eXPRESS Polymer Letters Vol.12, No.2 (2018) 126–135
Available online at www.expresspolymlett.com
https://doi.org/10.3144/expresspolymlett.2018.11

Factors influencing catalytic behavior of titanium complexes bearing bisphenolate ligands toward ring-opening polymerization of *L*-lactide and ε-caprolactone

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Received 2 August 2017; accepted in revised form 20 September 2017

Abstract. A series of titanium complexes bearing substituted diphenolate ligands (**R**CH(phenolate)$_2$, where **R** = H, CH_3, *o*-OTs-phenyl, *o*-F-phenyl, *o*-OMe-phenyl, 2,4-OMe-phenyl) was synthesized and studied as catalysts for the ring opening polymerization of *L*-lactide and ε-caprolactone. Ligands were designed to probe the role of chelate effect and steric effect in the catalytic performance. From the structure of triphenolate (with one extra coordination site than diphenolate ligand) Ti complex, **TriOTiO^{i}Pr$_2$**, we found no additional chelation to influence the catalytic activity of Ti complexes. It was found that bulky aryl groups in the diphenolate ligands decreased the rate of polymerization most. We conclude that steric effect is the most controlling factor in these polymerization reactions by using Ti complexes bearing diphenolate ligands as catalysts since it is responsible for the exclusion of needed space for incoming monomer by the bulky substituents on the catalyst.

Keywords: *biodegradable polymers, polycaprolactone, ring-opening polymerization, polylactide*

1. Introduction

Ring-opening polymerization (ROP) is the most common method to synthesize biodegradable polyesters, such as poly(lactide) (PLA) and poly(ε-caprolactone) (PCL) [1, 2]. These polymers have vast applications in many fields [3, 4]. Metal catalysts [5–7] have been commonly used as catalysts for the ROP of cyclic esters. Since PLA and PCL polymers have wide application in medical field, the minimization of residual hazardous metal in these polymers after synthesis is essential. For this reason as well as its low cost, titanium complexes [8–14] were chosen as popular catalysts in ROP. Among these titanium complexes, multi-phenol ligands have proven particularly useful because of its ease of synthesis and diverse structural variation [11–14].

Two main features of Ti diphenolate complexes that influence their catalytic performance were reported in the literature–chelate effect and steric effect (Figure 1). Chelate effect exerted by extra donor coordination on diphenolate ligand on Ti catalyst was found to enhance their catalytic performance. This effect was investigated by Takashima *et al*. [12] through the application of titanium catalysts bearing chalcogen-bridged diphenolate ligands in ε-caprolactone (CL) polymerization. Their results demonstrated that extra sulfur donor was more effective with regard to initiation. In a separate study, Takashima *et al*. [13] also

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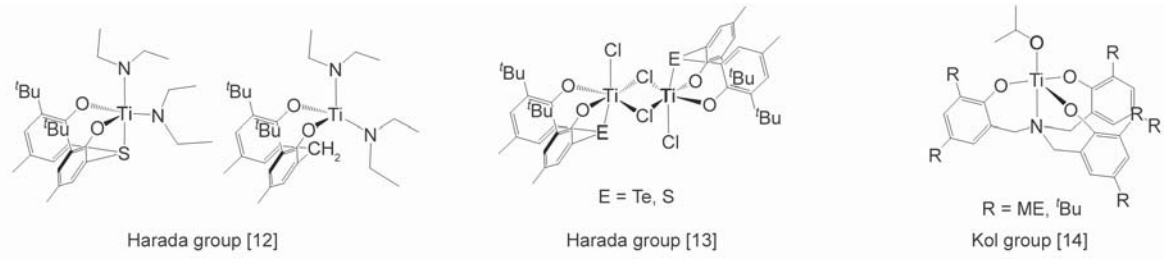

Figure 1. Current examples of Ti complexes with multi-phenolate ligands

found that the tellurium-bridged titanium complex was superior to the sulfur-bridged titanium complex catalytically. It is clear that donor effect on titanium diphenolate catalysts has an important role in determining its catalytic performance. On the other hand, Gendler *et al*. [14] studied the steric effect by the use of titanium aminotriphenolate complexes as the catalysts in *L*-lactide (LA) polymerization. Their results showed that less bulky substituents on diphenolate ligand favored the coordination of LA and enhanced LA polymerization activity.

In the previous literature chelate effect and steric effect were discussed separately. We wish to contemplate two factors on the same ligand in order to see which is more important in controlling the catalytic activity in ROP. The work on aluminum diphenolate complexes by Ko and Lin [15] was inspirational (Figure 2). They first used 2,2′-ethylidene-bis(4,6-di-tert-butylphenol) (EDBP) for the synthesis of $[(EDBP)Al(\mu\text{-}OBn)]_2$, which resulted in efficient catalytic activity in ROP of lactones with living/immortal property. Then they found catalytic activity increased when bridging methylene group on EDBP was replaced by *o*-OMe-phenyl group to give 2,2′-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butylphenol) (MEBBP) [16]. The additional aryl group offered extra donor coordination as well as extra steric hindrance. Modifying the *o*-OMe-phenyl group may give a great chance to probe the chelate effect and steric effect simultaneously. Herein we reported the syntheses of a series of titanium complexes bearing **R**CH(phenol)$_2$ (R = H, CH_3, *o*-OTs-, *o*-F-, *o*-OMe-, 2,4-OMe-phenyl) ligands and the results on how steric and chelate effects of the aryl ligand substituents may influence their catalytic behavior in CL and *L*-LA polymerization.

