Titanatranes containing tetradentate ligands with controlled steric hindrance

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Dedicated to Professor John G. Verkade in honor of his 72nd birthday.

Abstract

New monomeric titanatranes $ArOTi(OCMe_2CH_2)_xN(CH_2CH_2O)_{3-x}$ (Ar = 2,6-di-*i*-Pr-phenyl; $x = 0$, **5**; $x = 1$, **6**; $x = 2$, **7**; $x = 3$, **8**) were synthesized from the corresponding tetradentate ligands **1–4**, respectively, using an equimolar mixture of Ti(O-*i*-Pr)$_4$ and 2,6-di-*i*-Pr-phenol. These compounds show the catalytic activity for the ring opening polymerization of *l*-lactide.
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1. Introduction

Atranes synthesized from triethanolamine feature a wide variety of metallic and nonmetallic central atoms [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 a triethanolate-amine ligand and its derivatives have been reported in the literature [3]. While most of the extensive previous work on titanatrane has been focused on the modification of axial substituents trans to annular N → Ti bond [3a,3b,3c, 3d,3e,3f,3i,3j,3k,3l,3m,3p,3q], much less attention has been directed toward the electronic or steric modification of tri-ethanolamine in itself [3g,3h,3n,3o]. In this regard, here we describe new tetradentate trianionic triethoxyamine ligands $(N(CH_2CMe_2O)_x(CH_2CH_2O)_{3-x}{}^{3-})$ ($x = 1$, **2**; $x = 2$, **3**; $x = 3$, **4**) with controlled steric hindrance in a stepwise fashion. In addition, the synthesis, characterization and catalytic ability for the polymerization of lactide, for four titanatranes possessing imino-2,2′,2″-triethanolate (**1**), imino-2,2-dimethyl-2,2′,2′-triethanolate (**2**), imino-2,2,2′,2′-tetramethyl-2,2′,2″-triethanolate (**3**), and imino-2,2,2′,2′,2″,2″-hexamethyl-2,2′,2″-triethanolate (**4**) in Scheme 1 will be demonstrated. The corresponding four titanatranes **5–8** all possess an axial anionic 2,6-di-*i*-Pr-phenolate ligand.
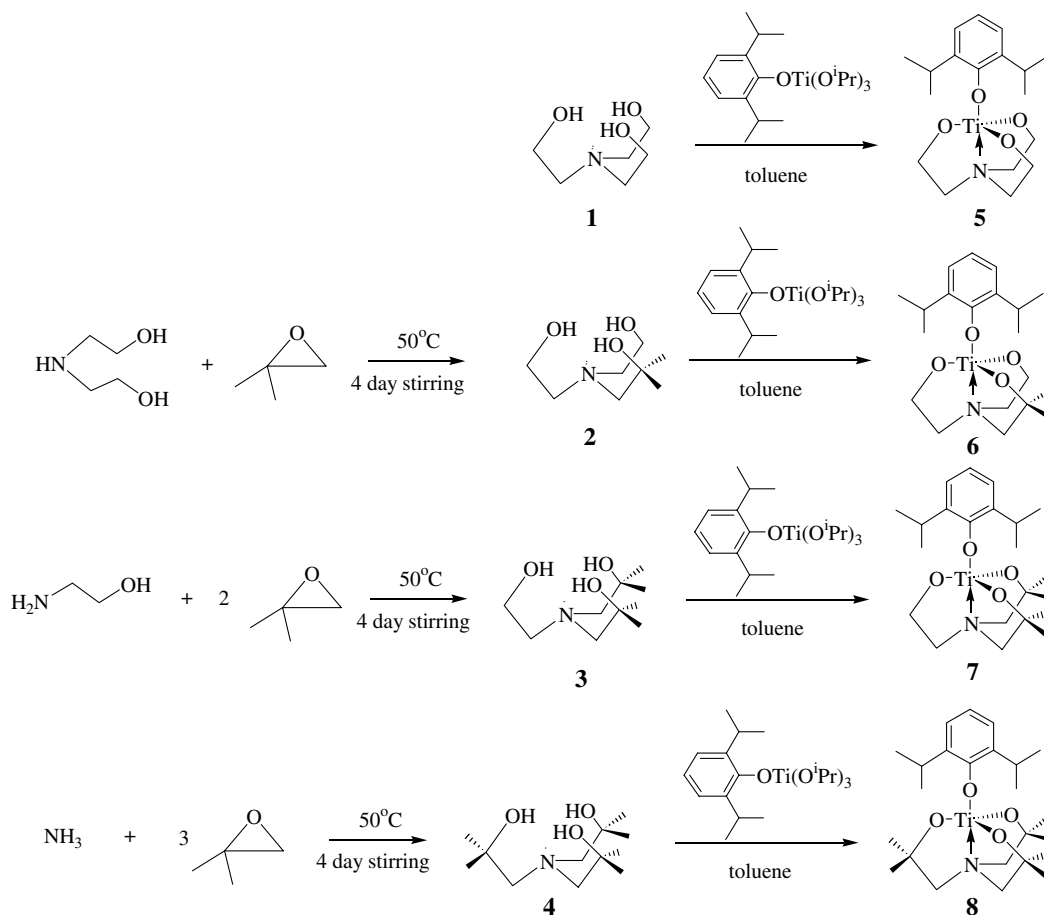
2. Experimental

