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Catalytic improvement of titanium complexes bearing bis(aminophenolate) in ring-opening polymerization of L-lactide and ε-caprolactone

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ABSTRACT

This study synthesized and examined a series of titanium aminophenoxide complexes as catalysts for the ring-opening polymerization of L-lactide and ε-caprolactone. These Ti complexes are more active for LA than for CL. The interaction between coordinating atoms of the ligands and the central metal ions has a considerable influence on the resulting catalyses. The complex with thiophenyl groups demonstrated the highest catalytic activity, due to the lability of thiophenyl groups. Rapid changes between association and dissociation can be used to tune the electronic density of Ti in order to avoid contending with the coordination of L-lactide and ε-caprolactone to increase activity. In addition, kinetic results indicate a first-order dependency on [$\mathbf{L^{OMe}Ti(O^iPr)_2}$] and a first-order dependency on [CL] and [LA] respectively.

1. Introduction

Aliphatic polyesters such as poly(ε-caprolactone) (PCL), poly(lactide) (PLA), and their copolymers have demonstrated wide applicability in a variety of fields [1], due to their biodegradability, biocompatibility, and permeability. The preparation of PCL and PLA has subsequently undergone intensive study and ring-opening polymerization (ROP) has been the most common approach. Many metal complexes [2] have been used as catalysts for the ROP of cycloesters; however, materials employed in medical applications require low cytoxicity. As a result, Ti complexes [3d] are the commonly used catalysts in ROP, due to the low cost of the precursor and the high oxidation state associated with polyanionic ligands. Salen type ligands (bis(iminophenol)) (Fig. 1) are commonly employed because the framework between the two nitrogen atoms can be altered according to one's objectives. For example, linear alkyl groups produce fluxional ligands, while cycloalkyl groups (e.g. the cyclohexyl group) produce the rigid and chiral ligands. The phenyl group produces a rigid ligand with higher electronic density. In addition, the substitute group on the phenol ring can be altered according to the steric or electronic properties. The three octahedral coordination isomers of metal complexes are presented in Fig. 2. The following literatures are the examples of the ROPs employing Ti complexes with Salen ligands [3].

In 2006, Gibson [3a] reported that the *trans*-Ti complex with Salen ligand provides greater catalytic activity than the *cis* form with regard to *rac*-lactide polymerization. In the same year, Gibson [3b] reported that electron-withdrawing substituents within the Salen framework of Ti complexes can reduce the propagation rate of lactide (LA) monomers.

Another similar ligand is bis(aminophenol) (Salan type) [4] (Fig. 3). The framework between two nitrogens can be altered and the functional groups (R_3) associated with the nitrogen may also be used to control the steric effect. In the following, we outline the important work on ε-caprolactone (CL) and LA polymerization using Ti and Zr bis(aminophenolate) complexes. Davidson [4c] reported that the steric bulky substituents on the phenolate ring decreased the polymerization rate of CL and LA using Zr complexes as the catalysts; however, the opposite is true for Ti complexes. Kol [4a] reported that the electron donating substituent (in the R_1 and R_2 positions) of ligands increases the activity of Ti complexes in LA polymerization but opposite results for Zr complexes. Kim [4d] reported a slight increase in catalytic activity from the methyl to benzyl groups in the R_3 position of Ti complexes. Few studies have investigated the steric effect (in the R_3 position of Ti complexes) on the catalytic activity of corresponding Ti complexes for ROP of lactide, due to difficulties involved in the synthesis of

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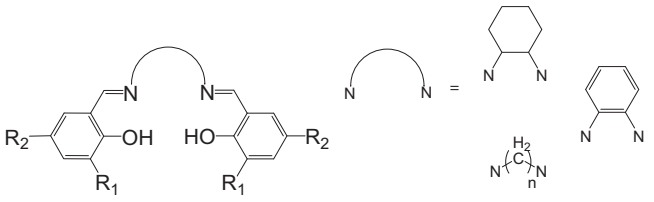

Fig. 1. Salen type ligands.

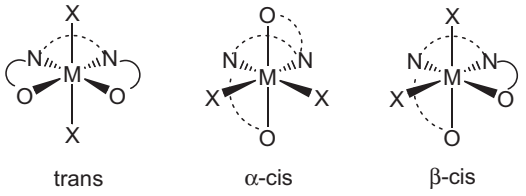

Fig. 2. Octahedral coordination isomers of metal complexes with Salen ligands.

bis(aminophenol) using bulky or coordinated groups in the R_3 position. In addition, the common coordination number of Ti complexes is six and the atoms in the R_3 position did not easily coordinate to Ti for the Ti complexes with bis(aminophenolate) and two alkoxide ligands. A survey of Ti complexes bearing Salen or Salan ligands for the cycloester polymerization showed that their catalytic activity is low because the coordination spheres of Ti atoms bearing Salen or Salan ligands are congested and the compound structure have to transform into less-six-coordination states to accept monomer or form the unlikely seven coordination states with monomer donating.

Neves [5] attempted to synthesize Zn complex using hexadentate bis(aminophenol). The synthesis of this Salan ligand is presented in Fig. 4. Inspired by this ligand, we planned to synthesize a series of bis(aminophenol) ligands with two extra pendent coordinating groups and their Ti complexes. If the size of Ti is too small to form a seven or eight coordination complex, the extra coordinated groups in the R_3 positions are useless and may even compete against the coordination of monomers, thereby decreasing the polymerization rate. If two extra pendent coordinating groups are labile and can help the Ti complexes to transform into less six coordination states, the polymerization rate of bis(aminophenolate)Ti complexes with two extra pendent coordinating groups will be faster than that of tetradentate bis(aminophenolate)Ti complexes. In addition, the pendent functional group can influence the catalytic activity of Ti complexes because the pendant atoms of coordinated ligands provide the metal with electrons through coordination, which weakens the metal-alkoxide bond [6]. Herein, we designed a series of Salan ligands and their Ti complexes. According to the result of CL and L-LA polymerization using these Ti complexes as the catalysts, the best pendent functional group for increasing the catalytic activity can be found out and it investigated the underlying catalytic mechanism.