2. Experimental section

2.1. Chemicals

Standard Schlenk techniques and a N_2-filled glovebox were used all over the isolation and treatment of all the compounds. Solvents, ε-caprolactone, *L*-lactide, and deuterated solvents were purified prior to use. EDBP was purchased from ALDRICH. 2,4-di-*tert*-butylphenol, formaldehyde (37 wt% sol. in water), 2-methoxybenzaldehyde, 2-fluorobenzaldehyde, 2,5-dimethoxybenzaldehyde, titanium (IV) isopropoxide, *p*-toulenesulfonic acid, deuterated chloroform, *L*-lactide, and ε-caprolactone were purchased from Acros. Benzyl alcohol was purchased from Alfa Aesar. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini2000-200 (200 MHz for ^1H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal tetramethylsilane or center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. GPC measurements were performed on a Jasco PU-2080 PLUS HPLC pump system equipped with a differential Jasco RI-2031 PLUS refractive index detector using THF (HPLC grade) as an eluent (flow rate 1.0 mL/min, at 40 °C). The chromatographic column was JORDI Gel DVB 103 Å, and the calibration curve was made by primary polystyrene standards to calculate Mn(GPC). **H-diOH** [17] and **OTs-diOH**

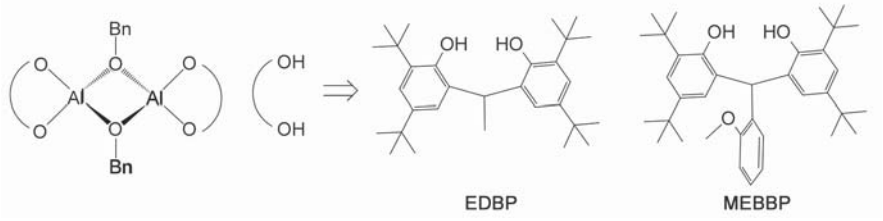

Figure 2. Structures of [(**EDBP**)Al(μ-OBn)]$_2$ and [(**MEBBP**)Al(μ-OBn)]$_2$

[18] were prepared by acid-catalyzed condensation following literature procedures. Me-Ti were prepared following literature procedures [11].

Synthesis of F-diOH

A mixture of 2,4-di-*tert*-butylphenol (4.12 g, 20 mmol) and 2-fluorobenzaldehyde (1.24 g, 10 mmol) with catalytic amount of *p*-toulenesulfonic acid was refluxed for one day in hexane (30 mL). The solution was at –20 °C for 2 days and colorless crystalline solids were obtained. Yield: 1.89 g (73%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.32~6.65 (8H, m, *H*-Ar), 5.88 (1H, s, C*H*), 4.42 (2H, s, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.16 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.53 (*C*OH), 142.81, 136.63, 130.60, 129.14, 128.97, 126.18, 124,39, 123.93, 123.27, 120.37, 115.76, 115.32 (*C*-Ar), 40.37 (CH), 34.86 (*o*-*C*(CH$_3$)$_3$), 34.29 (*p*-*C*(CH$_3$)$_3$), 31.42 (*o*-C(CH$_3$)$_3$), 29.84 (*p*-C(*C*H$_3$)$_3$). Elemental Analysis ($C_{35}H_{47}O_2F$) Found: C, 81.62%; H, 8.65%. Anal. Calcd: C, 81.04%; H, 9.13%.

Synthesis of OMe-diOH

Using a method is similar to that for ***o*-F-diOH** except 2-methoxybenzaldehyde was used in place of 2-fluorobenzaldehyde. Yield: 2.04 g (77%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.24 (1H, s, *H*-Ph(^{t}Bu)$_2$), 6.71 (1H, d, *J* = 2 Hz, *H*-Ph(^{t}Bu)$_2$), 6.93–6.99 (4H, m, *H*-Ar(*o*-OMe)), 5.92 (1H, s, C*H*), 4.95 (2H, s, O*H*), 3.80 (3H, s, OCH_3), 1.37 (18H, s, *o*-C(CH_3)$_3$), 1.16 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 156.72 (*C*OCH$_3$), 150.65 (*C*OH), 142.23 (4-*C*-Ph(^{t}Bu)$_2$), 136.45 (2-*C*-Ph(^{t}Bu)*2*), 130.46, 128.59, 126.91, 123.92, 122.78, 121.16, 110.87 (*C*-Ar), 55.74 (CO*C*H$_3$), 39.58 (*C*H), 34.95 (*o*-*C*(CH$_3$)$_3$), 34.27 (*p*-*C*(CH$_3$)$_3$), 31.48 (*o*-*C*(CH$_3$)$_3$), 29.81 (*p*-*C*(CH$_3$)$_3$). Elemental Analysis ($C_{36}H_{50}O_3$) Found: C, 81.92%; H, 8.99%. Anal. Calcd: C, 81.46%; H, 9.50%.

