Synthesis, characterization, and polymerization activity of (pentamethylcyclopentadienyl)titanatranes containing $\{(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_nN(CH_2CH_2O)_{3-n}\}^{3-}$ (n = 0–2) or $\{N(C_6H_4\text{-}2\text{-}O)_3\}^{3-}$

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ABSTRACT

(Pentamethylcyclopentadienyl)titanatranes, $Cp^*Ti\{(O\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_nN(CH_2CH_2O)_{3-n}\}$ (n = 0, **1**; n = 1, **2**; n = 2, **3**), featuring three five-membered chelating rings (**1**) to two six-membered chelating rings (**3**) in a stepwise fashion through **2** were synthesized from the corresponding tri-hydroxy chelating ligands **1L–3L**, respectively, using Cp^*TiCl_3 and triethylamine. $Cp^*Ti\{(O\text{-}2\text{-}C_6H_4)_3N\}$ (**4**) having three five-membered chelating rings from fully deprotonated $N(C_6H_4\text{-}2\text{-}OH)_3$ (**4L**) was also synthesized. X-ray analysis shows that **2** and **4** have slightly distorted trigonal bipyramidal geometry around Ti. These compounds exhibited good catalytic activity for the syndiospecific polymerization of styrene in the presence of MAO at various polymerization conditions.

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1. Introduction

The use of $N(CH_2CH_2O^-)_3$ (**1L**) ligand in the chemistry of atrane in which five-membered chelating rings are present has broadened its application across the periodic Table [1]. Many studies of new atrane systems have focused on main group elements such as silicon, phosphorus, aluminum, and tin [1–2]. Among the transition metallic atranes, many examples of titanium complexes bearing $N(CH_2CH_2O^-)_3$ ligand and its derivatives have been reported in the literature [3–5]. Recently, various silatranes [6], alumatranes [7], and titanatranes [8–9] containing all six-membered rings from fully deprotonated tris(aryloxo)amine ligand has been reported in the literature, whereas only two examples of titanatranes containing two different ring sizes have recently been reported by Verkade [9] and Nomura [10] groups. In this paper, we report the synthesis, characterization, and syndiospecific polymerization behavior of another examples of titanatranes **2** and **3** with two different ring sizes containing fully deprotonated $(HO\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)N(CH_2CH_2OH)_2$ (**2L**) and $(HO\text{-}2,4\text{-}Me_2C_6H_2\text{-}6\text{-}CH_2)_2N(CH_2CH_2OH)$ (**3L**), respectively. In addition, we report here the synthesis and X-ray structure of titanatrane **4** with three five-membered rings

from fully deprotonated $N(C_6H_4\text{-}2\text{-}OH)_3$ (**4L**). The syndiospecific polymerization activities of styrene for compounds **2–4** have also been compared with those of other well-known catalysts such as $Cp^*Ti(OCH_2CH_2)_3N$ (**1**) and Cp^*TiCl_3 (**5**).

2. Results and discussion

The general scheme for the synthesis of titanatranes containing tetradentate ligands **1L–4L** is shown in Scheme 1. The treatment of Cp^*TiCl_3 in methylene chloride with the same equivalent of the ligand precursors **1L–4L** in the presence of NEt_3 gave, after workup, the monomeric titanatranes **1–4**, respectively, as yellow or orange crystals in good isolated yield (**1**, 81%; **2**, 86%; **3**, 76%; **4**, 82%). Complexes **1–4** obtained are soluble in polar organic solvents such as methylene chloride and in toluene. They have some volatile nature and the HRMS of compounds exhibits molecular peaks for the corresponding complexes. All the compounds evaluated as catalysts in the present work were pre-purified by recrystallization in toluene.

