

(Pentamethylcyclopentadienyl)titanatrane:[†] A New Class of Catalyst for Syndiospecific Polymerization of Styrene

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A new type of catalyst for the syndiospecific polymerization of styrene, Cp^{*}Ti(N(CH₂CH₂O)₃)₃ (**3**), was prepared by either the reaction of triethanolamine with Cp^{*}TiCl₃ in the presence of triethylamine or the reaction of (N(CH₂CH₂O)₃)TiCl with LiCp^{*}. The former reaction route is more efficient in terms of yield and easy accessibility of a titanium starting compound. The X-ray analysis reveals that **3** exists in a monomeric form in the solid state and the Ti atom adopts essentially an η^5 bonding posture with regard to the Cp^{*} ring and a tetradentate bonding mode with regard to the triethanolamine ligand via a transannular interaction from the bridgehead N atom to Ti. The compound **3**, which is stable to air and heat and soluble in hydrocarbon solvents, shows very efficient catalytic activity for the syndiospecific polymerization of styrene in the presence of modified methylaluminoxane (MMAO) as cocatalyst.

Introduction

The use of the titanium/MAO catalyst system in the first preparation of syndiotactic polystyrene (sPS) by Ishihara et al. has spurred an active search for new types of sPS catalysts.¹ The great interest in sPS, a crystalline material with heat and chemical resistance properties far superior to those of atactic PS, has arisen due to the practical applications of this new thermoplastic polymer in the field of electronics and engineering industries.² A wide variety of new catalytic systems based on titanium or zirconium organometallic complexes have been reported in the literature.³ The examples include Cp^{*}TiX₃ (Cp^{*} = C₅H₅, C₅Me₅ and X = halide, alkyl, alkoxy)⁴ and (indenyl)TiCl₃⁵ and substituted indenyl derivatives,⁶ which are among the most active catalysts. While most of the extensive previous work on sPS catalysts has been focused on the modifica-

tion of the η^5 ligand system,⁶ much less attention has been directed toward the electronic modification of the catalytically active site by introducing electron-rich multidentate ligands in place of monodentate X₃ ligands. In this regard, the potentially tetradentate electron-rich trianionic triethoxyamine (N(CH₂CH₂O)₃³⁻, TEA), the fully deprotonated form of triethanolamine, would be suitable for modifying the active site of sPS catalysts. We report here the synthesis and structure of (pentamethylcyclopentadienyl)titanatrane (Cp^{*}Ti(TEA), **3**) and its very efficient catalytic behavior in the formation of sPS in the presence of MMAO as cocatalyst.

Experimental Section

General Procedure. All operations were performed under a pure argon atmosphere using a Vacuum Atmospheres drybox equipped with a Model HE 493 Dri-Train gas purifier or using standard Schlenk techniques.⁷ Argon was deoxygenated with activated Cu catalyst and dried with Drierite. *n*-Hexane and toluene were distilled under argon from sodium–potassium alloy and stored over activated molecular sieves 3A.⁸ Dichloromethane was distilled under argon from CaH₂.⁸ ¹H and ¹³C{¹H} FT-NMR spectra were recorded on a Bruker AM300 spectrometer. Electron impact mass spectra were obtained by Korea Basic Science Center, Taejon, Korea. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, NY.

Synthesis. All chemicals were purchased from Aldrich. Cp^{*}TiCl₃ (**1**)⁹ and (TEA)TiCl (**2**)¹⁰ were synthesized by the literature procedures.

Synthesis of Cp^{*}Ti(TEA) (3**). Route A.** A reddish solution of **1** (1.45 g, 5.0 mmol) in 40 mL of CH₂Cl₂ was added dropwise