2. Results and discussion

2.1. Synthesis and characterization of Ti complexes

All ligands were prepared through the condensation reactions of arylaldehydes and ethylenediamine to form diimines. The diimines were reduced using $NaBH_4$ and reacted with 2,4-di-*tert*-butyl-6-(chloromethyl)phenol to form hexadentate bis(aminophenol). All ligands reacted with a stoichiometric quantity of titanium isopropoxide in THF to produce a moderate yield of Ti compounds (Fig. 5). The formula and structure were confirmed by ^{1}H and ^{13}C NMR spectra, elemental analysis, and X-ray crystal analysis. The X-ray structure of **$L^FTi(O^iPr)_2$** (Fig. 6) illustrates the octahedral geometry of the Ti complex, with the *cis* position between two isopropoxides and the *trans* position between two phenolate groups. The axial angle of O(2)-Ti-O(1) is 168.80(7) and the equatorial angles between N(2)-Ti-N(1), O(4)-Ti-N(2), O(4)-Ti-O(3), and O(3)-Ti-N(1) are 73.84(6), 95.09(7), 107.73(7), and 89.87(7)°, respectively. The distances between the Ti atom and O(1), N(1), O(2), O(3), O(4) and N(2) are 1.8853(15), 2.3856(18), 1.8915(15), 1.8178(16), 1.8334(16), and 2.3910(18) Å, respectively, confirming the distortion of the structure from an ideal octahedral topology. In addition, the angles of C(47)-O(4)-Ti and C(50)-O(3)-Ti are 134.11(14) and 138.66(15)°, which exceeds 109.5°. This means that there are π bonds between Ti and oxygen of isopropoxides and shorter bond distances than the bonds between Ti and oxygen of phenolate groups. Compared with **$L^{Bn}Ti(O^iPr)_2$** [4d], the bonds of Ti—O^{i-Pr} are longer in **$L^FTi(O^iPr)_2$** than **$L^{Bn}Ti(O^iPr)_2$** (1.818(4) and 1.800(5) Å) and the angles of C—O^{i-Pr}—Ti are smaller in **$L^FTi(O^iPr)_2$** than **$L^{Bn}Ti(O^iPr)_2$** (138.3(4) and 148.9(5)°). There is no interaction between Ti and F (no coordination and resonance effect) but the bonding between Ti and O^{i-Pr} is changed.

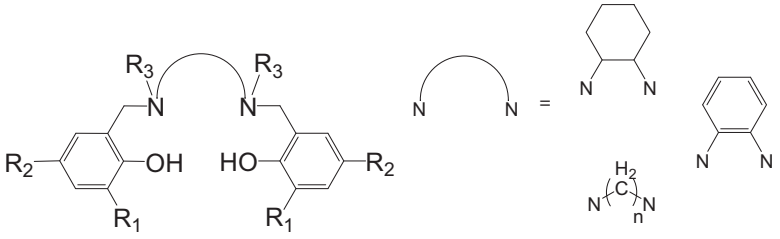

Fig. 3. Bis(aminophenol) ligands (Salan type).

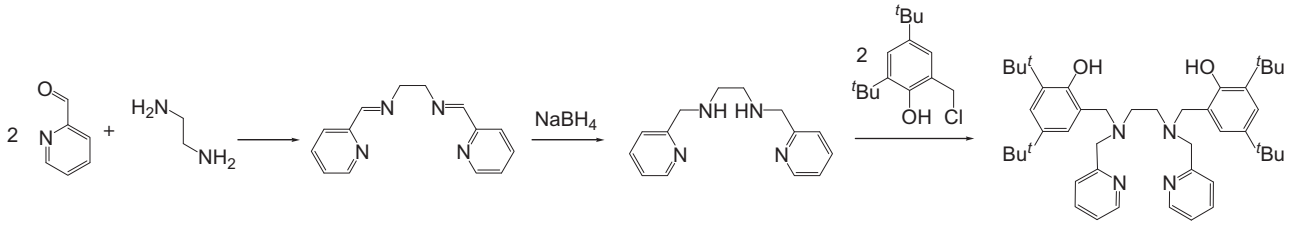

Fig. 4. Preparation of hexadentate bis(aminophenol) ligand.

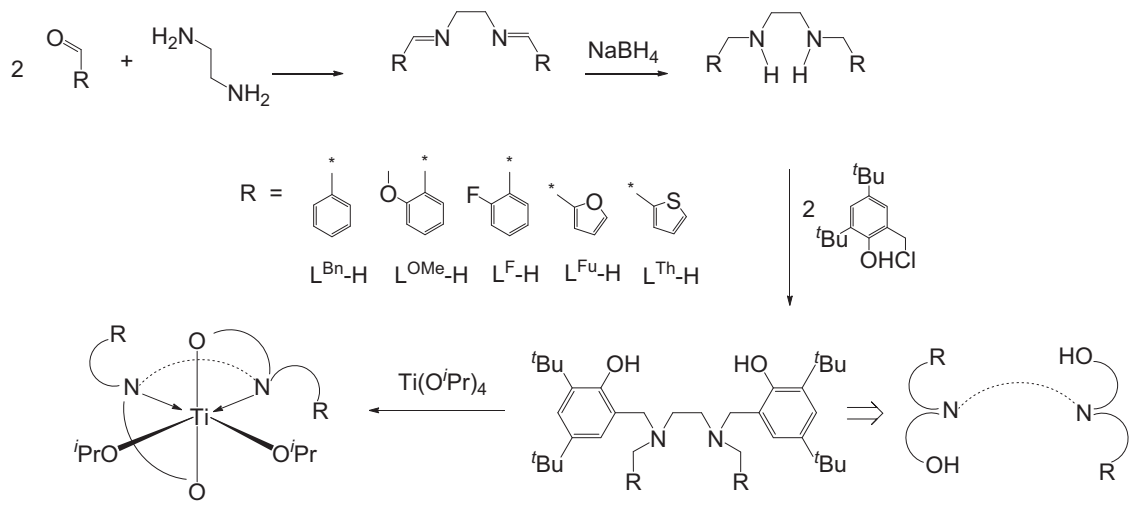

Fig. 5. Synthesis of bis(aminophenol) ligands and their Ti complexes.

