# Effect of ligand in ethylene/styrene copolymerization by [Me$_2$Si(C$_5$Me$_4$)(NR)]TiCl$_2$ (R = *tert*-Bu, cyclohexyl) and (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$)-MAO catalyst system

Kotohiro Nomura[*], Hiroshi Okumura, Takashi Komatsu,
Naofumi Naga, Yukio Imanishi

*Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan*

## Abstract

Copolymerization of ethylene with styrene using linked cyclopentadienyl-amide titanium(IV) complexes, [Me$_2$Si(C$_5$Me$_4$) (R)]TiCl$_2$ [R = *tert*-Bu (**1**), cyclohexyl (**2**)], and non-bridged (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (**3**)-MAO catalysts have been explored. Although the catalytic activity by **2** was lower than **1**, **2** showed more efficient styrene incorporation than **1** under the same conditions. Moreover, the resultant copolymer prepared by **2** possessed completely different microstructure from those by **1**, indicating that the nature of amide ligand affects both styrene incorporation and monomer sequence.
© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Titanium; Ethylene/styrene copolymerization; Constrained geometry catalyst

## 1. Introduction

Olefin polymerization by homogeneous transition metal catalysis attracts particular attention in the field of organometallic chemistry, catalysis, and of polymer chemistry. Many efforts have thus been reported concerning this topic especially using early transition metal complexes [1]. We especially focused to *non-bridged* half-metallocene type group 4B transition metal complexes of the type, Cp′M(L)X$_2$ (Cp′ = cyclopentadienyl group; M = Ti, Zr; L = anionic ligand such as OAr; X = halogen, alkyl, etc.) [2–10], because we expected that this type of complexes would exhibit unique characteristics as olefin poly-

merization catalysts that would be different from both ordinary metallocene type and so-called 'constrained geometry' (hybrid 'half-metallocene') type catalysts [1d,1e,11–16] like [Me$_2$Si(C$_5$Me$_4$)(N$^t$Bu)]TiCl$_2$ (**1**). Another reason why we focused to this type is that the synthesis is not so complicated (shorter synthetic steps with relatively high yields), and that the modification of ligand moiety, L, sterically and/or electronically should be thus easier especially than the ordinary bridged-type complexes [2–17].

We have recently reported that non-bridged (cyclopentadienyl)(aryloxy)titanium(IV) complexes-MAO catalyst system exhibited unique characteristics not only for ethylene homopolymerization, ethylene/α-olefin copolymerization [2], but also for styrene homopolymerization, ethylene/styrene copolymerization [17]. The activity could be tuned only by replacing substituent on Cp′ group (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-

* Corresponding author. Tel.: +81-743-72-6041;
fax: +81-743-72-6049.
*E-mail address:* nomurak@ms.aist-nara.ac.jp (K. Nomura).

$^{i}Pr_2C_6H_3$) (**3**) was thus found to be effective for styrene polymerization, whereas $Cp^*TiCl_2$(O-2,6-$^{i}Pr_2$ $C_6H_3$) was quite effective for both ethylene/$\alpha$-olefin copolymerization and ethylene homopolymerization.

It was also revealed that **3** would be a useful catalyst for preparing ethylene/styrene copolymer with high styrene contents with uniform comonomer distribution (we confirmed the comonomer distribution (even with narrow molecular weight distribution by GPC) by cross-fractionation chromatography, and GPC-IR, e.g. see [18]), and that the microstructure for the resultant copolymer was different from that prepared by **1** [17]. We believe that this is one of the unique characteristics for this kind of catalysts. However, we do not have clear reason why polystyrene structure possessed in the copolymer was atactic, although styrene homopolymerization by **3** afforded highly syndiotactic polystyrene exclusively. This should also be an important question to consider the catalytically-active species for both styrene polymerization and ethylene/styrene copolymerization especially using half-titanocene catalysts (e.g. syndiospecific styrene polymerization by half-titanocene complex catalysts, see [19]; for review, see [20]; ethylene/styrene copolymerization by Cp$'$TiX$_3$ (X = Cl, benzyl, OPh, etc., see [21]; and ethylene/styrene copolymerization by bridged Cp-amide titanium catalysts, see [22]). In addition, precise control of both monomer sequence and stereospecificity by ligand modification in ethylene/styrene copolymerization has been a challenging subject, because electronic and/or steric nature of ligand should directly affect not only the insertion mode (2,1- or 1,2-insertion), but also the comonomer incorporation. One example for preparing alternating poly(ethylene-*co*-styrene) with well defined isotactic polystyrene structure by using $[Me_2Si(Flu)(N^tBu)]TiMe^+[B(C_6F_5)_4]^-$ under the specified conditions (e.g. molar ratio of styrene/ethylene: ca. 40 at 50 °C) has been known, but this complex showed less styrene incorporation than **1**, and the percentage of copolymer based on total polymer formed strongly depended upon polymerization temperature [22g]. Okuda and coworkers also showed the ligand effect in ethylene/styrene copolymerization with several linked Cp$'$-amide titanium and zirconium complexes (**1**, $[Me_2Si(C_5Me_4)(NCH_2Ph)]TiCl_2$, $[Me_2Si(Ind)(N^tBu)]TiCl_2$, $[Me_2Si(Flu)(N^tBu)]ZrCl_2$, $[Me_2Si(3-Me_3Si-Ind)(N^tBu)]TiCl_2$, [22d]), and re-
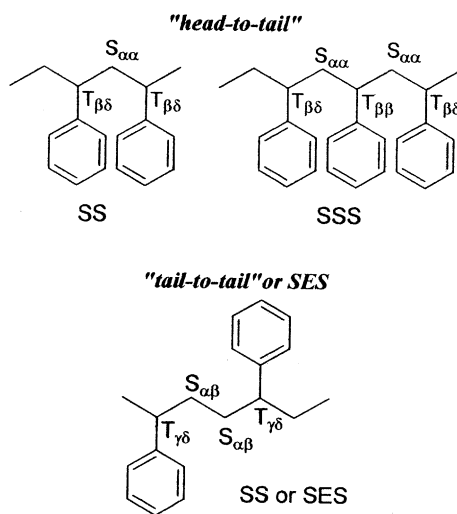


