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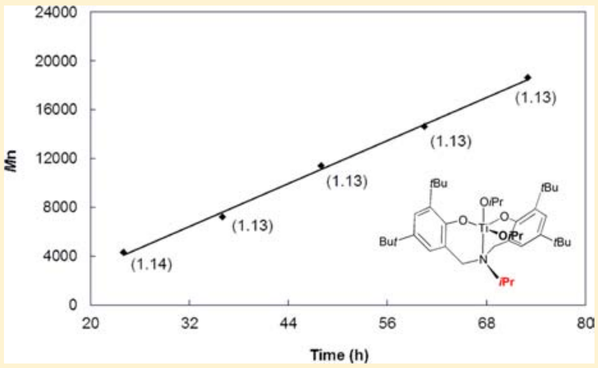
Titanium Complexes of Tridentate Aminebiphenolate Ligands Containing Distinct *N*-Alkyls: Profound N-Substituent Effect on Ring-Opening Polymerization Catalysis

Lan-Chang Liang,* Sheng-Ta Lin, and Chia-Cheng Chien

Department of Chemistry and Center for Nanoscience & Nanotechnology, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

Ⓢ *Supporting Information*

ABSTRACT: The synthesis, structural characterization, and reactivity studies of titanium complexes supported by tridentate amine biphenolate ligands of the type $[RN(CH_2\text{-}2\text{-}O\text{-}3,5\text{-}C_6H_2(t\text{Bu})_2)_2]^{2-}$ $\{[\text{R-ONO}]^{2-}$; R = *t*Bu (**1a**), *i*Pr (**1b**), *n*Pr (**1c**)$\}$ are described. Alcoholysis of $Ti(OiPr)_4$ with H_2[**1a−1c**] in diethyl ether solutions at 25 °C generates quantitatively the corresponding $[\text{R-ONO}]Ti(OiPr)_2$ (**2a−2c**) as a yellow crystalline solid. X-ray diffraction studies of **2b** and **2c** showed them to be five-coordinate, trigonal-bipyramidal species. Ring-opening polymerization of ε-caprolactone (ε-CL) catalyzed by **2b** and **2c** proved to be living, as evidenced by the narrow molecular weight distributions of the derived polymers and the linear dependence of number-averaged molecular weights on the monomer-to-catalyst ratios or polymerization time. Kinetic studies revealed that the polymerization rates are first-order in the concentration of ε-CL and first-order in that of **2b** and **2c**. The propagation rate of **2c** is ca. 15 times faster than that of **2b**, highlighting a profound substituent effect of primary versus secondary *N*-alkyls. In sharp contrast, reactions employing catalytic **2a** produce either low-molecular-weight oligomers or polymers characteristic of somewhat wider molecular weight distributions, depending on the polymerization temperatures.



INTRODUCTION

Group 4 complexes of chelating alkoxide or aryloxide ligands have long been recognized to have significant applications in polymerization catalysis.[1−4] For instance, a wide range of bi-, tri-, or tetradentate phenolate ligands have been developed for the preparation of complexes as alternatives to nonmetallocene catalysts for α-olefin polymerization.[5−15] On the other hand, the employment of phenolate complexes in catalytic ring-opening polymerization (ROP) of heterocycles such as lactides[16−26] or ε-caprolactone (ε-CL)[25,27−32] also receives increasing attention because of the biomedical functions of these polymeric materials as drug delivery excipients, adsorbable sutures, and substitutes for environmentally friendly thermoplastics.[33,34] Pioneering work by Kol and Okuda has independently shown that group 4 biphenolate complexes can act as excellent catalysts not only for polymerization of α-olefins but also for ROP of lactides.[14,35−43] It has been shown that the activities of these catalysts depend strongly on the identity of the peripheral substituents of the phenolate rings and/or the linkage connecting them.[22,44−46] Figure 1 depicts representative examples of chelating biphenolate ligands. Notably, while significant achievements on ROP catalysis have been made with metal complexes of a variety of tetradentate ligands, e.g., ONNO,[19] OSSO,[47,48] ONSO,[49] and ONOX (X = OR, NR_2),[22,45] etc., the constitution effect of tridentate variations, particularly ONO lacking an extra N-tethered donor, is not well established. We note that, although titanium complexes of tridentate ONO ligands bearing an N-substituted primary alkyl are known (e.g., R = Me, *n*Pr, CH_2Ph, CH_2Naphthyl),[27,45] their activities in ROP catalysis have yet to be explored thoroughly.