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to a solution of triethanolamine (0.75 g, 5.0 mmol) and triethylamine (2.1 mL, 15 mmol) in 40 mL of CH_2Cl_2 at -78°C . The reaction mixture was warmed to room temperature and stirred for 12 h before filtration. The residue, obtained by removing the solvent under vacuum, was redissolved in *n*-hexane, and the resulting mixture was filtered through a Celite bed. The removal of solvent from the yellow filtrate gave the desired product **3** in 81% yield (1.33 g). ^1H NMR (300.13 MHz, CDCl_3 , ppm): δ 4.24 (t, 6H, $\text{NCH}_2\text{CH}_2\text{O}$), 2.87 (t, 6H, $\text{NCH}_2\text{CH}_2\text{O}$), 1.86 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.1 MHz, CDCl_3 , ppm): δ 122.32 ($\text{C}_5(\text{CH}_3)_5$), 70.89 ($\text{NCH}_2\text{CH}_2\text{O}$), 56.14 ($\text{NCH}_2\text{CH}_2\text{O}$), 11.01 ($\text{C}_5(\text{CH}_3)_5$). EI-MS (% intensity): m/z 329 (100%, M^+), 299 (85%, $\text{M}^+ - \text{CH}_2\text{O}$), 269 (93%, $\text{M}^+ - 2\text{CH}_2\text{O}$), 241 (48%, $\text{M}^+ - 2\text{CH}_2\text{CH}_2\text{O}$), 226 (53%, $\text{M}^+ - \text{N}(\text{CH}_2\text{CH}_2\text{O})_2$), 194 (84%, $\text{M}^+ - \text{Cp}^*$), 182 (35%, $\text{M}^+ - \text{N}(\text{CH}_2\text{CH}_2\text{O})_3$). Anal. Calcd for $[\text{Cp}^*\text{Ti}(\text{TEA})]$, $\text{C}_{16}\text{H}_{27}\text{NO}_3\text{Ti}$: C, 58.33; H, 8.26; N, 4.25. Found: C, 58.49; H, 8.40; N, 4.30.

Route B. The pale yellow solid **2** (1.15 g, 5 mmol) and LiCp^* (0.71 g, 5 mmol) were placed in a Schlenk flask, and 20.0 mL of dry, freshly distilled toluene was added at -78°C . The reaction mixture was warmed to room temperature, resulting in a yellow suspension. The reaction mixture was stirred for 24 h and filtered. The residue, obtained by removing the solvent under vacuum, was redissolved in *n*-hexane, and the resulting mixture was filtered through a Celite bed. The removal of solvent from the yellow filtrate gave the desired product **3** in 56% yield (0.92 g). The spectroscopic data obtained from route B are the same as those from route A.

X-ray Structural Determination of 3. Crystals suitable for X-ray crystallography were obtained by slow cooling of a hexane solution of **3** in a refrigerator (-15°C). A total of 3313 independent reflections was measured on an Enraf-Nonius CAD4TSB diffractometer at 293 K with $\lambda(\text{Mo K}\alpha)$ radiation = 0.710 73 Å. The structure was solved by a semi-invariant direct method (SIR 92 in MolEN) and refined by full matrix least-squares calculation (SHELXL 93) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were placed at their geometrically calculated positions ($d_{\text{C-H}} = 0.96$ for methyl hydrogens, $d_{\text{C-H}} = 0.97$ for methylene hydrogens) and refined riding on the corresponding carbon atoms with isotropic thermal parameters (1.5 times the *U* value for methyl hydrogens, 1.2 times the *U* value for methylene hydrogens). All calculations were performed on a Silicon Graphics Indigo2XZ workstation. The detailed data are listed in Table 1.

Polymerization Procedure and Polymer Characterization. Styrene polymerizations were carried out in a 250 mL Schlenk flask with magnetic stirring. Toluene, the polymerization solvent, was distilled from sodium-potassium alloy under an argon atmosphere just before use. Styrene monomer was distilled from calcium hydride and stored in the refrigerator. Polymerizations were carried out as follows: toluene, styrene, MMAO (Akzo, 3A type), and the titanium compound were injected into a 250 mL Schlenk flask with magnetic stirring in that order at the desired temperatures of 30, 50, 70, and 90°C . After the desired reaction time was reached, reaction was terminated by the addition of 50 mL of methanol and the addition of 50 mL of 10% HCl in methanol followed. The resulting precipitated polymer was washed three times with 500 mL portions of methanol and dried in vacuo at 70°C for 12 h. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the sPS portion of the polymer obtained. Syndiotacticity of the extracted portion was confirmed by measuring ^{13}C NMR spectra at 100°C in 1,1,2,2-tetrachloroethane- d_2 . Molecular weights of polymers were determined by gel-permeation chromatography at 135°C in *o*-dichlorobenzene. The thermal properties of the polymers were investigated by the Thermal Analyst 200 DSC system under a nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. For each given polymerization run, two or three serial experiments were carried out to confirm the reproducibility of the

