

Review

Use of Titanium Complexes Bearing Diphenolate or Calix[*n*]arene Ligands in α -Olefin Polymerization and the ROP of Cyclic Esters

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Abstract: In this review, we discuss the use of titanium complexes bearing either bridged diphenolate or calix[*n*]arene ($n = 4, 6, 8$) ligation, in the formation of plastics from α -olefins or via the ring opening polymerization (ROP) of cyclic esters. The syntheses, molecular structures and catalytic behaviour of these systems are discussed, as well as where possible, the properties of the resultant polymers.

Keywords: polyolefins; polyesters; biodegradable polymers; titanium; calix[*n*]arene; diphenolate

1. Introduction

Global demand for plastics remains high in both newly expanding as well as established economies, which stems from the favourable characteristics, including cost, associated with many petrochemical derived polymers. This availability/affordability, as well as the high ‘tune ability’ of their mechanical properties allows for incredible versatility, and as such polyolefin-based plastics are ubiquitous and play a central role in modern day society. Nevertheless, excessive and uncontrolled use of these materials for single-use applications (eg. packaging) and their still somewhat limited recyclability come at a cost to the environment. As well as changes in recent social behaviour, one possible route towards tackling the environmental issues is to limit the application of polyolefin based single-use plastics, and develop more biodegradable alternatives. Ideally, such alternative polymers should retain the favourable characteristics of known plastics, whilst not taking centuries to degrade (or readily fragmenting into microplastics). The challenge is not easy, and will require intense research efforts. One promising route to biodegradable polymers is via the ring opening polymerization (ROP) of cyclic esters. Both the polymerization of polyolefins and the ROP of cyclic esters has benefited from catalyst development and the ability of coordination chemistry to manipulate the ligands at the metal center of the catalyst to both optimize catalytic activity and to tune polymer (or oligomer) properties. Early transition metals, particularly those of group IV, have seen widespread use in the polyolefin area, and in more recent years have also been scoped for the ROP of cyclic esters. Chelating ligands can help to stabilize the catalytically active species and also offer the opportunity to bring metals into close proximity with the possibility of favourable cooperative effects. One type of chelate ligand that have seen application in a variety of catalytic processes are the diphenolates. This also led to exploration of macrocyclic phenols known as calix[*n*]arenes (Figure 1, right) given that these macrocycles can be visualized as larger cyclic versions of the aforementioned diphenolates (Figure 1, Type II) [1–3]. Such systems offer several advantages, for example the ligands employed are commercially available or can readily be synthesized in multigrams quantities. In addition, access to vast numbers of structural motifs is possible via their ready functionalization; such modifications allow for the control of parameters such as thermal stability and/or solubility. In turn, the inherent chirality of some of these ligands and,

consequently, of their corresponding metal complexes can be particularly advantageous in the case of stereoselective reactions. In such a scenario, the cavity of the calix[*n*]arenes is ideal for selective substrate recognition [1]. All of these characteristics can be crucial in terms of catalysis. This review focuses on the use of both titanium diphenolates and titanocalix[*n*]arenes, the first examples of the latter were characterized back in the 1980s [4]. For the sake of clarity, titanium complexes bearing ligands derived from type I phenols (Figure 1, left) are not discussed here, since they have been extensively treated elsewhere [5].

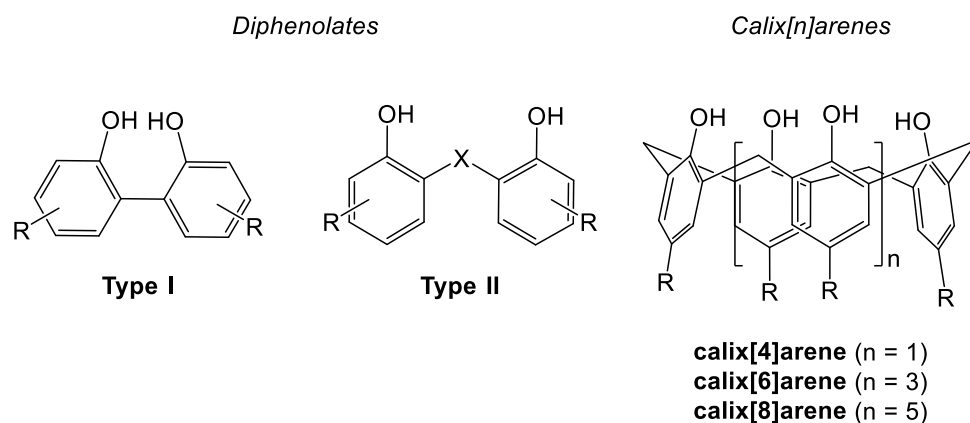


Figure 1. Phenol-based pro-ligands [1–5].

2. Olefin Polymerization

2.1. Titanium-Diphenolate Complexes

In 1989, Kakugo et al. reported the synthesis of titanium complexes (**1** and **2**, Figure 2) bearing a sulfur-bridged diphenolate ligand [6]. These compounds, activated by methylaluminoxane (MAO, Scheme 1) where tested in the polymerization of ethylene and of propylene (Table 1).

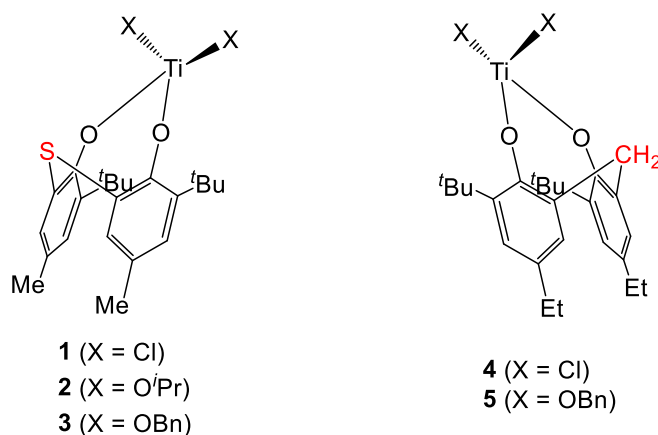
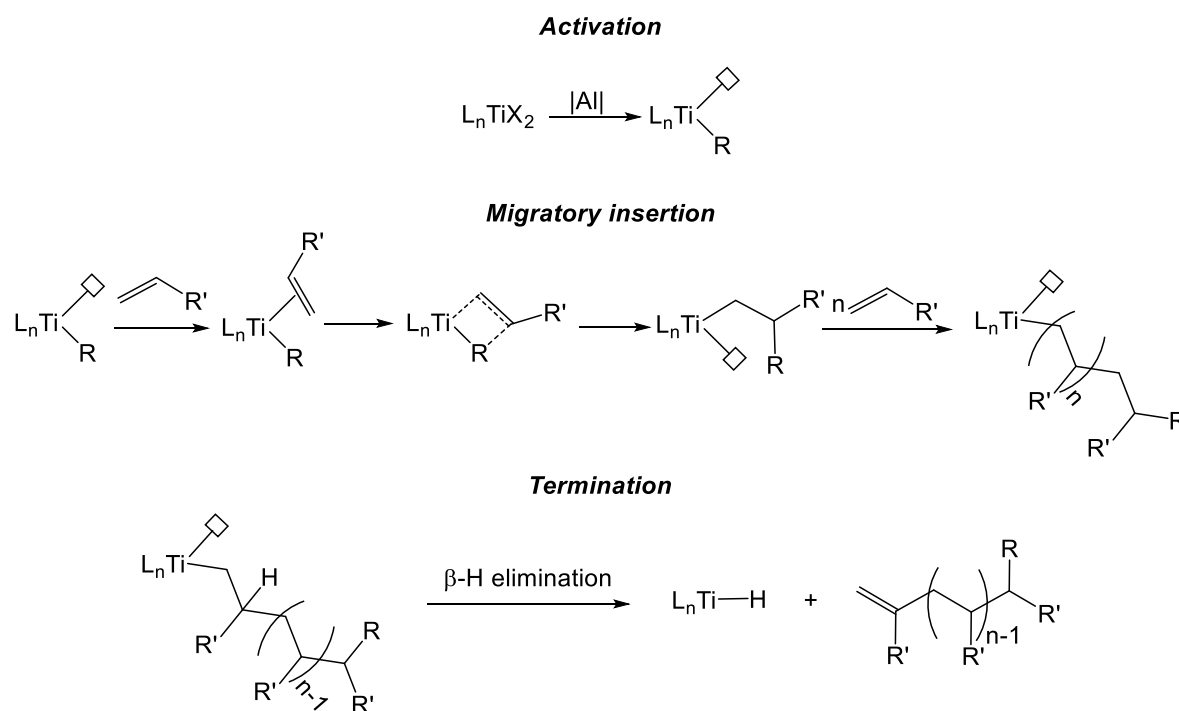