Scheme 1.

ported that the indenyl and the benzylamine analogues that would have more open structures promoted the highest styrene incorporation. Small percentage of head-to-tail styrene coupling ($T_{\beta\beta}$ and $S_{\alpha\alpha}$, Scheme 1) in addition to the tail-to-tail coupling of styrene unit or head-to-head bridged by an intervening ethylene unit ($S_{\alpha\beta}$) was also observed by the benzyl analogue [22d]. We also showed our preliminary results concerning the effect in cyclopentadienyl fragment in the previous communication [17].

Under these circumstances mentioned above, we had decided to explore the effect of ligand for ethylene/styrene copolymerization as well as for ethylene and/or styrene homopolymerization with various half-metallocene type titanium complexes containing Cp$'$-aryloxy and/or Cp$'$-amide ligand. In this paper, we thus wish to show one interesting example concerning the effect of amide ligand in ethylene/styrene copolymerization.

## 2. Results and discussion

We chose cyclohexyl analogue, $[Me_2Si(C_5Me_4) (NCy)]TiCl_2$ (**2**), not only because this complex possesses both bulky and electron-donating substituents like *tert*-butyl group in amide fragment which would stabilize the catalytically-active species under

polymerization conditions, but also because the styrene incorporation may be improved by reducing the steric bulk around the metal center by the replacement, as presented by [Me$_2$Si(C$_5$Me$_4$)(NCH$_2$Ph)]TiCl$_2$ [22d]. In addition, we have recently found that the replacement of methyl group into cyclohexyl group in Cp*TiCl$_2$(NMeR) (R = Me, Cy) drastically improved the catalytic activity for ethylene polymerization in the presence of methylaluminoxane (MAO) [23]. (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (3) was also chosen as the reference (see Chart 1).
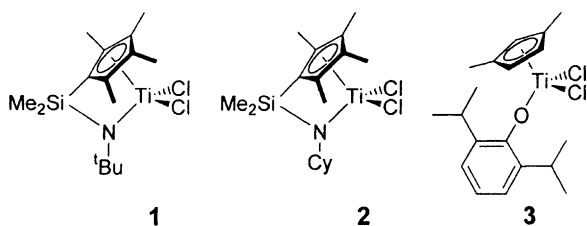


Chart 1

## 2.1. Copolymerization of ethylene with styrene by 1–3-MAO catalyst systems

Copolymerizations of ethylene with styrene by 1–3 were performed in toluene at 25 °C by using 100 ml scale autoclave in the presence of MAO. MAO white solid prepared by removing toluene and AlMe$_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.) was used as the cocatalyst, because the use of this MAO was effective to obtain poly(ethylene-co-1-butene) both with high molecular weight and narrow molecular weight distribution when 1 was used as the catalyst precursor [2b]. The polymerizations were terminated at the initial stage in order to control the monomer conversion less than 10% (to minimize the effect of monomer concentration during the copolymerization). The resultant polymer was separated by boiling acetone, and then by boiling tetrahydrofuran (THF). The results are summarized in Table 1.

It was revealed that both 1 and 3 exhibited the remarkable catalytic activities, and the resultant

Table 1
Ethylene/styrene copolymerization catalyzed by [Me$_2$Si(C$_5$Me$_4$)(NR)]TiCl$_2$-MAO system[a]