Synthesis of OMe$_2$-diOH

Using a method is similar to that for ***o*-F-diO**H except 2,5-dimethoxybenzaldehyde was used in place of 2-fluorobenzaldehyde. Yield: 1.94 g (69%). ^{1}H NMR ($CDCl_3$, 200 MHz) 6.90–6.61 (7H, m, *H*-Ar), 5.04 (2H, s, O*H*), 3.73 (3H, s, *o*-OCH_3), 3.66 (3H, s, *m*-OCH_3), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.18 (18H, s, *p*-C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 153.96 (*C*OH), 151.02, 150.70, 142.28, 136.51, 129.97, 126.73, 123.84, 122.84, 116.53, 113.08, 112.07 (*C*-Ar), 56.39 (*o*-OCH_3), 55.59 ($_p$-OCH_3), 39.98 (*C*H), 34.97 (*o*-*C*(CH$_3$)$_3$), 34.27 (*p*-*C*(CH$_3$)$_3$), 31.51 (*o*-C(*C*H$_3$)$_3$), 29.79 (*p*-*C*(CH$_3$)$_3$). Elemental Analysis ($C_{37}H_{52}O_4$) Found: C, 79.91%; H, 9.69%. Anal. Calcd: C, 79.24%; H, 9.35%.

Synthesis of TriO-H

A mixture of OTs-diOH (6.7 g, 10 mmol) and NaOH (0.4 g, 10 mmol) in ethanol (50 mL) was refluxed for one day and the solvent was removed from the mixture under vacuum. The residue was extracted with hexane (3×100 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated to 20 mL. The solution was at –20 °C for 2 days and white powder was obtained. Yield: 2.73 g (53%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.25–6.99, 6.94–6.82 (4H, m, ArOH) 7.28, 6.74 (4H, s, Bu$^t_2$ArOH), 5.79 (1H, s, C*H*), 5.00 (1H, s, O*H*) 4.83 (2H, s, O*H*), 1.38 (18H, s, *o*-C(CH_3)$_3$), 1.67 (18H, s, *p*-C(CH_3)$_3$). ^{1}3C NMR ($CDCl_3$, 50 MHz) δ 164.92 (*C*OH-Ph(^{t}Bu)$_2$), 159.91, 150.67, 142.37, 136.19, 134.97, 129.02, 127.11, 125.92, 124.22, 123.18, 115.39, 114.92 (*C*-Ar), 40.51 (*C*H), 34.83 (*o*-*C*(CH$_3$)$_3$), 34.25 (*p*-*C*(CH$_3$)$_3$), 31.42 (*o*-C(*C*H$_3$)$_3$), 29.92 (*p*-C(*C*H$_3$)$_3$). Elemental Analysis ($C_{35}H_{48}O_3$) Found: C, 81.55%; H, 9.09%. Anal. Calcd: C, 81.35%; H, 9.36%.

Synthesis of H-Ti

A mixture of H-diOH (2.12 g, 5 mmol) and Ti(OiPr)$_4$ (1.42 g, 5 mmol) in THF (50 mL), was stirred for 24 hr at room temperature. Volatile materials were removed under vacuum to give yellow powder and then it was washed with hexane (30 mL) and a yellow powder was obtained. Yield: 1.20 g (41%). ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.31, 7.11 (2H, s, Ar*H*), 4.72 (2H, sep, *J* = 6.0 Hz, OC*H*(CH$_3$)$_2$), 4.29 (1H, d, *J* = 14.0 Hz, Ar$_2$CH_2), 3.56 (1H, d, *J* = 14.0 Hz, (Ar)$_2$CH_2), 1.41 (18H, s, ArC(CH_3)$_3$), 1.31 (12H, d, *J* = 6.0 Hz, OCH(CH_3)$_2$). 1.29 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) : δ 159.44, 142.95, 135.60, 133.05, 134.77, 121.73, (*Ar*), 79.19 (OC*H*(CH$_3$)$_2$), 35.26 (Ar$_2$*C*H$_2$), 35.12 (Ar*C*(CH$_3$)$_3$), 34.56 (Ar*C*(CH$_3$)$_3$), 31.61 (ArC(*C*H$_3$)$_3$), and 26.27 (OCH(*C*H$_3$)$_2$). Elemental Analysis ($C_{35}H_{56}O_4Ti$) Found: C, 70.92%; H, 9.08%. Anal. Calcd: C, 71.41%; H, 9.59%.

Synthesis of F-Ti

Using a method is similar to that for **H-Ti**. Yield: 2.5 g (73%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.43~6.89

(8H, m, Ar*H*), 6.04 (1H, s, Ar_2CH), 4.71 (2H, br, $OCH(CH_3)_2$), 1.45 (18H, s, $ArC(CH_3)_3$), 1.31 (12H, br, $OCH(CH_3)_2$). 1.23 (18H, s, $ArC(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) : δ 158.47, 142.25, 135.33, 132.80, 131.23, 130.14, 127.79, 123.08, 121.13, 120.35, 115.59, 115.15 (*Ar*), 79.25 ($OCH(CH_3)_2$), 38.52 (Ar_2CH), 35.30 ($ArC(CH_3)_3$), 34.36 ($ArC(CH_3)_3$), 31.54 ($ArC(CH_3)_3$), 30.31 ($ArC(CH_3)_3$), and 26.46 ($OCH(CH_3)_2$). Elemental Analysis ($C_{41}H_{59}FO_4Ti$) Found: C, 72.12%; H, 8.52%. Anal. Calcd: C, 72.12%; H, 8.71%.