Figure 2. Titanium complexes bearing sulfur- and methylene-bridged diphenolates [6,7].

The chloride derivative **1** proved to be slightly better performing than its alkoxide congener **2** in both transformations. In fact, a slightly higher activity was exhibited by the former in ethylene polymerization (228 and 188 for **1** and **2**, respectively, Table 1, entries 1 and 2) while an important increase (*ca.* 2-fold) was observed in the reaction involving propylene (Table 1, entries 3 and 4). High molecular weights and narrow polydispersities were achieved in all cases. Notably, both complexes were shown to be more active than [Ti(O*i*Pr)₄] (Table 1, entry 5). In terms of microstructure, ¹³C NMR spectroscopic

analyses on the PP obtained in the presence of complex 1/MAO systems highlighted poor regio- and stereoregularity.



X = halide, alkoxide; |Al| = MAO, AlR_3 , AlR_nCl_{n-1}

R = Me, Et, i Bu; R' = H, Me, C_4H_9 , C_6H_5

Scheme 1. Simplified mechanism for the Ti-catalyzed olefin polymerization.

Table 1. Ethylene and propylene polymerization catalyzed by 1 and 2/MAO systems [6].

Entry	Complex	Monomer	Activity ^a	M_w (10^{-4})	M_w/M_n
1	1	ethylene	228	360	2.0
2	2	ethylene	188	420	2.5
3	1	propylene	186	>800	2.2
4	2	propylene	87	>800	2.0
5	$[Ti(OiPr)_4]$	propylene	4.8	41.5	6.9

Reaction conditions: $[Ti] = 1.1 \times 10^{-6}$ M, $Al_{MAO}/Ti = 4700$, $T = 20$ °C. For ethylene: toluene 10 mL, P = 1 atm, 20 s. For propylene: monomer 30 g, 1 h. ^a $g_{PE} \times g_{Ti}^{-1} \times s^{-1}$ (ethylene) and $g_{PP} \times g_{Ti}^{-1} \times h^{-1}$ (propylene).

Subsequently, complex 1 along with its benzyl derivative 3 and their methylene-bridged analogues 4 and 5 activated by MAO were employed in the polymerization of ethylene by Orpen et al. (Table 2) [7]. Also in this case, complex 1 proved to be more active than the benzyl complex 3. However, higher molecular weight and better control were achieved with the latter catalyst (Table 2, entries 1 and 2). The rather broad polydispersities suggested the formation of more than one active species when MAO is used as co-catalyst. Better performance of the chloride pre-catalyst over the benzyl congener was observed also in the case of complexes 4 and 5 (Table 2, entries 3 and 4). Interestingly, sulfur-bridged compounds were shown to be more active than their methylene-bridged analogues (cf. Table 2 entry 1 vs. entry 3). Complexes 1 and 3 were also tested for the polymerization of 1-hexene. With both systems, atactic but regioregular poly-1-hexene was obtained. The polymers isolated exhibited high molecular weights and narrow polydispersities (7800 vs. 19,000 Da and 1.78 vs. 1.71 for 1 and 3, respectively). Eventually, the polymerization of 1,3-butadiene was achieved in the presence of the 1/MAO system. The microstructure of the polymer was found to be 65% 1,4-*cis*, 20% 1,4-*trans* and 15%

1,2-vinyl, as determined by ^{13}C -NMR spectroscopic analyses. Interestingly, both **1** and **3** were found to be inactive when EtAlCl_2 was used as co-catalyst instead of MAO.

Table 2. Ethylene polymerization catalyzed by **1**, **3**, **4** and **5**/MAO systems [7].

Entry	Complex	Time (min)	Activity ($\text{kgPE} \times \text{molTi}^{-1} \times \text{h}^{-1}$)	M_n (10^{-3})	M_w/M_n
1	1	5	4740	29.5	11.9
2	3	15	504	50.0	7.0
3	4	10	390	nd	nd
4	5	15	180	nd	nd

Reaction conditions: $\text{Ti} = 0.02 \text{ mmol}$, $\text{Al}_{\text{MAO}}/\text{Ti} = 500$, $T = 20 \text{ }^\circ\text{C}$, toluene 200 mL, $P = 3 \text{ atm}$.

In order to further investigate the effect of the bridging unit on the efficiency of the catalyst, some tellurium-bridged diphenols and their corresponding titanium complexes were synthesized by Nakamura et al. (Figures 3 and 4) [8]. All complexes activated by MAO were tested in the polymerization of ethylene (Table 3).

