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# Polymerization of ε-caprolactone using bulky alkoxo-titanium complexes and structural analysis of [Ti(OBorneoxo)$_2$Cl$_2$(thf)$_2$]

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## Abstract

A variety of bisalkoxo titanium dichloride THF adducts [Ti(OR)$_2$Cl$_2$(thf)$_2$] {OR = adamantanoxo (**9**), (1*R*,2*S*,5*R*)-(−)-menthoxo (**10**), (1*S*-endo)-(−)-borneoxo (**11**)} have been prepared and characterized by spectroscopic techniques. The molecular structure of **11** has been determined by single-crystal X-ray diffraction studies. The parent Lewis acid bisalkoxo titanium dichloride derivatives and related alkoxo complexes [Ti(OR)$_2$(OPr$^i$)$_2$]$_2$ have been tested as initiators in ring-opening polymerization of ε-caprolactone and L-lactide.
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*Keywords:* Titanium; Alkoxo; Ring opening polymerization; ε-Caprolactone; X-ray structure determination

## 1. Introduction

Alkoxo ligands are known to stabilize early and middle transition metal centres in high oxidation states. Bulky aryloxo or trialkylsiloxo of group 4 and 5 have extensively been used in organometallic chemistry [1–4]. Typically in the chemistry developed with these derivatives the metal centre is surrounded by two attendant RO ligands as found in the {Ti(ArO)$_2$} fragment used as template for catalytic C–C coupling reactions [5]. Ti(ArO)$_2$X$_2$ complexes are used as catalyst for olefin polymerization [6,7] and for the Diels–Alder reaction [8,9]. In some ways bulky RO or ArO ligands may be viewed as Cp analogue having a predetermined steric pressure at the metal centre based on their substituents. Bearing this in mind, we are interested in the development of the bulky alkoxide chemistry of early transition metals with chiral RO groups [10] which can open an entrance into the synthesis of new chiral catalysts. Because of the current interest in poly(caprolactone) and poly(lactide) biodegradable and biocompatible polymers as potentially substitutes of nondegradable polymers and due that stereosequence distribution of PLA determines a number of physical properties, some chiral alkoxo titanium complexes have been tested as initiators in ring opening polymerization of ε-caprolactone and L-lactide.

A wide range of studies about the ring opening polymerization of cyclic esters and cyclic carbonates have been reported. Main group and earth rare based complexes have been employed in this area with excellent results [11,12]. Homoleptic metal alkoxo catalysts based on Sn, Fe, Al, Y or Ln have been been commonly employed, these systems allow the control of the polymerization parameters and give high molecular weight polymers in very good yields [13–15]. However, a great deal of attention has been

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paid in the past few years to the development of single site catalysts bearing sterically hindered ancillary ligands since they are capable of offering a better control over the stereoselectivity of lactide polymerisation [16,17]. Of particular interest to our present contribution is the work published on titanium alkoxides by Harada et al. [18], the reported study of polymerization of ε-caprolactone and L-lactide show that titanium complexes having chelating bisaryloxo ligands bridged by sulphur or tellurium $[Ti\{2,2'\text{-}E(4\text{-}Me\text{-}6Bu^t\text{-}C_6H_2O)_2\}(OPr^i)_2]_2$ (E = S, Te) or the methylene bridged analogue $[Ti\{2,2'\text{-}CH_2(4\text{-}Me\text{-}6Bu^t\text{-}C_6H_2O)_2\}(OPr^i)_2]$ initiate living polymerization of ε-caprolactone while the bis(aryloxide) titanium THF adduct $[Ti\{2,2'\text{-}CH_2(4\text{-}Me\text{-}6\text{-}Bu^t\text{-}C_6H_2O)_2\}Cl_2(thf)_2]$ is inactive under the same conditions. Recently Davidson et al. have reported the synthesis and behaviour of titanium amino bis(phenolate) complexes $[Ti\{2,2'\text{-}N(R')(CH_2)_2(4R\text{-}6R\text{-}C_6H_2O)_2\}(OPr^i)_2]$ ($R' = Me, CH_2Ph, CH_2$Naphtyl; R = Me, $Bu^t$) and bidentade chatechol based titanium aryloxides in ring opening polymerization of ε-caprolactone [19,20]. The use of titanium complexes prepared with less bulky bridged ligands as 2,2′-methylenebis(4-methylphenol) or nonbridged hindered phenols such as 2-*tert*-butyl-4-methyl-phenol resulted in a poorly controlled chain growth or no polymerization, as well as, $Ti(OBu^n)_4$ that leads to uncontrolled polymerization of cyclic esters [21].

