,4] Although

this homogeneous catalyst was reported to give a uniform polypropene even at $-20°C$, broad GPC curves were shown in polymers obtained at $0°C$. We have, therefore, investigated the propene polymerization with Cp*TiMe$_3$-based supported catalysts at $-20°C$ using $B(C_6F_5)_3$ as a cocatalyst in the presence of Oct$_3$Al. The results are summarized in Table 1. GPC curves of the polymers obtained with the homogeneous catalyst showed bimodal molecular weight distribution (Fig. 1). This result suggests that the homogeneous Cp*TiMe$_3$ catalyst is not uniform under the present conditions, although the uniform polymer was obtained in a short time polymerization (40−240 s) in the absence of Oct$_3$Al.[3, 4]

On the other hand, higher number average molecular weight and narrower molecular weight distribution were achieved with the unmodified SiO$_2$-supported catalyst compared with the homogeneous catalyst as shown in Fig. 1. Thus, the supported catalyst using unmodified SiO$_2$ was more homogeneous than the nonsupported catalyst, because the immobilization of Cp*TiMe$_3$ on SiO$_2$ probably prohibits the aggregation of titanium species. The polymers obtained with the modified SiO$_2$-supported catalysts (entry 3 and 4, Table 1) also showed the uniform GPC curves. These results support the effectiveness of the immobilization of Cp*TiMe$_3$ species on SiO$_2$ to keep the homogeneity.

The supported catalyst using SiO$_2$ modified with Me$_2$SiCl$_2$ showed the highest activity and the highest molecular weight among the catalysts employed. It is plausible that the monomer can coordinate easily to the titanium anchored on the surface through the -OSiMe$_2$O- spacer rather than the anchored on the unmodified SiO$_2$ because of less steric hindrance with SiO$_2$ surface (Sch. 1). The supported catalyst system modified with Ph$_2$SiCl$_2$ showed the lowest activity and gave polymers with the lowest molecular

Table 1. Results of Propene Polymerization with Cp*TiMe$_3$-Based Catalysts[a]

No.	Catalyst	Yield (g)	Activity (kg mol^{-1} h^{-1})	M_n^b ($\times 10^{-4}$)	M_w/M_n^b
1	Cp*TiMe$_3$[c]	0.60	10.0	4.6	6.7
2	Cp*TiMe$_3$/SiO$_2$[d]	0.54	9.0	5.7	5.0
3	Cp*TiMe$_3$/Me-SiO$_2$[e]	1.04	17.3	6.2	4.5
4	Cp*TiMe$_3$/Ph-SiO$_2$[f]	0.52	8.7	2.1	8.3

[a] Polymerization conditions: toluene = 30 mL, propene = 1 atm, $-20°C$, 1 h, Ti = 60 μmol, $B(C_6F_5)_3$ = 120 μmol, Oct$_3$Al = 0.6 mmol.
[b] Determined by GPC using universal calibration.
[c] In the absence of Oct$_3$Al.
[d] Unmodified SiO$_2$ was used as a carrier.
[e] SiO$_2$ modified with Me$_2$SiCl$_2$ was used as a carrier.
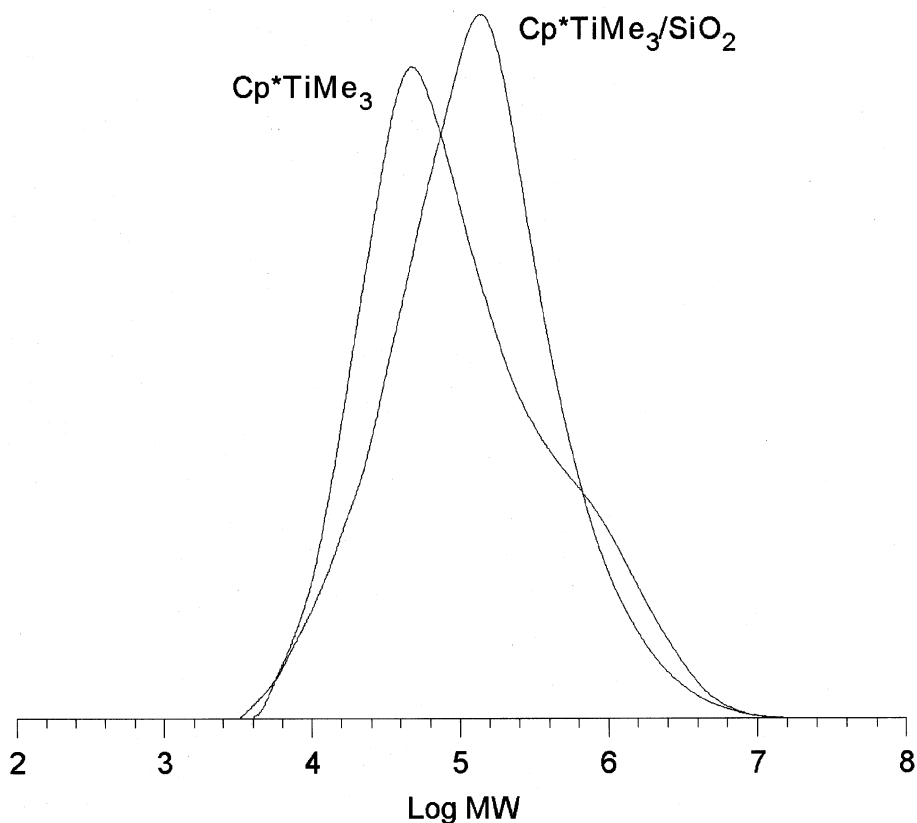[f] SiO$_2$ modified with Ph$_2$SiCl$_2$ was used as a carrier.