Synthesis of OMe-Ti

Using a method is similar to that for **H-Ti**. Yield: 2.2 g (64%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.42~6.71 (8H, m, Ar*H*), 5.89 (1H, s, Ar_2CH), 4.69 (2H, br, $OCH(CH_3)_2$), 3.27 (3H, s, OCH_3), 1.44 (18H, s, $ArC(CH_3)_3$), 1.32 (12H, br, $OCH(CH_3)_2$). 1.20 (18H, s, $ArC(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.67, 141.89, 134.87, 133.92, 132.97, 132.48, 129.07, 127.21, 123.77, 120.37, 119.71, 111.77 (*Ar*), 78.92 ($OCH(CH_3)_2$), 55.30 (OCH_3), 39.40 (Ar_2CH), 35.26 ($ArC(CH_3)_3$), 34.34 ($ArC(CH_3)_3$), 31.57 ($ArC(CH_3)_3$), 30.34 ($ArC(CH_3)_3$), and 26.46 ($OCH(CH_3)_2$). Elemental Analysis ($C_{42}H_{62}O_5Ti$) Found: C, 72.60%; H, 8.99%. Anal. Calcd: C, 72.00%; H, 8.99%.

Synthesis of OMe_2-Ti

Using a method is similar to that for **H-Ti**. Yield: 2.9 g (80%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.23~6.17 (7H, m, Ar*H*), 5.85 (1H, s, Ar_2CH), 4.71 (2H, br, $OCH(CH_3)_2$), 3.72 (3H, s, OCH_3), 3.26 (3H, s, OCH_3), 1.43 (18H, s, $ArC(CH_3)_3$), 1.33 (12H, br, $OCH(CH_3)_2$). 1.22 (18H, s, $ArC(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz) : δ 158.65, 153.08, 152.49, 141.91, 134.94, 133.77, 132.97, 123.62, 120.49, 115.63, 113.36, 111.73 (*Ar*), 78.93 ($OCH(CH_3)_2$), 56.11, 55.30 (OCH_3), 39.44 (Ar_2CH), 35.25 ($ArC(CH_3)_3$), 34.33 ($ArC(CH_3)_3$), 31.60 ($ArC(CH_3)_3$), 30.32 ($ArC(CH_3)_3$), and 26.43 ($OCH(CH_3)_2$). Elemental Analysis ($C_{43}H_{64}O_6Ti$) Found: C, 71.25%; H, 9.15%. Anal. Calcd: C, 71.25%; H, 8.90%.

Synthesis of OTs-Ti

A mixture of OTs-diOH (3.35 g, 5 mmol), ethanol (0.08 mL), and $Ti(O^iPr)_4$ (1.42 g, 5 mmol) in THF (50 mL), was stirred for 24 hr at room temperature. Volatile materials were removed under vacuum to give yellow powder and then it was washed with hexane (30 mL) and a yellow powder was obtained. However, the ^{1}H NMR spectrum showed the product was not pure. 0.3 g of OTs-Ti was set in NMR tube with THF 0.5 mL and CH_2Cl_2 0.5 mL in –20 °C. The yellow crystal was obtained after 1 week.

Synthesis of TriOTiO^{i}Pr$_2$

A mixture of TriO-H (2.58 g, 5 mmol) and $Ti(O^iPr)4$ (1.42 g, 5 mmol) in THF (50 mL), was stirred for 24 hr at room temperature. Volatile materials were removed under vacuum to give yellow powder and then it was washed with hexane (30 mL) and a yellow powder was obtained. However, the ^{1}H NMR spectrum showed the product was not pure. 0.2 g of $TriOTiO^iPr_2$ was set in NMR tube in –20 °C. The yellow crystal was obtained after 1 month.

2.2. General procedures for the polymerization of PCL and PLA

A typical polymerization procedure was exemplified by the synthesis of entry 1 (Table 1) using complex **H-Ti** as a catalyst. The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. Toluene (5.0 mL) was added to a mixture of complex **H-Ti** (0.1 mmol) and ε-caprolactone (1.14 g, 10 mmol) at 50 °C. After the solution was stirred for 2 hr, the reaction was then quenched by adding to a drop of ethanol, and the polymer was precipitated pouring into *n*-hexane (60.0 mL) to give white solids. The white solid was dissolved in CH_2Cl_2 (5.0 mL) and then *n*-hexane (70.0 mL) was added to give white crystalline solid. Yield: 0.90 g (79%). For LA polymerization, using a method similar to that for CL polymerization except *L*-LA was used in place of CL at 60 °C.

3. Results and discussion

3.1. Synthesis and characterization of Ti complexes

RCH(phenol)$_2$ ligands were synthesized in accordance with the methods outlined in the literature [16]. Ligands reacted with a stoichiometric quantity of titanium *iso*-propoxide in THF to produce a moderate yield of Ti complexes (Figure 3). The Ti complexes could be confirmed by the ^{1}H NMR spectrum of the disappearance of the hydrogen on phenolate group compared with related ligand spectrum (4.42–5.88 ppm). The formulae and structure were determined using ^{1}H and ^{13}C NMR spectra, elemental analysis, and X-ray crystal analysis (for **OTs-Ti** and **TriOTiO^{i}Pr$_2$**). All titanium complexes were isolated