## 2. Results and discussion

Complexes $[Ti(OR)_2(OPr^i)_2]_2$ {OR = adamantanoxo (OAdam (**1**)), (1*R*,2*S*,5*R*)-menthoxo (OMent (**2**)), (1*S*-endo)-(−)-borneoxo (OBorn (**3**)), (1,2:3,4-di-*O*-isopropylidene)-α-D-galactopyranoxo (ODAGP (**4**)), (1,2:5,6-di-*O*-isopropylidene)-α-D-glucofuranoxo (ODAGF (**5**))} and $[Ti(OR)_2Cl_2]$ {OR = OAdam (**6**), OMent (**7**), OBorn (**8**)} were previously synthesized in our group by an alcoholysis reaction of $Ti(OPr^i)_4$ and the appropriate amount of alcohol ROH and by a redistribution reaction between the tetraalkoxo derivatives $[Ti(OR)_4]$ and titanium tetrachloride in toluene, respectively (see Scheme 1) [22–24].

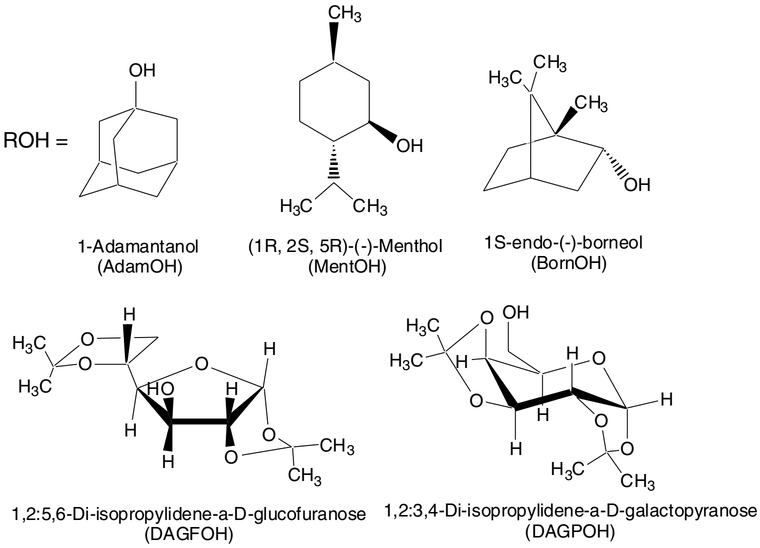
The complexity of titanium alkoxo coordination chemistry has often contributed to a substantial degree of uncertainty in the identity of the catalytically active species. The high solubility of the above-mentioned derivatives in common organic solvents avoid the isolation of suitable crystals in order to carry out an X-ray diffraction study. Spectroscopic techniques must be used instead to characterize them. In order to get some extra information about the distribution of the bulky alkoxo ligands and because of the synthesis of the dichloride alkoxo titanium derivatives is carry out in a neat way by warming the adducts under vacuum, the related THF adducts $[Ti(OR)_2Cl_2(thf)_2]$ {OR = OAdam (**9**), OMent (**10**), OBorn (**11**)} have been

$$Ti(OPr^i)_4 + 2\ ROH \xrightarrow{CH_2Cl_2} 1/2\ [\{Ti(OR)_2(OPr^i)_2\}_2] + 2\ Pr^iOH$$

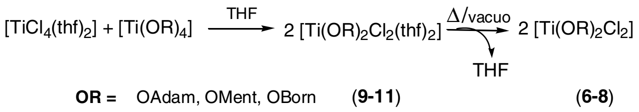
OR = OAdam (**1**), OMent (**2**), OBorn (**3**), ODAGP (**4**), ODAGF (**5**)

$$[TiCl_4] + [Ti(OR)_4] \xrightarrow{toluene} 2\ [Ti(OR)_2Cl_2]$$

OR = OAdam (**6**), OMent (**7**), OBorn (**8**)



Scheme 1.