We are currently exploring coordination and reaction chemistry employing metal complexes of chelating biphenolate ligands.[29,50−56] For instance, the constitution of titanium complexes of 2,2′-hydrocarbylphosphinobis(4,6-di-*tert*-butylphenolate) ($[\text{R-OPO}]^{2-}$; R = *t*Bu, Ph) was found to be a function of the phosphorus-bound substituents and so were their catalytic activities with respect to ROP of ε-CL.[29,51] Interestingly, while $[t\text{Bu-OPO}]Ti(OiPr)_2$ catalyzes ROP of ε-CL in a living fashion, $[\text{Ph-OPO}]Ti(OiPr)_2$ exhibits a somewhat higher propensity to undergo undesirable trans-esterification, as implied by the polydispersity index (PDI) values of derived polymers under identical conditions.[29] To better understand the decisive factors of tridentate biphenolate ligands on the structure and reactivity of the derived metal complexes, we became interested in ONO ligands given their isoelectronic characteristics with established OPO analogues.

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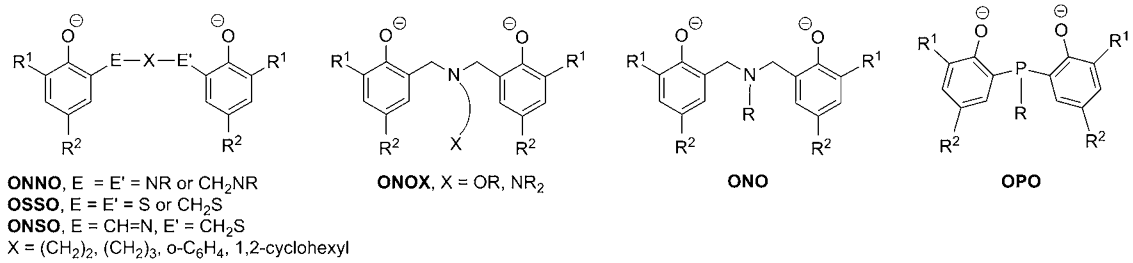
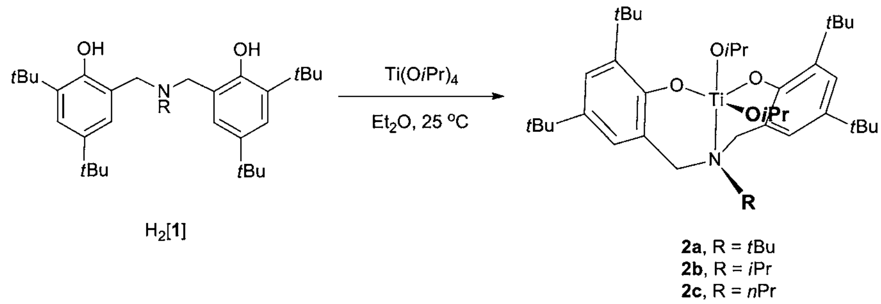


Figure 1. Representative examples of chelating biphenolate ligands.

Scheme 1



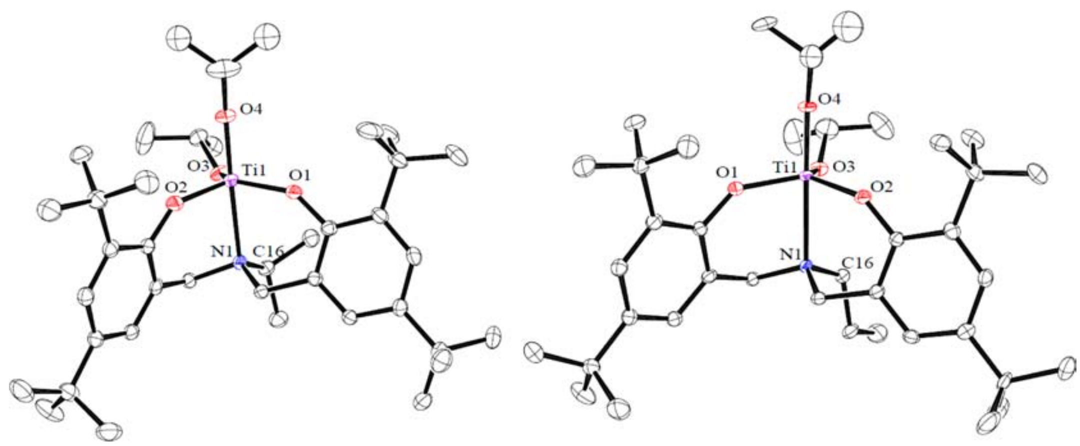


Figure 2. Molecular structures of [*i*Pr-ONO]Ti(O*i*Pr)$_2$ (**2b**, left) and [*n*Pr-ONO]Ti(O*i*Pr)$_2$ (**2c**, right) with thermal ellipsoids drawn at the 35% probability level.

