

Note

Synthesis, characterization, and catalytic activities in syndiospecific polymerization of styrene for half-sandwich titanium complexes with non-Cp tridentate dianionic ligands $\text{MeN}(\text{CH}_2\text{CR}_2\text{O}^-)_2$

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Abstract

New half-titanocenes, $\text{Cp}^*\text{TiCl}[(\text{OCR}_2\text{CH}_2)\text{NMe}(\text{CH}_2\text{CR}'_2\text{O})]$ [$\text{R}, \text{R}' = \text{H}$ (**1**), $\text{R}, \text{R}' = \text{Me}, \text{H}$ (**2**), $\text{R}, \text{R}' = \text{Me}$ (**3**)], were prepared from Cp^*TiCl_3 (**4**) with the corresponding alcohols in the presence of triethylamine. X-ray analysis shows that **1** has slightly distorted trigonal bipyramidal geometry around Ti. These complexes exhibited moderate catalytic activities for syndiospecific styrene polymerization in the presence of MAO and the activity increased in the order: **2** > **1** > **4** > **3** (at 50 °C), **1** > **2** > **4** > **3** (at 70 °C and 90 °C).

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1. Introduction

Syndiotactic polystyrene (sPS) [1], a relatively new material with high melting point and rapid crystalline rate, could be straightforwardly prepared by a wide variety of catalytic systems based on titanium/MAO or zirconium/MAO [2]. Among them, $\text{Cp}'\text{TiX}_3$ complexes ($\text{Cp}' =$ substituted/unsubstituted cyclopentadienyl or indenyl; $\text{X} =$ halide, alkyl, or alkoxy) [3] are the most active precursors for the preparation of sPS. Until now, many organometallic precursors have been evaluated for their sPS catalytic behavior as well as the influence of their structure on physical properties of obtained sPS polymers [2,3]. In the case of poly(α -olefin) catalysis, a number of $\text{Cp}'\text{Ti}(\text{L})_n\text{X}_{3-m}$ type complexes with one Cp ligand and a second non-Cp ligand have widely been explored in order to elucidate the relationship between structures of catalysts and catalytic activities [4];

however, there are relatively few reports for the syndiospecific polymerization of styrene using half-sandwich titanocene complexes containing one bi-, tri-, or tetradentate ligand (non-Cp type ligand) in replace of chlorides in $\text{Cp}'\text{TiCl}_3$. The literature examples include $\text{Cp}'\text{Ti}(\text{NC}_5\text{H}_4(\text{CR}_2\text{O}))\text{Cl}_2$ [$\text{NC}_5\text{H}_4(\text{CR}_2\text{O}) =$ bidentate pyridylalkoxide ligand] [5], $\text{Cp}'\text{Ti}(\text{ONO})\text{Cl}_2$ ($\text{ONO} =$ tridentate *N*-alkoxy- β -ketoiminate ligand) [5], $\text{Cp}^*\text{TiCl}(\text{OSO})$ ($\text{OSO} =$ tridentate sulfide-linked bis(phenol) ligand) [6], $\text{Cp}^*\text{Ti}[(\text{OCH}_2\text{CH}_2)_3\text{N}]$ [7], $\text{Cp}^*\text{TiCl}[(\text{OCH}_2\text{CH}_2)_2\text{NMe}]$ [8], $\text{Cp}'\text{TiCl}(\text{OPhCH}=\text{NPhOMe})$ [9], $\text{Cp}^*\text{TiCl}[(\text{OCH}(\text{R})\text{CH}_2)_2\text{NAr}]$ [10], and $\text{Cp}'\text{TiCl}[(\text{R}-2-\{2-\text{XC}_6\text{H}_4\})\text{N}=\text{CH})\text{C}_6\text{H}_2\text{O}]$ [11]. Recently, we have reported $\text{Cp}^*\text{TiCl}(\text{DEA-Me})$ (**1**) having the tridentate *N*-methyldiethanolamine ligand could be used as a good precursor for syndiospecific polymerization of styrene in the presence of MAO [8]. In addition, Li and coworkers reported the synthesis and characterization of titanium complexes $\text{Cp}^*\text{TiCl}[(\text{OCH}(\text{R})\text{CH}_2)_2\text{NAr}]$ ($\text{R} = \text{H}$ or Me ; $\text{Ar} = \text{Ph}$ or 2,6-dimethylphenyl) containing deprotonated tridentate ligand such as