Scheme 2.

cleanly synthesized using $TiCl_4(thf)_2$ as starting material (Scheme 2). The $^1H$ and $^{13}C$ NMR spectras of these adducts show the expected pattern of resonances for the corresponding bulky alkoxo ligands and two equivalents of THF. Except compounds **2**, **7** and **10** which are colourless oils, compounds (**1**–**11**) were isolated as beige or colourless crystalline material highly sensitive towards hydrolysis.

Previous work on bulky monodentade aryloxo and 2,2′-methylene-bis(phenol) ligands led to the isolation of a series of monomeric species. Diltworth et al. published the synthesis of $[Ti(2,6\text{-}Ph_2C_6H_3O)Cl_2]$ [25] by reaction of 2,6-diphenylphenol with $TiCl_4$ in toluene, which presents tetrahedral geometry around titanium atom due to the presence of bulky phenoxo ligands that causes only minor distortions in the tetrahedral angles. Okuda and co-workers have shown that $[Ti\{2,2'\text{-}CH_2(4\text{-}CH_3\text{-}6\text{-}Bu^tC_6H_2\text{-}O)_2\}Cl_2]$ coordinates one THF molecule forming a pentacoordinated titanium adduct in which the ligand oxygen atoms occupy the apical and the equatorial positions with the THF being axial and trans to one end of the chelating bisaryloxo [26]. Nevertheless, the most usual behaviour of starting tetrahedral titanium complexes is the formation of six-coordinated complex with labile donor solvents, as shown the isolation and characterization of $[Ti(2,6\text{-}(CH_3)_2C_6H_3O)_2Cl_2(THF)_2]$ [27] and the bridged-bisaryloxo titanium dichloride THF adduct $[Ti\{2,2'\text{-}CH_2(6\text{-}PhC_6H_3O)_2\}Cl_2(THF)_2]$ [28]. Similar structures have been observed for phosphine adducts $[Ti\{2,2'\text{-}CH_2CH_2(4\text{-}vinyl\text{-}6\text{-}CH_3C_6H_2O)_2\}Cl_2\,(dmpe)]$ (dmpe = dimethylphosphinoethane) with two aryloxo ligands linked by an ethylene bridge and its unlinked analogue [29], $[Ti\{2,2'\text{-}CH_2(4\text{-}CH_3\text{-}6\text{-}Bu^tC_6H_2O)_2\}Cl_2 \cdot dme]$ and $[Ti\{(2,6\text{-}(Pr^i)_2C_6H_3\text{-}O)_2\}(bipy)_2]$ [30].

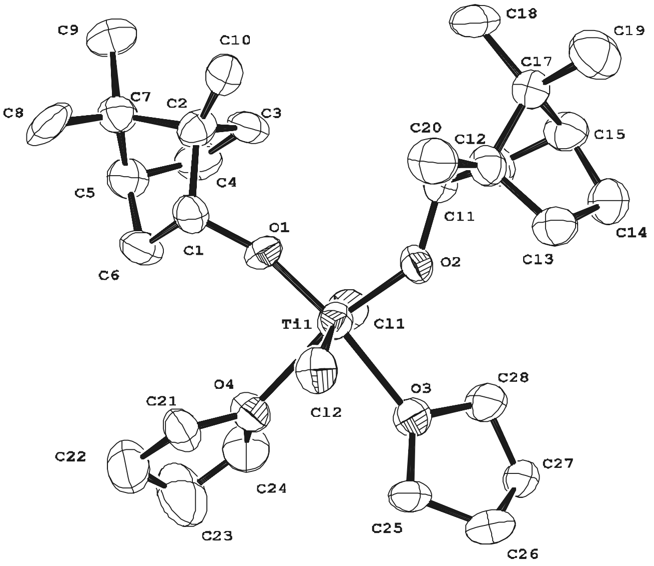


Fig. 1. ORTEP representation of the molecular structure of THF adduct **11**. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths and angles for $[Ti(OBorn)_2Cl_2(thf)_2]$ (**11**)