| Run no. | Catalyst | Ethylene (atm) | Styrene (ml) | Acetone soluble content[b] | Activity[c] | THF soluble fraction | | | | Content[d] of THF Insoluble fraction (wt.%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Content[d] (wt.%) | $M_w$[e] (×10$^{-4}$) | $M_w/M_n$[e] | Styrene (mol%)[f] | |
| 1 | 1 | 4 | 5 | 0.3 | 5110 | 1.5 | – | – | – | 98.1[g] |
| 2 | 1 | 4 | 10 | 0.3 | 5630 | 99.6 | 18 | 1.8 | 32.7 | tr. |
| 3 | 2 | 4 | 3 | tr. | 1370 | 99.8 | 4.8 | 1.7 | 40.9 | tr. |
| 4 | 2 | 4 | 5 | 0.3 | 1640 | 99.6 | 5.0 | 1.9 | 44.6 | tr. |
| 5 | 2 | 4 | 5 | 2.4 | 280[h] | 97.6 | 2.3 | 1.7 | 48.4 | tr. |
| 6 | 2 | 4 | 10 | tr. | 1980 | 99.8 | 4.5 | 1.8 | 45.7 | tr. |
| 7 | 2 | 6 | 3 | tr. | 1140 | 99.4 | 4.2 | 1.5 | 37.0 | 0.5 |
| 8 | 2 | 6 | 5 | tr. | 1430 | 99.7 | 3.0 | 2.3 | 42.0 | 0.2 |
| 9 | 2 | 8 | 3 | tr. | 1030 | 99.7 | 7.5 | 1.5 | 36.0 | 0.2 |
| 10 | 2 | 8 | 5 | tr. | 1340 | 99.5 | 7.3 | 1.7 | 41.2 | 0.4 |
| 11 | 3[i] | 4 | 3 | tr. | 3670 | 97.1 | 6.4 | 1.8 | 32.3 | 2.9 |
| 12 | 3[i] | 4 | 5 | 1.5 | 4280 | 98.2 | 6.0 | 2.1 | 38.5 | 0.7 |
| 13 | 3[i] | 4 | 10 | 1.1 | 4140 | 98.2 | 3.7 | 1.6 | 49.0 | 0.7 |

[a] Reaction conditions: catalyst 1.0 µmol (2 µmol/ml toluene), total volume of toluene and styrene = 30 ml, MAO white solid (Al/Ti = 2000, molar ratio), 25 °C, 10 min, 100 ml scale autoclave.
[b] Percentage of content in acetone soluble fraction based on polymer formed.
[c] Polymerization activity (kg polymer/mol Ti h), polymer yield in acetone insoluble fraction.
[d] Percentage of content based on whole polymer produced (in acetone insoluble fraction).
[e] GPC data in o-dichlorobenzene versus polystyrene standard.
[f] Styrene content (mol%) in copolymer by $^1$H NMR (C$_2$D$_2$Cl$_4$).
[g] Poly(ethylene-co-styrene) was obtained as THE insoluble fraction ($M_w$ = 2.52 × 10$^5$, $M_w/M_n$ = 2.0, styrene 12.2 mol%), catalyst 17.0 µmol.
[h] Polymerization at 0 °C, catalyst 67 µmol.
[i] (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (3) was used in place of 2.

polymers were poly(ethylene-*co*-styrene)s almost exclusively (runs 1–2, 11–13). It is clear that **3** showed more efficient styrene incorporation than **1** (run 1 versus run 12, and run 2 versus run 13). The $M_w$ value by **3** decreased with the increase in the styrene content (runs 11–13). Although **2** exhibited the lower activity under the same conditions (runs 2, 6, and 13), the activity seemed to be not so low as reported by [Me$_2$Si(C$_5$Me$_5$)(NCH$_2$Ph)]TiCl$_2$ (38 kg polymer/mol Ti h), in which 100 times decrease in the activity compared to **1** was observed under the same conditions [22d]. The $M_w/M_n$ values were narrow in all cases, and $M_w$ value by **1** was higher than those by **2** or **3**.

It turned out that **2** exhibited more efficient styrene incorporation than **1** or **3** under the same conditions, and the efficiency by **2** should be the highest among a series of linked Cp′-amide titanium complexes (Fig. 1) [22]. It seemed impossible to prepare the copolymer with styrene contents higher than ca. 50 mol%, but this is the same trend observed for this copolymerization by **1**. On the other hand, the styrene content in poly(ethylene-*co*-styrene) increased upon the increase in [styrene]/[ethylene] molar ratios, if **3** was used as the catalyst (runs 11–13). These results thus indicate that the nature of ligand directly affects the styrene incorporation.

The activity by **2** was not strongly affected by the ethylene pressure although the styrene content decreased at higher ethylene pressure (runs 3, 7, 9 or runs 4, 8, 10, Table 1), and relatively higher activity was observed under higher styrene concentrations (runs 3–4, 6 or runs 7–8, runs 9–10). The styrene content of 36.0 mol% could be obtained by **2** at 8 atm of ethylene with relatively low styrene molar ratio (run 9, [styrene]/[ethylene] = 0.87/0.97 mmol/ml) (e.g. ethylene concentrations under the reaction conditions were estimated by the equation quoted by Kissin [24a]), whereas styrene content of 32.7 mol% by **1** was attained at ethylene 4 atm with relatively higher styrene molar ratio (run 2, [styrene]/[ethylene] = 2.91/0.48 mmol/ml) (e.g. the ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported in [24b]). Both electronic and steric bulk of cyclohexyl substituent can be thus considered for the notable increase in the styrene incorporation. In addition, this complex was also found to be efficient catalyst for preparing the copolymer exclusively even at 0 °C (run 5), and this is also an interesting contrast with the fact that the attempted copolymerization using [Me$_2$Si(Flu)(N$^t$Bu)]TiX$_2$ gave only polyethylene at 0 °C even under the molar ratio of [styrene]/[ethylene] = 40 [22g].