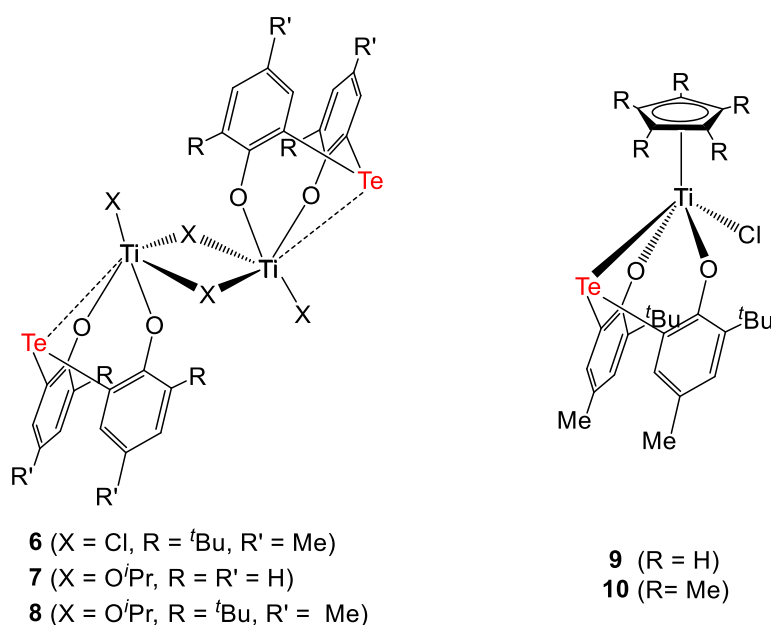


Figure 3. Tellurium-bridged diphenolate titanium complexes [8].

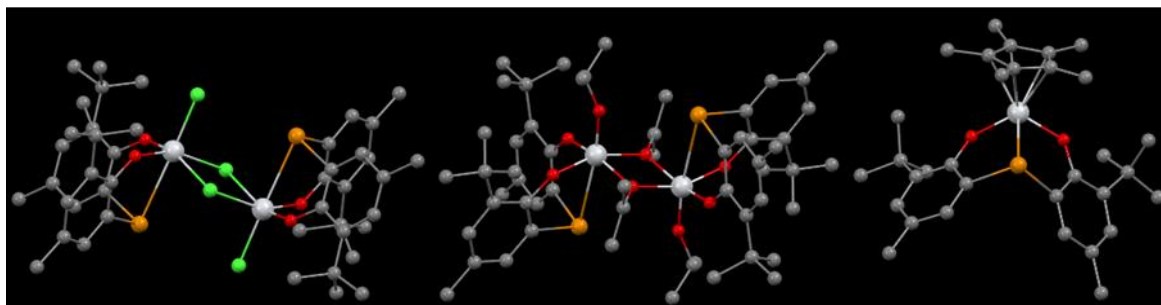


Figure 4. Molecular structures of complexes **6** (left), **8** (center) and **10** (right) [8].

Table 3. Ethylene polymerization catalyzed by **1**, **4**, **6** -**10**/MAO systems [8].

Entry	Complex	Time (h)	Activity (kg _{PE} × mol _{Ti} ⁻¹ × atm ⁻¹ × h ⁻¹)	M _n (10 ⁻⁴)	M _w /M _n
1	6	0.08	161	-	-
2	6	1	70	1.5	3.2
3	6	3	21	-	-
4	7	6	0.34	1.5	19
5	8	1	29	2.5	4.1
6	9	1	130	-	-
7	10	6	2.3	2.4	6.1
8	1	1	220	0.8	2.2
9	4	1	1.3	-	-

Reaction conditions: Ti = 5 × 10⁻⁶ mol, Al_{MAO}/Ti = 1000, T = 25 °C, toluene 15 mL, P = 1 atm.

The chloride complex **6** bearing bulky substituents proved to be very active (Table 3, entry 1). Interestingly, its alkoxide analogue **8** was ca. 5-times less performing (Table 3, entry 5), whilst the less sterically hindered compound **7** was almost inactive (Table 3, entry 4). Notably, good activity was exhibited by the Cp-containing complex **9**, while its Cp* analogue **10** was shown to be less performing (130 and 2.3 kg_{PE} × mol_{Ti}⁻¹ × atm⁻¹ × h⁻¹, Table 3, entries 6 and 7 for **9** and **10**, respectively). Such different reactivity was explained by considering the steric bulk around the Ti center exerted by the Cp* ligand. Complexes **1** and **4** were also tested under the same reaction conditions (Table 3, entries 8 and 9, respectively). Complex **4** was ca. two orders of magnitude less performing than **1**. Notably, the activity of the sulfur-containing catalyst was three times higher than that of the tellurium-based complex. This evidence was inconsistent with theoretical studies previously performed in order to predict the activity of these systems [9]. This was explained in terms of stability of the catalytically active species. In fact, the **6**/MAO system was shown to completely deactivate within 1 h, probably due to Al-Te exchange reactions. The poor performance of catalyst **4** was explained considering the higher flexibility of the sulfur and tellurium-containing ligands over the more rigid methylene-bridged congener.

Subsequently, Trivedi et al. reported the synthesis of titanium-isopropoxide complexes bearing various substituted methylene-bridged diphenols- (**11**–**13**) and binaphthols (**14**–**15**) (Figure 5) [10,11]. In a preliminary investigation, all complexes activated by ethylaluminum sequichloride (EASC) were tested in the polymerization of ethylene (Table 4). All systems proved to be active, following the trend **13** > **15** > **11** > **14** > **12**. Low molecular weight waxes were obtained in all cases, with M_w values spanning from 770 to 3400 Da. Good control was observed in all cases, with polydispersity values found in the range 1.3–1.9. Notably, under the same reaction conditions the metallocene catalyst Cp₂TiCl₂ was found to be inactive.

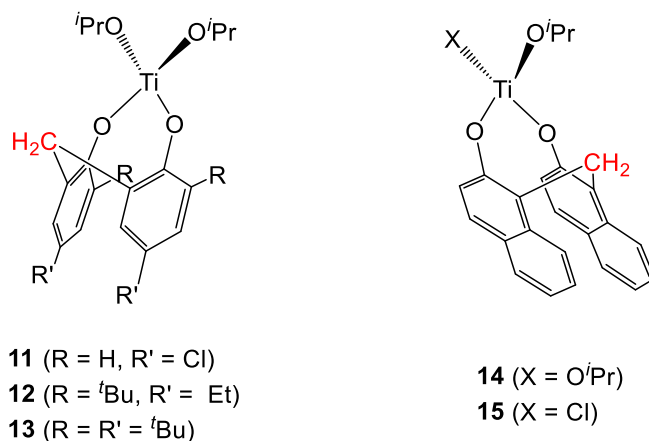
**Figure 5.** Titanium complexes bearing methylene-bridged diphenol and binaphthol derived ligands [10,11].

Table 4. Ethylene polymerization catalyzed by **11–15**/EASC systems [10,11].

Entry	Complex	Activity (kg _{PE} × g _{Ti} ⁻¹)	M _w	M _w /M _n
1	11	7.8	1900	1.7
2	12	3.5	770	1.3
3	13	11.0	1760	1.5
4	14	4.2	3380	1.9
5	15	9.5	1290	1.5
6	Cp ₂ TiCl ₂	-	-	-

Reaction conditions: T = 100 °C, 1 h, P = 20 atm, toluene.