We describe herein the synthesis of titanium complexes of [RN(CH$_2$-2-O-3,5-C$_6$H$_2$(*t*Bu)$_2$)$_2$]$^{2-}$ {[R-ONO]$^{2-}$; R = *t*Bu (**1a**), *i*Pr (**1b**)}[57] featuring an N-bound tertiary or secondary alkyl, complementary to those bearing an N-substituted primary alkyl such as [*n*Pr-ONO]$^{2-}$ (**1c**).[45] Although known, titanium complexes of **1c**,[45] to the best of our knowledge, were not employed for ROP catalysis with ε-CL. In this contribution, we aim to illustrate the structure and reactivity characteristics of titanium ONO complexes, particularly the N-alkyl substituent effect on ROP catalysis. Kinetic studies on ROP of ε-CL catalyzed by titanium complexes of [**1a**−**1c**]$^{2-}$ are described.

■ RESULTS AND DISCUSSION

Complex [**1c**]Ti(O*i*Pr)$_2$ (**2c**) was prepared according to literature procedures.[45] Similarly, the *tert*-butyl-substituted [**1a**]Ti(O^{i}Pr)$_2$ (**2a**) or isopropyl-derived [**1b**]Ti(O^{i}Pr)$_2$ (**2b**) was isolated as a yellow solid in quantitative yield by treating a diethyl ether solution of Ti(O*i*Pr)$_4$ with an equimolar amount of H$_2$[**1a**] or H$_2$[**1b**], respectively (Scheme 1). The solution NMR data of **2a**−**2c** are all consistent with a structure having time-averaged C_s symmetry; the mirror plane comprises the titanium center, the nitrogen donor, and two isopropoxide oxygen atoms, thereby reflecting the two phenolate rings. For instance, the ^{1}H NMR spectrum of **2b** at room temperature reveals two well-resolved septet resonances for the methine protons in the isopropoxide ligands and two sharp singlet resonances for the aryl *tert*-butyl groups. The nitrogen-bound benzylic protons are observed as two doublet resonances, reflecting their diastereotopic nature as a consequence of nitrogen coordination to titanium. A variable-temperature ^{1}H NMR study of **2b** (60 mM in toluene-d_8) revealed that the signals of isopropoxide methine protons gradually broaden upon heating and coalesce at temperatures higher than 80 °C and so do those of benzylic protons, indicating unambiguously the occurrence of a fluxional exchange process at elevated temperatures, presumably via an amine dissociation and inversion mechanism. In contrast, the isopropoxide methine and benzylic protons in the *tert*-butyl-substituted **2a** are observed as one septet and one singlet resonance, respectively, at room temperature. These signals do not resolve unless the

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temperature is decreased to −70 °C or lower (50 mM in toluene-d_8), likely reflective of the steric discrepancy of the *N*-alkyls incorporated. Complexes **2a**−**2c** are all thermally stable; no sign of decomposition was observed, as indicated by ^{1}H NMR studies (50 mM in toluene-d_8, 80 °C, 24 h).

Attempts to grow X-ray-quality crystals of **2a** were not successful. Yellow crystals of **2b** suitable for X-ray diffraction analysis were grown from a concentrated pentane solution at −35 °C, whereas pale-yellow crystals of **2c** were obtained by the slow evaporation of a pentane solution at room temperature. As depicted in Figure 2, both complexes are five-coordinate, trigonal-bipyramidal species. The nitrogen donor and one of the isopropoxide ligands are disposed axially, with N1−Ti−O4 = 178.37(8)° for **2b** and 176.95(16)° for **2c** (Table 1). The N-substituted alkyl group is positioned beneath the equatorial isopropoxide ligand. In view of the trans influence, the comparable bond distances of Ti1−O4 in both molecules indicate virtually identical electronic properties for these nitrogen donors. Although the Ti1−N1 distances are also similar, the Ti1−N1−C16 angle in **2b** [115.02(14)°] is larger than that in **2c** [111.2(2)°] and so is the dihedral angle defined by O3−Ti1−N1 and Ti1−N1−C16 (41.04° for **2b** and 32.94° for **2c**), clearly reflecting the steric discrepancy of these N-bound alkyls. Accordingly, a close contact is found for O3 and C16 in both complexes, as evidenced by the nonbonded distances of 2.99 Å for **2b** and 2.88 Å for **2c**, which are both substantially shorter than the expected van der Waals distance of 3.20 Å.[58] Space-filling models highlighting the close contact of O3 and C16 in both molecules are depicted in the Supporting Information. These results forecast that the intramolecular steric congestion should be even more severe for the five-coordinate, *tert*-butyl-substituted **2a**. The remaining bond distances and angles are unexceptional and comparable to those of five-coordinate amine- or phenolate-ligated titanium isopropoxide complexes.[15,27,45,59−61]