Crystal-related data indicated no coordination between Ti and fluorine; however, the ^{1}H NMR spectra of these complexes revealed interesting information. In Fig. 7, protons (a) (blue) are the four H atoms in the ethylenediamine group, protons (b) (green) are the four H atoms of methenes in the 2,4-di-*tert*-butyl-6-methylphenol group, and protons (c) (red) are the four H atoms of methenes in the pendent group (*R*). When *R* is a phenyl group (Ti–Bn), protons (c) are the singlet peak, which means that the benzyl group can freely rotate. A different situation may also occur, in which the protons (c) are the doublet of doublets peak when *R* is a 2-methylphenyl, 2-fluorophenyl, furan-2-yl, or thiophen-2-yl group. This splitting pattern is predictable regardless of the timescale of fluxionality of complex and therefore cannot be used as a diagnostic of coordination of the *R* group to the metal.

2.2. Polymerization of ε-caprolactone and L-lactide

Polymerizations of L-LA and CL using Ti complexes as an initiator in toluene were investigated at 120 °C (Table 1). As shown in Table 1, different Ti complexes demonstrated different degrees of catalytic rate (in L-LA and CL polymerization) using different ligands. As illustrated by entries 1, 3, 5, 7, and 9 of Table 1 for CL polymerization ([CL]/[Cat.] = 10, benzene-*d*6 1 mL in a sealed NMR tube), the catalytic rate was in the following order: $\mathbf{L^{Th}Ti(O^iPr)_2} > \mathbf{L^{Bn}Ti(O^iPr)_2} > \mathbf{L^{F}Ti(O^iPr)_2} > \mathbf{L^{OMe}Ti(O^iPr)_2} > \mathbf{L^{Fu}Ti(O^iPr)_2}$. All the CL polymerization associated with these complexes was completed within 80 h using [CL] = 5 M in 5 mL toluene at 120 °C (entries 2, 4, 6, 8, and 10 of Table 1). The $M_{n(GPC)}$ of these polymers appeared slightly larger than $M_{n(cal)}$ and $M_{n(NMR)}$ and their polydispersity index (PDI) was narrow, with the exception of $\mathbf{L^{Bn}Ti(O^iPr)_2}$ due to reduced transesterification resulting from a reduction in the protection of ligands.

As shown in entries 1, 3, 5, 7, and 9 of Table 2 for L-LA polymerization ([LA]/[Cat.] = 10, benzene-d_6 1 mL at 120 °C in a sealed NMR tube), the activity of $\mathbf{L^{Th}Ti(O^iPr)_2}$ still exceeded that of $\mathbf{L^{Bn}Ti(O^iPr)_2}$ and others had lower catalytic rate than $\mathbf{L^{Bn}Ti(O^iPr)_2}$. The L-LA polymerization using $\mathbf{L^{Th}Ti(O^iPr)_2}$ as the catalyst was finished in 20 h with [LA] = 5 M in 2 mL toluene at 100 °C (entries 2 of Table 2); however, other Ti complexes showed lower catalytic rate. The range of PDI of these polymers was 1.14–1.26. $\mathbf{L^{Th}Ti(O^iPr)_2}$ provided the best catalytic rate for both L-LA and CL polymerization, revealing the ability of sulfur atoms to increase the polymerization rate of Ti complexes. According to literature reports [4c,7], Ti complexes are in general more active for CL than for LA, but our results showed the opposite phenomenon. Few papers [8] reported that their Ti complexes showed higher activity for the polymerization of LA than for the polymerization of CL without explanations.

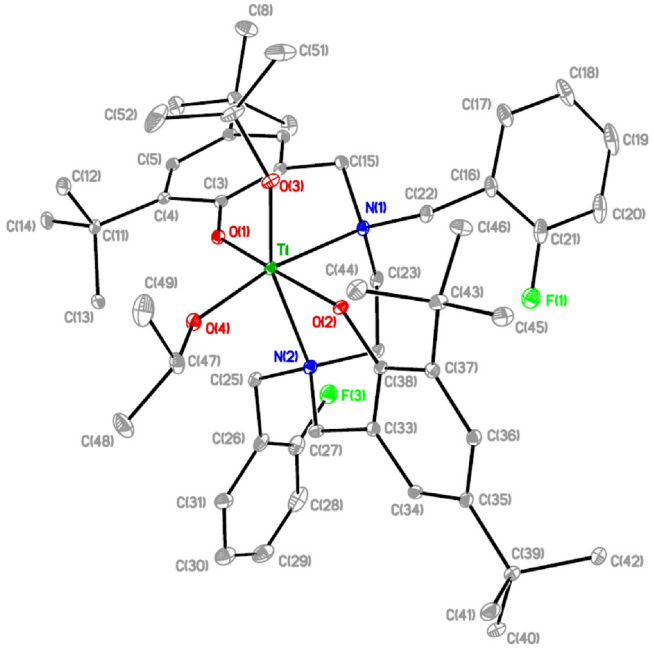

Fig. 6. Molecular structure of complex $\mathbf{L^FTi(O^iPr)_2}$ as 20% probability ellipsoids (all of the hydrogen atoms were omitted for clarity. The deposition numbers of crystallographic data: CCDC 949467).

Although $\mathbf{L^{Th}Ti(O^iPr)_2}$ presented the best catalytic activity, it did not necessarily have the highest polymerization rate. These Ti complexes have an octahedral geometric framework, which should require transformation to real active intermediates with a lower coordination number in order to accept monomers coordination; the induction period may be the time required for transformation. The pendent groups of the ligands may decrease the transformation time or increase the polymerization rate of their intermediate. Therefore, the polymerization of CL and LA by these Ti complexes was monitored by ^{1}H NMR to obtain the k_{obs} and the induction period of these catalysts (Table 3, Figures S1–S4, and Tables S1–S4). In addition, two d-solvents (C_6D_6 and $CDCl_3$) were used to investigate the solvent effect with different polarity. In Table 2, $\mathbf{L^{Th}Ti(O^iPr)_2}$ had a higher k_{obs} value than $\mathbf{L^{Bn}Ti(O^iPr)_2}$ for CL and LA polymerization in benzene-d_6 and $CDCl_3$; however,

Table 1
Polymerization of ε-caprolactone using each of the Ti complexes as an initiator.