Furthermore, the effect of the reaction conditions on the performance of complex **15** in the polymerization of ethylene was investigated (Table 5) [11]. A drop of activity was observed when EASC was replaced by other Al-based co-catalysts (Table 5, entries 1–5) Lower activities were also observed by reducing the temperature (Table 5, entries 6 and 7). On the other hand, a significant improvement of productivity was achieved by increasing the monomer pressure (Table 5, entries 8 and 9). The nature of the reaction medium was also considered, and the catalytic system was inactive in the case of the reaction carried out in hexane (Table 5, entry 10), while enhanced activity was observed when the standard solvent (toluene) was replaced by chlorobenzene (Table 5, entry 11).

Table 5. Effect of the reaction conditions on the ethylene polymerization promoted by **15** [11].

Entry	Solvent	[Al]	T (°C)	P _{ethylene} (atm)	Activity (kg _{PE} × g _{Ti} ⁻¹)	M _w	M _w /M _n	T _m (°C)
1	Toluene	EASC	100	20	9.5	1290	1.5	118
2	Toluene	Et ₂ AlCl	100	20	6.7	-	-	113
3	Toluene	MAO	100	20	2.1	-	-	136
4	Toluene	EtAlCl ₂	100	20	1.8	-	-	125
5	Toluene	Et ₃ Al	100	20	0.2	-	-	-
6	Toluene	EASC	30	20	0.4	-	-	-
7	Toluene	EASC	60	20	2.3	-	-	128
8	Toluene	EASC	100	7	3.5	890	1.3	111
9	Toluene	EASC	100	33	18.3	3200	1.6	119
10	Hexane	EASC	100	20	0.8	-	-	-
11	Chlorobenzene	EASC	100	20	12.4	1550	1.6	117

In all cases, low molecular weights and narrow polydispersities were observed (900–3200 Da and 1.3–1.7, respectively). Melting temperatures lower than that observed for HDPE and LDPE were detected (111–120 °C). Noteworthy, all polymers exhibited a degree of crystallinity in the range of 80–88%, as determined by X-ray diffraction analyses.

2.2. Titanocalix[n]arene Complexes

The first reports of the use of titanocalix[n]arenes for the polymerization of α-olefins dates back to 1999, when Ladipo et al. synthesized novel titanium-based complexes **16–22** bearing proximally bridged *p*-*tert*-butylcalix[4]arene ligands (Figure 6) [12]. When activated by MAO, these compounds exhibited moderated activity in the polymerization of ethylene (Table 6), but were inactive towards the polymerization of higher olefins such as propylene and 1-hexene.

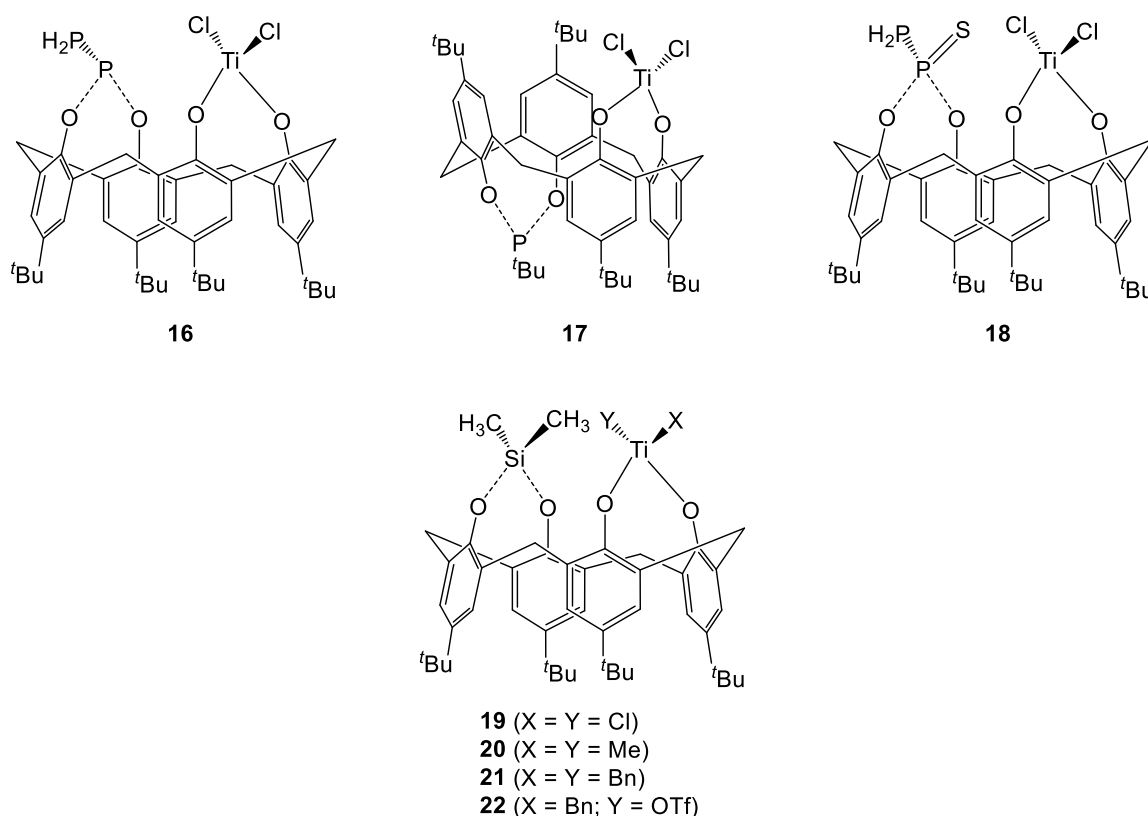


Figure 6. Titanium-calix[4]arene complexes disclosed by Ladipo et al. [12].

Table 6. Polymerization of ethylene catalyzed by 16–22/MAO systems [12].

Entry	Complex (mmol)	MAO (Al/Ti)	Time (min)	Activity (kg mol _{cat} ⁻¹ h ⁻¹)
1	16 (0.02)	500	30	9
2	17 (0.02)	500	30	70
3	18 (0.02)	500	30	15
4	19 (0.02)	500	30	35
5	20 (0.02)	500	30	15
6	21 (0.02)	500	30	25
7	22 (0.02)	500	30	24

Reaction conditions: Toluene (40 mL), ethylene 1 atm, 25 °C.

Frediani, Sémeril et al. employed the 1,3-di-*n*-propyloxycalix[4]arene complex **23** (Figures 7 and 8), activated by MAO, to afford ultrahigh molecular weight polyethylene [13]. The influence of the temperature as well as the [ethylene]/[Ti] ratio on the productivity of the polymerization were studied (Table 7). Indeed, an improvement of catalytic activity was obtained by either increasing the temperature (Table 7, entries 1–6) or by employing higher monomer concentrations (Table 7, entries 7–9).

¹H-NMR spectroscopic studies identified the active species as a titanium methyl cation. A similar species was observed by Proto et al. in their study concerning the polymerization of ethylene catalyzed by **24**/MAO systems [14].