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($\text{OCH}(\text{R})\text{CH}_2$) $_2$ NAr with mono-methylated carbons connected with oxygen atoms that could display the improved catalytic activities towards sPS [10]. These results prompt us to design and prepare the new non-Cp-type tridentate ligands such as (HOCMe $_2$ CH $_2$)NMe(CH $_2$ CR $_2$ OH) (R = H, **2L**; R = Me, **3L**) with controlled steric hindrance and their titanium complexes Cp * TiCl[(OCMe $_2$ CH $_2$)NMe(CH $_2$ CR $_2$ O)] (R = H, **2**; R = Me, **3**) for the syndiospecific polymerization of styrene. Reported herein are the synthesis and characterization of complexes **2** and **3** with one Cp * and one non-Cp tridentate ligand such as **2L** and **3L** as well as their efficient catalytic behavior in the formation of sPS in the presence of MAO as cocatalyst.

2. Experimental

2.1. General procedure

All reactions were carried out under dinitrogen atmosphere using standard Schlenk and glove box techniques [12]. All solvents were dried by distilling from sodium/benzophenone ketyl (toluene) or CaH $_2$ (methylene chloride) under a dinitrogen atmosphere and stored over the activated molecular sieves 3A [13]. CDCl $_3$ was dried over activated molecular sieves (4A) and were used after vacuum transfer to a Schlenk tube equipped with J. Young valve.

2.2. Measurements

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at ambient temperature on a Bruker DPX-300 NMR spectrometer using standard parameters. The chemical shifts are referenced to the residual peaks of CDCl $_3$ (7.24 ppm, ^1H NMR; 77.0 ppm, $^{13}\text{C}\{^1\text{H}\}$ NMR). Elemental analyses and mass data were performed by EA 1110-FISONS(CE) and ICP-MASS HP-4500, respectively. The thermal properties of polymers were investigated by Thermal Analyst 200 DSC (differential scanning calorimetry) system. The samples (about 3–4 mg) were heated to 300 °C under nitrogen atmosphere at a heating rate of 10 °C/min, and then cooled at 10 °C/min to 30 °C, and finally reheated to 300 °C at 10 °C/min. Molecular weights of sPS samples were determined at 140 °C in 1,2,4-trichlorobenzene by PL 220+220R GPC calibrated with standard polystyrenes.

2.3. Synthesis

All chemicals were purchased from Aldrich. MAO was purchased in Witco. Compound **1** was synthesized in the yield of 90% by the literature procedure [8].

2.4. Synthesis of ligand

(HOCH $_2$ CH $_2$)NMe(CH $_2$ CMe $_2$ OH) (**2L**)

Isobutylene oxide (3.61 g, 55.0 mmol) and (2-methylamino)ethanol (3.83 g, 50.0 mmol) was added to a 10 mL screw cap vial containing stirring bar. The vial was tightly

sealed by Teflon tape and paraffin film. The mixture was maintained at room temperature for overnight and was then heated for 5 days at 50 °C. The removal of volatile compounds at reduced pressure gave the desired product **2L** (7.29 g, 99%) as colorless oil.