## 2.2. Microstructure of poly(ethylene-co-styrene)s prepared by 1–3

Fig. 2 shows $^{13}$C NMR spectrum (methylene and methine region) of the copolymer (THF soluble fraction) prepared by **1**. Fig. 3 also shows the $^{13}$C NMR spectrum of the copolymer prepared by **3**. As reported previously [17], the copolymer prepared by **3** (Fig. 3) showed the resonances at $\delta = 40.7$ (T$_{\beta\beta}$, three styrene unit connected to head-to-tail coupling, Scheme 1), 43.1–43.5 and 43.8–44.5 ppm (S$_{\alpha\alpha}$ and T$_{\beta\delta}$, two styrene unit connected to head-to-tail coupling) in addition to the resonances at $\delta = 34.3$ and 35.1 ppm, which are attributed to S$_{\alpha\beta}$ (tail-to-tail coupling of styrene unit or head-to-head bridged by an intervening ethylene unit, Scheme 1).[1] This is an especially
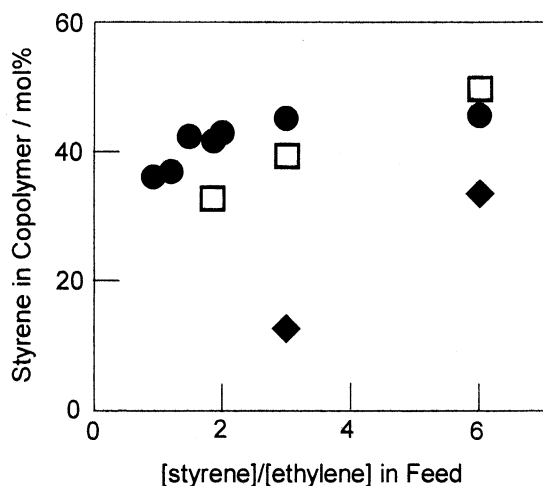


Fig. 1. Plots of styrene content (mol%) in poly(ethylene-*co*-styrene)s vs. [styrene]/[ethylene] (molar ratio) in feed for ethylene/styrene copolymerization by **1**–**3**-MAO catalyst systems (Table 1). Catalyst: **1** (◆), **2** (●), and **3** (□).

---

[1] It seemed very difficult to calculate *r*-parameters from the triad sequence distribution only from these NMR spectra, since the signals for S$_{\alpha\delta}$, and S$_{\alpha\gamma}$ at $\delta = 36.8$ and 37.0 ppm as well as those for S$_{\gamma\gamma}$, S$_{\gamma\delta}$ and S$_{\delta\delta}$ at $\delta = 29.7$ ppm are difficult to separate.
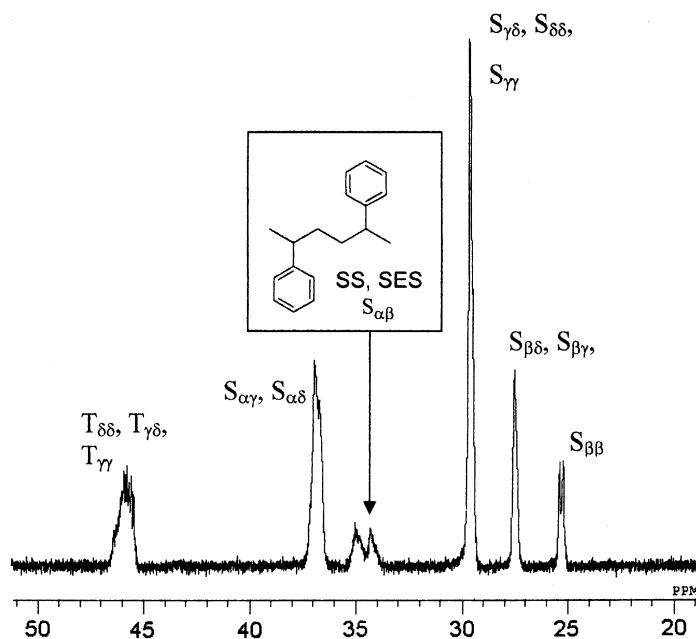
Fig. 2. $^{13}$C NMR spectrum (in CDCl$_3$ at 60 °C) of poly(ethylene-*co*-styrene) (methylene and methine region, THF soluble fraction) prepared by **1** (run 2, Table 1, styrene 32.7 mol%).
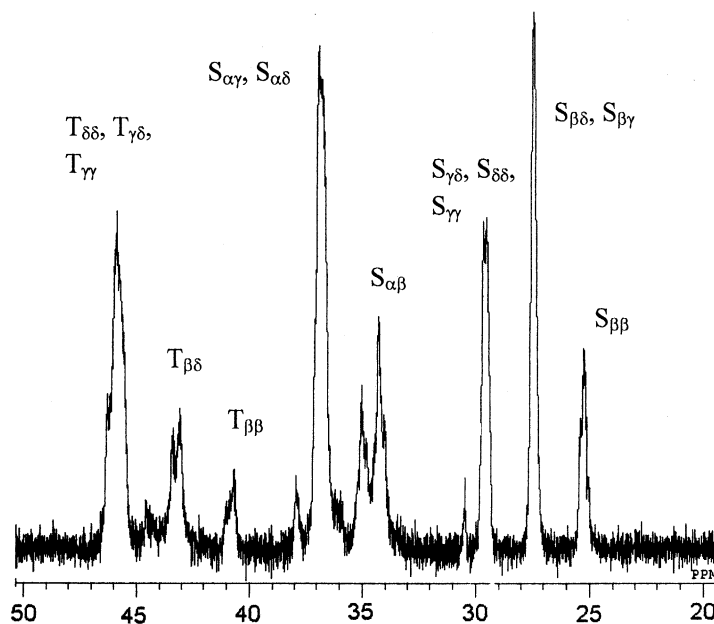


