

Synthesis, X-ray Structure, and *l*-Lactide/ ϵ -Caprolactone Polymerization Behavior of Monomeric Aryloxytitanatrane

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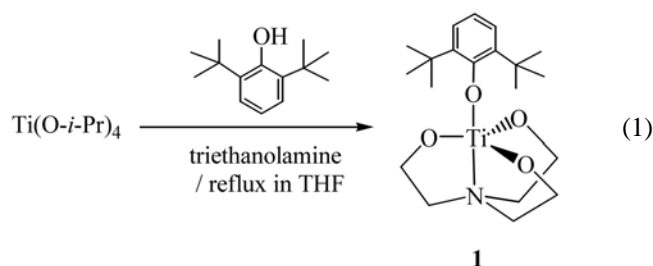
The chemistry of atrane coordinated by the central nitrogen atom as well as all three arms of deprotonated triethanolamine ligand, imino-2,2',2''-triethanolate, has been intensively studied over the past few decades and its examples are now known across the periodic table.¹ Most studies have focused on the use of main group elements such as silicon, phosphorus, aluminum, and tin in the formation of atrane.¹ In view of the well known significant number of similarities in the chemistries of tin and titanium, relatively few reports have appeared concerning metallic titanatranes with a transannular N \rightarrow Ti bond from bridgehead N atom in triethanolateamine ligand to Ti atom.² Besides tetradentate imino-2,2',2''-triethanolate ligand, one or two more coordinating ligands for titanatranes are needed because the central titanium atom in titanatranes is five-coordinate or six-coordinate with a trigonal bipyramidal or an octahedral coordination pattern, respectively. Cyclopentadienyl ligand can formally be considered as facial tridentate ligand,³ and thus mononuclear five-coordinate titanatranes containing Cp ligands looks reasonable as reported in the literature;^{2j,2k} however, titanatrane with aryloxy or alkyloxy groups favored oxygen-bridged dimeric structural geometry.^{2b-2f,4} Although the structure of 2-(diphenylmethyl)-4,6-di-*tert*-butylphenoxytitanatrane has recently been revealed,^{2g} examples of structurally characterized monomeric titanatranes containing both monodentate aryloxy or alkyloxy groups and triethanolateamine are very rare.

In this paper, we report the synthesis, characterization, and polymerization behavior of monomeric titanatrane complex having simple and commercially available 2,6-di-*tert*-butylphenoxy ligand. We chose 2,6-di-*tert*-butylphenol as an axial ligand for monomeric titanatrane because the presence of two sterically bulky substituents in 2,6 position of phenol may help titanatranes exist as a monomeric specie. Furthermore, the studies for titanium alkoxides⁴⁻⁶ for ring opening

polymerization (ROP) of *l*-lactide (*l*-LA) or ϵ -caprolactone (ϵ -CL) are now one of popular research fields in the homogeneous catalysis. In this regard, a new mononuclear titanatrane obtained was used as a catalyst for the ROP of *l*-LA and ϵ -CL.

The treatment of Ti(O-*i*-Pr)₄ with 1 equivalent of 2,6-di-*tert*-butylphenol and 1 equivalent of triethanolamine in THF gave, after workup, novel mononuclear titanatranes **1** as orange-yellow crystals in 81% isolated yield. After recrystallization using toluene, **1** was used as a catalyst for making polylactide (PLA) and polycaprolactone (PCL). Compound **1** in the solid state was stable in air for few weeks and it was slightly decomposed in the CDCl₃ solutions in capped NMR tubes at room temperature after few days. It is soluble in polar organic solvents and toluene, but insoluble in alkanes such as *n*-hexane. It has been fully characterized by ¹H and ¹³C{¹H}-NMR spectroscopic data and elemental analysis.

In order to confirm the molecular structure and to elucidate the metal-ligand bonding in this titanatrane, the single-crystal X-ray diffraction studies for **1** were performed.⁷ Single-crystal X-ray structure, selected bond distances and selected bond angles for **1** are shown in Figure 1. In contrast to the often observed oxygen-bridged dimeric structural feature for titanatranes,^{2b-2f,4} the crystal structures show monomeric character, which is consistent with their NMR spectra, presumably because of the steric bulk of the axially located di-*tert*-butylphenolate ligand. The Ti atom adopts a tetradentate-bonding mode with triethanolamine *via* a transannular interaction from the bridgehead N atom to Ti. The overall coordination geometry of the complexes is slightly distorted trigonal bipyramidal (TBP), with axial amino nitrogen and axial oxygen of di-*tert*-butylphenolate ligand and equatorial three oxygens, as evident from the sum of angles between the equatorial oxygens around the titanium of 346.23(5)°. As a result, the acute O(equatorial)-Ti-N angles (77.44(5)°) and obtuse O(equatorial)-Ti-O(axial) angles (102.56(5)°) reflect the displacement of the Ti toward axial oxygen. In addition, it is noteworthy that axial oxygen atom, titanium atom and N atom form linearity with very small deviation of 0.20(7)°, which is the smallest deviation when comparing with literature values of deviations of 0.20(8)-1.46(3)° for mononuclear titanatranes and those of 15.5(1)-51.05(8)° for dinuclear or multinuclear oxo-bridged titanatranes.² Furthermore, the fact that the C8-O1-Ti bond angle (166.48(14)°) deviates from linearity by about 23.52°,