Table 1. Crystallographic Data for the Structural Analysis of $\text{Cp}^*\text{Ti}(\text{TEA})$ (3**)**

empirical formula	$\text{C}_{16}\text{H}_{27}\text{NO}_3\text{Ti}$
fw	329.28
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
<i>a</i> (Å)	9.6723(17)
<i>b</i> (Å)	13.8922(16)
<i>c</i> (Å)	12.6782(14)
β (deg)	92.794(16)
<i>V</i> (Å ³)	1701.5(4)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.285
$\lambda(\text{Mo K}\alpha)$	0.710 73
<i>F</i> (000)	704
μ (cm ⁻¹)	5.0
cryst size (mm)	$0.30 \times 0.30 \times 0.30$
θ range (deg)	$2 < \theta < 25$
scan type	$\omega/2\theta$
<i>hkl</i>	+11, +16, ± 15
no. of rflns total	3313
no. of data ($I > 2\sigma(I)$)	1551
no. of params refined	231
$R1(I > 2\sigma(I))^a$	0.0852
$wR2(I > 2\sigma(I))^b$	0.1978
GOF ($I > 2\sigma(I)$)	1.138
diff peak and hole (e Å ⁻³)	0.48, -0.42

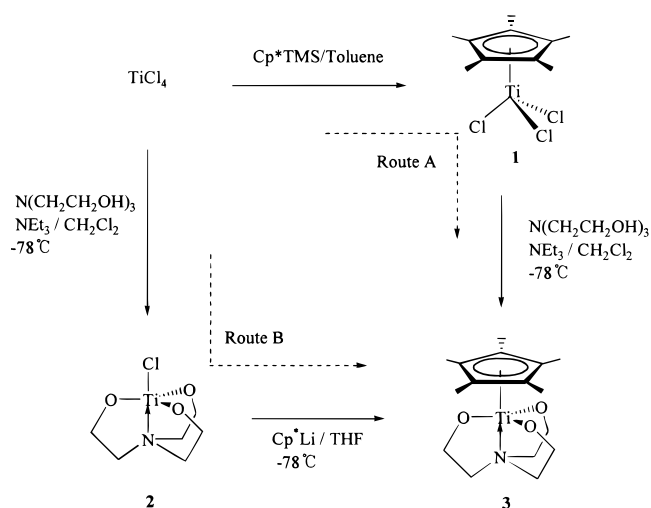
^a The structure was refined in F_o^2 using all data; the value of *R*1 is given for comparison with older refinements based on F_o with a typical threshold of $F_o > 4\sigma(F_o)$. $R1 = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 1.6216P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Distances and Angles for Compound 3

Bond Distances (Å)			
Ti-O(1)	1.880(7)	Ti-O(2)	1.879(7)
Ti-O(3)	1.869(8)	Ti-N	2.342(9)
Ti-C(1)	2.439(10)	Ti-C(2)	2.445(9)
Ti-C(3)	2.427(10)	Ti-C(4)	2.444(10)
Ti-C(5)	2.416(10)	Ti-CENT ^a	2.119(10)
Bond Angles (deg)			
CENT-Ti-O(2)	104.12(3)	CENT-Ti-O(1)	104.47(3)
CENT-Ti-N	179.77(3)	CENT-Ti-O(3)	104.98(3)

^a CENT = centroid of the five-membered ring.

Scheme 1



formation of the polymer and the average values of these serial experimental results are given.

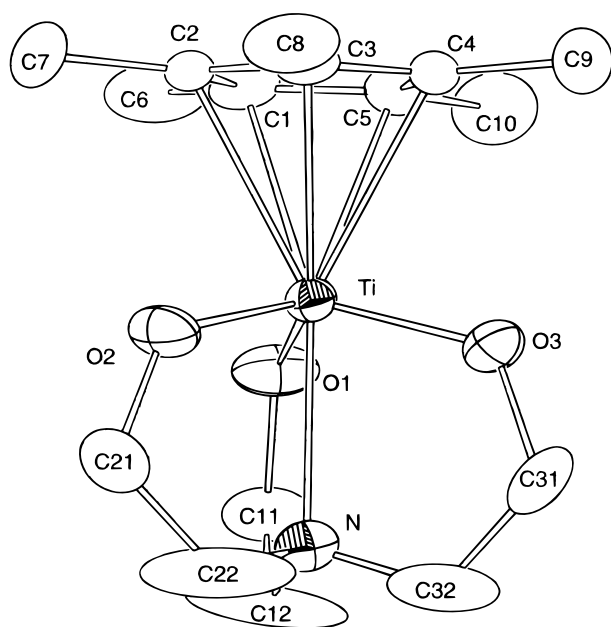
Results and Discussion

Yellow crystalline **3** was prepared by the two different synthetic routes outlined in Scheme 1. Route A utilizes