Fig. 3. $^{13}$C NMR spectrum (in CDCl$_3$ at 60 °C) of poly(ethylene-*co*-styrene)s (methylene and methine region, THF soluble fraction) prepared by **3** (run 13, Table 1, styrene 49.0 mol%).
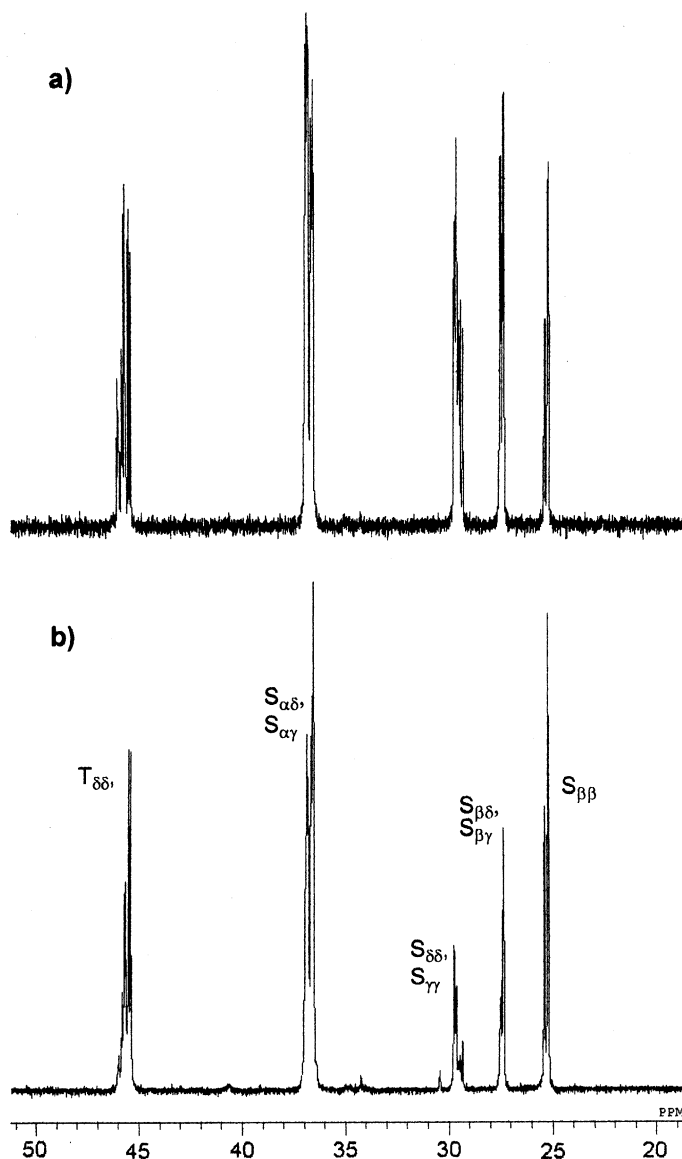
Fig. 4. $^{13}$C NMR spectra (in CDCl$_3$ at 60 °C) of poly(ethylene-*co*-styrene)s (methylene and methine region, THF soluble fraction) prepared by **2**-MAO catalyst system: (a) run 7, styrene 37.0 mol%, (b) run 4, styrene 44.6 mol%.

interesting contrast with that prepared by **1** (Fig. 2), and the preparation of poly(ethylene-*co*-styrene)s with higher styrene contents than 50% can be thus possible with the efficient manner by **3**.

Fig. 4a shows $^{13}$C NMR spectrum (methylene and methine region) of the copolymer (THF soluble fraction) prepared by **2** (run 7, styrene content 37.0 mol%). Three resonances attributed to $T_{\delta\delta}$, $S_{\alpha\gamma}$ and $S_{\beta\beta}$ carbons were observed in addition to resonances attributed to $S_{\alpha\delta}$, $S_{\beta\delta}$ and $S_{\gamma\gamma}$ carbons (Scheme 2), but no resonances attributed to $S_{\alpha\beta}$ carbon were observed. Moreover, no resonances attributed to $S_{\alpha\alpha}$ and $T_{\beta\delta}$ carbon (two styrene unit connected to head-to-tail coupling, Scheme 1), which
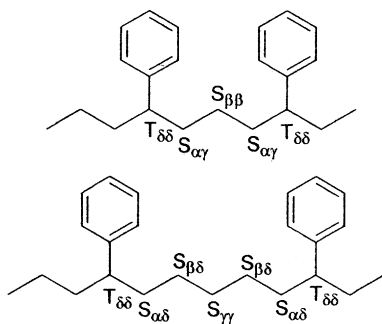
Scheme 2.

were observed for the copolymer prepared by indenyl analogue, [Me$_2$Si(Ind)(N$^t$Bu)]TiCl$_2$ [22d], were seen, although styrene incorporation was remarkably improved by **2**. The result presented here is an interesting contrast especially with that prepared by **1**, because no resonances ascribed to styrene repeated units including the typical resonance attributed to S$_{\alpha\beta}$ carbon (styrene repeat unit by tail-to-tail coupling, Scheme 1) for the copolymer by **1** were observed.