Entry	LTi(O^iPr)$_2$	Time (h)	Conv.[a]	$M_{n(Cal)}$[b]	$M_{n(NMR)}$[a]	$M_{n(GPC)}$[c]	PDI[c]
1[d]	L^{Th}	7.75	90				
2[e]		40	>99	2900	2300	2200	1.02
3[d]	L^{Bn}	30.5	93				
4[e]		40	>99	2900	1900	2900	1.26
5[d]	L^{F}	51.25	91				
6[e]		40	62	1900	800	1900	1.20
7[d]	L^{OMe}	56.5	86				
8[e]		40	54	1600	1400	1800	1.25
9[d]	L^{Fu}	75.5	93				
10[e]		40	28	–[f]	–[f]	–[f]	–[f]

[a] Obtained from ^{1}H NMR analysis.
[b] Calculated from the molecular weight of monomer × [monomer]$_0$/2[Cat]$_0$ × conversion yield + Mw(Pr^iOH).
[c] Obtained from GPC analysis and calibration based on the polystyrene standard. $M_{n(GPC)}$ is the value obtained from GPC times 0.56.
[d] Reaction condition: benzene-d_6 (1 mL) in sealed NMR tube, [CL] = 1.0 M, 120 °C, [CL]:[Cat] = 10:1.
[e] Reaction condition: toluene (5 mL) in Schlenk flask, [CL] = 5.0 M, 100 °C, [CL]:[Cat] = 50:1.
[f] Not available.

Table 2
Polymerization of L-lactide using each of the Ti complexes as an initiator.

Entry	LTi(O^iPr)$_2$	Time (h)	Conv.[a]	$M_{n(Cal)}$[b]	$M_{n(NMR)}$[a]	$M_{n(GPC)}$[c]	PDI[c]
1[d]	L^{Th}	10.5	91				
2[e]		20	>99	7300	–[f]	5400	1.26
3[d]	L^{Bn}	15	95				
4[e]		20	37	2700	–[f]	2400	1.16
5[d]	L^{F}	26	91				
6[e]		20	43	3100	–[f]	3000	1.14
7[d]	L^{OMe}	38.75	91				
8[e]		20	24	1800	–[f]	2400	1.22
9[d]	L^{Fu}	51	91				
10[e]		20	53	3900	–[f]	2200	1.21

[a] Obtained from ^{1}H NMR analysis.
[b] Calculated from the molecular weight of monomer × [monomer]$_0$/2[Cat]$_0$ × conversion yield + Mw(Pr^iOH).
[c] Obtained from GPC analysis and calibration based on the polystyrene standard. $M_{n(GPC)}$ is the value obtained from GPC times 0.58.
[d] Reaction condition: benzene-d_6 (1 mL) in sealed NMR tube, [LA] = 1.0 M, 120 °C, [LA]:[Cat] = 10:1.
[e] Reaction condition: toluene (2 mL) in Schlenk flask, [LA] = 5 M, 100 °C, [LA]:[Cat] = 100:1.
[f] Not available.

$L^{Th}Ti(O^iPr)_2$ had a longer induction period than **$L^{Bn}Ti(O^iPr)_2$** for LA polymerization. This indicates that thiophenyl groups increase the polymerization rate because the S is a soft atom and the weaker bonds between Ti and S allow thiophenyl groups to dissociate easily, thereby avoiding the competition with monomers. The lability of thiophenyl groups still provides Ti electrons through coordination, which decreases the bond between Ti and alkoxide and increases the polymerization rate. However, this does not help to decrease transformation time. The transformation time involved in LA polymerization was shorter than that of CL, indicating that LA is helpful in the transformation of these Ti complexes into the active intermediates. In addition, Ti complexes in $CDCl_3$ resulted

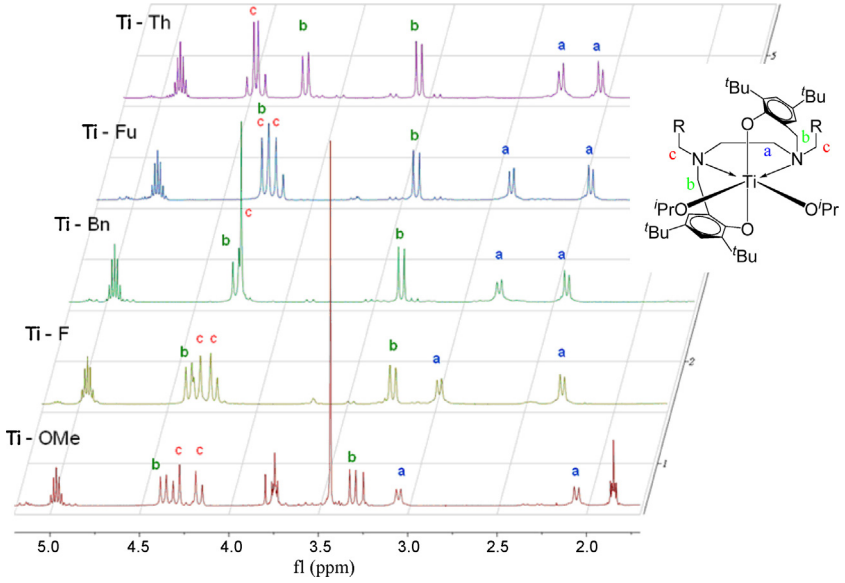

Fig. 7. ^{1}H NMR spectra of Ti complexes. (For interpretation of the references to colour in this figure citation, the reader is referred to the web version of this article.).

Table 3
Kinetic study of polymerization of ε-caprolactone and L-lactide using each of the Ti complexes as an initiator in a sealed NMR tube in C_6D_6 and $CDCl_3$, respectively.

Catalyst $LTi(O^iPr)_2$	C_6D_6				$CDCl_3$			
	CL		LA		CL		LA	
Entry	k_{obs}	Ip[a]	k_{obs}	Ip[a]	k_{obs}	Ip[a]	k_{obs}	Ip[a]
L^{Th}	0.551	3.5	0.274	3.5	0.215	9	0.242	3.75
L^{Bn}	0.082	6.5	0.242	2.75	0.048	14	0.098	2
L^{F}	0.075	19.5	0.128	7.5	0.064	30	0.055	5
L^{OMe}	0.057	13.5	0.080	8	0.093	22	0.054	4
L^{Fu}	0.065	38.5	0.068	15.75	0.053	38	0.048	7

[a] Ip = Induction period (h).

in lower k_{obs} and longer induction periods, compared with C_6D_6. All the Ti complexes with hexadentate ligands in $CDCl_3$ showed greater activity than $L^{Bn}Ti(O^iPr)_2$ in CL polymerization (Table 3) and it means the pendent groups of ligands are beneficial in polar $CDCl_3$ and increase the polymerization rate (k_{obs}).