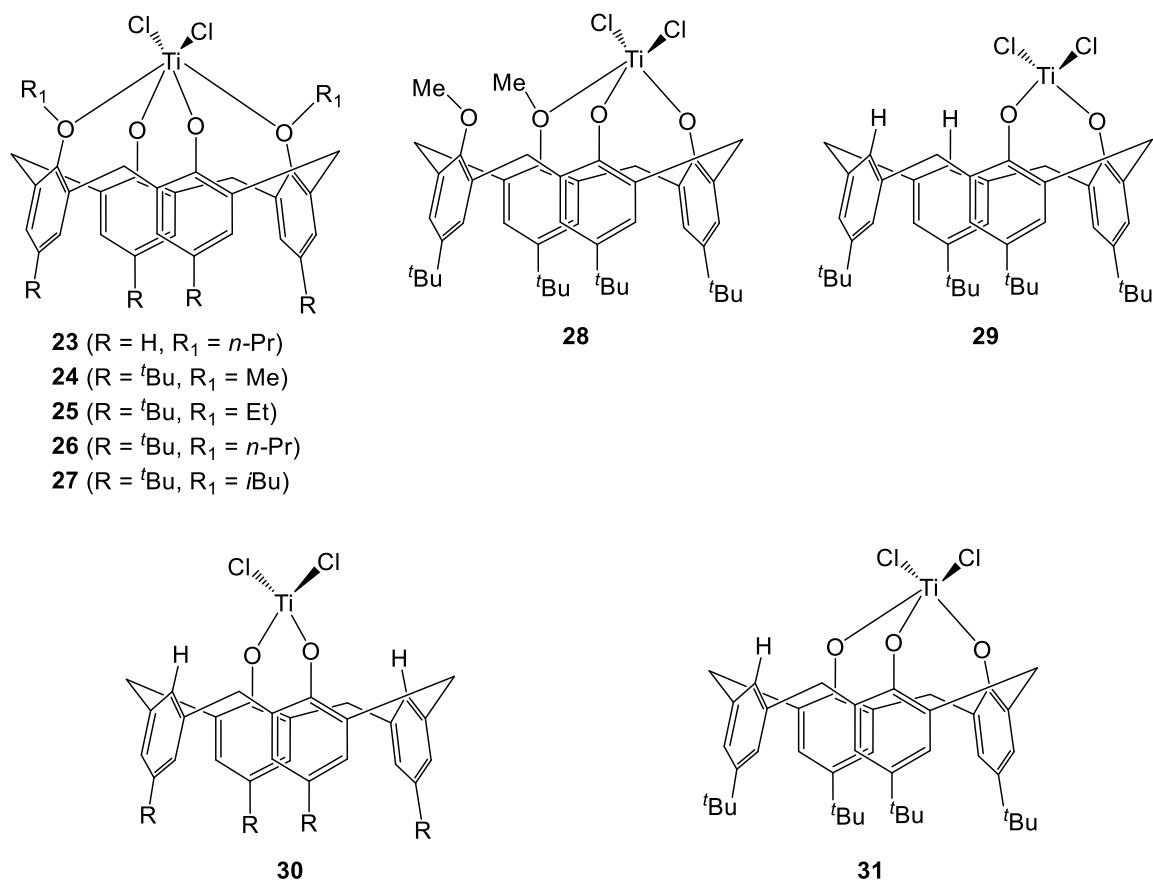


Figure 7. Proximal and distal titanocalix[4]arene complexes [13–15].

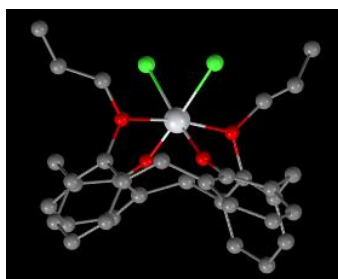


Figure 8. Molecular structure of **23** [13].

Table 7. Polymerization of ethylene catalyzed by **23**/MAO [13].

Entry	T (°C)	[ethylene] (M)	Activity (kg _{polym.} · mol _{cat} ⁻¹ h ⁻¹)	T _m (°C)	M _n ^a (10 ⁻⁶)
1	45	0.5	10.6	135.8	3.98
2	60	0.5	29.8	136.9	3.44
3	75	0.5	43.7	137.0	2.54
4	90	0.5	60.0	134.2	0.96
5	105	0.5	54.5	137.0	0.73
6	120	0.5	27.0	135.5	0.60
7	60	0.25	9.8	138.3	3.24
8	60	0.75	53.8	137.8	3.53
9	60	1.00	82.4	138.3	4.22

Reaction conditions: [Ti] = 2.1 × 10⁻⁵ M, Al/Ti = 1440, Toluene 200 mL, 2 h. ^a Viscosimetric average molar mass.

Subsequently, Taoufik, Bonnamour et al. extended these studies and investigated the effect of varying the 1,3-dialkyloxy R groups (for R = methyl, ethyl, *n*-propyl and *i*-butyl) on the catalytic activity of complexes **24–27** (Figure 9) during ethylene polymerization [15]. In the same study, a couple of 1,2-dialkoxycalix[4]arene derivatives were also studied such as the previously encountered **19** containing a chelating siloxide SiMe₂ and the methyloxy **28**. Depleted calix[4]arene complexes **29–31** bearing 1,2- or 1,3-titanium dichloride motifs were also investigated (Table 8). Whilst the behavior of the 1,2- and 1,3-systems was different, it was determined that within each series increasing the number of alkyloxy groups present was detrimental to the catalytic activity. Moderate activity was exhibited by complex **19** containing the chelating 1,2-siloxide moiety (Table 8, entry 1). Interestingly, low productivity values spanning from 14 to 21 kg_{PE} · mol_{cat}⁻¹ h⁻¹, were achieved in the presence of complexes **24–27**, regardless of the chain length of the 1,3-alkoxide substituents (Table 3, entries 2–5). The highest productivity was obtained in the presence of the 1,2-depleted complex **29** (Table 8, entries 7) while significantly lower activity was observed in the case of its 1,3-analogue **30** (Table 8, entry 8). In all cases, high number average molecular weights were determined. Noteworthy, the highest values (spanning from 2.3 to 3.2 × 10⁶ g mol⁻¹) were observed for the PEs synthesized in the presence of complexes **24–27**. These numbers were found to be consistent with the range observed for Ultra High Molecular Weight (UHMW) PE. On the other hand, lower *M_n* values consistent with High Density (HD) PE were achieved in the presence of the depleted complexes **19** and **29** (1.7 and 1.4 × 10⁶ g mol⁻¹, respectively).

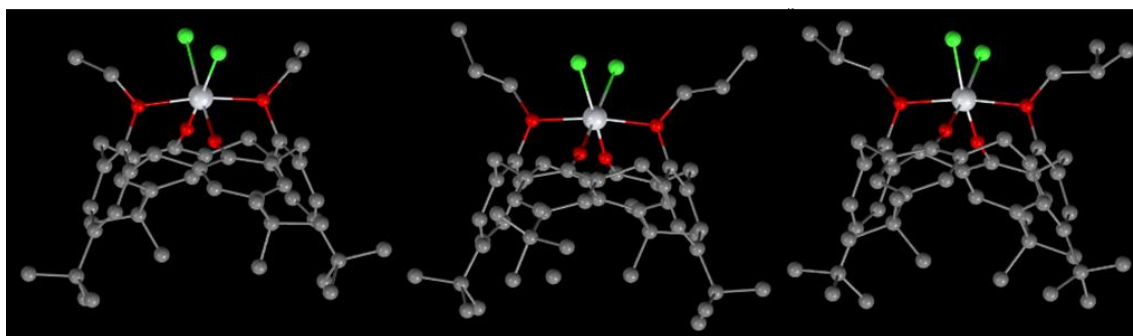


Figure 9. Molecular structures of complexes **25** (left), **26** (center) and **27** (right) [15].