2.1. General considerations

All reactions were carried out under dinitrogen atmosphere using standard Schlenk and glove box techniques [4]. All solvents were dried by distilling from sodium/

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Scheme 1.

benzophenone ketyl (toluene, tetrahydrofuran (THF), diethylether and hexane) or CaH$_2$ (methylene chloride) under a nitrogen atmosphere and stored over the activated molecular sieves 3A [5]. All deuterium solvents were dried over activated molecular sieves (4A) and were used after vacuum transfer to a Schlenk tube equipped with J. Young valve. ^{1}H and ^{13}C{^{1}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, ^{1}H NMR; 77.0 ppm, ^{13}C{^{1}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 system under nitrogen atmosphere at a heating rate of 10 °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, 10^4, 10^5 Å) in series, and a Wyatt Optilab DSP interferometric refractometer as a detector. The columns were calibrated with polystyrene standards.

2.2. Synthesis

All chemicals were purchased from Aldrich. Compound **5** was synthesized in the yield of 85% by the modified literature procedure, [6] in which toluene was used instead of THF as a solvent.

2.3. Synthesis of 2

Isobutylene oxide (3.61 g, 55.0 mmol) and diethanolamine (5.26 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 4 days at 50 °C. The removal of volatile compounds at reduced pressure gave the desired product **2** (8.60 g, 97%) as colorless oil (see Scheme 1).

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 4.51 (br s, 3H, O*H*), 3.57 (t, 4H, *J* = 4.8 Hz, OC*H*$_2$), 2.64 (t, 4H, *J* = 4.8 Hz, OCH$_2$C*H*$_2$N), 2.41 (s, 2H, OCMe$_2$C*H*$_2$N), 1.15 (s, 6H, *Me*).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.46 MHz): δ 70.7 (OCMe$_2$-*C*H$_2$N), 66.8 (O*C*Me$_2$), 59.9 (O*C*H$_2$), 59.2 (O*C*H$_2$-CH$_2$N), 27.7 (*Me*).

HRMS (EI) *m/z* calcd: 177.2414. Found: 177.2419.

2.4. Synthesis of 3

Ligand **3** as a colorless oil was prepared in a yield of 97% (10.0 g) by reacting isobutylene oxide (7.93 g, 110.0 mmol) with ethanolamine (3.05 g, 50.0 mmol) in a manner analogous to the procedure for the ligand **2** (see Scheme 1).

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 3.95 (br s, 3H, O*H*), 3.59 (t, 2H, $J = 5.3$ Hz, OC*H*$_2$CH$_2$), 2.76 (t, 2H, $J = 5.3$ Hz, OCH$_2$C*H*$_2$), 2.58 (s, 4H, OCMe$_2$C*H*$_2$N), 1.17 (s, 12H, *Me*).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.46 MHz): δ 71.0 (C*Me*$_2$CH$_2$N), 68.8 (O*C*Me$_2$), 61.3 (O*C*H$_2$), 60.3 (O*C*H$_2$CH$_2$N), 28.1 (*Me*).

HRMS (EI) *m/z* calcd: 205.2946. Found: 205.2948.