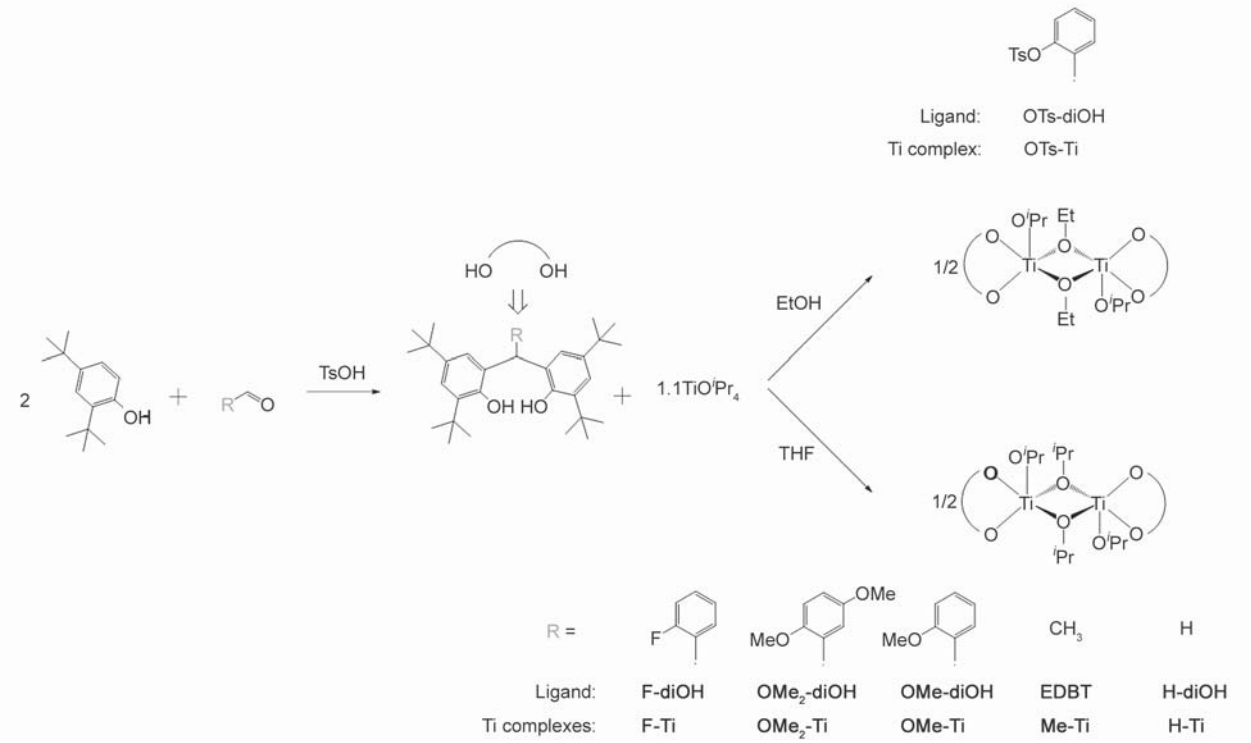

Figure 3. Synthesis of **RCH(phenol)$_2$** ligands and their Ti complexes

as dinuclear titanium *iso*-propoxide complexes except in the case of OTs-Ti where isolation of *iso*-propoxide complex failed and ethoxide complex was obtained instead (Figure 4).

From the crystal structure of **OTs-Ti** (Figure 4), it is clear that the tosyl group does not coordinate to the Ti center. The axial angle of O(6)–Ti–O(7A) is 167.19(8)° and the equatorial angles between O(1)–Ti–O(2), O(2)–Ti–O(7), and O(1)–Ti–O(7) are 109.48(8), 127.16(8), and 118.25(8)°, respectively.

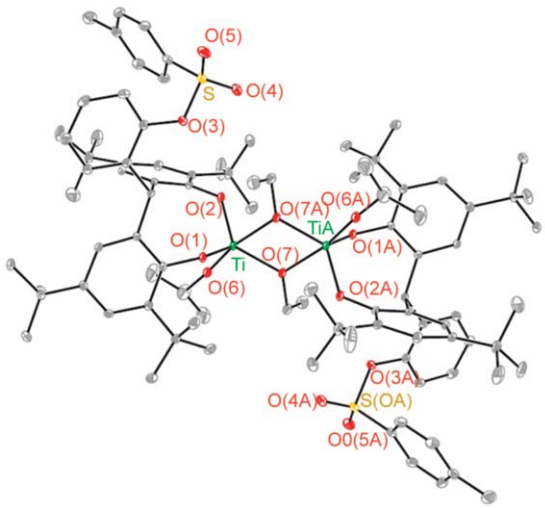

Figure 4. Molecular structures of **OTs-Ti** as 30% ellipsoids. CCDC deposition number: 1041595 (hydrogen atoms were omitted for clarity)

The distance between the Ti atom and O(1), O(2), O(6), O(7) and O(7A) are 1.8646(18), 1.8511(18), 1.7647(19), 1.9513(18) and 2.0809(18) Å, respectively. These findings confirm that the structure is distorted from an ideal trigonal bipyramidal geometry. The bond of Ti-O(6) is shorter than other Ti-O bonds due to the most electron donating feature of the terminal *iso*-propoxide. The average bond distance between the O atom of diphenolate ligand and the Ti of **OTs-Ti** is 1.8578 Å, which is comparable to that of Ti diethoxides complex bearing an EDBP ligand (1.8485 Å) [11]. In structural chemistry, the **structural parameter** (τ) is the number that indicates what the geometry of the coordination center is [19]. **OTs-Ti** presents a distorted trigonal bipyramidal geometry with τ = 0.468; however, the Ti complex in Figure 5b presents a distorted square pyramidal geometry with τ = 0.104. The bond distance between H atom in the bridging carbon and the Ti of **OTs-Ti** is 2.851 Å (Figure 5a), which is clearly longer than that of the Ti complex in Figure 5b (2.288 Å). The difference between these two Ti complexes can be attributed to the fact that a steric bulky substituent, such as the OTs group, repels the bridging ethoxide and thereby drives the substituent away. This provides evidence to support the supposition that the steric effect alters the geometry of Ti complexes and may also influence the catalytic activity in *L*-LA and CL polymerization.