Table 8. Polymerization of ethylene catalysed by **19**- and **24–30**/MAO systems [15].

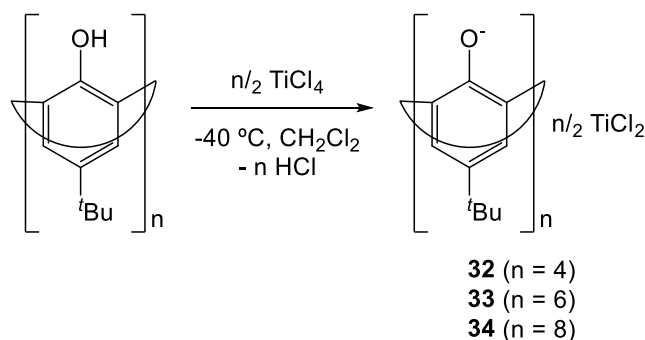
Entry	Complex	Activity (kg _{polym.} · mol _{cat} ⁻¹ h ⁻¹)	<i>M_n</i> (10 ⁻⁶)	<i>M_w</i> / <i>M_n</i>	<i>T_m</i> (°C)
1	19	113	1.7	4.4	137.4
2	24	14	2.9	2.7	132.0
3	25	16	2.7	2.5	131.8
4	26	21	3.2	2.9	131.4
5	27	16	2.3	3.0	133.2
6	28	185	2.6	3.3	134.6
7	29	350	1.4	5.4	133.6
8	30	83	n.d. ^a	n.d. ^a	137.4

Reaction conditions: P_{ethylene} = 30 bar, T = 50 °C, [Ti] = 2.1 × 10⁻⁵ M, Toluene 50 mL, 2 h. ^a Not determined.

In order to explain such differences, it was proposed that the increased protection around the metal center in complexes **24–27** would limit chain transfer reactions, enabling the growth of longer PE chains. Such a statement was supported by the trend of the molecular weight distributions. In fact, broad polydispersities were observed in the case of less hindered complexes **19** and **29** (4.4 and 5.4, respectively), while narrower values (spanning from 2.7 to 3.0) were achieved in the case of the more protected congeners **24–27**.

A number of other less well-defined titanium calix[*n*]arenes have also been employed for ethylene polymerization [16–19]. In this regard, Li et al. reported the synthesis of titanocalixarene complexes by

treating at $-40\text{ }^{\circ}\text{C}$ in dichloromethane *p*-*tert*-butylcalix[*n*]arene ($n = 4, 6$ and 8) with different amount of $[\text{TiCl}_4]$ (Scheme 2) [16]. The formation of Ti-O bonds was determined via ^1H -NMR spectroscopy, by monitoring the disappearance of the diagnostic OH signal normally observed at low field. Elemental analyses performed on each sample suggested the formation of di-, tri- and tetranuclear complexes for **32**, **33** and **34**, respectively.



Scheme 2. Synthesis of multinuclear titanocalix[*n*]arene ($n = 4, 6, 8$) complexes [16].

Such complexes, activated by MAO, were employed as catalysts in the polymerization of ethylene (Table 9). All catalysts exhibited moderate activity affording high molecular weight PEs ($1.2 - 5.6 \times 10^6 \text{ g mol}^{-1}$). The trend of productivity was found to be $\mathbf{32} < \mathbf{33} < \mathbf{34}$ suggesting that larger rings allow for a better Ti-monomer interaction. No influence of calixarene size was observed on the molecular weights of the polymers synthesized.

Table 9. Polymerization of ethylene catalyzed by **32–34**/MAO systems [16].

Entry	Complex	Activity ($\text{g}_{\text{polym}} \text{ mol}_{\text{cat}}^{-1} \text{ h}^{-1}$)	M_w (10^{-6})	T_m ($^{\circ}\text{C}$)
1	32	1.36	1.22	136.7
2	33	1.84	5.06	141.5
3	34	2.04	1.74	139.6

Reaction conditions: $T = 40\text{ }^{\circ}\text{C}$, $[\text{Ti}] = 10\text{ }\mu\text{M}$, $\text{Al/Ti} = 500$, toluene 50 mL, 0.5 h.

The polymerization of styrene was also investigated (Table 10). The activity of the catalytic systems was found to be the same as observed for ethylene polymerization. Interestingly, high syndiotacticity was achieved in the presence of **32** and **33** (Table 10, entries 1 and 2, 90.6 and 92.3%, respectively), while atactic PS was isolated by using the larger analogue **34** (Table 10, entry 3).

Table 10. Polymerization of styrene catalyzed by **32–34**/MAO systems [16].

Entry	Complex	Activity ($\text{g}_{\text{polym}} \cdot \text{mol}_{\text{cat}}^{-1} \text{ h}^{-1}$)	S-PS (%)	T_m ($^{\circ}\text{C}$)
1	32	6.59	90.6	265.6
2	33	6.89	92.3	270.4
3	34	7.56	-	-

Reaction conditions: $T = 80\text{ }^{\circ}\text{C}$, $[\text{Ti}] = 10\text{ }\mu\text{M}$, $\text{Al/Ti} = 500$, toluene 10 mL, 1 h, styrene 15 mL.

Subsequently, Chen et al. studied in detail the effect of the reaction conditions on ethylene polymerization catalysed by **32**/ AlR_3 systems (Table 11) [17]. By using $\text{Al}(i\text{Bu})_3$ as co-catalyst, a positive effect on the productivity of the polymerization was observed by progressively increasing the Al/Ti ratio (Table 11, entries 1–4). Indeed, no conversion was obtained with an Al/Ti ratio of 10, while moderate activity was achieved by slightly increasing the amount of co-catalyst (Table 11, entries

1 and 2). Double the amount of polymer was collected by moving from an Al/Ti ratio of 15 to 20 (Table 11, entry 3), while only a slight improvement was achieved by doubling the ratio (Table 11, entry 4). A progressive drop of the polymer melting point was detected when increasing the amount of co-catalyst, possibly due to chain-transfer processes. The productivity of the process was shown to be dependent also on the polymerization temperature. Indeed, when performing the reaction at 35 or 60 °C good activities were observed (Table 11, entries 7 and 8). On the other hand, at 0 and 100 °C the catalyst exhibited only moderate activity (Table 11, entries 5 and 9). This was explained assuming the incomplete activation of the catalyst at low temperature and partial decomposition of the catalytic species under more forcing conditions. This assumption was confirmed by prolonging the reaction time (4 h instead of 1 h). In fact, while the amount of collected polymer doubled in the case of the reaction performed at 0 °C, no improvement was observed in the test carried out at higher temperature (Table 11, entries 6 and 10). Finally, the effect of different Al-alkyl co-activators was studied (Table 11, entries 11–14). Interestingly, the efficiency of the process was shown to follow the trend: AlEt₃ > Al(*i*Bu)₃ > AlEt₂Cl > Al(*i*Bu)₂Cl.