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2b and 2c

	2b	2c
Ti1−O1	1.8679(17)	1.846(3)
Ti1−O2	1.8408(17)	1.862(3)
Ti1−N1	2.346(2)	2.367(4)
Ti1−O3	1.8162(17)	1.798(4)
Ti1−O4	1.7819(18)	1.780(3)
O1−Ti1−O2	118.10(8)	121.51(16)
O1−Ti1−O3	124.93(8)	115.10(16)
O2−Ti1−O3	111.91(8)	118.46(16)
N1−Ti1−O1	81.49(7)	82.82(13)
N1−Ti1−O2	83.97(7)	81.23(13)
N1−Ti1−O3	82.25(7)	83.80(14)
O4−Ti1−O1	97.11(8)	97.17(15)
O4−Ti1−O2	97.45(8)	96.22(15)
O4−Ti1−O3	97.91(9)	98.93(17)
N1−Ti1−O4	178.37(8)	176.95(16)

The reactivity of **2a**−**2c** with respect to ROP of ε-CL was investigated.[62] Table 2 summarizes the polymerization results. All polymeric products were characterized by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC), which revealed a monomodal trace in each case. Consistent with the steric sizes of the *N*-alkyls in these titanium complexes, the polymerization rate follows the order **2a** < **2b** < **2c**. While **2c** completely reacts with 300 equiv of ε-CL to produce poly(ε-caprolactone) (PCL) effectively under the conditions employed (entries 5−9), both **2a** and **2b** react much slower (entries 1 and 3, respectively). The sluggish polymerization rate of **2a** may also be attributed to the somewhat stronger electron-releasing *N-tert*-butyl, which presumably lowers the electrophilicity of titanium and thus discourages monomer coordination. The discrepancy in the reactivity of the isopropyl-substituted **2b** and the *n*-propyl-derived **2c** is in accordance with the sterics of *N*-alkyls in these titanium complexes, as probed by X-ray studies. Nevertheless, the PDI values of PCLs derived from **2b** (entry 3) and **2c** (entry 6) are both low, suggesting that ROP catalyzed by these complexes is likely well-defined. As illustrated in entry 1, the product derived from **2a** is best described as low-molecular-weight oligomers. The polymerization rates of **2a** and **2b** may be efficiently increased upon heating to 80 °C (entries 2 and 4), but wider molecular weight distributions of the derived polymers result, implying that undesired transesterification takes place. It has been shown that [*t*Bu-OPO]Ti(O*i*Pr)$_2$ is a living catalyst for ROP of ε-CL at 80 °C.[29] The reactivity discrepancy between **2a** and [*t*Bu-OPO]Ti(O*i*Pr)$_2$ thus underscores apparently the constitution effect of these biphenolate ligands. In contrast to ε-CL, the titanium complexes **2a**−**2c** are inactive for *rac*-lactide or L-lactide polymerization under various conditions (e.g., toluene, 25 or 80 °C, 24 h; melt at 150 °C, 24 h), as evidenced by ^{1}H NMR studies.

Table 2. ROP of ε-CL by Catalysts 2a−2c[a]

entry	catalyst	[ε-CL]/[cat]	conv (%)[b]	M_n (calcd, kg mol^{-1})[c]	M_n (exp, kg mol^{-1})[d]	corrected M_n (exp, kg mol^{-1})[e]	PDI[d]
1	**2a**	100	12	1.4	N/A	N/A	N/A
2[f]	**2a**	100	94	10.7	11.1	6.2	1.35
3	**2b**	100	72	8.3	10.1	5.6	1.14
4[f]	**2b**	100	>99	11.4	13.6	7.6	1.40
5	**2c**	50	>99	5.7	8.4	4.7	1.17
6	**2c**	100	>99	11.4	15.9	8.9	1.18
7	**2c**	150	>99	17.0	20.5	11.5	1.20
8	**2c**	200	>99	22.7	27.6	15.5	1.17
9	**2c**	300	>99	34.0	38.0	21.3	1.18

[a]Unless otherwise noted, $[cat]_0$ = 1.0 mM in 10 mL toluene, 25 °C, 24 h. [b]Determined by ^{1}H NMR analysis. [c]Calculated from {fw of ε-CL × ($[\varepsilon\text{-CL}]_0/[cat]_0$) × conversion} + fw of *i*PrOH, assuming one propagating chain per titanium atom. [d]Measured by GPC in THF, calibrated with polystyrene standards. [e]Multiplied by a factor of 0.56.[63,64] [f]80 °C.