Figure 1. GPC curves of polypropenes obtained with Cp*TiMe₃ and Cp*TiMe₃/SiO₂ catalysts.

weight. These results can be interpreted by the above hypothesis: contrary to the dimethylsilyl group, the bulky diphenylsilyl group in the spacer prohibits monomer coordination. The above results imply that the nature of an active site such as propagation and chain transfer can be turned by the modification of SiO₂ surface.

Table 2 summarizes the microstructures of polypropenes determined from the ^{13}C NMR spectra shown in Fig. 2. In addition to the resonance of regioregular main chain carbons, the resonance of regioirregular structures were observed in some spectra. The content of chemical inversion was calculated by Eq. 1.

$$\text{Chemical inversion } (\%) = \frac{[T_{\beta\gamma}]}{[T_{\beta\beta}] + [T_{\beta\gamma}] + [T_{\alpha\beta}] + [T_{\alpha\gamma}]}$$

There were very few chemical inversions in the polymer obtained from the homogeneous system. In the supported systems, however, chemical
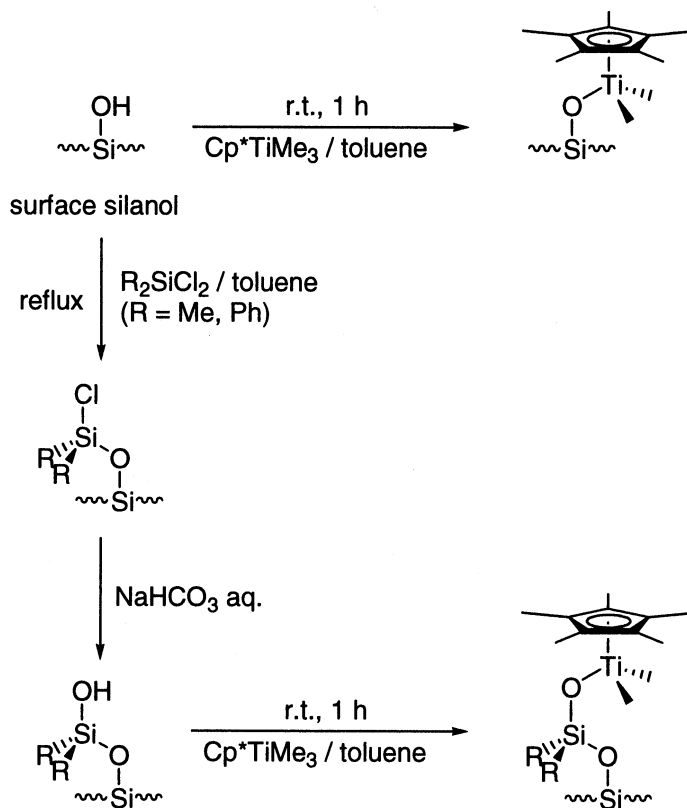
Scheme 1. Synthetic routes for the SiO_2-supported catalysts.

inversions were detected and increased in the following order: unmodified SiO_2 (6.0%) < Me_2SiCl_2-modified SiO_2 (10.5%) < Ph_2SiCl_2-modified SiO_2 (15.5%). The glass transition temperature was found to decrease according to the content of chemical inversion. We have previously reported that

Table 2. Microstructures of Polypropenes Obtained with Cp^*TiMe_3-Based Catalysts