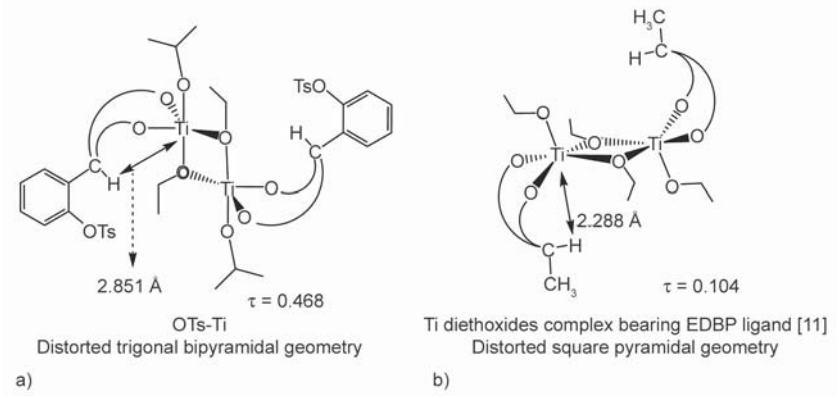

Figure 5. Comparison of molecular structures of of (a) **OTs-Ti** and (b) Ti diethoxides complex bearing an EDBP ligand [11]

3.2. Polymerization of ε-caprolactone and *L*-lactide

As shown in Table 1, using Ti complexes as catalysts for the polymerizations of *L*-LA and CL in toluene were investigated at 60 and 50 °C, respectively. As shown in entries 1–5 of Table 1 for CL polymerization ([CL]/[Cat.] = 100, toluene 5 mL), all CL polymerization processes associated with these complexes were completed within 2–4.5 hr. In addition, the $M_{n(GPC)}$ of these polymers appears similar to $M_{n(cal)}$; however, the dispersities ($Đ_M$s) of the polymers catalyzed by **F-Ti**, **OMe-Ti**, and **OMe_2-Ti** are broad ($Đ_M$ = 1.34–1.50). The catalytic rates were in the following order: **H-Ti** > **Me-Ti** > **F-Ti** > **OMe-Ti** > **OMe_2-Ti**. As shown in entries 6–10 of Table 1 for *L*-LA polymerization ([LA]/[Cat.] = 100, toluene 5 mL at 60 °C), the activity of **Me-Ti** exceeded that all other complexes, with **OMe_2-Ti** appearing to be the least efficient. The $M_{n(GPC)}$ of these PLAs also appears similar to $M_{n(cal)}$ except the PLA catalyzed by **F-Ti**. Their ability of polymer control of PLA was more efficient than that of PCL with a limited $Đ_M$ ($Đ_M$ = 1.06–1.20) and anticipated molecular weight as well as theoretical molecular weight calculated assuming the growth of four *iso*-propoxides. It implied that the transesterification in CL polymerization occurred easily compared with *L*-LA polymerization.

We also conducted kinetic studies to determine the k_{obs} in order to elucidate the catalytic behavior of these titanium complexes in the polymerization of CL and *L*-LA (Table 2–4, Figures 6 and 7). The results indicated that all the polymerization rate is a first-order dependency on monomer concentration in all polymerizations by using various Ti complexes as catalysts according to Equation (1). In Table 2, the

Table 1. Polymerization of ε-caprolactone and *L*-lactide using each of the Ti complexes as catalysts

Entry	Cat.	Monomer	Time [h]	Conv.[a]	$M_{n(Cal)}$[b]	$M_{n(GPC)}$[c]	$Đ_M$[c]
1[d]	**H-Ti**	CL	2.0	>99	5800	4800	1.18
2[d]	**Me-Ti**	CL	2.5	91	5200	4100	1.11
3[d]	**F-Ti**	CL	2.5	88	5100	7100	1.50
4[d]	**OMe-Ti**	CL	3.0	90	5200	7000	1.34
5[d]	**OMe_2-Ti**	CL	4.5	92	5300	6200	1.47
6[e]	**H-Ti**	LA	2.0	91	6600	4600	1.06
7[e]	**Me-Ti**	LA	2.0	94	6800	5000	1.07
8[e]	**F-Ti**	LA	3.7	92	6600	11000	1.18
9[e]	**OMe-Ti**	LA	5.0	91	6700	8200	1.20
10[e]	**OMe_2-Ti**	LA	5.0	85	5700	5600	1.12

[a]Obtained from ^{1}H NMR analysis.
[b]Calculated from the molecular weight of monomer·([monomer]$_0$/2[Cat]$_0$)·conversion yield + $M_{w(Pr^iOH)}$.
[c]Obtained from GPC analysis with calibration based on the polystyrene standard. Values obtained from GPC times 0.56 for PCL and 0.58 for PLA.
[d]Reaction condition: toluene 5 mL, [CL] = 2.0 M, 50 °C, [CL]:[Cat] = 100:1.
[e]Reaction condition: toluene 5 mL, [LA] = 2.0 M, 60 °C, [LA]:[Cat] = 100:1.