| | | | |
|---|---|---|---|
| *Bond length (Å)* | | | |
| Ti1–O1 | 1.734(7) | Ti1–Cl2 | 2.377(3) |
| Ti1–O2 | 1.757(6) | Ti1–Cl1 | 2.391(3) |
| Ti1–O3 | 2.189(7) | O1–C1 | 1.438(12) |
| Ti1–O4 | 2.270(7) | O2–C11 | 1.451(12) |
| *Bond angle (°)* | | | |
| O1–Ti1–O2 | 100.4(3) | O4–Ti1–Cl2 | 83.2(2) |
| O1–Ti1–O3 | 172.2(3) | O1–Ti1–Cl1 | 95.2(2) |
| O2–Ti1–O3 | 87.4(3) | O2–Ti1–Cl1 | 94.3(2) |
| O1–Ti1–O4 | 91.7(3) | O3–Ti1–Cl1 | 84.2(2) |
| O2–Ti1–O4 | 167.9(3) | O4–Ti1–Cl1 | 84.1(2) |
| O3–Ti1–O4 | 80.5(3) | Cl2–Ti1–Cl1 | 164.50(13) |
| O1–Ti1–Cl2 | 94.0(2) | C1–O1–Ti1 | 164.2(6) |
| O2–Ti1–Cl2 | 96.3(2) | C11–O2–Ti1 | 141.8(6) |
| O3–Ti1–Cl2 | 84.8(2) | | |

In order to know the situation in our case, the molecular structure of complex **11** has been determined by single-crystal X-ray diffraction studies. Selected bond lengths and angles are listed in Table 1. The ORTEP plot in Fig. 1 shows the molecular structure of adduct **11** which exhibit a distorted octahedral geometry around the central titanium atom with the alkoxide groups being *cis* to each other, while the chlorine atoms are *trans* to each other, and the two THF ligands are *trans* to the alkoxides. The Cl(2)–Ti–Cl(1) angle 164.50(13)° shows the slight deformation of the two chlorine atoms from the exact *trans* position. The central metal atom lie on the basal plane defined by O(1), O(2), O(3) and O(4), as shown by the sum of bond angles around the metal which is exactly 360° (100.4(3)°; 87.4(3)°, 91.7(3)°, 80.5(3)°). The (Born)O–Ti–O(Born) angle 100.4(3)° is in the range found for aryloxo titanium complexes such as in the aryloxo titanium dichloride THF adduct $[Ti(2,6\text{-}(CH_3)_2C_6H_3O)_2\text{-}Cl_2(THF)_2]$ and the bridged-bisaryloxo titanium dichloride THF adduct $[Ti\{2,2'\text{-}CH_2(6\text{-}PhC_6H_3O)_2\}Cl_2(THF)_2]$, 99.2(5)° and 97.8(1)°, respectively. The two Ti–O(Born) distances [Ti–O(1) = 1.734(7), Ti–O(2) = 1.757(6) Å] are slightly shorter than those of the bisaryloxo adducts (av. 1.788 Å) [16], besides the C(1)–O(1)–Ti(1) and C(11)–O(2)–Ti(1) angles open up to 164.2(6)° and 141.8(6)°, respectively, suggesting the existence of $\pi(O \rightarrow Ti)$ donation to the titanium in addition to the σ-interaction.

Several groups have used bulky bis(phenolate) titanium complexes as initiators in living ring-polymerization of cyclic esters [18,31] and cyclic carbonates [32,33]. In this study of ring-opening polymerization by titanium complexes $[Ti(OR)_2(OPr^i)_2]_2$ (**1**–**5**) and $[Ti(OR)_2Cl_2]$ (**6**–**8**) ε-caprolactone (ε-CL) has been chosen as monomer. The catalytic activity of these species is summarised in Table 2. The polylactone molecular weight was determined by gel permeation chromatography (GPC). When 100 equivalent of ε-CL was added at 25 °C to a $CH_2Cl_2$ solution of titanium