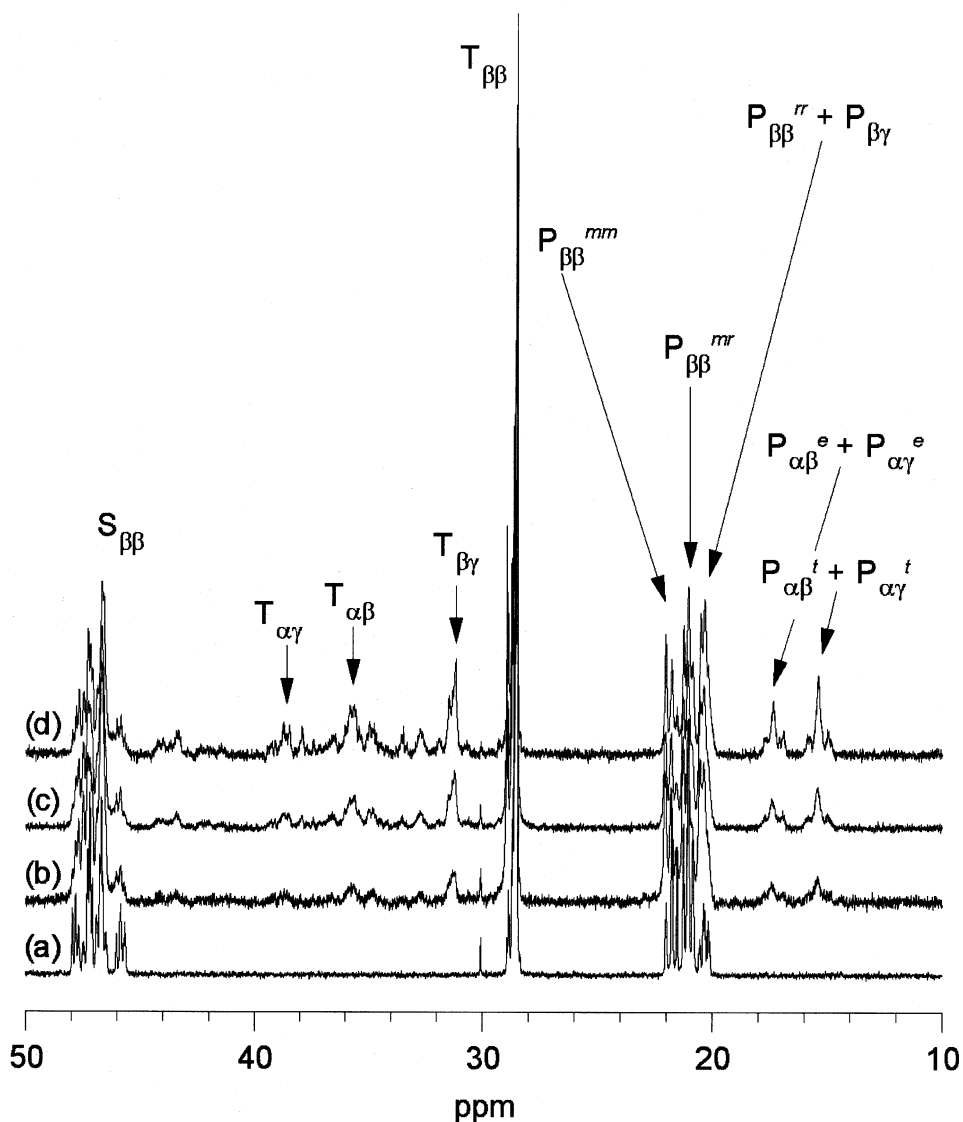| No.	Catalyst	Triad Tacticity (%)[a]			Chemical Inversion (%)[a]	T_g (°C)[b]
		[mm]	[mr]	[rr]		
1	Cp^*TiMe_3	28.7	53.0	18.3	0.1	− 5
2	Cp^*TiMe_3/SiO_2	30.0	41.8	28.2	6.0	− 10
3	$Cp^*TiMe_3/Me\text{-}SiO_2$	27.7	45.2	27.1	10.5	− 12
4	$Cp^*TiMe_3/Ph\text{-}SiO_2$	28.6	48.0	23.4	15.5	− 14

[a] Determined from 125 MHz ^{13}C NMR.
[b] Determined by DSC.

Figure 2. 125 MHz ^{13}C NMR spectra of polypropenes obtained with Cp*TiMe$_3$-based catalysts. (a) Cp*TiMe$_3$, (b) Cp*TiMe$_3$/SiO$_2$, (c) Cp*TiMe$_3$/Me-SiO$_2$, (d) Cp*TiMe$_3$/Ph-SiO$_2$.

polypropene obtained by SiO$_2$-supported CpTiCl$_3$ catalyst combined with various alkylaluminum compounds contained chemical inversion between 14−19%.[12] These results indicate that the regiospecificity of CpTiX$_3$-based catalysts can be controlled by the modification of SiO$_2$, as well as cocatalyst used.

Microtacticity of the polypropenes were also investigated by ^{13}C NMR, and the results are listed in Table 2. Syndiotactic triad increased in the

opposite order with that of the chemical reaction. Both anchoring on surface and introducing spacer were found to affect the regio- and stereospecificity of Cp*TiMe$_3$-based catalysts.

CONCLUSION

In summary, it was found that immobilization of Cp*TiMe$_3$ on SiO$_2$ enhanced the homogeneity and stability of active species, and the regio- and stereospecificity of the catalysts were conveniently turned by the modification of SiO$_2$.

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