^1H NMR (CDCl $_3$, 300.13 MHz, ppm): δ 3.56 (t, J = 5.4 Hz, 2H, NCH $_2$ CH $_2$), 3.41 (br s, 2H, OH), 2.60 (t, J = 5.5 Hz, 2H, NCH $_2$ CH $_2$), 2.37 (s, 3H, NMe), 2.34 (s, 2H, CMe $_2$ CH $_2$ N), 1.12 (s, 6H, CMe $_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl $_3$, 75.46 MHz, ppm): δ 70.72 (OCH $_2$), 68.29 (OCMe $_2$), 61.75 (NCH $_2$), 59.75 (NCH $_2$), 45.46 (NMe), 27.62 (OCMe $_2$).

HRMS (EI) m/z calc: 147.1259. Found: 147.1252.

2.5. Synthesis of ligand MeN(CH $_2$ CMe $_2$ OH) $_2$ (**3L**)

Ligand **3L** as a white solid was prepared in a yield of 97% (8.50 g) by reacting isobutylene oxide (7.93 g, 110.0 mmol) with methylamine (1.55 g, 50.0 mmol) in a manner analogous to the procedure for the ligand **2L**.

^1H NMR (CDCl $_3$, 300.13 MHz, ppm): δ 3.86 (s, 2H, OH), 2.46 (s, 4H, CMe $_2$ CH $_2$ N), 2.42 (s, 3H, NMe), 1.10 (s, 12H, CMe $_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl $_3$, 75.46 MHz, ppm): δ 72.05 (OCMe $_2$), 71.48 (OCMe $_2$), 61.39 (NCH $_2$), 60.49 (NMe), 28.21 (OCMe $_2$).

HRMS (EI) m/z calc: 175.1572. Found: 175.1568.

2.6. Synthesis of Cp * TiCl[(OCH $_2$ CH $_2$)NMe(CH $_2$ CMe $_2$ O)] (**2**)

A reddish solution of Cp * TiCl $_3$ (1.45 g, 5.0 mmol) in 40 mL CH $_2$ Cl $_2$ was added dropwise to a solution of **2L** (0.74 g, 5.0 mmol) and triethylamine (2.1 mL, 15 mmol) in 40 mL CH $_2$ Cl $_2$ at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 12 h before filtration. The residue, obtained by removing the solvent under vacuum, was redissolved in toluene and the resulting mixture was filtered through a Celite bed. The removal of solvent from the yellow filtrate gave the desired product **2** in the yield of 88% (1.60 g).

^1H NMR (CDCl $_3$, 300.13 MHz, ppm): δ 4.36–4.28 (m, 2H, CH $_2$ O), 2.86–2.79 (m, 1H, CH $_2$ CH $_2$ N), 2.72 (d, J = 3.3 Hz, 2H, CMe $_2$ CH $_2$ N), 2.70–2.61 (m, 1H, CH $_2$ CH $_2$ N), 2.58 (s, 3H, NMe), 1.97 (s, 15H, C $_5$ Me $_5$), 1.22 (d, J = 10 Hz, 6H, CMe $_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl $_3$, 75.46 MHz, ppm): δ 125.8 (C $_5$ Me $_5$), 85.95 (OCH $_2$), 72.88 (OCMe $_2$), 68.29 (CH $_2$ CH $_2$ N), 61.60 (CMe $_2$ CH $_2$ N), 47.79 (NMe), 31.92 (OCMe $_2$), 31.16 (OCMe $_2$), 12.00 (C $_5$ Me $_5$).

Elemental Anal. Calc. for C $_{17}$ H $_{30}$ ClNO $_2$ Ti: C, 56.13; H, 8.31; N, 3.85. Found: C, 56.18; H, 8.11; N, 4.02%.

2.7. Synthesis of Cp * TiCl[(OCMe $_2$ CH $_2$) $_2$ NMe] (**3**)

The desired product **3** as a yellow crystal was prepared from Cp * TiCl $_3$ (1.45 g, 5.0 mmol), **3L** (0.88 g, 5.0 mmol),

and triethylamine (2.1 mL, 15 mmol) in a yield of 89% (1.74 g) in a manner analogous to the procedure for **2**.