2.3. Kinetic study of the polymerization of CL and LA catalyzed using $L^{OMe}Ti(O^iPr)_2$

Kinetic studies were performed with respect to the ratio of $[M]_0/[\mathbf{L^{OMe}Ti(O^iPr)_2}]$ ([CL] = 2.0 M in toluene 5 mL and [LA] = 1.25 M in $CDCl_3$ 1 mL) at 100 °C shown in Tables S5, S6, and Figures S5, S6, S7, and S8. Preliminary results indicate a first-order dependency on [CL] and [LA] respectively (Figures S5 and S7). By plotting $\ln k_{obs}$ vs. $\ln[\mathbf{L^{OMe}Ti(O^iPr)_2}]$, both $\mathbf{L^{OMe}Ti(O^iPr)_2}$ orders of 1, k_{app} values of 1.82 and 0.40 were discovered for CL and LA (Figures S6 and S8), respectively. The polymerization of CL and LA using $\mathbf{L^{OMe}Ti(O^iPr)_2}$ at 100 °C demonstrated the following rate law:

$$-d[CL]/dt = 1.82 \times [CL]^1[\mathbf{L^{OMe}Ti(O^iPr)_2}]^1$$

$$-d[LA]/dt = 0.40 \times [LA]^1[\mathbf{L^{OMe}Ti(O^iPr)_2}]^1$$

2.4. Mechanistic studies of polymerization

According to the kinetic characteristics, one monomer is consumed in every polymerization cycle and the Ti complexes retain the mononuclear form because the order of the monomer and Ti complex is 1. Because the Ti complex is in a hexa-coordinated form, it is incapable of bonding with a monomer. This may be explained by the I_a mechanism, in which coordination of the monomer weakens the N atom of the Salan ligand and N atom dissociates to form a six-coordinate intermediate **A** (Fig. 8). After the initiation of the monomer (by isopropoxide) to form the six-coordinate structure **B** or **C**, structure **C** is more active than **D** if the pendent group **R** is labile because **R** is easily replaced by the monomer, which increases reactivity. This is the reason that the thiophen-2-yl methyl group presented the highest catalytic activity. In addition, CL polymerization presented a longer induction period than LA polymerization, which indicates that LA more efficiently coordinates with Ti than with CL, thereby promoting the formation of structure **A**.

3. Conclusions

A series of Salan ligands was synthesized and associated titanium complexes in catalyzing the polymerization of CL and LA were studied. The polymerization rate of CL and LA was altered according to pendent group. Among these Ti complexes, only thiophen-2-yl methyl group enhanced the polymerization rate of CL and LA but was not helpful for decreasing the induction period. The underlying mechanism may be the coordination of Ti by the monomer to form a seven-coordinate intermediate, which subsequently transformed into a six-coordinate active species. During the process of polymerization, the N atom of Salan ligand easily bonded with Ti to form a six-coordinate structure, which decreased activity. The thiophen-2-yl methyl group prevented the coordination of the N atom and was easily replaced by the monomer due to its lability.

3.1. Experimental

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. 2,4-Di-*tert*-butylphenol, sodium borohydride, formaldehyde, 37 wt% sol. in water, triethylamine, thionyl chloride, ethylenediamine anhydrous, benzaldehyde, 2-methoxybenzaldehyde, 2-fluorobenzaldehyde, thiophene-2-carbaldehyde, furan-2-carbaldehyde, titanium (IV) isopropoxide, sodium hydride, deuterated chloroform, L-lactide, and ε-caprolactone were purchased from Acros. Benzyl alcohol was purchased from Alfa. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 2000-200 (200 MHz for ^1H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS 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). 2,4-Di-*tert*-butyl-6-(chloromethyl)phenol [9], L^{Bn}–H_2 [4d], and $L^{Bn}{}_2Ti(O^iPr)_2$ [4d] were prepared by acid-catalyzed condensation following literature procedures.

3.2. Synthesis of N,N′-bis(2-methoxybenzyl)-N,N′-bis[(3,5-di-tert-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (L^{OMe}–H_2)

A mixture of ethylenediamine (6.01 g, 100 mmol) and 2-methoxybenzaldehyde (27.2 g, 200 mmol) was refluxed for 1 day in ethanol (150 mL). The reaction solution was cooled down in ice bath and sodium borohydride (7.57 g, 200 mmol) was transferred to the solution slowly. After 1 h, the solution was refluxed again for 1 day. Volatile materials were removed under vacuum to yield yellow oil. The oil was dissolved in CH_2Cl_2 (200 mL) and the solution was washed with water (2/200 ml) and the solvent removed at reduced pressure to give the white powders. The white powders were set with 2,4-di-*tert*-butyl-6-(chloromethyl)phenol (53.55 g, 210 mmol) and NEt_3 (28 mL, 200 mmol) in ethanol 400 mL and refluxed for 1 month. Volatile materials were removed under vacuum to yield yellow oil. The oil was dissolved in CH_2Cl_2 (200 mL) and the solution was washed with water (2/200 ml) and several drops of HCl. The yellow oil was obtained when CH_2Cl_2 was