2.5. Synthesis of 4

Ligand **4** as a colorless solid was prepared in a yield of 98% (4.60 g) by reacting isobutylene oxide (4.76 g, 66.0 mmol) with 2 M solution of ammonia in methanol (10.0 mL, 20.0 mmol) in a manner analogous to the procedure for the ligand **2** (see Scheme 1).

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 3.38 (br s, 3H, O*H*), 2.70 (s, 6H, C*H*$_2$), 1.20 (s, 18H, *Me*).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.46 MHz): δ 70.9 (N*C*H$_2$), 70.3 (O*C*Me$_2$), 28.7 (*Me*).

HRMS (EI) *m/z* calcd: 233.3477. Found: 233.3480.

2.6. Synthesis of 6

To a toluene solution composed of 2,6-di-*i*-Pr-phenol (0.891 g, 5.00 mmol) in 10 mL of toluene was added dropwise at room temperature a solution of Ti(O-*i*-Pr)$_4$ (1.42 g, 5.00 mmol) in 10 mL of toluene. After 2 h, the reaction solution was added dropwise to the solution of **2** (0.89 g, 5.00 mmol) in 10 mL of toluene. The reaction mixture was stirred at room temperature overnight, and then the volatiles were evaporated under vacuum, leaving a yellow solid, to which was added 15 mL of toluene. The yellow solution was filtered, and the desired product **6** was isolated as pale yellow crystals after the solution remained at −15 °C in a refrigerator for a few days (1.65 g, 83%) (see Scheme 1).

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 6.99 (d, $J = 7.5$ Hz, 2H, aryl-*H*), 6.81 (t , $J = 7.5$ Hz, 1H, aryl-*H*), 4.47 (m, 4H, OC*H*$_2$), 3.62 (m, 2H, C*H*Me$_2$), 3.25 (m, 4H, C*H*$_2$C*H*$_2$N), 3.22(s, 2H, OCMe$_2$C*H*$_2$N) 1.35 (s, 6H, OC*Me*$_2$), 1.23 (d, $J = 6.80$ Hz, 12H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.46 MHz): δ 160.1, 137.8, 122.5, 120.2 (aryl), 84.20 (O*C*Me$_2$), 71.02 (O*C*H$_2$), 68.26 (OCMe$_2$*C*H$_2$), 60.05 (O*C*H$_2$CH$_2$), 30.36 (OC*Me*$_2$), 26.80 (*C*HMe$_2$), 23.33 (CH*Me*$_2$).

Elemental Anal. Calc. for C$_{20}$H$_{33}$NO$_4$Ti C, 60.15; H, 8.33; N, 3.51. Found: C, 60.19; H, 8.57; N, 3.73%.

2.7. Synthesis of 7

The desired product **7** as a yellow crystal was prepared in a yield of 82% in a manner analogous to the procedure for **6** (see Scheme 1).

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 6.99 (d, $J = 7.5$ Hz, 2H, aryl-*H*), 6.81 (t , $J = 7.5$ Hz, 1H, aryl-*H*), 4.45 (t, $J = 5.2$ Hz, 2H, OC*H*$_2$), 3.63 (m, 2H, C*H*Me$_2$), 3.30–3.17 (m, 6H, CH$_2$CH$_2$N and CMe$_2$C*H*$_2$N), 1.34 (s, 6H, OC*Me*$_2$), 1.32 (s, 6H, OC*Me*$_2$), 1.23 (d, $J = 6.8$ Hz, 12H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.46 MHz): δ 160.1, 137.8, 122.5, 120.0 (aryl), 83.47 (O*C*Me$_2$), 71.35 (O*C*Me$_2$CH$_2$), 71.05 (O*C*H$_2$), 63.82 (O*C*H$_2$CH$_2$), 31.16 (OC*Me*$_2$), 30.53 (OC*Me*$_2$), 26.77 (*C*HMe$_2$), 23.35 (CH*Me*$_2$).

Elemental Anal. Calc. for C$_{22}$H$_{37}$NO$_4$Ti: C, 61.82; H, 8.78; N, 3.28. Found: C, 62.18; H, 8.66; N, 3.14%.

2.8. Synthesis of 8

The desired product **8** as a deep yellow crystal was prepared in a yield of 78% in a manner analogous to the procedure for **6**. (See Scheme 1).