It should be noted that the intensity of resonances attributed to S$_{\beta\delta}$ and S$_{\gamma\gamma}$ carbons decreased, if the styrene content in the copolymer was increased up to 44.6 mol% (Fig. 4b). Only trace (negligible) amount of the styrene repeated units (S$_{\alpha\beta}$) were observed for the poly(ethylene-*co*-styrene) prepared by **2**[2] in spite of that the copolymer contain 44.6 mol% of styrene (which was independently determined by $^1$H NMR). It is clear that this is a crucial reason for the difficulty to prepare the copolymer with styrene content higher than ca. 50 mol%, because styrene should be incorporated into the copolymer after inserted ethylene even at almost equal molar ratio if **2** was employed as the catalyst. Although the polystyrene structure was atactic, this should be an interesting example to prepare the copolymer with a controlled insertion manner only by simple replacement of amide fragment from **1**. One probable assumption based on our previous results for ethylene/α-olefin copolymerization with Cp′-aryloxy

---

[2] The broad resonance observed at 41 ppm in Fig. 4b should be due to the T$_{\beta\beta}$ of styrene repeated units. However, we suspect that this would be due to the atactic polystyrene contaminated in the copolymer. The peak at 30.5 ppm is due to the impurity (2,6-di-*tert*-butyl-*p*-creasol as the added stabilizing agent) in the copolymer.

titanium catalysts [2e,2f] is that the difference observed here concerning the microstructure between **1** and **2** may be due to the flexibility of the catalytically active species. The steric bulk should be reduced by replacing *tert*-butyl group (**1**) into cyclohexyl group (**2**) in [Me$_2$Si(C$_5$Me$_4$)(NR)]TiCl$_2$, and this would be one probable reason for improved styrene incorporation. Although this might be a probable reason for explaining the improved styrene incorporation for **2** from **1**, however, we do not have a clear explanation why **2** incorporates styrene in an alternating manner.

## 3. Summary

We have shown that **2** exhibits more efficient styrene incorporation than **1** in the copolymerization, affording the copolymer with almost alternating manner. The styrene incorporation and microstructure for the resultant poly(ethylene-*co*-styrene)s strongly depended upon the ligand in half-metallocene type titanium complexes (**1**–**3**). We do not have an exact reason why **2** incorporate styrene in an alternating manner with regioregular insertion, but this should be an important finding for designing efficient catalyst precursor for controlled copolymerization. We are doing more research concerning this chemistry, and further results will be introduced in the near future.

## 4. Experimental

All synthetic experiments were carried out under a nitrogen atmosphere in a vacuum atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Toluene for the polymerization was distilled over sodium and benzophenone under nitrogen atmosphere, and was stored in a sealed bottle in the drybox in the presence of molecular sieves (mixture of 3A and 4A 1/16, and 13X). Reagent grade of styrene was distilled under nitrogen in the presence of CaH$_2$ after the standard purification procedure, and was stored in a Schlenk tube under N$_2$ in the freezer. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd.) and was used

as received. $(1,3\text{-}Me_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**3**) was prepared according to the previous report [2b]. $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**) was purchased from Kanto Chemical Co. Ltd. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt.% (Al) toluene solution, Tosoh Finechem Co.] were removed in vacuo in the drybox, and used as a white solid.

All $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, $^1H$; 100.40 MHz, $^{13}C$). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves. $^{13}C$ NMR spectra for the poly(ethylene-*co*-styrene)s were performed by using JEOL LA400 spectrometer (CDCl$_3$) with proton decoupling at 60 °C. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 10,000. $^1H$ NMR spectra for the copolymer (calculation of styrene content in the copolymer) were measured in the same manner (tetrachloroethane-d$_4$) at 100 °C. The polymer solutions were prepared by dissolving polymers in solvent up to 10 wt.%.

Molecular weight and molecular weight distribution of the resultant copolymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH$_{HR}$-H HT × 2) at 140 °C using *o*-dichlorobenzene containing 0.05% (w/v) 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

### 4.1. Synthesis of [Me₂Si(C₅Me₄)(NCy)]TiCl₂ (2)

Compound **2** was prepared similarly according to the reported procedure [25], by the reaction of $[Me_2Si(C_5Me_4H)(NHCy)]$, $^nBuLi$, $TiCl_4$ in the presence of $NEt_3$ in toluene. The mixed solution of toluene/*n*-hexane in the freezer prepared after the filtration and concentration procedure gave yellow microcrystals. Yield 50%. $^1H$ NMR (CDCl$_3$): δ 4.76 (m, 1H, N–C*H*–), 2.21 and 2.08 (s, 12H, C$_5$*Me*$_4$), 1.84 (dd or m), 1.63 (d or m), 1.24–1.51 (m), 1.01–1.11,

0.84–1.00 (m). $^{13}C$ NMR (CDCl$_3$): δ 140.7, 136.0, 102.0, 64.0, 34.9, 26.2, 25.8, 16.0, 13.0, 4.9.