Table 2
Ring-opening polymerization of ε-caprolactone in presence of $[Ti(OR)_2(OPr^i)_2]_2$ and $[Ti(OR)_2Cl_2]$

| Complex | Initiator | $T$ (°C) | Time (h) | [M]/[I][a] | Conversion[b] (%) | $M_n/10^3$ | $M_w/M_n$[c] | $M_n/10^3$ (calcd)[d] |
|---|---|---|---|---|---|---|---|---|
| **1** | $[Ti(OAdam)_2(OPr^i)_2]_2$ | 25 | 24 | 100 | 77 | 10.9 | 2.09 | 11.1 |
| **2** | $[Ti(OMent)_2(OPr^i)_2]_2$ | 25 | 8 | 100 | 100 | 8.0 | 1.78 | 9.1 |
| **3** | $[Ti(OBorn)_2(OPr^i)_2]_2$ | 25 | 8 | 100 | 100 | 5.7 | 2.28 | 6.9 |
| **4** | $[Ti(ODAGP)_2(OPr^i)_2]_2$ | 25 | 8 | 100 | 100 | 7.1 | 1.64 | 8.5 |
| **5** | $[Ti(ODAGF)_2(OPr^i)_2]_2$ | 25 | 24 | 100 | 100 | 4.8 | 1.45 | 6.3 |
| **6** | $[Ti(OAdam)_2Cl_2]$ | 25 | 24 | 100 | 65 | 6.0 | 1.45 | 7.8 |
| **7** | $[Ti(OMent)_2Cl_2]$ | 25 | 24 | 100 | 69 | 7.4 | 1.05 | 8.1 |
| **8** | $[Ti(OBorn)_2Cl_2]$ | 25 | 24 | 100 | 60 | 6.6 | 2.30 | 7.6 |

[a] [M] = 1.5 mol/L.

[b] Conversion was determined from the relative intensity of the NMR signals.

[c] Measured by GPC in THF calibrated with standard polystyrene samples.

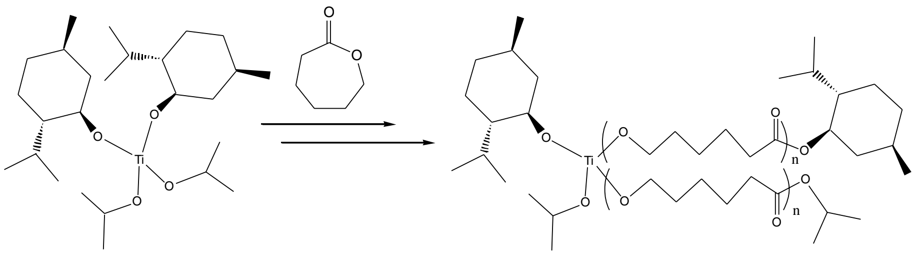
[d] $M_n$ (calcd) = (MW of ε-CL) × 100 × (polymer yield).

alcoholate complexes $[Ti(OR)_2(OPr^i)_2]_2$ the polymerization of the monomer takes place to give conversions of 77–100% for periods of 8–24 h. These complexes show marked differences in their efficiency in this process. The produced polymers present molecular weight distributions ($M_w/M_n$) in the range of 1.45–2.28 and $M_n$ from 4800 to 10900 (Entries 1–5).

The $^1$H NMR spectrum of the poly (ε-caprolactone) obtained by complex $[Ti(OMent)_2(OPr^i)_2]_2$ shows a resonance for the $CH_2$–OH end group at 3.63 ppm together with the signals of terminal isopropyl ester at 1.20 and 4.98 ppm and terminal menthyl ester –$CH$–O– at 4.60 ppm indicating that the growing end groups are both the titanium isopropoxo and menthoxo species what implies the formation of two different types of polymer molecules from every molecule of initiator. Therefore the ring cleavage of the lactone occurs between the acyl-oxygen bond and the propagation of the polymerization occurs by the addition of monomer to the active polymer chains end (See Scheme 3). A similar behaviour has been observed for the rest of titanium alcoholate complexes of the type $[Ti(OR)_2(OPr^i)_2]_2$.