^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 7.00 (d, $J = 7.5$ Hz, 2H, aryl-*H*), 6.81 (t, $J = 7.5$ Hz, 1H, aryl-*H*), 3.67 (m, 2H, C*H*Me$_2$), 3.26 (s, 6H, OCMe$_2$C*H*$_2$), 1.35 (s, 18H, OC*Me*$_2$), 1.24 (d, $J = 6.8$ Hz, 12H, CH*Me*$_2$).

^{13}C{^{1}H} NMR (CDCl$_3$, 75.46 MHz): δ 160.2, 137.8, 122.4, 119.6 (aryl), 82.80 (O*C*Me$_2$), 74.74 (O*C*Me$_2$CH$_2$), 30.34 (OC*Me*$_2$), 26.73 (*C*HMe$_2$), 23.35(CH*Me*$_2$).

Table 1
Crystallographic data and parameters for **6** and **7**

	6	7
Empirical formula	C$_{20}$H$_{33}$NO$_4$Ti	C$_{22}$H$_{37}$NO$_4$Ti
Formula weight	399.37	427.43
Temperature (K)	130	100
Wavelength (Å)	0.71073	0.74999
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
Unit cell dimensions		
a (Å)	8.8687(12)	8.8570(18)
b (Å)	13.4020(18)	13.965(3)
c (Å)	18.312(3)	18.493(4)
α (°)	90	90
β (°)	103.506(2)	90
γ (°)	90	90
V (Å^3)	2116.4(5)	2287.4(8)
Z	4	4
D_{calc} (Mg/m^3)	1.253	1.241
Absorption coefficient (mm^{-1})	0.427	0.400
$F(000)$	856	920
θ Range for data collection (°)	2.29–28.28	1.10–28.64
Index ranges	$-8 \leqslant h \leqslant 11$, $-8 \leqslant k \leqslant 17$, $-23 \leqslant l \leqslant 23$	$0 \leqslant h \leqslant 11$, $-18 \leqslant k \leqslant 18$, $-24 \leqslant l \leqslant 24$
Reflections collected	8168	10 587
Independent reflections [R_{int}]	3869 [0.0495]	5835 [0.0906]
Data/restraints/parameters	3869/0/239	5835/0/263
Goodness-of-fit on F^2	0.723	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0442$, $wR_2 = 0.0700$	$R_1 = 0.0603$, $wR_2 = 0.1632$
R indices (all data)	$R_1 = 0.0872$, $wR_2 = 0.0742$	$R_1 = 0.0624$, $wR_2 = 0.1606$
Largest difference in peak and hole (e Å^{-3})	0.296 and −0.357	0.800 and −0.961

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

Elemental Anal. Calc. for $C_{24}H_{41}NO_4Ti$: C, 63.29; H, 9.07; N, 3.08. Found: C, 63.52; H, 9.15; N, 2.97%.

2.9. X-ray structure determination for 6 and 7

The crystallographic measurements were performed at 130 K for **6** using a Bruker CCD-1000 diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation or 100 K for **7** using synchrotron radiation ($\lambda = 0.74999$ Å) on a 4AMXW ADSC Quantum-210 detector with a silicon double crystal monochromator at the Pohang Accelerator Laboratory, Korea. Specimens of suitable quality and size ($0.1 \times 0.1 \times 0.1$ mm^3) were selected, mounted, and centered in the X-ray or synchrotron 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 [7]. Final refinement based on the reflections ($I > 2.0(I)$) converged at $R_1 = 0.0442$, $wR_2 = 0.0700$, and GOF = 0.723 for **6** and at $R_1 = 0.0603$, $wR_2 = 0.1632$, and GOF = 1.049 for **7**. Further details are listed in Table 1.

3. Polymerization procedure

Solution polymerizations of LA were carried out by charging a stirring bar and LA to a 5 mL vial in the glove box and then the flask was immersed at the oil bath of 100 °C. Polymerization began with the addition of 1 mL stock toluene solution of the titanium compound. After 10 h, the polymerization was terminated by the addition of 5 mL of MeOH. The reaction mixture was washed with excess methanol several times. The precipitated polymer was collected by filtration, washed with methanol (40 mL, washing for five times), and dried in a vacuum oven at 40 °C for 12 h. In the case of the bulk polymerization, no solvent was used and polymerization was carried out in a manner analogous to the solution polymerization except for the polymerization temperature of 130 °C.