The treatment of titanatranes **1–4** with 1.0–10.0 eq. of $AlMe_3$ in toluene gave, after workup, only unreacted starting materials **1–4**, respectively, even though heteroleptic aluminum/titanium complexes via the facile reaction between alkoxytitanatranes and the same equivalent per Ti of $AlMe_3$ have been recently reported in the literature [10] (see Section 3). The steric bulk of methyl
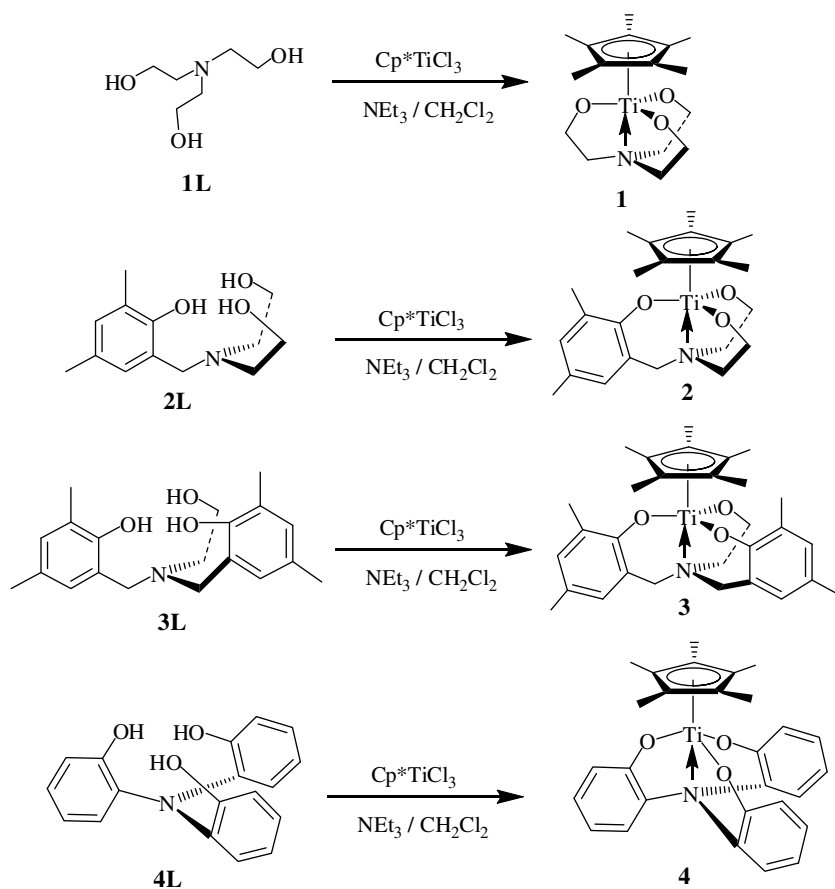
Scheme 1. Synthetic routes for 1–4.

substituents in pentamethylcyclopentadienyl ring may also prevent from the formation of aluminum adducts. Furthermore, attempted use of trilithiated species instead of neutral ligands 1L–4L in toluene or diethylether was not successful and a mixture of several unidentified compounds was obtained. In addition, the reaction between (HO-2,4-Me$_2$C$_6$H$_2$-6-CH$_2$)$_3$N and Cp*TiCl$_3$ in the presence of NEt$_3$ did not allow to give the product having three six-membered chelating rings because the steric bulk of methyl substituents in tetradentate ligand has a significant influence of the product formation [11] (see Section 3).

The ^{1}H NMR spectra of 1–4 display well-defined resonances with their expected integrations. In comparison to the free tetradentate precursors 1L–3L, all signals of CH$_2$O and NCH$_2$CH$_2$ in 1–3 are shifted to downfield, which is a consequence of the complexation with Lewis acidic titanium metal. In the ^{1}H NMR spectra for complexes 1–3, the extent of downfield shift in ^{1}H NMR spectra is greater for OCH$_2$ resonances (0.6–0.8 ppm) than for CH$_2$N resonances (−0.1–0.4 ppm). The greater extent of downfield shifts of OCH$_2$ NMR resonance than those of CH$_2$N 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 (see Table 1). 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. ^{1}H and ^{13}C{^{1}H} NMR indicate that all complexes show monomeric structural feature in solution. Thus, the ligands are coordinated to the titanium atom in a tetradentate 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

2 and 4 was performed in spite of the presence of severe disorder for the structure of 4. Single-crystal X-ray structure, selected bond distances, and selected bond angles for 2 and 4 are shown in Figs. 1 and 2, respectively. The crystal structures of 2 and 4 show mononuclear characters, which are consistent with its NMR spectra. The Ti atom adopts essentially an η^5 bonding posture with pentamethylcyclopentadienyl ring and a tetradentate bonding mode with 2L or 4L via a transannular interaction from the bridgehead N atom to Ti, giving a slightly distorted trigonal bipyramidal local geometry around Ti.