### 4.2. Typical reaction procedure for copolymerization of ethylene with styrene by 1–3-MAO catalyst

Typical example (run 3) is as follows: toluene (24.5 ml), MAO were added into the autoclave (100 ml, stainless steel) in the drybox, and the reaction apparatus was then replaced with ethylene. The reaction mixture was then pressurized to the prescribed ethylene pressure soon after the addition of styrene and a toluene solution (0.5 ml) containing **2**. The mixture was stirred for 10 min, and the polymerization was terminated with the addition of EtOH (15 ml). The solution was then poured into EtOH (100 ml), and the resultant polymer was adequately washed with EtOH and then dried in vacuo for several hours.

According to the previous report, the resultant polymer mixture was separated into three fractions, and atactic polystyrene prepared only by MAO was extracted with acetone. Poly(ethylene-*co*-styrene) was extracted with THF, and polyethylene and polystyrene (or the copolymer with low styrene content) which were the by-product in this reaction was separated as THF insoluble fraction. The basic experimental procedure is as follows: the polymer sample obtained in the copolymerization experiment was added into a round bottom flask containing acetone (100 ml) equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate acetone soluble and insoluble fractions. Then the acetone insoluble fraction was dried and added into a round bottom flask containing THF (100 ml) equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate THF soluble and insoluble fractions. These fractions were analyzed by $^1H$, $^{13}C$ NMR and GPC.

### Acknowledgements

## References

[1] (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143;
(b) W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3903;
(c) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143;
(d) J. Suhm, J. Heinemann, C. Wörner, P. Müller, F. Stricker, J. Kressler, J. Okuda, R. Mülhaupt, Macromol. Symp. 129 (1998) 1;
(e) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587;
(f) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 429.

[2] (a) K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, Organometallics 17 (1998) 2152;
(b) K. Nomura, N. Naga, M. Miki, K. Yanagi, Macromolecules 31 (1998) 7588;
(c) K. Nomura, T. Komatsu, Y. Imanishi, J. Mol. Catal. A 152 (2000) 249;
(d) K. Nomura, T. Komatsu, Y. Imanishi, J. Mol. Catal. A 159 (2000) 127;
(e) K. Nomura, K. Oya, T. Komatsu, Y. Imanishi, Macromolecules 33 (2000) 3187;
(f) K. Nomura, K. Oya, Y. Imanishi, J. Mol. Catal. A 174 (2001) 127.

[3] S.A.A. Shah, H. Dorn, A. Voigt, H.W. Roesky, E. Parisini, H.-G. Schmidt, M. Noltemeyer, Organometallics 15 (1996) 3176.

[4] S. Doherty, R.J. Errington, A.P. Jarvis, S. Collins, W. Clegg, M.R.J. Elsegood, Organometallics 17 (1998) 3408.

[5] D.W. Stephan, J.C. Stewart, F. Guérin, R.E.V.H. Spence, W. Xu, D.G. Harrison, Organometallics 18 (1999) 1116.

[6] J. Richter, F.T. Edelmann, M. Noltemeyer, H.-G. Schmidt, M. Schmulinson, M.S. Eisen, J. Mol. Catal. A 130 (1998) 149.

[7] (a) L.R. Sita, J.R. Babcock, Organometallics 17 (1998) 5228;
(b) K.C. Jayaratne, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 958;
(c) K.C. Jayaratne, R.J. Keaton, D.A. Henningsen, L.R. Sita, J. Am. Chem. Soc. 122 (2000) 10490;
(d) R.J. Keaton, K.C. Jayaratne, D.A. Henningsen, L.A. Koterwas, L.R. Sita, J. Am. Chem. Soc. 123 (2001) 6197.

[8] R. Vollmerhaus, P. Shao, N.J. Taylor, S. Collins, Organometallics 18 (1999) 2731.

[9] A. Antiñolo, F. Carrillo-Hermosilla, A. Corrochano, J. Fernández-Baeza, A. Lara-Sanchez, M.R. Ribeiro, M. Lanfranchi, A. Otero, M.A. Pellinghelli, M.F. Portela, J.V. Santos, Organometallics 19 (2000) 2837.

[10] P.-J. Sinnema, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 598 (2000) 179.

[11] (a) J.A.M. Canich, G.G. Hlatky, H.W. Turner, US Patent 542236 (1990);
(b) J.A.M. Canich, Exxon, US Patent 5026798 (1991);
(c) J.A.M. Canich, Exxon, Eur. Patent Appl. 420436 (1991).

[12] (a) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S.-Y. Lai, Dow, Eur. Patent 416815 (1991), Jpn. Patent 2623070 (1997);
(b) J.C. Stevens, D.R. Neithamer, Dow, Eur. Patent 418022 (1991).