4. Result and discussion

Ligands **2**–**4** 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 several 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. The new tetradentate ligands **2**–**4** could be isolated in pure form by removal of the solvent at reduced pressure. **2** and **3** were obtained as sticky oil, but **4** obtained only as solid state.

The treatment of Ti(O-*i*-Pr)₄ with 1 equiv. of 2,6-di-*i*-Pr-phenol and one equiv. of the ligand precursors **1**–**4** in toluene gave, after workup, the novel titanatranes **5**–**8** as pale or deep yellow crystals in 78–85% isolated

yield. These four products in the solid state were stable in air for a few weeks and, according to ^{1}H NMR spectroscopy, they decomposed slightly after a few days at room temperature in CDCl₃ solutions contained in capped NMR tubes. They are soluble in polar organic solvents and in toluene. As expected, **5**, **6**, and **7** are totally insoluble in alkanes such as *n*-hexane; however, compound **8** is unexpectedly soluble even in hydrocarbon solvents such as *n*-hexane and *n*-pentane. All the compounds evaluated as catalysts in the present work were pre-purified by recrystallization in toluene.

The ^{1}H NMR spectra of ligands **1**–**4** and complexes **5**–**8** display well-defined resonances with their expected integrations. In comparison to the free tetradentate precursors **1**–**4**, all signals in **5**–**8** are shifted to downfield, which is a consequence of the complexation with Lewis acidic titanium metal. In the ^{1}H NMR spectra, the extent of downfield shift in ^{1}H NMR spectra is greater for OCH_2 resonances (0.9 ppm) than for CH_2N resonances (0.6–0.8 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. 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 intra-molecular ligand exchange at ambient temperature. In addition, the ^{1}H and ^{13}C{^{1}H} NMR indicate that 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 in this titanatrane, the single-crystal X-ray diffraction studies for **6** and **7** were performed. Single-crystal X-ray structure, selected bond distances, and selected bond angles for **6** and **7** are shown in Figs. 1 and 2, respectively. In contrast to the often observed oxygen-bridged dimeric structural feature for titanatranes [3b,3d,3e,3f,3l,3p], the crystal structures of **6** and **7** show mononuclear characters, which are consistent with their NMR spectra, presumably because of the steric bulk of the axially located di-*i*-Pr-phenolate ligand. In addition to the three anionic oxygens, the titanium atom in **6** and **7** is ligated via a transannular interaction stemming from the bridgehead amino nitrogen, giving a slightly distorted trigonal bipyramidal local geometry around the metal. The amino nitrogen N and oxygen atom of di-*i*-Pr-phenolate ligand occupy the axial positions of a trigonal bipyramidal coordination array. The three five-membered rings adopt an envelope conformation similar to all the previously investigated monomeric atranes and azatranes [3,8]. The sum of the angles around the equatorial oxygens is 347.70(8)° for **6** and 347.11(7)° for **7**. As a result, the acute O$_{eq}$–Ti–N angles
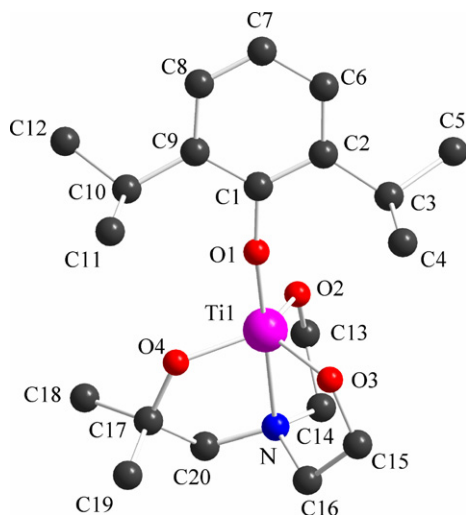
Fig. 1. Molecular drawing of compound **6** and atom labeling. (H atoms were omitted for clarity) Selected bond distances (Å): Ti1–O1 = 1.828(2), Ti1–O2 = 1.833(2), Ti1–O3 = 1.832(2), Ti1–O4 = 1.827(2), Ti1–N = 2.306(2). Selected bond angle (°): C1–O1–Ti1 = 163.79(16), O1–Ti1–N = 179.59(7), O1–Ti1–O2 = 101.39(8), O1–Ti1–O3 = 102.10(8), O1–Ti1–O4 = 102.04(8), O2–Ti1–O3 = 114.56(8), O2–Ti1–O4 = 115.41(8), O3–Ti1–O4 = 117.73(8), O2–Ti1–N = 78.86(7), O3–Ti1–N = 78.06(7), O4–Ti1–N = 77.56(8).
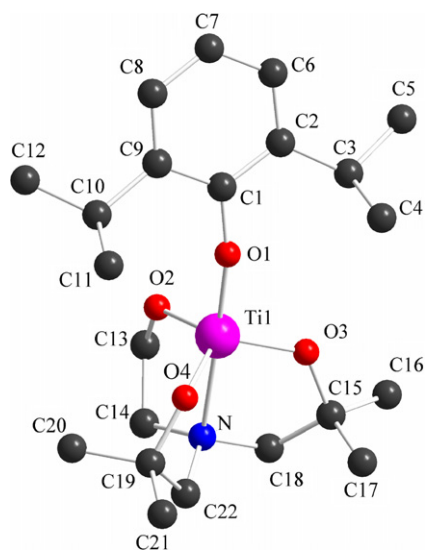