The catalytic activities of **2c** were examined with various equivalents of monomers (entries 5−9). Notably, the number-averaged molecular weights (M_n) of PCLs produced increase proportionally to the monomer-to-catalyst ratios (Figure 3). The PDI values of the derived PCLs in these cases are consistently low. These results imply that **2c** is a single-site catalyst and the polymer chain grows at a nearly constant rate. ROP of ε-CL catalyzed by **2c** thus proceeds in a living fashion.

Given the comparable PDI values of PCLs derived from **2b** and **2c** (entries 3 and 6), the activities of **2b** were also probed closely. In the presence of 500 equiv of monomers, **2b** polymerizes ε-CL to give PCLs with M_n values increasing linearly as a function of the polymerization time (Figure 4). The PDIs remain virtually identical and considerably low,

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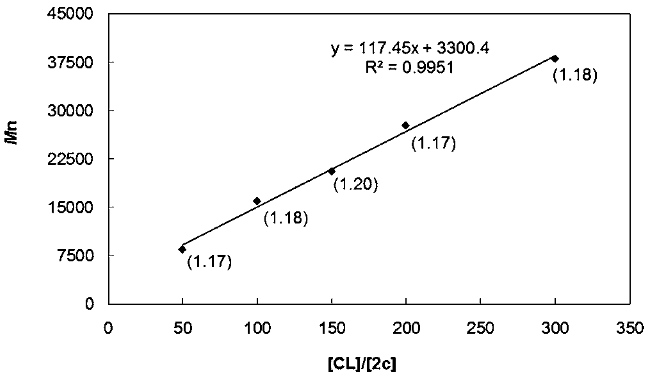

Figure 3. Linear plot of M_n (uncorrected) of PCLs prepared by **2c** versus monomer consumed to catalyst ratios (entries 5−9 in Table 2). Numbers shown in parentheses indicate their corresponding PDIs.

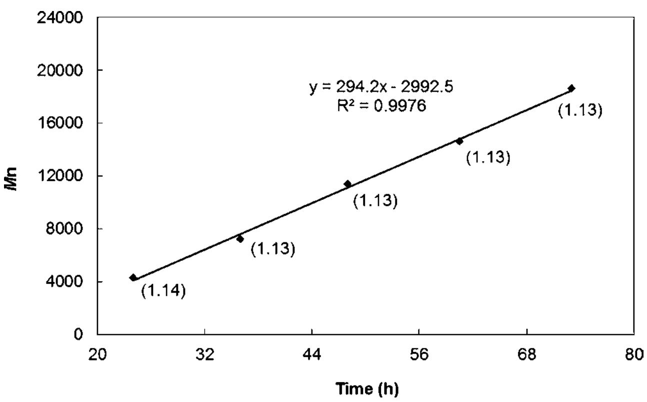

Figure 4. Linear plot of M_n (uncorrected) of PCLs prepared by **2b** versus polymerization time. Conditions: $[\mathbf{2b}]_0$ = 1.0 mM, $[\varepsilon\text{-CL}]_0$ = 500 mM, toluene, 25 °C. Numbers shown in parentheses indicate their corresponding PDIs.

thereby also featuring a living polymerization system although at a slower rate than that of **2c** for steric reasons. End-group analyses of the derived PCLs by ^{1}H NMR spectroscopy confirmed the incorporation of an isopropyl ester group (δ 4.98 for methine and δ 1.21 for methyl; Figure 5), suggesting that ROP was initiated by insertion of the coordinated ε-CL into the Ti−O*i*Pr bond followed by ring opening to cleave the acyl−oxygen bond for chain propagation. ROP catalysis thus proceeds by a coordination−insertion mechanism.[65]

To acquire mechanistic insights and better understand the N-substituent effect, we attempted kinetic studies on ROP catalysis with these titanium complexes. A comparison of the kinetic data derived from complexes **2b** and **2c** is of particular interest because they are both living ROP catalysts and composed of isomeric *N*-alkyl groups that are electronically similar but sterically distinguishable, as indicated by X-ray structural data. Monomer conversions with time at various concentrations of **2b** or **2c** were monitored by ^{1}H NMR spectroscopy in toluene-d_8 at 25 °C. As depicted in Figures 6 and 7, these data fit pseudo-first-order kinetics with the rate law shown in eq 1, although some induction periods are observed.[66−70]