The corresponding dichloride complexes allow the polymerization of ε-CL under similar experimental conditions to those previously used. The produced polymers present molecular weight distributions ($M_w/M_n$) in the range 1.05–2.30 and $M_n$ from 6000 to 7400 (Entries 6–8). In the $^1$H NMR spectrum of the poly(ε-caprolactone) obtained by $[Ti(OBorn)_2Cl_2]$ a resonance for the –$CH_2$–OH end group appears at 3.60 ppm. In addition, two signals attributed to the borneoxo moiety are observed at δ 4.85 and 0.8 ppm, indicating the partial incorporation of bulky alcoholate groups into the resulting polymer chains (see Fig. 3). Therefore, the polymerization should proceed by the reaction of ε-CL with both chlorine and the borneoxo ligands bound to titanium, as previously observed when using monodentade aryloxo titanium dichloride complexes [28]. When compare with the isopropoxo complexes the corresponding dichloride derivatives are better Lewis acid, however, the monomer conversions are inferior to that obtained using $[Ti(OR)_2(OPr^i)_2]_2$ as initiators as previously observed by Aida and co-workers for $[Ti\{2,2'\text{-}CH_2(4\text{-}CH_3\text{-}6Bu^tC_6H_2O)_2\}Cl_2]$ and $[Ti\{2,2'\text{-}CH_2(4\text{-}CH_3\text{-}6Bu^tC_6H_2O)_2\}(OPr^i)_2]$ being necessary the addition of propylene oxide as cocatalyst with the former complex [28]. The molecular weight of the obtained polymers is determined by the polymerization reaction and also by the extent of competitive side reactions. These systems show, in general, low molecular weights and medium polydispersity indexes at high conversions, consistent with the presence of back-biting processes of the active chain end to form oligomers, as well as, transesterification products promoted by active alkoxo end-groups.

The dichloride complexes **7** and **8** were also applied to the polymerization of L-lactide. The extent of polymerization in these samples was found to be 76% and 95%, respectively, within 72 h in toluene at 100 °C. These preliminary results are comparable to that obtained by Harada et al. with $[Ti\{2,2'\text{-}S(4\text{-}CH_3\text{-}6Bu^tC_6H_2O)_2\}(NEt)_2]$ [34] as initiator.



Scheme 3.

## 3. Conclusions

We have shown that the titanium complexes with bulky alkoxide ligands initiate the living ring opening polymerization of ε-caprolactone with different efficiency, affording polyesters with low molecular weights but comparable to those obtained by other reported bisaryloxide titanium complexes [28]. Ring opening polymerization of lactone suffers competitive side reactions leading to broadening of polydispersity indexes. Further experiments to investigate the influence of chiral ligands in the ring opening polymerization of D,L-lactide using titanium complexes are currently under way.

## 4. Experimental

*General remarks.* All reactions were performed using standard Schlenk tube and dry box techniques under an atmosphere of dry nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before used. [Ti(OAdam)$_4$], [Ti(OMent)$_4$], [Ti(OBorn)$_4$], [Ti(ODAGF)$_2$(OPr$^i$)$_2$]$_2$, [Ti(ODAGP)$_2$(OPr$^i$)$_2$]$_2$, [Ti(OMent)$_2$(OPr$^i$)$_2$]$_2$, [Ti(OAdam)$_2$(OPr$^i$)$_2$]$_2$ and [Ti(OBorn)$_2$(OPr$^i$)$_2$]$_2$ were prepared as previously described [22–24]. 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, (1*R*,2*S*,5*R*)-(−)-menthol, (1*S*-endo)-(−)-borneol, adamantanol and TiCl$_4$(thf)$_2$ were purchased from Aldrich and used as received. ε-Caprolactone was purchased from Aldrich and was refluxed over CaH$_2$, distilled and stored under an argon atmosphere prior to use.

IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer (4000–400 cm$^{-1}$) as nujol mulls between polyethylene pellets and KBr disks. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on Varian FT-300 and Varian FT-400 spectrometers and chemical shifts were measured relative to residual $^1$H and $^{13}$C resonances in the deuterated solvents. Elemental analyses were carried out with a Perkin–Elmer 2400 micro-analyzer. Molecular weight and molecular weight distribution were determined against polystyrene standards by GPC (Planta piloto de Química fina, Universidad de Alcalá).