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 equatorial atoms is 344.46(7)° for 2 and 339.0(7)° for 4. As a result, the acute O–Ti–N angles and the obtuse Cp(centroid)–Ti–O angles reflect a displacement of the titanium atom toward the axial Cp(centroid). (See Table 2) Furthermore, the Cp(centroid)–Ti–N angle deviates from linearity by 7.53(7)° for 2 and 2.3(20)° for 4. This deviation shows somewhat large deviation compared with the deviation range 0.23–1.46° reported for angle deviation of Cp(centroid), Ti atom and N atom for other (cyclopentadienyl)titanatranes containing tetradentate triethanolateamine ligand [4] because of the broken symmetry in chelating ligand 2L. Cp ring for 2 and 4 exhibit highly regular pentahapto coordinations. The distance between the Cp(centroid) and Ti ranges 2.136(2) Å for 2 and 2.036(10) Å for 4, which are similar to those observed for other structurally characterized (cyclopentadienyl)titanatrane complexes [4]. The Ti to Cp carbon distances, listed in Figs. 1 and 2, fall in a range observed for other known (cyclopentadienyl)titanatrane complexes [4]. The average Ti–O distance of 1.8849(15) for 2 and 1.898(14) Å for 4 and the
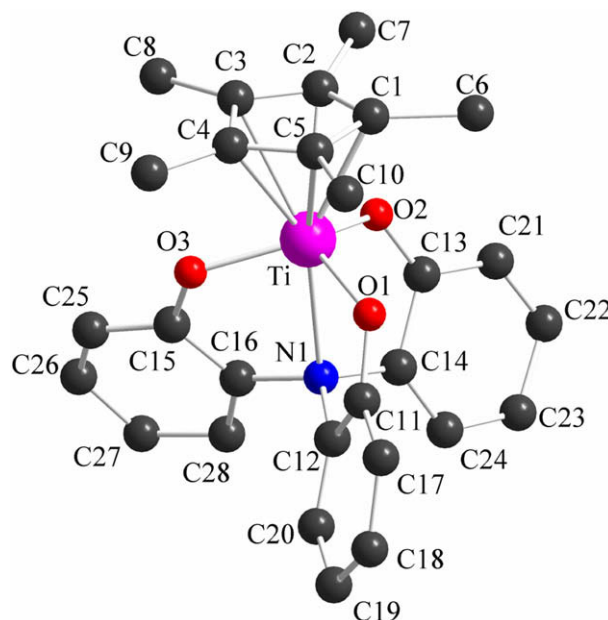
Table 1
Comparison of ^{1}H NMR chemical shifts for **1L–4L** and **1–4** dissolved in CDCl$_3$

Compound	Peak assignment					
	Aryl-*H*	CH$_2$O	NCH$_2$-aryl	NCH$_2$CH$_2$	Aryl-*Me*	C$_5$(CH$_3$)$_5$
1L		3.44		2.46		
1		4.24		2.87		1.86
2L	6.83, 6.61	3.73	3.77	2.74	2.19	
2	6.86, 6.66	4.43 – 4.31	3.68	2.80 – 2.61	2.34, 2.20	1.99
3L	6.83, 6.67	3.85	3.71	2.67	2.18	
3	6.88, 6.61	4.43	3.37	2.58	2.35, 2.21	2.14
4L	7.08–6.84					
4	7.43, 7.06, 6.72, 6.54					2.15
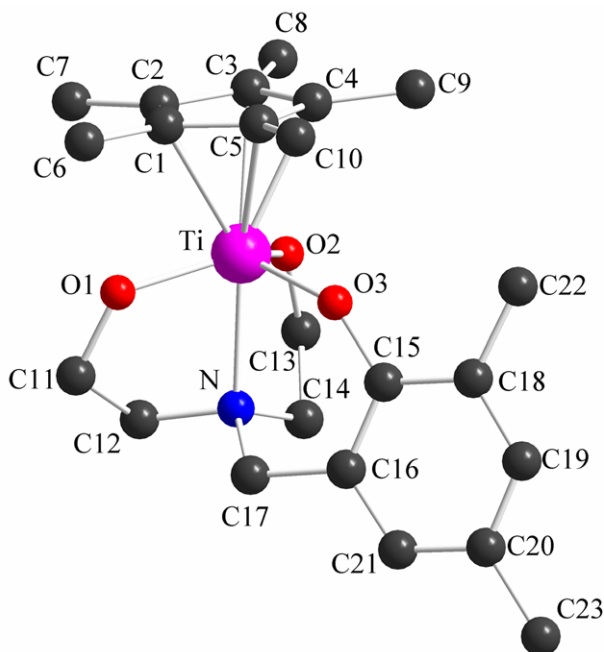
Fig. 1. Molecular drawing of compound **2** and atom labeling. (H atoms were omitted for clarity) Selected bond distances (Å): Ti–O1 = 1.8767(16), Ti–O2 = 1.8656(16), Ti–O3 = 1.9125(15), Ti1–N = 2.3176(18), Cp(centroid)–Ti = 2.136(2), Ti–C1 = 2.461(2), Ti–C2 = 2.439(2), Ti–C3 = 2.461(2), Ti–C4 = 2.434(2), Ti–C5 = 2.458(2). Selected bond angle (°): O1–Ti–O2 = 118.32(7), O1–Ti–O3 = 117.10(7), O2–Ti–O3 = 109.04(7), O1–Ti–N = 74.36(6), O2–Ti–N = 74.89(7), O3–Ti–N = 81.06(6), Ti–O1–C11 = 127.33(13), Ti–O2–C13 = 128.03(14), Ti–O3–C15 = 139.85(12), Ti–N–C12 = 103.24(12), Ti–N–C14 = 106.97(12), Ti–N–C17 = 113.13(17), Cp(centroid)–Ti–N = 172.47(7), Cp(centroid)–Ti–O1 = 100.23(7), Cp(centroid)–Ti–O2 = 103.82(7), Cp(centroid)–Ti–O3 = 106.24(7).