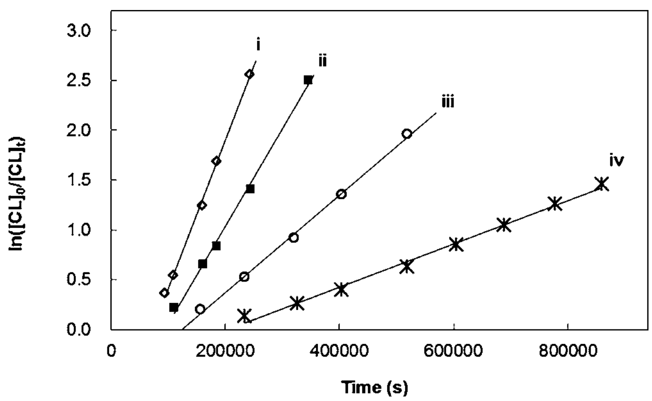

Figure 6. Semilogarithmic plots of ε-CL conversion with time employing **2b** in toluene-d_8 at 25 °C. $[\varepsilon\text{-CL}]_0$ = 1.807 M; i, $[\mathbf{2b}]_0$ = 112.5 mM, $k_{obs} = 1.49(4) \times 10^{-5}$ s^{-1}, linear fit R = 0.9982; ii, $[\mathbf{2b}]_0$ = 45.0 mM, $k_{obs} = 9.73(36) \times 10^{-6}$ s^{-1}, linear fit R = 0.9959; iii, $[\mathbf{2b}]_0$ = 18.0 mM, $k_{obs} = 4.88(15) \times 10^{-6}$ s^{-1}, linear fit R = 0.9972; iv, $[\mathbf{2b}]_0$ = 7.2 mM, $k_{obs} = 2.16(7) \times 10^{-6}$ s^{-1}, linear fit R = 0.9936.

$$-\mathrm{d}[\varepsilon\text{-CL}]/\mathrm{d}t = k_{obs}[\varepsilon\text{-CL}]^1 \quad (1)$$

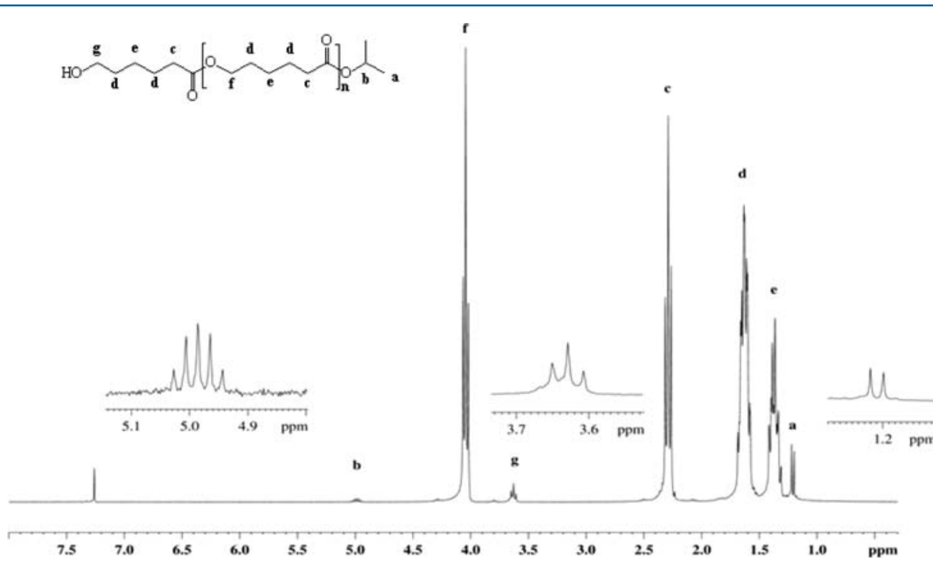

Figure 5. ^{1}H NMR spectrum of PCL (in $CDCl_3$) prepared by **2b**-catalyzed ROP of ε-CL.

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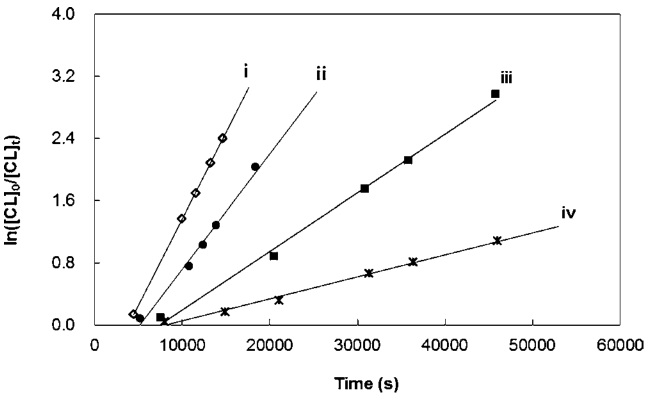

Figure 7. Semilogarithmic plots of ε-CL conversion with time employing **2c** in toluene-d_8 at 25 °C. $[\varepsilon\text{-CL}]_0$ = 1.807 M; i, $[\mathbf{2c}]_0$ = 112.5 mM, $k_{obs} = 2.23(2) \times 10^{-4}$ s^{-1}, linear fit R = 0.9997; ii, $[\mathbf{2c}]_0$ = 45.0 mM, $k_{obs} = 1.48(8) \times 10^{-4}$ s^{-1}, linear fit R = 0.9907; iii, $[\mathbf{2c}]_0$ = 18.0 mM, $k_{obs} = 7.54(31) \times 10^{-5}$ s^{-1}, linear fit R = 0.9951; iv, $[\mathbf{2c}]_0$ = 7.2 mM, $k_{obs} = 2.84(11) \times 10^{-5}$ s^{-1}, linear fit R = 0.9937.

where $k_{obs} = k_p[\mathbf{2}]^m$ and k_p = propagation rate constant.