^1H NMR (CDCl_3 , 300.13 MHz, ppm): δ 2.67 (q, $J = 11.6$ Hz, 4 H, CH_2N), 2.58 (s, 3H, NMe), 2.04 (s, 15H, C_5Me_5), 1.18 (d, $J = 4.4$ Hz, 12 H, CMe_2).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.46 MHz, ppm): δ 125.1 (C_5Me_5), 88.13 (OCMe_2), 73.68 (NCH_2), 50.29 (NMe), 28.59 (OCMe_2), 12.17 (C_5Me_5).

Elemental Anal. Calc. for $\text{C}_{19}\text{H}_{34}\text{ClNO}_2\text{Ti}$: C, 58.24; H, 8.75; N, 3.57. Found: C, 58.42; H, 8.91; N, 3.44%.

3. X-ray structure determination for **1**

The crystallographic measurements were performed at 293.2 K using a Bruker SMART 1K CCD diffractometer with Mo $\text{K}\alpha$ ($\lambda = 0.71073$ Å) radiation. Specimens of suitable quality and size ($0.1 \times 0.1 \times 0.1$ mm³) were selected, mounted, and centered in the X-ray beam by using a video camera. The structures were solved by the direct method and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms [14]. Final refinement based on the reflections ($I > 2.0\sigma(I)$) converged at $R_1 = 0.0512$, $wR_2 = 0.1378$, and $\text{GOF} = 1.047$. Further details are listed in Table 1.

3.1. Polymerization procedure

Polymerizations were carried out in 250 mL Schlenk flask with magnetic stirring. Toluene, the polymerization solvent, was distilled from sodium/benzophenone ketyl under dinitrogen atmosphere just before use. Styrene monomer was distilled from calcium hydride and stored at refrigerator. MAO was used as a solid form, which is obtained by the removal of all volatiles under vacuo from solution MAO purchased in Witco. Polymerizations were carried out as following: solid MAO, toluene, styrene, and the titanium compound were injected into a 250 mL Schlenk flask with magnetic stirring in that order at the desired temperatures of 50 °C, 70 °C, and 90 °C. After 10 min was reached, the reaction was terminated by the addition of 50 mL of methanol and the addition of 50 mL of 10% HCl in methanol was followed. The resulting precipitated polymer was washed three times each with 500 mL of methanol and dried in vacuo at 70 °C for 12 h.

4. Results and discussion

Ligands **2L** and **3L** were prepared by the reaction between suitable amine sources and slightly more than appropriate equivalents of isobutylene oxide as shown in Scheme 1. They were mixed in a 10 mL screw cap vial and allowed to stand overnight at room temperature. The mixture was then heated for 5 days at 50 °C to ensure complete reaction. NMR studies in benzene- d_6 indicate that this reaction is essentially complete after 3 days at 50 °C.

Table 1
Crystallographic data and parameters for **1**

	1
Empirical formula	$\text{C}_{15}\text{H}_{26}\text{ClNO}_2\text{Ti}$
Formula weight	335.72
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Pna21$
Unit cell dimensions	
a (Å)	14.149(6)
b (Å)	9.478(5)
c (Å)	12.511(7)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	1677.8(15)
Z	4
D_{calc} (g/cm ³)	1.329
Absorption coefficient (mm ⁻¹)	0.670
$F(000)$	712
Theta range for data collection (°)	2.59–27.92
Index ranges	$-18 \leq h \leq 11$, $-10 \leq k \leq 11$, $-15 \leq l \leq 16$
Reflections collected	9186
Independent reflections [R_{int}]	3657 [0.0312]
Data/restraints/parameters	3657/1/187
Goodness-of-fit on F^2	1.047
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0512$, $wR_2 = 0.1378$
R indices (all data)	$R_1 = 0.0630$, $wR_2 = 0.1529$
Largest difference in peak and hole (e Å ⁻³)	0.694 and -0.253