Fig. 2. Molecular drawing of compound **4** and atom labeling. (H atoms were omitted for clarity) Selected bond distances (Å): Ti–O1 = 1.898(14), Ti–O2 = 1.904(13), Ti–O3 = 1.893(14), Ti1–N = 2.395(16), Cp(centroid)–Ti = 2.036(10), Ti–C1 = 2.29(13), Ti–C2 = 2.21(14) Ti–C3 = 2.42(7), Ti–C4 = 2.35(5), Ti–C5 = 2.44(7). Selected bond angle (°): O1–Ti–O2 = 110.4(6), O1–Ti–O3 = 114.8(7), O2–Ti–O3 = 113.8(7), O1–Ti–N = 74.4(6), O2–Ti–N = 74.0(5), O3–Ti–N = 74.6(6), Ti–O1–C11 = 122.5(13), Ti–O2–C13 = 122.2(11), Ti–O3–C15 = 122.0(14), Ti–N–C12 = 103.5(11), Ti–N–C14 = 104.8(12), Ti–N–C16 = 103.5(11), Cp(centroid)–Ti–N = 177.7(20), Cp(centroid)–Ti–O1 = 105.1(20), Cp(centroid)–Ti–O2 = 108.2(19), Cp(centroid)–Ti–O3 = 103.7(20).

transannular Ti–N bond distance of 2.3176(18) for **2** and 2.395(16) Å for **4** are similar to those observed for other structurally characterized titanium trialkanolamine derivatives [4,5,8–11]. Other selected bond distances and angles are listed in Figs. 1 and 2. Also, details for comparison of bond lengths and bond angles for compounds **1**, **2**, and **4** are listed in Table 2.

The newly synthesized catalyst precursors **1–4** 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 because syndiotactic polystyrene (SPS) [12] could be straightforwardly prepared by Cp′TiX$_3$/MAO catalytic systems (Cp′ = substituted/unsubstituted cyclopentadienyl or indenyl; X = halide, alkyl, or alkoxy) [13]. The polymerization results are summarized in Table 3 in terms of the activity of the catalyst, SI (syndiotacticity), T_m (melting temperature), M_w, M_n, 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

Table 2
Comparison of bond lengths and bond angles for **1**, **2**, and **4**

	1[4a]	**2**	**4**
Ave. Ti–O (Å)	1.876(7)	1.8849(15)	1.898(14)
Ti–N (Å)	2.342(9)	2.3176(18)	2.395(16)
Cp(centroid)–Ti (Å)	2.119(10)	2.136(2)	2.036(10)
Ave. Ti–C(Cp*) (Å)	2.434(10)	2.451(2)	2.34(9)
Ave. O–Ti–N (°)	75.46(3)	76.77(6)	74.3(6)
Ave. Cp(centroid)–Ti–O (°)	104.52(3)	103.43(7)	105.7(20)
Cp(centroid)–Ti–N (°)	179.77(3)	172.47(7)	177.7(20)

values, we also carried out the control polymerization experiment using mother complex Cp*TiCl$_3$ (**5**)/MAO system and the blank polymerization test without any catalysts **1–5** 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 polymerization temperature affects considerably the activities of the catalysts and the molecular weights of SPS polymers.

Table 3
Data for the syndiospecific polymerization of styrene using **1–5**[a]