[13] (a) J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, Organometallics 14 (1995) 789;
(b) K.L. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, Organometallics 14 (1995) 3129.

[14] D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, Organometallics 14 (1995) 3132.

[15] D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.

[16] A.L. McKnight, M.A. Masood, R.M. Waymouth, Organometallics 16 (1997) 2879.

[17] K. Nomura, T. Komatsu, Y. Imanishi, Macromolecules 33 (2000) 8122.

[18] K. Nomura, Proceedings of the presentation at ISOM XIV C6, Cambridge, MA, USA, August 2001 (unpublished results). K. Nomura, H. Okumura, T. Komatsu, N. Naga, Macromolecules, in press.

[19] (a) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, Polym. Prepr. Jpn. 35 (1986) 240;
(b) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, Macromolecules 19 (1986) 2465;
(c) A. Zambelli, P. Longo, C. Pellecchia, A. Grassi, Macromolecules 20 (1987) 2035;
(d) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, Macromolecules 21 (1988) 3356;
(e) A. Zambelli, L. Oliva, C. Pellecchia, Macromolecules 22 (1989) 2129;
(f) T.H. Newman, R.E. Campbell, M.T. Malanga, Metcon 93 (1993) 315;
(g) T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, Macromolecules 26 (1993) 5822;
(h) N. Tomotsu, M. Kuramoto, M. Takeuchi, H. Maezawa, Metallocenes 96 (1996) 211;
(i) J.C.W. Chien, Metallocenes 96 (1996) 223;
(j) W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, Macromolecules 30 (1997) 7647;
(k) N. Tomotsu, H. Shouzaki, M. Takeuchi, Polym. Prepr. Jpn. 47 (1998) 1597;
(l) Q. Wu, Z. Ye, S. Lin, Macromol. Chem. Phys. 198 (1998) 1823;
(m) W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, Macromolecules 30 (1997) 7647.

[20] (a) N. Tomotsu, N. Ishihara, Catal. Surveys Jpn. 1 (1997) 97;
(b) N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, J. Mol. Catal. A 128 (1998) 167;
(c) N. Tomotsu, N. Ishihara, J. Synth, Org. Chem. Jpn. 57 (1999) 450.

[21] (a) P. Longo, A. Grassi, L. Oliva, Makromol. Chem. 191 (1990) 2387;
(b) S. Naganuma, M. Kuramoto, Idemitsu Kosan Co., Jpn. Patent (Kokai) H3-7705 (1991);
(c) S. Naganuma, T. Tasaki, S. Machida, Idemitsu Kosan Co., Jpn. Patent (Kokai) H4-130114 (1992);

(d) P. Aaltonen, J. Seppälä, Eur. Polym. J. 30 (1994) 683;

(e) C. Pellecchia, D. Pappalardo, M. D'Arco, A. Zambelli, Macromolecules 29 (1996) 1158;

(f) L. Oliva, S. Mazza, P. Longo, Macromol. Chem. Phys. 197 (1996) 3115;

(g) L. Oliva, L. Izzo, P. Longo, Macromol. Rapid Commun. 17 (1996) 745;

(h) G. Xu, S. Lin, Macromolecules 30 (1997) 685;

(i) D.-H. Lee, K.-B. Yoon, H.-Y. Kim, S.-S. Woo, S.K. Noh, J. Appl. Polym. Sci. 67 (1998) 2187;

(j) Q. Wu, Z. Ye, Q. Gao, S. Lin, Macromol. Chem. Phys.199 (1998) 1715.

[22] (a) J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S. Lai, Dow, Eur. Patent 416815 A2 (1990);

(b) Y. Wakabayashi, A. Miyashita, Polym. Prepr. Jpn. 44 (1995) 192;

(c) F.G. Sernetz, R. Mülhaupt, R.M. Waymouth, Macromol. Chem. Phys. 197 (1996) 1071;

(d) F.G. Sernetz, R. Mülhaupt, F. Amor, T. Eberle, J. Okuda, J. Polym. Sci. Part A: Polym. Chem. 35 (1997) 1571;

(e) F.G. Sernetz, R. Mülhaupt, J. Polym. Sci. Part A: Polym. Chem. 35 (1997) 2549;

(f) R.E. Campbell, M.H. Mcadon, P.N. Nickias, J.T. Patton, O.D. Redwine, F.J. Timmers, Dow WO 98/09999 (1998);

(g) G. Xu, Macromolecules 31 (1998) 2395;

(h) T. Arai, T. Ohtsu, S. Suzuki, Macromol. Rapid. Commun. 19 (1998) 327.

[23] K. Nomura, Some results presented at ISOM XIV C6, Cambridge, MA, USA, August 2001 (submitted for publication).

[24] (a) Y.V. Kissin, Isospecific Polymerization of Olefin with Heterogeneous Ziegler-Natta Catalysts, Springer, New York, 1985, p. 3;

(b) A. Sahgal, H.M. La, W. Hayduk, Can. J. Chem. Eng. 56 (1978) 354.

[25] M. Nabika, K. Nomura, Sumitomo Chemical Co., US Patent 5965758 (1999).