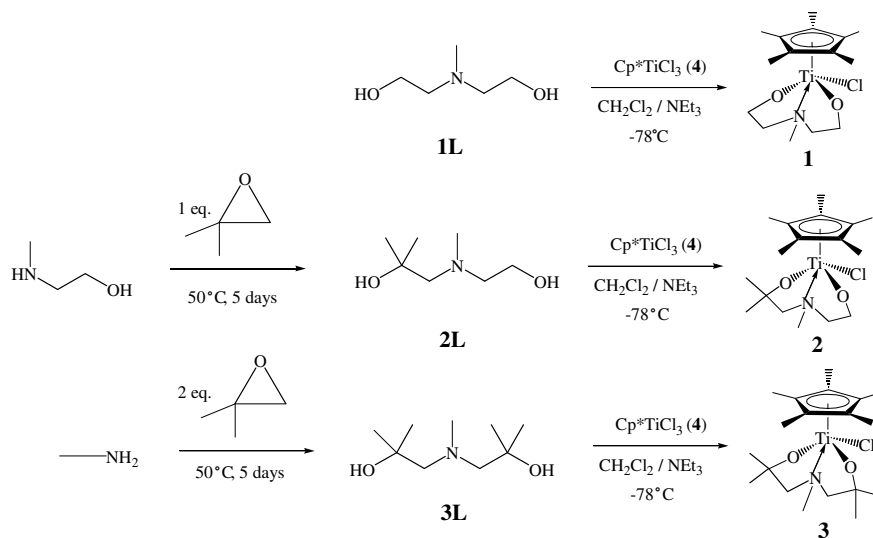
$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ and } wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right\}^{1/2}.$$

The new tridentate ligands **2L** and **3L** could be isolated in pure form by removal of the solvent at reduced pressure. **2L** is obtained as sticky oil, but **3L** obtained only as solid state.

The treatment of Cp^*TiCl_3 with the same equivalent of the ligand precursors **1L**–**3L** in methylene chloride gave, after workup, the novel complexes **1**–**3**, respectively, as pale or deep yellow crystals in good isolated yield (**1**, 90%; **2**, 88%; **3**, 89%). Complex **1** was obtained with somewhat higher yield of 90% in this study than the yield of 75% at the previously reported literature though the same synthetic procedure described in Section 2 was applied. These products in the solid state were stable in air for a few weeks and, according to ^1H NMR spectroscopy, they decomposed slightly after a few days at room temperature in CDCl_3 solutions contained in capped NMR tubes. They are soluble in polar organic solvents such as methylene chloride and in toluene. As expected, **1** and **2** are totally insoluble in alkanes such as n -hexane and n -pentane; however, compound **3** is unexpectedly soluble even in hydrocarbon solvents such as n -hexane. All the compounds evaluated as catalysts in the present work were pre-purified by recrystallization in toluene.

The ^1H NMR spectra of ligands **1L**–**3L** and complexes **1**–**3** display well-defined resonances with their expected integrations. In comparison to the free tridentate precursor

Results and Discussion



Scheme 1.

sors **1L–3L**, all signals in **1–3** are shifted to downfield, which is a consequence of the complexation with Lewis acidic titanium metal. In the ^1H NMR spectra for complexes **1** and **2**, the extent of downfield shift in ^1H NMR spectra is greater for OCH_2 resonances (0.7–0.8 ppm) than for CH_2N resonances (0.2–0.3 ppm). The greater extent of downfield shifts of OCH_2 NMR resonance than those of CH_2N resonance suggests a strong bond between O atom and Ti atom and a weak interaction between the N atom and the Ti atom upon complexation. Similar downfield shift of CH_2N resonance (0.21 ppm) was observed for complex **3**. The solution structure therefore is consistent with the structure in the solid since the Ti–O bonds are of normal length and the Ti–N bond is long and weak. The NMR signals were sharp and variable-temperature studies showed no evidence of inter- or intramolecular ligand exchange at ambient temperature. In addition, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ -NMR indicate that all complexes show monomeric structural feature in solution. Thus, the ligands are coordinated to the titanium atom in a tridentate manner and this interpretation is supported by the structural studies described below.