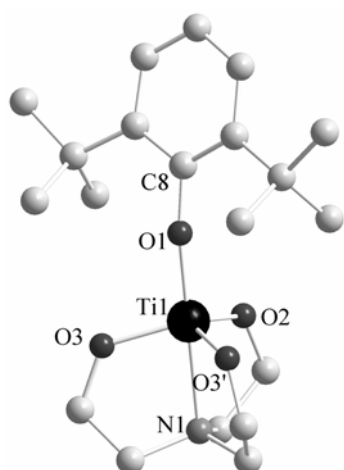


Figure 1. Molecular drawing of compound **1** and atom labeling. (H atoms were omitted for clarity) Selected bond distances (Å): Ti1-O1 = 1.836(2), Ti1-O2 = 1.841(2), Ti1-O3 = 1.832(1), Ti1-O3' = 1.832(1), Ti1-N1 = 2.292(2). Selected bond angle (°): C8-O1-Ti1 = 166.48(14), O1-Ti1-N1 = 179.80(7), O1-Ti1-O2 = 101.85(8), O1-Ti1-O3 = 102.91(4), O2-Ti1-O3 = 114.83(4), O3-Ti1-O3' = 116.57(6).

which is interestingly smallest compared with deviation of 30.5–52.28° reported for other di- or multinuclear oxo-bridged titanatrane,^{2,4} means the existence of strong electron donation from O atom to Ti atom. The average Ti-O bond distance (including the equatorial and axial oxygens) are similar to those observed for other structurally characterized titanatrane.² Interestingly, the transannular Ti-N bond distance (2.292(2) Å) fall at the short end of the range between 2.264(3) Å and 2.400(3) Å found in the structurally characterized titanatrane derivatives.² The degree of titanatrane TBP character (60.4%) is estimated from the approach of Ti-N distance to the sum of the titanium and nitrogen ionic radii of 1.97 Å relative to that for the sum of the van der Waals radii of 2.784 Å.^{8,9} This observation confirms the existence of transannular interaction in our new titanatrane system.

A wide variety of catalytic alkoxide systems based on tin, aluminum, zinc, magnesium, iron, and lanthanide organometallic complexes have been reported as catalysts for the polymerization of *l*-LA.⁵ Although titanium alkoxides have been well known for the homogeneous catalysts of olefin polymerization,¹⁰ only few examples for titanium alkoxides as catalysts in the ROP of *l*-LA are reported in the literature.^{4,6} Here we report preliminary results on the use of another Ti alkoxide catalyst. In this regard, complex **1** was examined for the solution polymerization activity with *l*-LA and ϵ -CL (Table 1). From the polymerization data in Table 1, it appears that the initiating group is the highly bulky di-*tert*-butylphenolate group, which was shown to be present in ¹H NMR of isolated PLA and PCL sample. In particular, complex **1** yields polymers with broader polydispersities than expected. This is presumably transesterification reactions can occur during propagation leading to bimodal and unimodal molecular weight distributions with a side tail or shoulder as was observed in the polymers in the GPC trace.

Table 1. ROP Data for *l*-LA and ϵ -CL Catalyzed by **1**

Type of monomer	g polymer	Tm (°C) ^c	M _w ^d	M _n ^d	M _w /M _n ^d
<i>l</i> -LA ^a	1.25	166.52	13,900	6,800	2.04
ϵ -CL ^b	0.99	53.83	33,700	15,900	2.12

^aPolymerization Condition: 1.44 g of *l*-LA, toluene 5 mL, polymerization temperature = 110 °C, polymerization time = 24 hr, [*l*-LA]/[Ti] = 100.

^bPolymerization Condition: 1.14 g of ϵ -CL, toluene 5 mL, polymerization temperature = 110 °C, polymerization time = 24 hr, [ϵ -CL]/[Ti] = 100.

^cDetermined by DSC. ^dWeight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity (M_w/M_n) were determined by GPC.

The thermal analysis of the crystalline PCL and PLA polymers exhibit sharp endothermic melting temperatures at 53.83 and 166.52 °C, respectively.