Table 3. Polymerization of Styrene Using the Cp*Ti(TEA) (3)/MMAO System in 100 mL of Toluene

run no.	T_p (°C)	Al/Ti	time (min)	Cp*Ti(TEA) (3)					Cp*TiCl ₃ (1)				
				amt of crude PS (g)	A^c ($\times 10^{-7}$)	conversn (%)	T_m^d (°C)	SI ^e (%)	amt of crude PS (g)	A^c ($\times 10^{-7}$)	conversn (%)	T_m^d (°C)	SI ^e (%)
1 ^a	30	500	10	0.518	0.37	11.4	277.7	98.6	0.25	0.18	5.5	273.7	96.8
2 ^a	30	1000	10	0.907	0.64	19.9	276.4	98.7	0.88	0.62	19.3	274.6	97.7
3 ^a	50	500	10	1.29	0.91	28.4	275.9	98.4	1.00	0.71	22.0	274.3	96.5
4 ^a	50	1000	5	2.70	3.81	59.3	274.3	98.3					
5 ^a	50	1000	10	3.36	2.37	73.8	274.6	98.4	2.62	1.84	57.6	272.9	96.0
6 ^a	50	1000	20	3.93	1.39	86.4	274.9	98.5					
7 ^a	50	1000	30	4.75	1.12	100	275.0	98.3					
8 ^a	50	1000	60	4.89	0.58	100	274.8	98.4					
9 ^b	50	1000	10	1.69	2.39	37.1	274.0	98.5					
10 ^a	70	500	10	3.58	2.46	78.7	273.7	98.1	2.44	1.72	53.6	273.1	96.2
11 ^a	70	1000	10	4.01	2.83	88.1	273.4	98.2	3.00	2.12	65.9	272.7	95.4
12 ^a	90	500	10	2.92	2.06	64.2	273.9	98.1	2.40	1.69	52.7	272.1	94.8
13 ^a	90	1000	10	2.05	1.45	45.1	273.7	98.2	1.36	0.96	29.9	272.5	95.0

^a Polymerization conditions: [styrene] = 0.436 M (5 mL); [1] or [3] = 0.195 mM. ^b Polymerization conditions: [styrene] = 0.218 M (2.5 mL); [3] = 0.195 mM. ^c A = activity = g of sPS/(mol of Ti)(mol of styrene)h. ^d Determined by DSC. ^e SI = 2-butanone-insoluble portion whose tacticity was established by ¹³C NMR in 1,1,2,2-tetrachloroethane-*d*₂.

**Figure 1.** ORTEP drawing of Cp*Ti(TEA) (3) showing 50% probability thermal ellipsoids and atom labeling.

Cp*TiCl₃ (1)⁹ and triethanolamine, and route B employs (TEA)TiCl₂ (2)¹⁰ and LiCp*. The former reaction route is more efficient in terms of yield and easy accessibility of a titanium intermediate in pure form. The compound 3 was characterized by NMR spectroscopy, elemental analysis, EI-MS, and X-ray diffraction (see the Experimental Section).

In contrast to the often observed oxygen-bridged dimeric structural feature for titanatranes,¹¹ the crystal structure of 3 indicates that Cp*Ti(TEA) molecules are discrete in the solid state. The molecular structure shown in Figure 1 reveals that the Ti atom adopts essentially an η^5 bonding posture with regard to the Cp* ring and a tetradentate bonding mode with regard to the TEA ligand via a transannular interaction from the bridgehead N atom to Ti. The overall coordination geometry of the complex is trigonal bipyramidal. The

centroid of the Cp* ring, the Ti atom and the N atom form an angle of nearly 180° and lie on the pseudo-3-fold axis. The average Ti to Cp* carbon distance of 2.434 Å is in a reasonable range for Ti–Cp distances.¹² The average Ti–O distance of 1.876 Å is similar to those in other structurally characterized titanatranes, but the Ti–N distance of 2.342(9) Å is longer than the observed range of 2.264(3)–2.333(1) Å, presumably due to the trans influence of the Cp* ring.^{11,13} Other selected bond distances and angles are listed in Table 2.