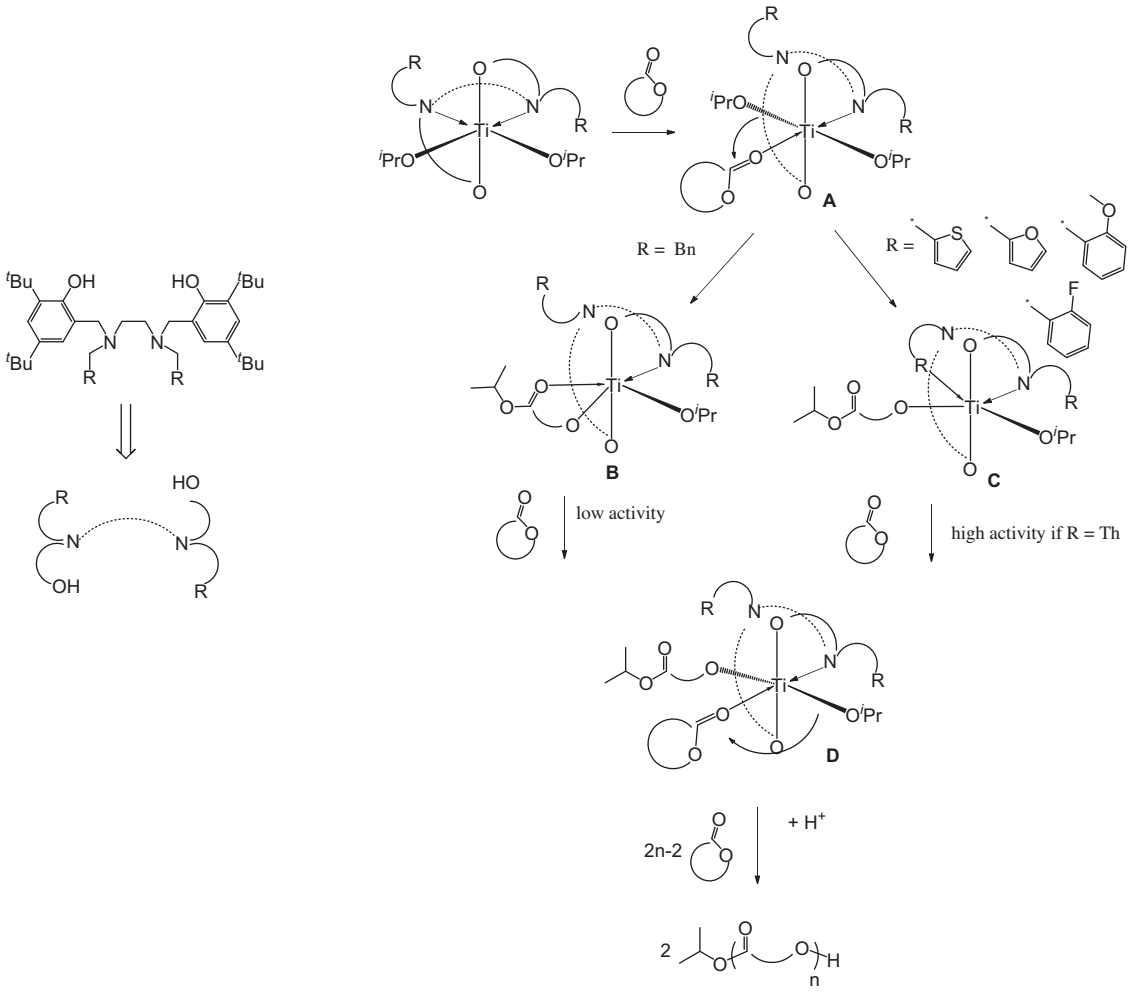

Fig. 8. Possible mechanisms underlying of the polymerization by Salan Ti complex.

removed and ethanol (250 mL) was added to dissolve the oil. The white powder was obtained and filtered after 10 day at −20 °C. Yield: 49.38 g (67%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 10.76 (2H, s, ArO*H*), 7.20–6.77 (12H, m, Ar*H*), 3.73 (6H, s, BnOCH_3), 3.64 (4H, s, NCH_2 BnOCH$_3$), 3.56 (4H, s, NCH_2Ar), 2.67 (4H, s, NCH_2CH_2N), 1.36 (18H, s, ArC(CH_3)$_3$), 1.24 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.00, 154.18, 140.12, 135.31, 131.37, 128.84, 125.11, 123.41, 122.60, 121.42, 120.33, 110.31 (*Ar*), 58.73 (NCH$_2$ BnOCH$_3$), 54.97 (BnOCH$_3$), 53.29 (NCH$_2$Ar), 50.20 (NCH$_2$CH$_2$N), 34.79 (ArC(CH$_3$)$_3$), 34.06 (ArC(CH$_3$)$_3$), 31.67 (ArC(CH$_3$)$_3$),29.53 (ArC(CH$_3$)$_3$). Elemental Analysis ($C_{48}H_{68}N_2O_4$) Found: N, 3.48%; C, 78.44%; H, 9.22%. Anal. Calcd: N, 3.80%; C, 78.22%; H, 9.30%. ESI-MS(+) *m*/*z* calcd = 737.06. Found: 737.34.

3.3. Synthesis of N,N′-bis(2-fluorobenzyl)-N,N′-bis[(3,5-di-tert-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (L^F–H_2)

Using a method is similar to that for L^{OMe}–H_2. Yield: 59.17 g (83%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 10.27 (2H, s, ArO*H*), 7.22–6.80 (12H, m, Ar*H*), 3.67 (4H, s, NCH_2BnF), 3.59 (4H, s, NCH_2Ar), 2.71 (4H, s, NCH_2CH_2N), 1.39 (18H, s, ArC(CH_3)$_3$), 1.26 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 162.64 (d, J_{CF} = 205.2 Hz), 160.19, 153.82, 140.65, 135.64, 131.94, 131.90, 129.46, 129.38, 124.18, 124.15, 123.68, 123.01, 120.94, 115.55, 115.32 (*Ar*), 58.93 (NCH$_2$BnF), 50.85 (NCH$_2$Ar), 50.25 (NCH$_2$CH$_2$N), 34.83 (ArC(CH$_3$)$_3$), 34.11 (ArC(CH$_3$)$_3$), 31.67 (ArC(CH$_3$)$_3$), 29.55 (ArC(CH$_3$)$_3$). Elemental analysis ($C_{46}H_{62}F_2N_2O_2$) found: N, 3.31%; C, 77.29%; H, 8.69%. Anal. Calcd: N, 3.93%; C, 77.49%; H, 8.76%. ESI-MS(+) *m*/*z* calcd = 712.99. Found: 713.43.