Table 2. Kinetic study of polymerization of ε-caprolactone and *L*-lactide using each of the Ti complexes as catalysts

Cat.	CL	LA
	k_{obs} (error)	
H-Ti	0.0265 (4)	0.0208 (8)
Me-Ti	0.0207 (9)	0.0268 (8)
F-Ti	0.0150 (4)	0.0113 (2)
OMe-Ti	0.0147 (4)	0.0082 (1)
OMe_2-Ti	0.0104 (2)	0.0067 (2)

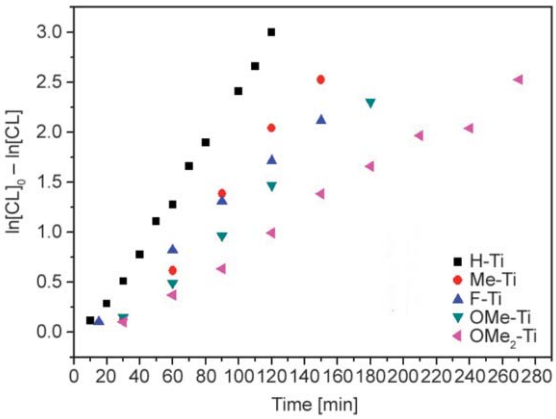

Figure 6. First-order kinetic plots for CL polymerizations with time with different Ti complexes

trend in the activity of titanium complexes with regard to the polymerization of CL is **H-Ti** > **Me-Ti** > **F-Ti** > **OMe-Ti** > **OMe_2-Ti**, which is similar to that of LA (**Me-Ti** > **H-Ti** > **F-Ti** > **OMe-Ti** > **OMe_2-Ti**). This indicates that increasing the size of the aryl group of **RCH(phenol)$_2$** decreases the polymerization rate because the steric bulky aryl group occupies the space around the catalytic Ti center, which hinders the coordination of CL and *L*-LA from titanium atom. The electronic effect of the aryl group with various substituents in the ligand should be neglected because it and other two phenolates were linked with the single bonds, implied that there is no electronic effect between them. Further, if the donating group in the *ortho*-position of the aryl ring is able to coordinate Ti atom, then catalytic activity would be influenced by Equation (1):

$$-\frac{d[\text{monomer}]}{dt} = k_{obs}[\text{monomer}] \quad (1)$$

To understand the relationship between polymerization activity and the donating group in the *ortho*-position of the aryl ring, a triphenol ligand (**TriO-H**) and

Table 3. The variations of [PCL] in ROP process with these Ti complexes in toluene 5 mL, [CL] = 2.0 M at 50 °C

Time [min]	H-Ti	Me-Ti	F-Ti	OMe-Ti	OMe_2-Ti
	Conv. [%]				
10	11				
15			10		
20	25				
30	40	12		14	10
40	54				
50	67				
60	72	46	56	39	31
70	81				
80	85				
90		75	73	62	47
100	91				
110	93				
120	95	87	82	77	63
130					
150		92	88		75
210					86
240					87
270					92
k_{obs}	0.02655 (44)	0.02073 (92)	0.01497 (39)	0.01465 (42)	0.01037 (22)
Induction period [min]	9.0 (12)	25.0 (44)	6.0 (26)	22.0 (31)	22.0 (33)

Table 4. The variations of [PLA] in ROP process with these Ti complexes in toluene 5 mL, [LA] = 2.0 M at 60 °C

Time [min]	Me-Ti	H-Ti	F-Ti	OMe-Ti	OMe_2-Ti
	Conv. [%]				
10	12	15	12		
20	37	37			
30	50	50	30	17	15
40	60	61			
50	69	68			
60	78	72	50	38	25
70	83	76			
80	88	80			
90	89	84	63	51	40
110		91			
120			76	60	52
150					62
180					67
190			88		
210				82	73
220			92		
240					79
300				91	
k_{obs}	0.02675 (75)	0.02078 (75)	0.01131 (19)	0.00821 (13)	0.00672 (17)
Induction period [min]	4.4 (16)	0	0	5.0 (25)	11.0 (38)

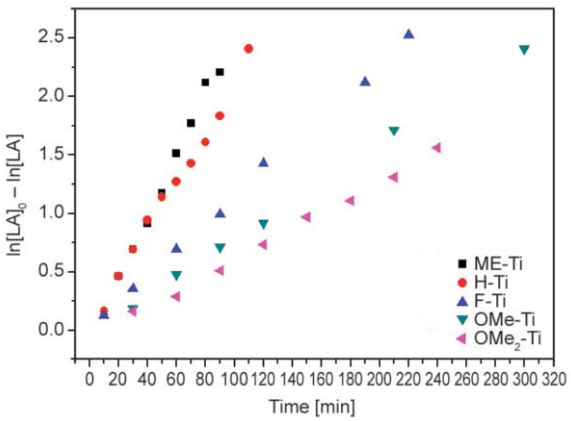

Figure 7. First-order kinetic plots for LA polymerizations with time with different Ti complexes

its Ti complex were synthesized (Figure 8) in order to evaluate the likelihood of coordination between the donating groups and Ti atoms. Our results revealed the production of a di-nuclear Ti complex (**TriOTiO^{i}Pr$_2$**) comprised two triphenolate ligands, two Ti atoms, and four terminal *iso*-propoxides (Figure 9). Two Ti atoms are connected by two phenolate groups from two different triphenolate ligands; however this is an indication that the donating group in the *ortho*-position of the aryl ring is unable to coordinate with Ti, even in a di-nuclear form. The crystal structure also revealed that the hydrogen bond was not negligible interaction in the molecular structure. In Figure 9, two Ti atoms of di-nuclear complex presented a different situation. Here the hydrogen bond of O(4)-H(3) (2.280 Å) caused the 2,4-di-*tert*-butylphenol to approach the Ti(1) atom; however, the bond distances of O(5)-H(8) and O(6)-H(8) were 3.945 and 4.488 Å, which clearly indicated that no interaction existed between H(8) and the two O atoms of *iso*-propoxides. The bond length of Ti(1)-H(11A) is 2.434 Å, which is shorter than that of Ti(2)-H(52A) (2.954 Å).