Catalyst	T_p (°C)	PS (g)	A[b]	SI[c] (%)	T_m[d] (°C)	T_c[d] (°C)	M_w[e]	M_n[e]	M_w/M_n[e]
1	50	1.89	13.3	97	269	235	760400	314500	2.42
	70	2.42	17.1	94	270	237	376600	172700	2.18
	90	1.43	10.1	87	271	239	199400	95200	2.09
					262				
2	50	1.23	8.68	90	270	236	598300	257400	2.32
	70	1.71	12.1	91	270	238	345800	166700	2.07
					263				
	90	1.47	10.4	89	272	241	134100	65700	2.04
					262				
3	50	1.07	7.55	90	270	238	446400	140900	3.17
					262				
	70	3.35	23.6	94	271	236	332600	163300	2.04
	90	2.39	16.9	92	271	239	165300	86100	1.92
					261				
4	50	1.03	7.27	87	268	236	710600	377700	1.88
	70	1.77	12.5	90	270	236	495500	233500	2.12
	90	1.61	11.4	89	271	239	168100	85100	1.98
					261				
Cp*TiCl₃ (**5**)	50	0.84	5.93	100	268	237	485000	312300	1.55
					249				
	70	2.01	14.2	95	271	238	355800	216500	1.64
					262				
					249				
	90	1.99	14.0	93	271	239	167600	99400	1.69
					261				
					249				

[a] Polymerization condition: toluene solvent = 50 mL; [Al]/[Ti] = 1000; styrene = 5.0 mL (43.6 mmol), t_p = 10 min; [Ti] = 0.0195 mmol, [s-MAO] = 1.16 g (19.5 mmol).
[b] Activity: g of PS/(mmol of Ti · mmol styrene · h).
[c] Syndiotacticity determined from the amount of polymer insoluble in 2-butanone.
[d] Determined by DSC (heating rate: 10 °C/min).
[e] Determined by GPC.

The polymerization data in Table 3 and Fig. 3 reveal that **1–5**/MAO systems have the maximum activities at 70 °C. Especially the catalytic activity of the complex **3** increase rapidly with raising polymerization temperature from 50 °C to 70 °C and then decrease quickly with further elevating polymerization temperature from 70 °C to 90 °C, as shown in Fig. 3. In the case of other complexes, the slope of increase from 50 °C to 70 °C and decrease from 70 °C to 90 °C is gentle. These results indicate that tetradentate chelating

Fig. 3. Plot of the catalytic activity and M_w of SPS vs. polymerization temperature.

ligands **1L–4L** with different steric hindrance and electronic effects seem to play an important role in stabilizing the active species generated from the reaction between the precursor **1–5** and MAO.

Although Nomura et al. [10] have reported that addition of AlMe₃ increases the ethylene-polymerization activity of titanatrane-type catalysts which are structurally related complexes **2** and **3**, solid-MAO without free AlMe₃ was used as a cocatalyst in the polymerization because the activities decreased upon the addition of a small amount of AlMe₃. However, the selective cleavage of one or two of three Ti–O bonds would afford the catalytically active cationic methyl-Ti species in the presence MAO. In order to investigate the possibility of cleavage of the Ti–O bond by reaction of AlMe₃, reactions of **1–4** with excess amount of AlMe₃ were performed but no desired products such as alkylated titanatranes or aluminum adduct of titanatranes [10] were obtained. In this regard, the active species may be formed by only MAO, not AlMe₃ in the syndiospecific polymerization of styrene using these titanatranes **1–4**.

According to Zambelli et al. [14], the syndiotactic-specific polymerization of styrene might be an 'electrophillic' 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 **1**/MAO > **2**/MAO > **3**/MAO > **4**/MAO > **5**/MAO at 50 °C, **3**/MAO > **1**/MAO > **5**/MAO > **4**/MAO > **2**/MAO at 70 °C, and **3**/MAO > **5**/MAO > **4**/MAO > **2**/MAO > **1**/MAO at 90 °C. If the electronic properties of Ti centers and thereby the electron-donating ability of ligands **1L–4L** are the only governing factors of determining the catalytic efficiency of compounds **1–5** in the syndiospecific polymerization of styrene, a catalytic order would be **1**/MAO > **2**/MAO > **3**/MAO > **4**/MAO > **5**/MAO, which accord with the polymerization result only at 50 °C, not at 70 °C and 90 °C, suggesting that other factor such as, among others, the steric hindrance of tetradentate ligands is also important governing key to the order of the catalytic activities. The steric bulkiness of
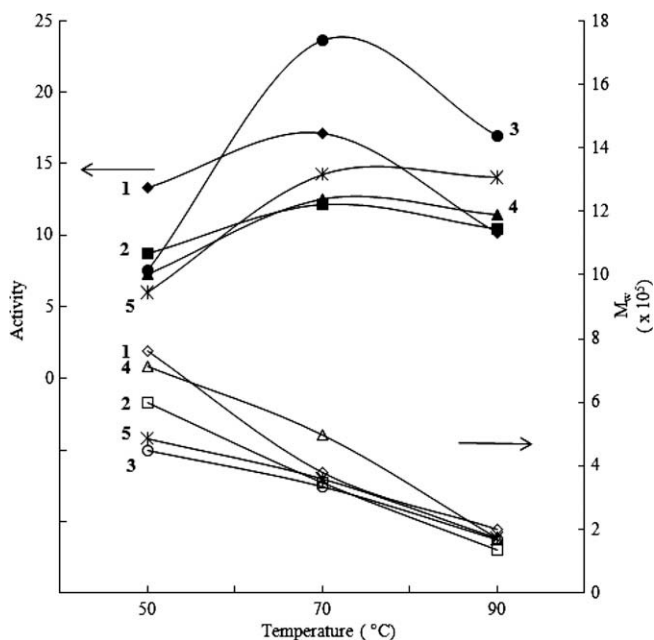
tetradentate ligands decreases in the order of **3** > **2** > **1** ~ **4**. Coupled use of this steric trend and the foregoing electronic tendency in interpreting the measured order of the catalytic activities at the polymerization temperature of 70 °C and 90 °C would provide some qualitative gauge in determining the relative importance of both factors. Especially, **3**/MAO showed the highest catalytic activity at high polymerization temperature among five complexes, and in the aspect of polymer engineering industry **3**/MAO is important because better mass transportation and temperature control are a key issue for the solution polymerization process at high temperature. In addition, there is a tendency in the activity increase in the styrene polymerization at the low polymerization temperature of 50 °C along with the increase of the number of five-membered rings in compounds **1**–**3**; however, the ring size effect disappeared at the higher polymerization temperatures of 70 °C and 90 °C, though Verkade's group have recently reported lactide polymerization activity at the high polymerization temperature of 130 °C increased as the number of five-membered ring in the chelating tetradentate ligand increased [9].