In order to confirm the molecular structure and to elucidate the metal–ligand bonding, the single-crystal X-ray diffraction study for **1** was performed. Single-crystal X-ray structure, selected bond distances, and selected bond angles for **1** are shown in Fig. 1. The crystal structure of **1** shows mononuclear characters, which are consistent with its NMR spectra. The Ti atom adopts essentially an η^5 bonding posture with Cp* ring and a tridentate bonding mode with *N*-methyl-diethanolamine via a transannular interaction from the bridgehead N atom to Ti, giving a slightly distorted trigonal bipyramidal local geometry around the metal. The amino nitrogen N and the centroid of Cp* ligand occupy the axial positions of a trigonal bipyramidal coordination array. The sum of the angles around the

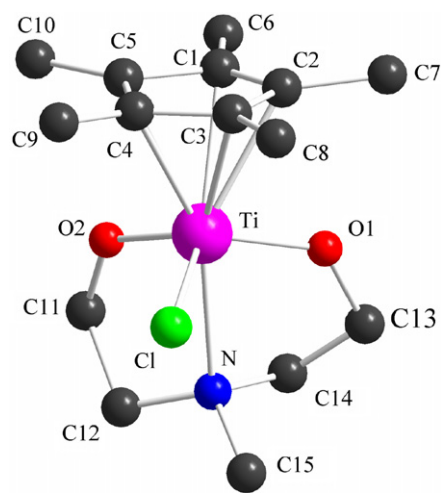


Fig. 1. Molecular drawing of compound **1** and atom labeling. (H atoms were omitted for clarity) Selected bond distances (Å): Ti–O1 = 1.862(4), Ti–O2 = 1.850(5), Ti1–N = 2.460(3), Ti–Cl = 2.3392(15), Cp(centroid)–Ti = 2.129(5), Ti–C1 = 2.395(3), Ti–C2 = 2.423(5), Ti–C3 = 2.442(6), Ti–C4 = 2.464(5), Ti–C5 = 2.482(6). Selected bond angle (°): O1–Ti–O2 = 116.99(13), O1–Ti–Cl = 112.17(18), O2–Ti–Cl = 112.19(19), O1–Ti–N = 72.6(2), O2–Ti–N = 74.0(2), Cl–Ti–N = 79.61(8), Ti–O1–C13 = 129.3(4), Ti–O2–C11 = 129.6(4), Ti–N–C12 = 104.5(4), Ti–N–C14 = 99.4(3), Ti–N–C15 = 120.8(3), Cp(centroid)–Ti–N = 174.7(3), Cp(centroid)–Ti–O1 = 103.9(3), Cp(centroid)–Ti–O2 = 104.3(3), Cp(centroid)–Ti–Cl = 105.9(3).

equatorial atoms is $341.35(17)^\circ$. As a result, the acute O or Cl–Ti–N angles [avg = $75.4(2)^\circ$] and the obtuse O or Cl–Ti–Cp(centroid) angles [avg = $104.7(3)^\circ$] reflect a displacement of the titanium atom toward the axial Cp(centroid). Furthermore, the N–Ti–Cp(centroid) angle deviates from linearity by $6.3(3)^\circ$. This deviation shows somewhat large deviation compared with the deviation range 0.34 – 1.46° reported for angle deviation of Cp(centroid), Ti atom and N atom for other cyclopentadienyltitanium complexes.