To ascertain the order (m) in titanium catalysts **2b** and **2c**, k_{obs} versus [**2b**] and [**2c**] were plotted (Figure 8). The plots are

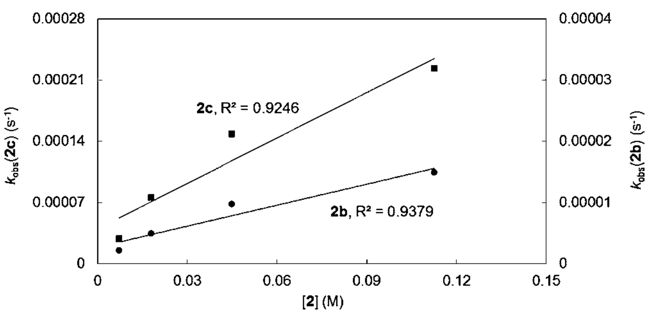

Figure 8. Plots of k_{obs} versus [**2b**] and [**2c**] for ROP of ε-CL in toluene-d_8 at 25 °C ($[\varepsilon\text{-CL}]_0$ = 1.807 M).

linear, indicating first-order dependency of the rate on these titanium catalysts. The overall kinetic law is thus expressed as eq 2, with $k_p = 1.15(50) \times 10^{-4}$ and $1.73(32) \times 10^{-3}$ L mol^{-1} s^{-1} at 25 °C for **2b** and **2c**, respectively. These results are also consistent with a coordination−insertion mechanism involving a single titanium site. Interestingly, although the *N*-alkyl substituents in **2b** and **2c** are isomeric and ROP catalyzed by both complexes follows an identical kinetic law, the propagation rate of the *n*-propyl-substituted **2c** is ca. 15 times faster than the isopropyl-derived **2b**.

$$-\mathrm{d}[\varepsilon\text{-CL}]/\mathrm{d}t = k_p[\mathbf{2}][\varepsilon\text{-CL}] \quad (2)$$

CONCLUSIONS

We have prepared a series of titanium isopropoxide complexes supported by tridentate aminebiphenolate ligands that contain a tertiary, secondary, or primary N-substituted alkyl. These complexes are all active catalysts for ROP of ε-CL. Their polymerization rates apparently decrease with increasing steric sizes of these distinct *N*-alkyls. Both isopropyl-derived **2b** and *n*-propyl-substituted **2c** act as single-site, living catalysts. Mechanistic studies suggest a coordination−insertion mechanism involving an overall second-order rate law. A profound discrepancy in the propagation rates of *n*-propyl- and isopropyl-substituted catalysts is revealed, highlighting dramatic effects of subtle ligand changes on catalyst activities.

EXPERIMENTAL SECTION

General Procedures. Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. All solvents were reagent-grade or better and were purified by standard methods. The NMR spectra were recorded on a Varian Unity or Bruker AV instrument. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane. Coupling constants (J) are listed in hertz. ^{1}H NMR spectra are referenced using the residual solvent peak at δ 7.16 for C_6D_6. ^{13}C NMR spectra are referenced using the internal solvent peak at δ 128.39 for C_6D_6. The assignment of the carbon atoms for all new compounds is based on DEPT ^{13}C NMR spectroscopy. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer.

GPC analyses were carried out at 45 °C on a JASCO instrument equipped with two Waters Styragel HR columns in series and a JASCO RI-2031 refractive index detector. High-performance liquid chromatography (HPLC) grade tetrahydrofuran (THF) was supplied at a constant flow rate of 1.0 mL/min with a JASCO PU-2080 isocratic HPLC pump. Molecular weights (M_n and M_w) were determined by interpolation from calibration plots established with polystyrene standards.

Materials. Compounds H_2[**1a**],[57] H_2[**1b**],[57] H_2[**1c**],[45] and **2c**[45] were prepared according to literature procedures. All other chemicals were obtained from commercial vendors and used as received.