A survey of the structures of triphenolate Ti alkoxide [20] revealed a preference for the tri-nuclear form

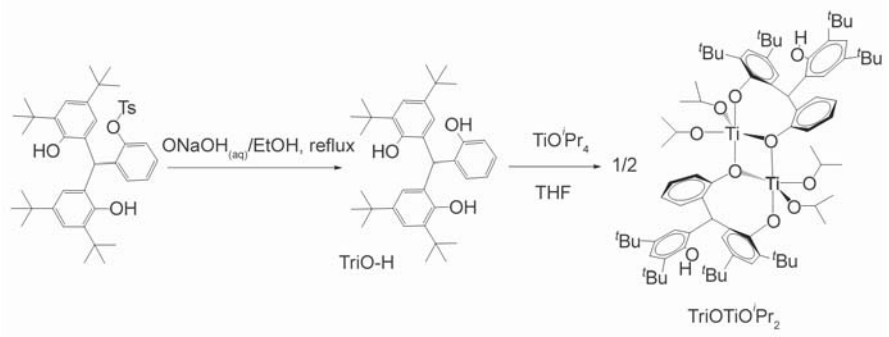

Figure 8. Synthesis of **TriOTiO^{i}Pr$_2$**

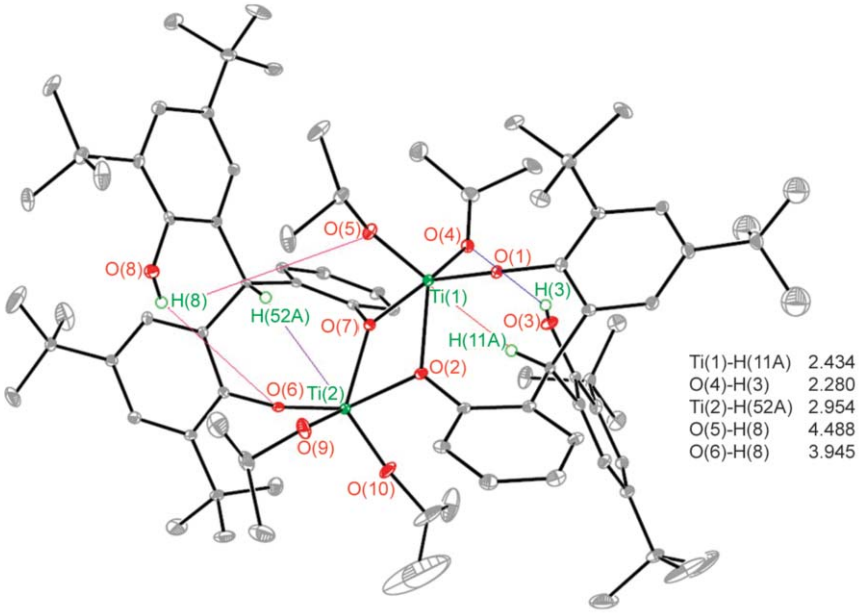

Figure 9. Molecular structure of **TriOTiO^{i}Pr$_2$** as 30% ellipsoids with selecting bond lengths. CCDC deposition number: 1042342 (hydrogen atoms were omitted for clarity)

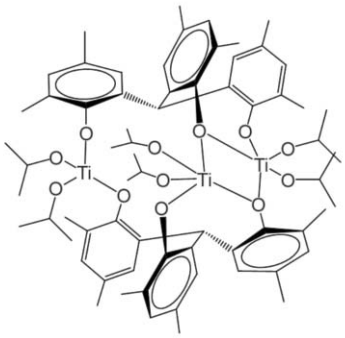

Figure 10. Molecular structures of Ti complexes bearing trisphenol [18]

(Figure 10). All phenol groups from ligands underwent acid-base reaction with alkoxide; however, molecular structure of **TriOTiO^{i}Pr$_2$** showed that the phenols and *iso*-propoxides were in the same molecule and spatial effect prevented phenols and *iso*-propoxides from undergoing an acid-base reaction. In addition, oxygen atoms from the phenolates were more suitable than that of *iso*-propoxides as bridging atoms.

4. Conclusions

A series of **RCH(phenol)$_2$** ligands were synthesized and associated titanium complexes in catalyzing the polymerization of CL and *L*-LA were studied. The rate of CL and *L*-LA polymerization was altered according to the aryl groups of **ArCH(phenol)$_2$**. Among these Ti complexes, steric tiny substituents, such as hydrogen or a methyl group, resulted in the highest polymerization rate, whereas increasing the size of the aryl group decreased the rate of polymerization. According to the molecular structure of **TriOTiO^{i}Pr$_2$**, the donating group in the *ortho*-position of the aryl ring was unable to coordinate with Ti atom. It would be reasonable to suppose that the steric effect influences catalytic ability, such that the ligand of the Ti complex would have to occupy the space around the Ti center in order to hinder monomer coordination. This conjecture is in line with previous findings [14].

Acknowledgements

This study is supported by Kaohsiung Medical University NSYSU-KMU JOINT RESEARCH PROJECT, (#NSYSUKMU 105-I004), and the Ministry of Science and Technology (Grant MOST 105-2113-M-037-007). We thank Center for Research Resources and Development at Kaohsiung Medical University for the instrumentation and equipment support.

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