The catalytic efficiency in terms of M_w decreases in the order of **1**/MAO > **4**/MAO > **2**/MAO > **5**/MAO > **3**/MAO at 50 °C, **4**/MAO > **1**/MAO > **5**/MAO > **2**/MAO > **3**/MAO at 70 °C and **1**/MAO > **3**/MAO ~ **4**/MAO ~ **5**/MAO > **2**/MAO at 90 °C. Along with the increase of polymerization temperature, the rapid decrease of molecular weight of SPS obtained by **1**–**5**/MAO was observed. It is interesting to note that as the number of five-membered ring in the encapsulating tripod ligand from **3** to **1** through **2** increased, M_w for SPS polymers obtained at the polymerization temperature of 50 °C and 70 °C, and polydispersity index at 70 °C and 90 °C also increased [9]. The properties of SPS were determined using $^{13}C\{^1H\}$ NMR and DSC. All systems afford SPS with high syndiotacticity and T_m values of 249–272 °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 [15].

3. Experimental

3.1. General procedure

All reactions were carried out under dinitrogen atmosphere using standard Schlenk and glove box techniques [16]. 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 [17]. CDCl$_3$ was dried over activated molecular sieves (4A) and were used after vacuum transfer to a Schlenk tube equipped with J. Young valve.

3.2. Measurements

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature on a Bruker AVANCE 400 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, $^{13}C\{^1H\}$ 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.

3.3. Synthesis

All chemicals were purchased from Aldrich. MAO was purchased in Witco. Compounds **1** [4], **2L**–**3L** [9], and **4L** [18] was synthesized by the literature procedure.

3.4. Synthesis of compound **2**

A reddish solution of Cp*TiCl$_3$ (0.58 g, 2.0 mmol) in 40 mL CH$_2$Cl$_2$ was added dropwise to a solution of (HO-2,4-Me$_2$C$_6$H$_2$-6-CH$_2$)N(CH$_2$CH$_2$OH)$_2$ (**2L**) (0.48 g, 2.0 mmol) and triethylamine (0.42 mL, 6.0 mmol) in 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 and wormed up to room temperature and then stirred 12 h. The resulting solution was filtered with Celite pad. The filtrate was condensed and added by hexane and then kept at −20 °C. Yellow powder was obtained. (0.72 g, 86%) Additionally yellow crystal suitable for X-ray crystallography was obtained.

^1H NMR (CDCl$_3$, 400.147 MHz): δ 6.86 (s, 1H, aryl-H), 6.66 (s, 1H, aryl-H), 4.43–4.31 (m, 4H, CH_2O), 3.68 (s, 2H, NCH_2-aryl), 2.80–2.61 (m, 4H, NCH_2CH$_2$), 2.34 (s, 3H, aryl-Me), 2.20 (s, 3H, aryl-Me), 1.99 (s, 15H, C$_5$(CH_3)$_5$).