Fig. 2. Molecular drawing of compound **7** and atom labeling. (H atoms were omitted for clarity) Selected bond distances (Å): Ti1–O1 = 1.831(2), Ti1–O2 = 1.837(2), Ti1–O3 = 1.826(2), Ti1–O4 = 1.841(2), Ti1–N = 2.301(2). Selected bond angle (°): C1–O1–Ti1 = 162.06(14), O1–Ti1–N = 178.51(7), O1–Ti1–O2 = 101.25(8), O1–Ti1–O3 = 102.55(7), O1–Ti1–O4 = 102.59(7), O2–Ti1–O3 = 113.68(7), O2–Ti1–O4 = 117.89(7), O3–Ti1–O4 = 115.54(7), O2–Ti1–N = 77.39(7), O3–Ti1–N = 78.62(7), O4–Ti1–N = 77.63(7).

[avg = 78.16(7)° for **6** and 77.88(7)° for **7**] and the obtuse O_{eq}–Ti–O_{ax} angles [avg = 101.84(8)° for **6** and 102.13(8)° for **7**] reflect a displacement of the titanium atom toward the axial oxygen. Furthermore, the N_{ax}–Ti–O_{ax} angle deviates from linearity by 0.41(7)° in **6** and by 1.49(7)° in **7**. This deviation in **6** falls near the short end of the

deviation range 0.20(8)–1.46(3)° reported for other mononuclear titanatranes [3h,3i,3k,3m]; however, **7** shows somewhat large deviation compared with the deviations for other mononuclear titanatranes, although values of 15.5(1)–51.05(8)° for this angle have been described for di- or multinuclear oxo-bridged titanatranes [3b,3d,3e, 3f,3j,3l,3p]. The average Ti–O bond distance for all four oxygens in each of **6** [1.830(2) Å] and **7** [1.834(2) Å] is similar to the average of this distance observed for other structurally characterized titanatranes [3b,3d,3e,3f,3-h,3i,3j,3k,3l,3m,3p]. In addition, the transannular Ti–N bond distance in **6**[2.306(2) Å] and **7** [2.301(2) Å] falls into the middle range of 2.264(3)–2.400(3) Å found in previously structurally characterized titanium trialkanolamine derivatives [3b,3d,3e,3f,3h,3i,3j,3k,3l,3m,3p,3q]. This observation confirms the existence of the transannular interaction.

Polylactide (PLA) is the biodegradable and renewable polymeric material as the controlled drug-release devices, absorbable sutures, medical implants for orthopedic use, disposable degradable plastic articles and scaffolds for tissue engineering [9]. Until now, a large variety of catalytic systems based on tin, aluminum, zinc, magnesium, iron, lanthanide and lithium organometallic complexes containing initiating groups such as amides, carboxylates, and alkoxides for the ring opening polymerization (ROP) of lactide (LA) have been reported in the literature [10]; however, in spite of the shortest history for titanium alkoxides in the field of the ROP of LA, titanium alkoxides have been extensively studied since 2002 [3q,6,11].