### 4.1. Preparation of [Ti(OAdam)$_2$Cl$_2$(thf)$_2$] (**9**)

A THF (10 mL) solution of [Ti(OAdam)$_4$] (1.24 g, 1.9 mmol) was added to a stirred THF (20 mL) solution of TiCl$_4$(thf)$_2$ (0.61 g, 1.9 mmol). The resulting solution was stirred for 6 h at room temperature and the solvent removed under vacuum to give a light brown solid. Recrystallization from toluene at −30 °C gave beige needles (1.47 g, 69%). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 1.61$ (ps t, 12H, $H_\delta$), 1.89 (m, 4H, THF) 1.98 (ps d, 12H, $H_\beta$), 2.18 (m, 6H, $H_\gamma$). 3.89 (m, 4H, THF). $^{13}$C{$^1$H} NMR (75 MHz, CDCl$_3$, 25 °C): $\delta = 25.7$ (THF), 31.2 (C$_\delta$), 35.8 (C$_\gamma$), 45.4 (C$_\beta$), 68.8 (THF), 82.7 (C$_\alpha$). IR (KBr disk, cm$^{-1}$): 811 (m), 885 (br), 925 (s), 981 (m), 1089 (s), 1118 (s), 1224 (w), 1299 (w), 1355 (m), 1452 (m), 2846 (s), 2898 (s), 2913.93 (s). Anal. Calc. for C$_{28}$H$_{38}$Cl$_2$O$_4$Ti: C, 60.34; H, 6.87. Found: C, 60.23; H, 6.76%.

### 4.2. Preparation of [Ti(OMent)$_2$Cl$_2$(thf)$_2$] (**10**)

A THF (10 mL) solution of [Ti(OMent)$_4$] (1.94 g, 2.9 mmol) was slowly added to a stirred toluene solution of TiCl$_4$(thf)$_2$ (0.94 g, 2.9 mmol). The resulting solution was stirred for 6 h at room temperature and the solvent removed under vacuum. The product was obtained as an yellow oil spectroscopically pure after being rinsed twice with cold pentane (2.70 g, 82%). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 0.81$ (d, 6H, C$H_3$, $^3J_{\mathrm{H,H}} = 6.9$ Hz), 0.86 (d, 6H, C$H_3$, $^3J_{\mathrm{H,H}} = 3.4$ Hz), 0.89 (d, 6H, C$H_3$, $^3J_{\mathrm{H,H}} = 2.9$ Hz), 0.91–0.99 (m, 4H, C(4)–$H$), 1.15–1.29 (m, 2H, –C$H$), 1.35–1.45 (m, 4H, C(3)–$H$), 1.54–1.62 (m, 4H, C(6)–$H$), 1.91 (m, 4H, THF), 2.2 (m, 2H, C(2)–$H$), 2.3 (m, 2H, C(5)–$H$), 4.02 (m, 4H, THF), 4.5 (m, 2H, C(1)–$H$). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 25 °C): $\delta = 15.9$ ($C$H$_3$), 21.1 ($C$H$_3$), 22.1 ($C$H$_3$), 22.8 (C$_3$), 25.5 ($C$H), 25.8 (THF), 31.7 (C$_5$), 34.2 (C$_4$), 45.1 (C$_6$), 50.6 (C$_2$), 70.5 (THF), 94.2 (C$_1$). IR (nujol-polyethylene, cm$^{-1}$): 422 (m), 493 (m), 617 (m), 727 (s), 856 (s), 925 (m), 995 (s), 1039 (s), 1079 (s), 1099 (s), 1132 (s), 1321 (m), 1344 (s), 1367 (s), 1457 (s), 2657 (m), 2728 (m).

### 4.3. Preparation of [Ti(OBorn)$_2$Cl$_2$(thf)$_2$] (**11**)

A THF (10 mL) solution of [Ti(OBorn)$_4$] (0.86 g, 1.3 mmol) was slowly added to a stirred toluene solution of TiCl$_4$(thf)$_2$ (0.42 g, 1.3 mmol). The resulting solution was stirred for 6 h at room temperature and the solvent removed under vacuum to give a white solid. The crude product was recrystallized from Et$_2$O to obtain a white crystalline solid (1.31 g, 90%). $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): $\delta = 0.86$ (s, 6 H, C$H_3$), 0.99 (s, 12H, C$H_3$), 1.29–1.34 (m, 6H, C(4)–$H$, C(6)–$H_{\mathrm{ax}}$), 1.68 (m, 2H, C(3)–$H_{\mathrm{ax}}$), 1.76 (m, 2H, C(3)–$H_{\mathrm{ec}}$), 1.91 (m, 4H, THF), 2.05 (m, 2H, C(5)–$H$), 2.41 (m, 2H, C(6)–$H_{\mathrm{ec}}$), 3.91 (m, 4H, THF), 5.18 (m, 2H, C(1)–$H$). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 25 °C): $\delta = 13.8$ ($C$H$_3$), 18.8 ($C$H$_3$), 20.2 ($C$H$_3$), 25.7 (THF), 26.9 (C$_4$), 28.2 (C$_3$), 39.5 (C$_6$), 45.0 (C$_5$), 48.0 ($C$(CH$_3$)$_2$), 52.3 (C$_2$), 69.5 (THF),101.6 (C$_1$). IR (KBr disk, cm$^{-1}$): 703 (w), 827 (s), 921 (s), 1022 (s), 1029 (s), 1056 (s), 1108 (m), 1137 (w), 1234 (w), 1307 (w), 1349 (m), 1367 (m), 1388 (m), 1452 (m), 1475 (m), 1621 (m), 2877 (s), 2952 (s), 2981 (s). Anal. Calc. for C$_{28}$H$_{42}$Cl$_2$O$_4$Ti: C, 59.90; H, 7.54. Found: C, 59.62; H, 7.44%.