anatrane containing tetradentate triethanolamine ligand [7a,7c,15]. Cp ring exhibits highly regular pentahapto coordination. The distance between the Cp (centroid) and Ti ranges 2.129(5) Å which are similar to those observed for other structurally characterized Cp–Ti complexes [5–11]. The Ti to Cp carbon distances, listed in Fig. 1, fall in a range observed for other known Ti–Cp complexes [5–11]. The average Ti–O distance of 1.856(5) Å and the Ti–Cl distance of 2.3392(15) Å are similar to those observed for other structurally characterized titanium complexes [5–11,15]. The transannular Ti–N bond distance of 2.460(3) is even larger than that of the range (2.264(3)–2.342(9) Å) found in the other structurally characterized titanium tri-alkanolamine derivatives [7a,7c,15]. Other selected bond distances and angles are listed in Fig. 1.

The newly synthesized catalyst precursors **1–3** are examined as catalysts for syndiospecific polymerization of styrene in the presence of MAO, which is used as a solid-state for the reproducibility of activity.

The polymerization results are summarized in Table 2 in terms of the activity of the catalyst, M_n , M_w , and M_w/M_n . To probe the nature of the polymerization reaction, we carried out polymerizations at various temperatures such as 50, 70, and 90 °C. In order to assess the significance of the quoted activity values, we also carried out the blank polymerization test without any catalysts **1–4** and the control polymerization experiment using mother complex Cp*TiCl₃ (**4**)/MAO system in the same polymerization condition. Blank polymerization using MAO itself gave a trace amount (about less than 5.0 mg) of sticky atactic polystyrene attached to magnetic stirring bar. The catalytic activity and the polymerization condition of **1**/MAO and **4**/MAO measured in this study are slightly different from the earlier reported results presumably mainly owing to the use of different source of MAO [8]. The polymerization temperature affects considerably the

activities of the catalysts and the molecular weights of SPS polymers.

The polymerization data in Table 2 reveal that activities for **1–3**/MAO systems increase until the polymerization temperature T_p increases up to 90 °C. Especially with the increase of polymerization temperature, the catalytic activity of the complexes **1** and **3** rapidly increase at first (from 50 °C to 70 °C) and then slowly increase (from 70 °C to 90 °C), as shown in Fig. 2. In the case of complex **2**, the slope of increase is constant from 50 °C to 90 °C. Contrarily, the catalytic activity for **4**/MAO system gave the optimum activity at 70 °C. These results indicate that tridentate chelating ligands **1L–3L** with steric hindrance seem to play an important role in stabilizing the active species generated from the reaction between the precursor **1–3** and MAO. Basically, all complexes exhibited remarkable thermal stability at high polymerization temperature.

According to Zambelli et al. [17], the syndiospecific polymerization of styrene might be an ‘electrophilic’ polyinsertion reaction at metal center, suggesting that titanium compounds with metal centers rich in electron density would be more effective catalysts. The polymerization data reveal that the catalytic efficiency in terms of activity decreases in the order of **2**/MAO > **1**/MAO > **4**/MAO > **3**/MAO at 50 °C and **1**/MAO > **2**/MAO > **4**/MAO > **3**/MAO at 70 °C and 90 °C. If the steric properties of metal centers and thereby the steric hindrance ability of the tridentate ligands **1L–3L** are the only governing factors of determining the catalytic efficiency of compounds **1** to **4** in the syndiospecific polymerization of styrene, a catalytic order would be **3**/MAO > **2**/MAO > **1**/MAO > **4**/MAO which is somewhat different from the polymerization results, suggesting that other factor such as, among others, the electronic effect of tridentate ligands is also important governing key to the order of the catalytic activities.