3.4. Synthesis of N,N′-bis(furan-2-ylmethyl)-N,N′-bis[(3,5-di-tert-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (L^{Fu}–H_2)

Using a method is similar to that for L^{OMe}–H_2. Yield: 44.01 g (67%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 10.30 (2H, s, ArO*H*), 7.34 ~ 7.21 (4H, m, Ar*H*), 6.82 (2H, d, *J* = 1.0 Hz, Furan*H*), 6.28 (2H, dd, *J* = 1.6, 1.0 Hz, Furan*H*), 6.08 (2H, d, *J* = 1.6 Hz, Furan*H*), 3.72 (4H, s, NCH_2Furan), 3.67 (4H, s, NCH_2Ar), 2.72 (4H, s, NCH_2CH_2N), 1.40 (18H, s, ArC(CH_3)$_3$), 1.28 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.14, 150.21, 142.45, 140.60, 135.68, 123.79, 123.00, 120.90, 110.21, 109.84 (*Ar*), 58.66 (NCH$_2$Furan), 50.04 (NCH$_2$Ar), 48.48 (NCH$_2$CH$_2$N), 34.84 (ArC(CH$_3$)$_3$), 34.12 (ArC(CH$_3$)$_3$), 31.69 (ArC(CH$_3$)$_3$), 29.57 (ArC(CH$_3$)$_3$). Elemental analysis ($C_{42}H_{60}N_2O_4$) found: N, 4.35%; C, 76.74%; H, 9.44%. Anal. Calcd: N, 4.26%; C, 76.79%; H, 9.21%. ESI-MS(+) *m*/*z* calcd = 656.94. Found: 657.23.

3.5. N,N′-bis(thiophen-2-ylmethyl)-N,N′-bis[(3,5-di-tert-butyl-2-hydroxyphenyl)methylene]-1,2-diaminoethane (L^{Th}–H_2)

Using a method is similar to that for L^{OMe}–H_2. Yield: 48.92 g (71%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 10.19 (2H, s, ArO*H*), 7.22–6.90

(6H, m, Ar*H*, Thio*H*), 6.83 (2H, d, *J* = 1 Hz, Thio*H*), 6.77 (2H, d, *J* = 1.8 Hz, Thio*H*), 3.80 (4H, s, NCH_2Thio), 3.73 (4H, s, NCH_2Ar), 2.75 (4H, s, NCH_2CH_2N), 1.42 (18H, s, ArC(CH_3)$_3$), 1.28 (18H, s, ArC(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ 153.92, 140.75, 138.07, 135.78, 127.77, 126.77, 125.69, 123.85, 123.11, 120.75 (*Ar*), 58.55 (NCH_2Thio), 51.02 (NCH_2Ar), 49.85 (NCH_2CH_2N), 34.86 (ArC(CH$_3$)$_3$), 34.13 (ArC(CH$_3$)$_3$), 31.67 (ArC(CH_3)$_3$), 29.53 (ArC(CH_3)$_3$). Elemental analysis ($C_{42}H_{60}N_2O_2S_2$) found: N, 3.62%; C, 73.22%; H, 8.98%. Anal. Calcd: N, 4.07%; C, 73.21%; H, 8.87%. ESI-MS(+) *m*/*z* calcd = 689.07. Found: 689.29.

3.6. Synthesis of $L^{OMe}Ti(O^iPr)_2$

A mixture of L^{OMe}–H_2 (7.37 g, 10 mmol) and Ti(O^{i}Pr)$_4$ (2.84 g, 10 mmol) in THF (50 mL) was stirred for 24 h. 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: 6.57 g (73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32–6.64 (H, m, Ar*H*), 4.97 (2H, m, *J* = 6 Hz, OC*H*(CH$_3$)$_2$), 4.27 (2H, d, *J* = 20.5, 14.6 Hz, NCH_2PhOCH$_3$), 4.20 (2H, d, *J* = 20.5, 14.6 Hz, NCH_2PhOCH$_3$), 4.41 (2H, d, *J* = 25.6, 13 Hz, NCH_2Ar), 3.31 (2H, d, *J* = 25.6, 13 Hz, NCH_2Ar), 3.43(6H, s, NCH$_2$PhOCH_3), 3.05 (2H, d, *J* = 19.6 Hz, NCH_2CH_2N), 2.55 (2H, d, *J* = 19.6 Hz, NCH_2CH_2N), 1.49 (18H, s, ArC(CH_3)$_3$), 1.23 (18H, s, ArC(CH_3)$_3$), 1.23 (12H, dd, *J* = 54.4, 6 Hz, OCH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 0 MHz): δ 159.46, 159.39, 138.15, 135.55, 134.82, 129.31, 124.20, 122.98, 122.30, 120.07, 111.44 (*Ar*), 77.17 (OCH(CH$_3$)$_2$), 59.90 (NCH$_2$ BnOCH$_3$), 55.36 (BnOCH$_3$), 52.92 (NCH$_2$Ar), 45.93 (NCH$_2$CH$_2$N), 35.07 (ArC(CH$_3$)$_3$), 34.09 (ArC(CH$_3$)$_3$), 31.83 (ArC(CH$_3$)$_3$), 30.36 (ArC(CH_3)$_3$), 26.74 and 26.28 (OCH(CH_3)$_2$). Elemental analysis ($C_{54}H_{80}N_2O_6Ti$) Found: N, 2.90%; C, 71.32%; H, 9.08%. Anal. Calcd: N, 3.11%; C, 71.98%; H, 8.95%. Mp:258 °C.