### 4.4. Polymerization of ε-caprolactone (general procedure)

To a dichloromethane solution (15 mL) of complex [Ti(OR)$_2$(OPr$^i$)$_2$]$_2$ or [Ti(OR)$_2$Cl$_2$] (0.46 mmol) was added ε-caprolactone (4.88 mL, 46 mmol) by syringe with vigorous magnetic stirring at room temperature. To follow the polymerization an aliquot of the reaction was periodically

Table 3
Crystal and structure refinement data for complex **11**

| | |
|---|---|
| Empirical formula | $C_{28}H_{50}Cl_2O_4Ti$ |
| Formula weight | 569.48 |
| $T$ (K) | 150(2) |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| $a$ (Å) | 7.4410(6) |
| $b$ (Å) | 18.845(3) |
| $c$ (Å) | 21.258(3) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 90 |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 2980.9(6) |
| $Z$ | 4 |
| $D_c$ (g/cm$^3$) | 1.269 |
| $\mu$ (mm$^{-1}$) | 0.496 |
| Crystal dimension (mm) | 0.3 × 0.1 × 0.1 |
| $F(000)$ | 1224 |
| $\theta$ Limits (°) | 2.16–25.5 |
| Limiting indices | $-8 < h < 9$, $-22 < k < 22$, $-25 < l < 25$ |
| Reflections collected/unique ($R_{int}$) | 20475/5558 (0.2320) |
| Reflections observed [$I > 2\sigma(I)$] | 2228 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$[a] = 0.0813, $wR_2$[b] = 0.1885 |
| Goodness-of-fit on $F^2$ | 1.111 |
| Absolute structure parameter | −0.12(10) |
| Largest difference in peak and hole (e Å$^{-3}$) | 0.675 and −0.887 |

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

subjected to $^1$H NMR spectroscopy, in order to determine the conversion of the monomer. After reaction time the reaction mixture was quenched by methanol to precipitate the polymer, which was dried under vacuum and weighted. The sample was subjected to $^1$H NMR spectroscopy ($CDCl_3$) and GPC to determine the average molecular weights $M_n$, $M_w$ of the produced polymer and $M_n/M_w$ values. The monomer conversion was determined from the relative intensity of the NMR signals at $\delta$ 4.20 and 4.02 ppm corresponding to the O$CH_2$ resonance in ε-caprolactone and poly (ε-caprolactone), respectively.

### 4.5. X-ray data collection and structure determination of [Ti(OBorn)$_2$Cl$_2$(thf)$_2$] (**11**)

Colourless needle crystals of **11** were obtained from $Et_2O$ at −25 °C. A summary of crystal data, data collection and refinement parameters for the structural analysis is given in Table 3. The crystal was glues with a mineral oil to a glass fiber and mounted on Kappa-CCD Bruker-Nonius diffractometer with area detector and equipped with an Oxford Cryostream 700 unit. Data were collected using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$). Data collection was performed at 150 K, with an exposure time of 60 s per frame (5 sets; 391 frames). Raw data were corrected for Lorenz and polarization effects.

Structure was solved by direct methods, completed by the subsequent difference Fourier techniques and refined by full-matrix least-squares on $F^2$ (SHELXL-97) [35]. Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. The hydrogen atoms were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system [36].

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## Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 296847, for compound **11**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http//www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.019.

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