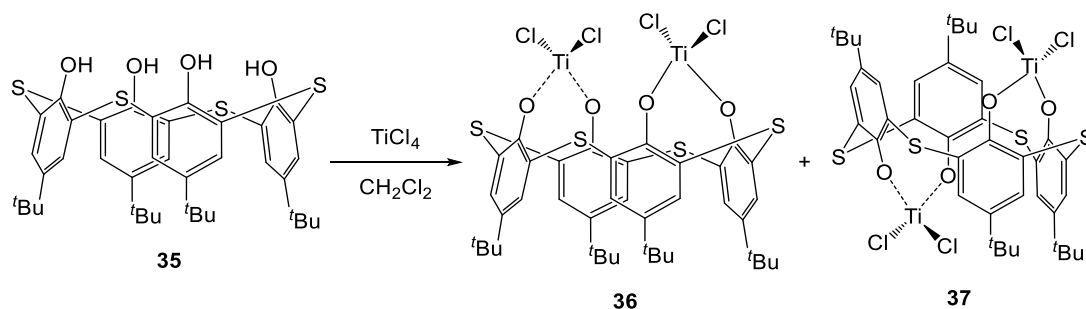
Table 11. Effect of the reaction conditions on the ethylene polymerization catalyzed by **32**/AlR₃ systems [17].

Entry	AlR ₃	Al/Ti	T (°C)	Time (h)	Activity (g _{polym} · mol _{cat} ⁻¹ h ⁻¹)	T _m (°C)
1	Al(<i>i</i> Bu) ₃	10	35	1	-	-
3	Al(<i>i</i> Bu) ₃	15	35	1	31.5	137.9
3	Al(<i>i</i> Bu) ₃	20	35	1	60.7	137.8
4	Al(<i>i</i> Bu) ₃	40	35	1	66.2	136.1
5	Al(<i>i</i> Bu) ₃	20	0	1	28.7	136.7
6	Al(<i>i</i> Bu) ₃	20	0	4	15.7	nd
7	Al(<i>i</i> Bu) ₃	20	35	1	60.7	137.8
8	Al(<i>i</i> Bu) ₃	20	60	1	60.0	137.5
9	Al(<i>i</i> Bu) ₃	20	100	1	37.3	134.6
10	Al(<i>i</i> Bu) ₃	20	100	4	9.7	nd
11	AlEt ₃	40	35	1	83.3	nd
12	Al(<i>i</i> Bu) ₃	40	35	1	66.2	nd
13	AlEt ₂ Cl	40	35	1	30.0	nd
14	Al(<i>i</i> Bu) ₂ Cl	40	35	1	14.7	nd

Reaction conditions: [Ti] = 5 × 10⁻⁴ M, P_{ethylene} = 1.0 MPa

Examples of ethylene polymerization catalyzed by titanocalix[*n*]arene complexes are also found in the patent literature [18,19]. Diaz-Barrios et al. patented the preparation of an additive by treating *p*-*tert*-butylcalix[8]arene with a hundred-fold excess of trimethylaluminum. This species was then reacted with [TiCl₄] in the presence of magnesium dichloride affording a supported catalyst with a titanium content of 7.7%. Such a compound was further employed in the polymerization of ethylene affording a polymer with a melt flow index of 0.76 g/10 min and bulk density of 0.27 g/mL.

Titanium-based complexes bearing thiacalix[4]arenes are less explored than their conventional calix[4]arenes counterparts. In 2002, Morohashi, Miyano et al. disclosed the synthesis of the first dinuclear titanium-thiacalix[4]arene complex (Scheme 3) [20].



Scheme 3. Synthesis of Ti-thiacalix[4]arene complexes **36** and **37** [20].

By treating *p*-*tert*-butylthiacalix[4]arene **35** with $[\text{TiCl}_4]$, the cone- and the 1,2-semi-alternate complexes **36** (Figure 10) and **37** were obtained. The isolation of the two species was possible due to their differing solubility in dichloromethane. Lately, Capacchione et al. investigated the efficiency of these compounds, activated by MAO, in the polymerization of ethylene (Table 12) [21]. Both complexes exhibited a maximum of activity at 25 °C (Table 12, entries 2 and 8, for **36** and **37**, respectively, while a drop of productivity was observed at both lower (0 °C) and higher (50 °C) temperatures. This was ascribed to the incomplete activation of the catalyst in the former case and to its partial decomposition in the latter. Complex **37** exhibited significant lower activity compared to the *cone* isomer, probably due to the steric effect exerted by the *p*-*tert*-butyl substituent of the calixarene moiety. High melting points, spanning from 133 to 143 °C, were observed in all cases, suggesting the production of highly linear PEs. This assumption was also confirmed by ^{13}C -NMR spectroscopy.

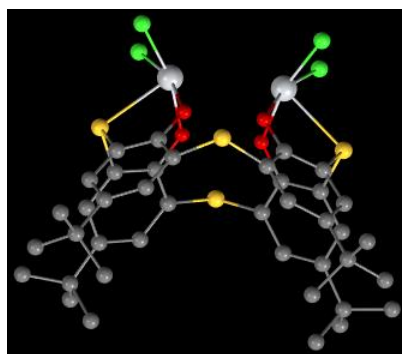


Figure 10. Molecular structure of **36** [21].

Table 12. Polymerization of ethylene catalysed by **36** and **37**/MAO systems [21].

Entry	Complex	T (°C)	Time (h)	P_{ethylene} (atm)	Activity ^b	M_n (10^{-4})	M_w/M_n	T_m (°C)
1	36	0	2	1	19	1.9	29.3 ^c	133.1
2	36	25	2	1	25	1.1	26.6 ^c	132.8
3	36	50	2	1	4.7	1.1	41.3 ^c	132.0
4	36	25 ^a	1.5	5	15	30	2.6	134.1
5	36	25 ^a	1	5	13	25	3.9	138.4
6	36	50 ^a	1	5	11	4.6	15.8 ^c	133.0
7	37	0	2	1	6.5	35	4.0	142.1
8	37	25	2	1	7.7	4.5	11.6 ^c	136.8
9	37	50	2	1	4.3	1.5	41.2 ^c	133.4
10	37	25 ^a	1	5	14	1.2	54.7 ^c	136.5
11	37	50 ^a	1	5	12	42	13.2 ^c	132.9

Reaction conditions: $[\text{Ti}] = 2.5 \times 10^{-5}\text{M}$, Al/Ti = 1000, toluene 15 mL, 2h. ^a toluene 150 mL. ^b $\text{kgPE} \times (\text{molTi})^{-1} \times P_{\text{ethylene}}^{-1} \times \text{h}^{-1}$. ^c bimodal.