3.7. Synthesis of $L^FTi(O^iPr)_2$

Using a method is similar to that for **$L^{OMe}Ti(O^iPr)_2$**. Yield: 5.96 g (68%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.32–6.63 (12H, m, Ar*H*), 4.94 (2H, m, *J* = 6 Hz, OC*H*(CH$_3$)$_2$), 4.37 (2H, d, *J* = 15.6 Hz, NCH_2BnF), 4.29 (2H, d, *J* = 15.6 Hz, NCH_2BnF), 4.38 (2H, d, *J* = 13 Hz, NCH_2Ar), 3.25 (2H, d, *J* = 13 Hz, NCH_2Ar), 2.99 (2H, d, *J* = 20 Hz, NCH_2CH_2N), 2.29 (2H, d, *J* = 20 Hz, NCH_2CH_2N), 1.50 (18H, s, ArC(CH_3)$_3$), 1.24 (18H, s, ArC(CH_3)$_3$), 1.22 (12H, dd, *J* = 58, 6 Hz, OCH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 162.28 (d, J_{CF} = 245.8 Hz), 161.05, 159.33, 138.69, 135.52, 134.88, 134.83, 130.16, 130.07, 124.28, 123.71, 123.67, 123.30, 123.27, 120.35, 120.20, 115.93, 115.69 (*Ar*), 77.60 (OCH(CH$_3$)$_2$), 59.92 (NCH$_2$ BnF), 52.49 (NCH_2Ar), 46.14 (NCH_2CH_2N), 35.10 (ArC(CH$_3$)$_3$), 34.12 (ArC(CH$_3$)$_3$), 31.78 (ArC(CH$_3$)$_3$), 30.38 (ArC(CH_3)$_3$), 26.72 and 26.24 (OCH(CH_3)$_2$). Elemental analysis ($C_{52}H_{74}F_2N_2O_4Ti$) found: N, 3.19%; C, 71.38%; H, 8.74%. Anal. Calcd: N, 3.19%; C, 71.21%; H, 8.50%. Mp: 266 °C.

3.8. Synthesis of $L^{Th}Ti(O^iPr)_2$

Using a method similar to that for **$L^{OMe}Ti(O^iPr)_2$**. Yield: 6.05 g (71%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30 (2H, dd, *J* = 5.2, 1.2 Hz, Thio*H*), 7.22 (2H, d, *J* = 2.4 Hz, Ar*H*), 7.00 (2H, d, *J* = 5.4 Hz, d, *J* = 3.4 Hz, Thio*H*), 6.76 (2H, d, *J* = 3.4 Hz, d, *J* = 1 Hz, Thio*H*), 6.74 (2H, d, *J* = 2.4 Hz, Ar*H*), 4.90 (2H, m, OC*H*(CH$_3$)$_2$), 4.48 (2H, d, *J* = 15.6 Hz, NCH_2Thio), 4.44 (2H, d, *J* = 15.6 Hz, NCH_2Thio), 4.20 (2H, d, *J* = 13.2 Hz, NCH_2Ar), 3.56 (2H, d, *J* = 13.2 Hz, NCH_2Ar), 2.76 (2H, d, *J* = 10 Hz, NCH_2CH_2N), 2.53 (2H, d, *J* = 10 Hz, NCH_2CH_2N), 1.51 (18H, s, ArC(CH_3)$_3$), 1.27 (18H, s, ArC(CH_3)$_3$), 1.15 (12H, dd, *J* = 58, 6 Hz, OCH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.88, 138.91, 135.59, 134.80, 130.41, 126.91, 126.48, 124.35, 123.49, 123.47 (*Ar*,*Thio*), 77.86 (OCH(CH$_3$)$_2$), 59.59 (NCH$_2$ Thio), 53.58 (NCH_2Ar), 47.20 (NCH_2CH_2N), 35.13 (ArC(CH$_3$)$_3$), 34.14 (ArC(CH$_3$)$_3$), 31.82 (ArC(CH$_3$)$_3$), 30.43 (ArC(CH_3)$_3$), 26.62 and 26.19 (OCH(CH_3)$_2$). Anal. Calcd (found) for ($C_{48}H_{72}N_2O_4S_2Ti$) Found: N, 3.13%; C, 67.60%; H, 8.29%. Anal. Calcd: N, 3.28%; C, 67.58%; H, 8.51%. Mp: 244 °C.

3.9. Synthesis of $L^{Fu}Ti(O^iPr)_2$

Using a method similar to that for **$L^{OMe}Ti(O^iPr)_2$**. Yield: 5.17 g (63%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.40 (2H, dd, *J* = 1.6, 0.8 Hz, Ar*H*), 7.20 (2H, d, *J* = 2.4 Hz, Ar*H*), 6.72 (2H, d, *J* = 2 Hz, Furan*H*), 6.34 (2H, dd, *J* = 3.2, 1.8 Hz, Furan*H*), 6.13 (2H, d, *J* = 2.8 Hz, Furan*H*), 4.86 (2H, m, *J* = 6 Hz, OC*H*(CH$_3$)$_2$), 4.21 (2H, d, *J* = 15.4 Hz, NCH_2Furan), 4.31 (2H, d, *J* = 13.6 Hz, NCH_2Ar), 3.42 (2H, d, *J* = 13.6 Hz, NCH_2Ar), 2.89 (2H, d, *J* = 10.2 Hz, NCH_2CH_2N), 2.65 (2H, d, *J* = 10.2 Hz, NCH_2CH_2N), 1.51 (18H, s, ArC(CH_3)$_3$), 1.27 (18H, s, ArC(CH_3)$_3$), 1.14 (12H, dd, *J* = 59.2, 6 Hz, OCH(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 159.47, 149.63, 143.00, 138.67, 135.52, 124.33, 123.24, 123.17, 112.14, 110.24 (*Ar*,*Furan*), 77.60 (OCH(CH$_3$)$_2$), 60.27 (NCH$_2$ Furan), 51.23 (NCH$_2$Ar), 47.00 (NCH$_2$CH$_2$N), 35.09 (ArC(CH$_3$)$_3$), 34.11 (ArC(CH$_3$)$_3$), 31.79 (ArC(CH$_3$)$_3$), 30.36 (ArC(CH_3)$_3$), 26.64 and 26.19 (OCH(CH$_3$)$_2$). Anal. Calcd (found) for ($C_{48}H_{72}N_2O_6Ti$) Found: N, 3.59%; C, 70.44%; H, 9.31%. Anal. Calcd: N, 3.41%; C, 70.22%; H, 8.84%. Mp: 230 °C.

3.10. General procedures for the polymerization

A typical polymerization procedure was exemplified by the synthesis of entry 7 (Table 1) using complex **$L^{OMe}Ti(O^iPr)_2$** 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 $L^{OMe}Ti(O^iPr)_2$ (0.1 mmol) and ε-caprolactone (1.14 g, 10 mmol) at 120 °C. After the solution was stirred for 80 h, the reaction was then quenched by adding to a drop of ethanol, and the polymer was precipitated pouring into *n*-hexane (30.0 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: 0.88 g (77%).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.07.003.

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