$^{13}C\{^1H\}$ NMR (CDCl$_3$, 100.626 MHz): δ 160.25 (aryl-C), 131.31 (aryl-C), 127.89 (aryl-C), 126.34 (aryl-C), 124.97 (aryl-C), 124.47 (C_5(CH$_3$)$_5$), 122.66 (aryl-C), 71.54 (CH$_2$O), 55.70 (NCH$_2$-aryl), 55.18 (NCH$_2$CH$_2$), 20.22 (aryl-Me), 18.93 (aryl-Me), 11.69 (C$_5$(CH$_3$)$_5$).

HRMS (EI) *m/z* Calc. 419.1939. Found: 419.1932.

Elemental Anal. Calc. for C$_{23}$H$_{33}$NO$_3$Ti: C, 65.87; H, 7.93; N, 3.34. Found: C, 65.80; H, 7.84; N, 3.38%.

3.5. Synthesis of compound **3**

The desired product **3** as an orange crystal was prepared from Cp*TiCl$_3$ (0.58 g, 2.0 mmol), (HO-2,4-Me$_2$C$_6$H$_2$-6-CH$_2$)$_2$N(CH$_2$CH$_2$OH) (**3L**) (0.66 g, 2.0 mmol), and triethylamine (0.42 ml, 6.0 mmol) in a yield of 76% (0.77 g) in a manner analogous to the procedure for **2**.

^1H NMR (CDCl$_3$, 400.147 MHz): δ 6.88 (s, 2H, aryl-H), 6.61 (s, 2H, aryl-H), 4.43 (broad, 2H, CH_2O), 3.37 (broad, 4H, NCH_2-aryl), 2.58 (broad, 2H, NCH_2CH$_2$), 2.35 (s, 6H, aryl-Me), 2.21 (s, 6H, aryl-Me), 2.14 (s, 15H, C$_5$(CH_3)$_5$).

$^{13}C\{^1H\}$ NMR (CDCl$_3$, 100.626 MHz): δ 159.82 (aryl-C), 131.20 (aryl-C), 127.32 (aryl-C), 127.07 (aryl-C), 126.85 (C_5(CH$_3$)$_5$), 124.28 (aryl-C), 122.49 (aryl-C), 72.42 (CH$_2$O), 56.65 (NCH$_2$-aryl and NCH$_2$CH$_2$), 20.27 (aryl-Me), 19.62 (aryl-Me), 12.41 (C$_5$(CH$_3$)$_5$).

HRMS (EI) *m/z* Calc. 509.2409. Found: 509.2407.

Elemental Anal. Calc. for C$_{30}$H$_{39}$NO$_3$Ti: C, 70.72; H, 7.72; N, 2.75. Found: C, 70.65; H, 7.73; N, 2.82%.

3.6. Synthesis of compound **4**

The desired product **4** as a yellow crystal was prepared from Cp*TiCl$_3$ (0.58 g, 2.0 mmol), N(C$_6$H$_4$-2-OH)$_3$ (**4L**) (0.59 g, 2.0 mmol), and triethylamine (0.42 ml, 6.0 mmol) in a yield of 82% (0.80 g) in a manner analogous to the procedure for **2**.

^1H NMR (CDCl$_3$, 400.147 MHz): δ 7.43 (d, J = 10.5 Hz, 3H, aryl-H), 7.06 (t, J = 9.8 Hz, 3H, aryl-H), 6.72 (t, J = 10.2 Hz, 3H, aryl-H), 6.54 (d, J = 10.8 Hz, 3H, aryl-H), 2.15 (s, 15H, C$_5$(CH_3)$_5$).

$^{13}C\{^1H\}$ NMR (CDCl$_3$, 100.626 MHz): δ 163.96 (aryl-C), 140.61 (aryl-C), 128.92 (aryl-C), 128.49 (aryl-C), 125.99 (C_5(CH$_3$)$_5$), 119.23 (aryl-C), 116.61 (aryl-C), 11.56 (C$_5$(CH$_3$)$_5$).