To investigate the effect of the substituents in tetradentate ligand on the polymerization behavior, the compounds **5–8** are examined as catalysts for the ring opening polymerization of *l*-LA. Our results on the use of titanium alkoxide catalysts **5–8** for the bulk and solution polymerization of *l*-LA are summarized in Table 2 in terms of the activity of the catalyst, yield, T_m, and molecular weight. The PLA samples were analyzed by GPC and DSC.

Because compounds **5–8**, regardless of the polymerization condition, gave PLA with more than 90% yield within 10 h, they showed slightly higher catalytic activity than previously reported titanium alkoxides [6,11] but they still exhibited lower activity than other metal alkoxides in the ROP of LA [10]. In spite of no big differences in yield, the catalytic efficiency decreases in the order of **5–6 > 7 > 8** in bulk polymerization and in the order of **5 > 6 > 7 > 8** in solution polymerization, indicating that the steric effects of the methyl substituents in the tetradentate ligands **1–4** are best optimized when no substituents are present. Interestingly, no discrimination in activity between bulk and solution polymerization for **5–8** was found. Among **5–8**, compound **5** gave a PLA with the highest molecular weight and also the increase of the methyl substituents in tetradentate ligands exert a bad influence on the molecular weight; however, the differences between the bulk and solution conditions are not clear. So, the molecular weights of all the resulting polymers obtained

Table 2
Ring opening polymerization of *l*-LA using **5**–**8**

Entry	Catalyst	Yield (%)[c]	T_m (°C)[d]	M_n[e]	M_w[e]	PDI[e]
1[a]	**5**	95.8	166.8	10600	23800	2.25
2[b]		95.1	167.3	14800	24100	1.63
3[a]	**6**	96.2	161.1	8300	15300	1.84
4[b]		93.8	163.9	7300	13000	1.80
5[a]	**7**	93.8	161.2	6200	11700	1.90
6[b]		91.0	163.0	6900	11900	1.72
7[a]	**8**	90.3	161.0	6200	12000	1.93
8[b]		89.6	164.5	7200	12200	1.69

[a] Bulk polymerization condition: $T_p = 130$ °C, [LA]/[Ti] = 200, catalysts = 0.05 mmol, time = 10 h.

[b] Solution polymerization condition: $T_p = 100$ °C, [LA]/[Ti] = 200, catalysts = 0.05 mmol, time = 10 h, toluene 1 ml.

[c] Isolated yield.

[d] Determined by DSC.

[e] Determined by GPC.

by bulk and solution polymerization using **5**–**8** are in the range $M_w = 11700$–23800 with $M_w/M_n = 1.84$–2.25 and $M_w = 11900$–24100 with $M_w/M_n = 1.63$–1.80, respectively. Not unexpectedly, the polydispersity index (PDI) values of PLA obtained by the solution polymerization are narrower than that prepared by the bulk polymerization. Interestingly, M_n values for PLA obtained from solution polymerization are even higher than that from bulk polymerization except for **6**. Furthermore, catalysts **5**–**8** yield polymers with somewhat large polydispersities and low molecular weights. This may be attributed to a rate of initiation that is slower than the rate of polymer propagation, thus allowing more time for the occurrence of transesterification reactions during propagation. Although the polymerizations were carried out at an elevated temperature, the PLA polydispersity indices are in an acceptable range (1.63–2.25 in Table 2). In addition, all catalytic systems afford PLA with T_m values of greater than 161.0 °C, even at a high polymerization temperature. Interestingly, T_m of PLA obtained from the solution polymerization is higher than T_m from the bulk polymerization. It appears that the initiating group is the highly bulky di-*i*-Pr-phenolate group, which was shown by ^{1}H NMR spectra of the isolated PLA samples. However, no dependence of polymer yield on the degree of polymerization or molecular weight support that not-simple ROP mechanism with complicated transesterification for our catalytic system is involved.

In summary, we have synthesized a novel series of four titanatranes with controlled steric hindrance in a stepwise fashion. These complexes function, with a trend in efficiency roughly decreasing the number of methyl groups in tetradentate ligand they possess, as single-site initiators for the ring opening polymerization of *l*-LA.

5. Supplementary material

CCDC 638141 and 638142 contain the supplementary crystallographic data for this **6** and **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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