In summary, we report a mononuclear titanatrane complex containing di-*tert*-butylphenolate ligand that act as a single-site initiator for the polymerization of ϵ -CL to PCL and *l*-LA to isotactic PLA.

Experimental Section

General Considerations. All chemicals were purchased from Aldrich and were used as supplied unless otherwise indicated. All reactions were carried out under an argon atmosphere using standard Schlenk and glove box techniques.¹¹ All solvents (toluene, tetrahydrofuran (THF)) were dried by distilling from sodium-potassium alloy/benzophenone ketyl under a nitrogen atmosphere and stored over the activated molecular sieves 3A.¹² CDCl₃ was obtained from Aldrich and dried over activated molecular sieves (4A), and used after vacuum transfer to a Schlenk tube equipped with J. Young valve. ϵ -CL was distilled under reduced pressure (90 °C/7 micron Hg pressure) from calcium hydride and stored *in vacuo* over 4 Å molecular sieves. *l*-LA were purified twice by sublimation at 70 °C under 7 micron Hg pressure before use.

Measurements. ¹H and ¹³C{¹H} spectra were recorded at ambient temperature on a Bruker DPX-300 NMR spectrometer using standard parameters. The chemical shifts are referenced to the peaks of residual CDCl₃ (δ 7.24, ¹H NMR; δ 77.0, ¹³C{¹H} NMR). Elemental analyses were performed by Korea Basic Science Center, Seoul, Korea. The thermal properties of polymers were investigated by Thermal Analyst 200 DSC system under nitrogen atmosphere at a heating rate of 20 °C/min. Molecular weights of polymers were determined by gel permeation chromatography (GPC) and the measurements were carried out at room temperature with THF as the eluent (1 mL/min) using a Waters 510 pump, a Waters 717 Plus Autosampler, four Polymer Laboratories PLgel columns (100, 500, 10⁴, 10⁵ Å) in series, and a Wyatt Optilab DSP interferometric refractometer as a detector. The columns were calibrated with polystyrene standards.

Synthesis of Compound 1. In a 250 mL Schlenk flask containing a stirring bar, 2,6-di-*tert*-butylphenol (1.03 g, 5.00 mmol), Ti(O-*i*-Pr)₄ (1.42 g, 5.00 mmol), and triethanol-

amine (0.746 g, 5.00 mmol) were charged in the order given. Then 50 mL of THF was added and the reaction mixture was refluxed overnight. After cooling to room temperature, volatiles were evaporated under vacuum, leaving an orange-yellow solid to which was added 15 mL of toluene. The orange solution was filtered and the desired product **1** was isolated as orange-yellow crystals after the solution remained at $-15\text{ }^{\circ}\text{C}$ in a refrigerator for several days (1.62 g, 81%). ^1H NMR (CDCl_3 , 300.13 MHz): 7.19 (d, $J = 7.7$ Hz, 2H, aryl-*H*), 6.75 (t, $J = 7.7$ Hz, 1H, aryl-*H*), 4.53 (t, $J = 5.1$ Hz, 6H, CH_2O), 3.27 (t, $J = 5.1$ Hz, 6H, NCH_2), 1.47 (s, 18H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.47 MHz): 163.9, 139.8, 124.6, 119.4 (aryl), 71.41 (CH_2O), 56.79 (NCH_2), 34.83 ($\text{C}(\text{CH}_3)_3$), 30.64 ($\text{C}(\text{CH}_3)_3$). Elemental Anal. Calcd for $\text{C}_{20}\text{H}_{33}\text{NO}_4\text{Ti}$: C, 60.15; H, 8.33; N, 3.51. Found C, 60.25; H, 8.27; N, 3.65.

Polymerization. In a typical polymerization run, the appropriate amount of titanium catalyst **1** was dissolved in toluene (5 mL) to which monomer was added and the vessel was heated to $110\text{ }^{\circ}\text{C}$ for 24 hr. The vessel was then exposed to air to terminate polymerization. The polymer was precipitated with methanol and washed with copious amounts of methanol and dried *in vacuo*.

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- Crystal data for **1** ($\text{C}_{20}\text{H}_{33}\text{NO}_4\text{Ti}$): Orthorhombic, space group = Pnma , $a = 12.703(2)\text{ \AA}$, $b = 15.542(3)\text{ \AA}$, $c = 10.3669(17)\text{ \AA}$, $\alpha = \beta = \gamma = 90.00\text{ deg}$, $V = 2046.7(6)\text{ \AA}^3$, $Z = 4$, $F(000) = 856$, $D = 1.296\text{ g m}^{-3}$, $R_1 = 0.0360$, $wR_2 = 0.1033$ for 2170 reflections with $I_o > 2\sigma(I_o)$. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-632491). This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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