X-ray Crystallography. Crystallographic data for **2b** and **2c** are available in the Supporting Information. Data were collected on a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 using *SHELXL-97*.[71] All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. The structure of **2c** contains disordered pentane. Attempts to obtain a suitable disorder model failed. The *SQUEEZE* procedure of the *PLATON* program[72] was used to obtain a new set of F^2 (hkl) values without the contribution of solvent molecules, leading to the presence of significant voids in this structure. The refinement reduced the R1 value to 0.0916. CCDC numbers are 892253−892254.

Synthesis of 2a. A diethyl ether solution (8 mL) of H_2[**1a**] (0.61 mmol) was added to a diethyl ether solution (6 mL) of Ti(O*i*Pr)$_4$ (0.61 mmol) at 25 °C. The solution was stirred at room temperature for 2 h and evaporated to dryness under reduced pressure to remove liberated isopropyl alcohol. The residue was redissolved in diethyl ether and filtered through a pad of Celite. Removal of all volatiles from the filtrate afforded the product as a yellow solid. Yield: 99%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.43 (d, 2, J = 2.3, Ar*H*), 6.96 (d, 2, J = 2.0, Ar*H*), 5.31 (septet, 2, J = 6.1, OC*H*Me$_2$), 3.73 (br s, 4, ArC*H*$_2$), 1.64 (s, 18, ArC*Me*$_3$), 1.45 (br s, 12, OCH*Me*$_2$), 1.33 (s, 18, ArC*Me*$_3$), 1.20 (s, 9, NC*Me*$_3$). ^{13}C NMR (C_6D_6, 125 Hz): δ 161.85 (*C*), 142.15 (*C*), 135.61 (*C*), 128.14 (*C*), 125.56 (CH), 123.22 (CH), 80.90 (br s, OCHMe$_2$), 61.82 (NCMe$_3$), 56.44 (ArCH$_2$N), 35.66 (ArCMe$_3$), 34.83 (ArCMe$_3$), 32.39 (ArC*Me*$_3$), 30.40 (ArC*Me*$_3$), 27.20 (OCH*Me*$_2$), 27.02 (NC*Me*$_3$). Anal. Calcd for $C_{40}H_{67}NO_4Ti$: C, 71.28; H, 10.03; N, 2.08. Found: C, 71.62; H, 10.40; N, 2.08.

Synthesis of 2b. The procedures were similar to those of **2a**, producing the product as a yellow solid. Yield: 99%. ^{1}H NMR (C_6D_6, 500 MHz): δ 7.50 (d, 2, J = 2.1, Ar*H*), 6.99 (d, 2, J = 1.8, Ar*H*), 5.33 (septet, 1, J = 6, OC*H*Me$_2$), 4.95 (septet, 1, J = 6, OC*H*Me$_2$), 4.17 (d, 2, J = 13.7, ArC*H*$_A$H$_B$), 3.47 (d, 2, J = 13.7, ArCH$_A$*H*$_B$), 3.21 (septet, 1, J = 6.8, NC*H*Me$_2$), 1.71 (s, 18, ArC*Me*$_3$), 1.41 (d, 6, J = 6.0, OCH*Me*$_2$), 1.37 (s, 18, ArC*Me*$_3$), 1.30 (d, 6, J = 6.0, OCH*Me*$_2$), 0.77 (d, 6, J = 6.8, NCH*Me*$_2$). ^{13}C NMR (C_6D_6, 75 MHz): δ 160.83 (*C*), 141.39 (*C*), 135.97 (*C*), 125.68 (*C*), 124.60 (CH), 123.75 (CH), 80.00 (OCHMe$_2$), 79.32 (OCHMe$_2$), 58.96 (ArCH$_2$N), 53.21 (NCHMe$_2$), 35.74 (ArCMe$_3$), 34.81 (ArCMe$_3$), 32.43 (ArC*Me*$_3$), 30.45 (ArC*Me*$_3$), 27.10 (OCH*Me*$_2$), 26.72 (OCH*Me*$_2$), 17.57 (NCH*Me*$_2$). Anal. Calcd

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for $C_{39}H_{65}NO_4Ti$: C, 70.98; H, 9.93; N, 2.12. Found: C, 71.14; H, 9.69; N, 2.07.

Catalytic ROP of ε-CL. A toluene solution of **2** (1.0 mM) was added to a toluene solution of ε-CL (with a prescribed concentration based on $[\varepsilon\text{-CL}]_0/[\mathbf{2}]_0$ ratios shown in Table 2). Toluene was added, if necessary, to make a total volume of the reaction solution of 10 mL. The solution was stirred at 25 or 80 °C in a prescribed oil bath for 24 h and quenched with a methanol solution of HCl. The solid thus precipitated was washed with hexane, isolated, and dried under reduced pressure until constant weight.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, space-filling models, and crystal data and structure refinement for **2b** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lcliang@mail.nsysu.edu.tw.

Notes

The authors declare no competing financial interest.

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