In addition, the catalytic efficiency in terms of M_w decreases in the order of **4**/MAO > **1**/MAO > **3**/MAO > **2**/MAO at 50 °C and **1**/MAO > **2**/MAO > **4**/MAO >

Table 2
Data for the syndiospecific polymerization of styrene using **1–4**

Entry	Catalyst ^a	T_p (°C)	PS (g)	A^b ($\times 10^7$)	M_n^c	M_w^c	M_w/M_n^c
1	1	50	1.04	0.734	216800	381100	1.76
2		70	3.07	2.17	208800	385900	1.85
3		90	3.30	2.33	147100	254100	1.73
4	2	50	1.62	1.14	180100	328700	1.83
5		70	2.10	1.48	187300	361800	1.93
6		90	2.40	1.69	116800	220800	1.89
7	3	50	0.30	0.212	167700	369200	2.20
8		70	1.33	0.939	123600	253100	2.05
9		90	1.70	1.20	91400	179400	1.96
10	4	50	0.84	0.593	312300	485000	1.55
11		70	2.01	1.42	216500	355800	1.64
12		90	1.99	1.40	99400	167600	1.69

^a Polymerization condition: toluene solvent = 50 mL; [Al]/[Ti] = 1000; styrene = 5.0 mL, t_p = 10 min; [Ti] = 0.0195 mmol; [s-MAO] = 1.16 g (19.5 mmol).

^b Activity: g PS/(mol Ti · mol styrene · hour).

^c Determined by GPC.

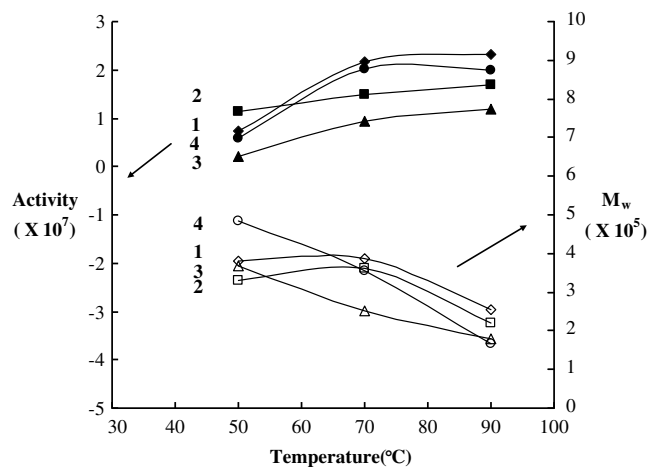


Fig. 2. Plot of the catalytic activity and M_w of SPS vs. polymerization temperature.

3/MAO at 70 °C and 90 °C. The molecular weights of sPS obtained by 3/MAO and 4/MAO decrease monotonously with the polymerization temperature; however, the molecular weights by 1/MAO and 2/MAO increase until 70 °C. Along with the increase of polymerization temperature, the rapid decrease of molecular weight of sPS obtained by 4/MAO was observed. The properties of sPS were determined using $^{13}\text{C}\{^1\text{H}\}$ NMR and DSC. All systems afford sPS with high syndiotacticity and T_m values of 268–272 °C over the entire range studied. Especially, DSC data show that a melting point of about 270 °C during the first heating for all obtained polymers was observed, but two or three melting points were observed during the second heating. This may be owing to different crystalline polymorphic structure of sPS produced by our systems [16].

5. Conclusion

In this paper, we have demonstrated the synthetic significance of the catalytic system of $\text{Cp}^*\text{TiCl}[(\text{OCR}_2\text{CH}_2)\text{-NMe}(\text{CH}_2\text{CR}'_2\text{O})]$ ($\text{R} = \text{R}' = \text{H}$, **1**; $\text{R} = \text{Me}$, $\text{R}' = \text{H}$, **2**; $\text{R} = \text{R}' = \text{Me}$, **3**) in generating syndiotactic polystyrene with high molecular weight and with high syndiotacticity index. Furthermore, dimethyl substituents in the tridentate ligand of titanium complexes **1–3** impose electronic and steric effect in different extent on the metal centers of catalysts involved in the syndiospecific polymerization of styrene and hence affect the catalytic activities. Further studies on the regulation of molecular weight distribution of polyethylene using complex **1–3** are now in progress.

Supplementary material

CCDC 657105 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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