Table 4
Crystallographic data and parameters for **2** and **4**

	2	**4**
Empirical formula	$C_{23}H_{33}O_3NTi$	$C_{42}H_{39}N_{1.50}O_{4.50}Ti_{1.50}$
Formula weight	419.40	708.60
Temperature	293(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/n}$	$C2$
Unit cell dimensions	$a = 13.226(6)$ Å	$42.052(6)$ Å
	$b = 10.752(5)$ Å	$8.7799(11)$ Å
	$c = 16.087(8)$ Å	$9.8489(13)$ Å
	$\alpha = 90°$	$90°$
	$\beta = 107.316(11)°$	$99.940(9)°$
	$\gamma = 90°$	$90°$
Volume	$2185.7(18)$ Å^3	$3581.7(8)$ Å^3
Z	4	4
D_{calc}	1.275 g/cm^3	1.314 g/cm^3
Absorption coefficient	0.414 mm^{-1}	0.388 mm^{-1}
$F(000)$	896	1482
Theta range for data collection	2.31–28.11°	0.98–28.09°
Index ranges	$-16 \leqslant h \leqslant 17$	$-51 \leqslant h \leqslant 54$
	$-14 \leqslant k \leqslant 13$	$-11 \leqslant k \leqslant 11$
	$-20 \leqslant l \leqslant 11$	$-12 \leqslant l \leqslant 11$
Reflections collected	12543	15651
Independent reflections	4893 [$R_{(int)} = 0.0347$]	6617 [$R_{(int)} = 0.1292$]
Data/restraints/parameters	4893/0/260	6617/228/625
Goodness-of-fit on F^2	1.037	1.006
Final R indices [$I > 2$ sigma(I)]	$R_1 = 0.0431$, $wR_2 = 0.1189$	$R_1 = 0.1039$, $wR_2 = 0.2026$
R indices (all data)	$R_1 = 0.0561$, $wR_2 = 0.1285$	$R_1 = 0.2364$, $wR_2 = 0.2565$
Largest difference peak and hole	0.362 and -0.418 e Å^{-3}	0.326 and -0.517 e Å^{-3}

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$.

HRMS (EI) *m/z* Calc. 473.1470. Found: 473.1475.

Elemental Anal. Calc. for $C_{28}H_{27}NO_3Ti$: C, 71.04; H, 5.75; N, 2.96. Found: C, 71.12; H, 6.25; N, 3.36%.

*3.7. Attempted synthesis of Cp*Ti(O-2,4-Me₂C₆H₂-6-CH₂)₃N*

A reddish solution of Cp*TiCl₃ (0.58 g, 2.0 mmol) in 40 mL CH₂Cl₂ was added dropwise to a solution of (HO-2,4-Me₂C₆H₂-6-CH₂)₃ N (0.84 g, 2.0 mmol) and triethylamine (0.42 mL, 6.0 mmol) in CH₂Cl₂ 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 and wormed up to room temperature and then stirred 12 h. The resulting solution was filtered with Celite pad. The filtrate was condensed and added by hexane and then kept at −20 °C. A mixture of reddish orange and colorless powders, which is a mixture of starting materials, was obtained.

3.8. Attempted synthesis of aluminum adduct of 1–4

1.0–10.0 eq. of AlMe₃ (2.0–20.0 mmol) was added dropwise at −78 °C to a 10.0 mL of toluene solution of **1–4** (2.0 mmol). The reaction mixture was stirred at room temperature for overnight, and then the resultant volatiles were evaporated in vacuo, leaving an orange-yellow solid. The resultant solids were extracted with *n*-hexane. The orange solution was filtered, and the desired product was then collected from the refrigerator as yellow powders, which prove to be corresponding starting materials **1–4**.

3.9. X-ray structure determination for 2 and 4

The crystallographic measurements were performed at ambient temperature using a Bruker SMART 1K CCD diffractometer for **2** and APEX II CCD diffractometer for **4** with Mo K$_\alpha$ (λ = 0.71073 Å) radiation. Specimens of suitable quality and size were selected, mounted, and centered in the X-ray beam by using a video camera. Cell parameters were determined and refined by the SMART program [19]. Data reduction was performed using SAINT software [20]. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [21]. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package (version 5.1) with anisotropic thermal parameters for all non-hydrogen atoms [22]. X-ray crystal structures of **2** and **4** were drawn by Diamond Program version 2.1e. Details for crystallographic data and parameters are listed in Table 4.

3.10. 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 under nitrogen and then kept cold until used. 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 3 times each with 500 mL of methanol and dried in vacuo at 70 °C for 12 h.

4. Conclusion

In this paper, we have demonstrated the synthetic significance of the catalytic system of Cp*Ti{(O-2,4-Me₂C₆H₂-6-CH₂)$_n$N(CH₂CH₂O)$_{3-n}$} (n = 0,**1**; n = 1, **2**; n = 2, **3**) and Cp*Ti{(O-2-C₆H₄)₃N} (**4**) in generating syndiotactic polystyrene with high

activities and with high molecular weight. Furthermore, the ring size and steric bulkiness in the tetradentate ligand of titanium complexes **1–4** impose electronic and steric effect in different extent on the Ti centers of catalysts involved in the syndiospecific polymerization of styrene and hence affect the catalytic activities. Further studies on polyethylene and copolymerization using complex **1–4** are now in progress.

5. Supplementary material

CCDC 678853 and 678854 contain the supplementary crystallographic data for compounds **2** and **4**. 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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