Polymerizations of styrene involving the 3/MMAO system were performed in toluene under various conditions. The polymerization data, summarized in Table 3 along with those for the 1/MMAO system, reveal that the catalytic system 3/MMAO is more efficient in producing highly syndiotactic polystyrene in terms of activity, conversion, stereospecificity, and T_m at all polymerization temperatures. The syndiotacticity and the molecular weights of all the resulting polymers from the 3/MMAO system exceed 98% and are in the range $M_w = (1.05\text{--}3.84) \times 10^5$ with $M_w/M_n = 1.50\text{--}4.07$, respectively. Further characteristics worthy of mention for 3 are its air and thermal stability and good solubility in hydrocarbon solvents such as pentane and hexane, which render its handling, purification, and characterization amenable.¹⁴ The increase of the catalytic activity with an increase of MMAO concentration is as expected, except for the polymerization temperature of 90 °C, but high activity was observed even at the low [Al]/[Ti] ratio of 500. The catalytic activity also increases as the polymerization temperature T_p increases up to 70 °C. Many homogeneous metallocene catalysts based on η^5 ligands lead to a precipitous lowering of stereospecificity and T_m value with increasing T_p .^{5,15} However, the 3/MMAO system affords polystyrenes with high stereospecificity of greater than 98% and high T_m value of

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273.4–277.7 °C over the entire T_p range studied. It is apparent that the **3**/MMAO system is interesting in this regard, in that higher T_m 's are consistently found at all polymerization temperatures. Polymerization proceeded rapidly and 100% conversion was reached within $1/2$ h at a T_p value of 50 °C. The molecular weight distribution becomes broad as T_p increases, as expected for a homogeneous catalyst system.

The coupled presence of the ancillary ligand Cp^* and the transannular interaction appears to be essential for the high catalytic efficiency of **3**, since the use of Cp or Cl instead of Cp^* or removal of the transannular interaction led to a catalytically inefficient system for syndiospecific polymerization of styrene. In the case of the unsubstituted Cp analogue $CpTi(TEA)$,^{10,11a} polymerization of styrene in toluene with MMAO ($[Ti] = 0.195$ mM, $[Al]/[Ti] = 1,000$, $[Sty] = 0.872$ M, $T_p = 50$ °C, and time 1 h) gave low activity (0.24×10^6 g of PS/(mol of Ti)(mol of styrene)h), low conversion (9.2%), and low syndiospecificity (72.8%). In addition, the **2**/MMAO system does not show any catalytic activity for styrene polymerization. Also, $Cp^*Ti((OCH_2)_3CCH_3)$,¹⁶ which has no transannular interaction, showed an extremely low activity of 0.20×10^6 g of PS/((mol of Ti)(mol of

styrene)h)) and conversion of 3.7% for the polymerization of styrene when similar polymerization conditions were employed.

In conclusion, we have synthesized a new type of catalyst for syndiospecific polymerization of styrene, $Cp^*Ti(TEA)$, whose demonstrated physical and polymerization properties coincide with important attributes for an industrially viable polymerization catalyst.

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Supporting Information Available: Tables of crystal data, atomic coordinates, thermal parameters, and bond distances and angles for $Cp^*Ti(TEA)$ (**3**) (8 pages). Ordering information is given on any current masthead page.

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(16) The yellow compound $Cp^*Ti((OCH_2)_3CCH_3)$ was synthesized in 76% yield according to route A using 1,1,1-tris(hydroxymethyl)ethane instead of triethanolamine. 1H NMR (300.13 MHz, $CDCl_3$, ppm): δ 3.96 (s, 2H), 3.94 (s, 2H), 3.49 (s, 2H), 2.06 (s, 15H, $C_5(CH_3)_5$), 0.72 (s, 3H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.1 MHz, $CDCl_3$, ppm): δ 124.0, 74.61, 37.45, 19.38, 11.79. EI-MS (% intensity): m/z 300 (100%, M^+), 270 (62%, $M^+ - CH_2O$), 240 (89%, $M^+ - 2CH_2O$), 215 (20%, $M^+ - (CH_3)C(CH_2O)_2$), 181 (30%, $M^+ - CH_3C(CH_2O)$).