3. Ring Opening Polymerization (ROP)

3.1. Ti-diphenolate complexes

In the early 2000s, Takeuchi et al. investigated the ring opening polymerization (ROP) of ϵ -caprolactone (ϵ -CL) and other oxocyclic monomers, namely propylene oxide (PO) and oxetane (OX), catalyzed by complexes **38–43** (Figure 11) [22,23]. The isopropoxy adducts **39** and **42** proved to be active in the ROP of ϵ -CL, affording high molecular weight polymers with good control. The degree of polymerization was found to be ca. half of the expected value, suggesting the growth of two polymer chains for each Ti center. Neither of the two catalysts was active in the ROP of propylene oxide. Similarly, no polymerization was observed in the presence of the more Lewis acidic chloro-derivatives **38** and **41**. However, $^1\text{H-NMR}$ spectroscopy analysis on the crude reaction mixture suggested the presence of the ring opening product 1-chloro-2-propanol. This was thought to proceed from the formation of a chlorotitanium monoalcoholate species followed by its protonolysis by the water present in the deuterated solvent. [22] Subsequently, the same group disclosed the synthesis of ϵ -CL/OX (X = Cl or *i*Pr) block copolymers catalyzed by the chlorotitanium monotriflate complexes **40** and **43**. [23] In this scenario, the cationic polymerization of OX is followed, after quenching of the electrophilic growing end, by the anionic ROP of ϵ -caprolactone (Scheme 4).

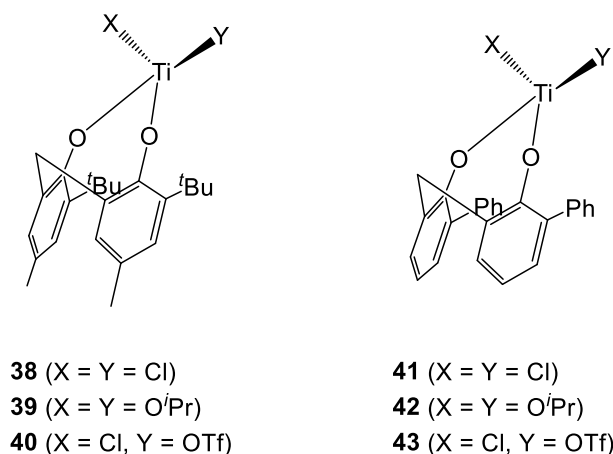
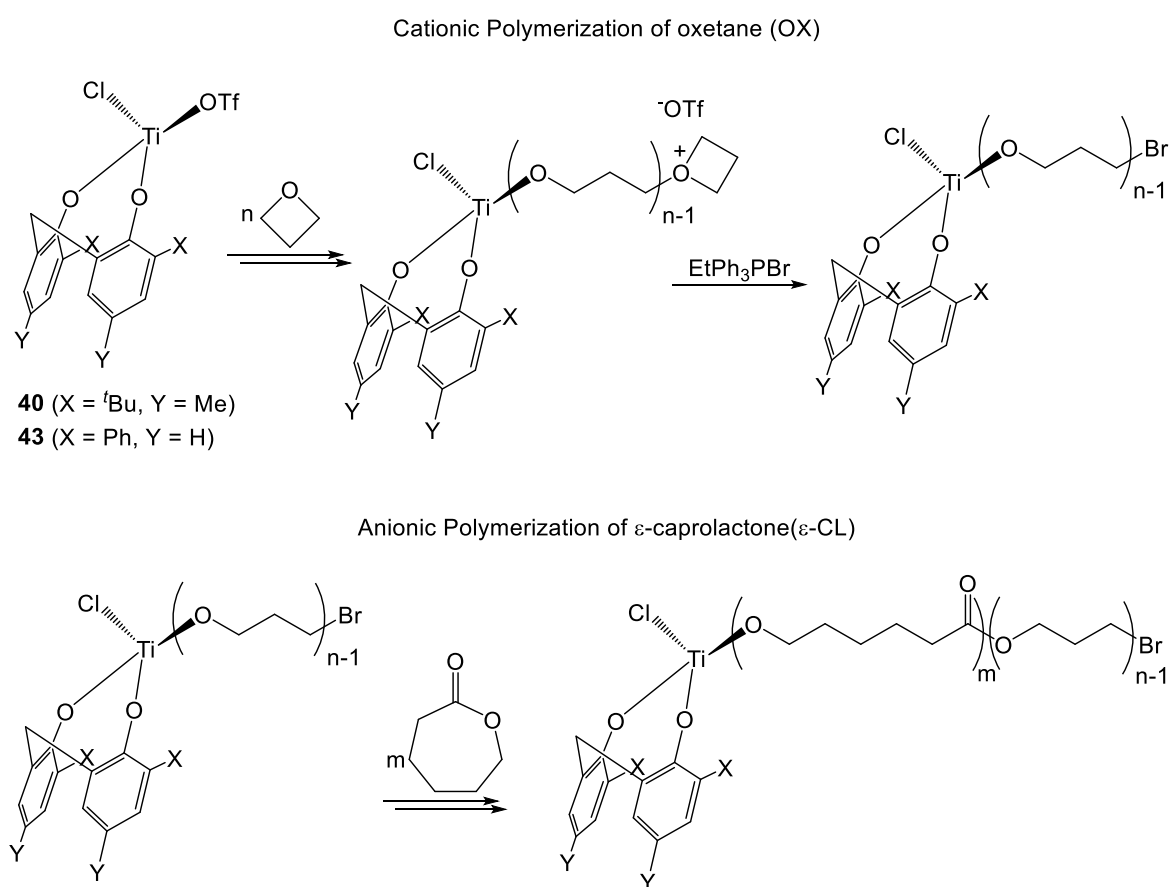


Figure 11. Diphenolate complexes employed in ROP of oxocyclic monomers [22,23].

Based on the promising results achieved in the polymerization of ethylene [6–8], Harada et al. investigated the use of complexes **1**, **5**, **6**, **8** and **10** in the ROP of ϵ -CL (Table 13) with a view to obtaining a biodegradable polymer [24]. The compound bearing the sulfur-bridged ligand (**1**) proved to be active both in the presence and in the absence of solvent (Table 13, entries 1–3). In fact, almost complete conversion was achieved in 6 h in all cases. The highest M_n was obtained in toluene, while the lowest in anisole; the control of the process was shown to follow the opposite trend. Under solvent-free conditions, the Te-bridged catalysts **6** exhibited low activity. In fact, only moderate conversion was achieved after 12 h at 100 °C (Table 13, entry 4). By running the reaction in toluene at 50 °C, no reaction was observed, while 88% conversion was achieved by increasing the temperature (Table 13, entry 5 and 6, respectively). Similar outcomes were obtained by replacing toluene with anisole or dioxane in the presence of a lower catalyst loading (Table 13, entries 7 and 8). Similarly to the previous case, the highest M_n was observed in the reaction in toluene, while the polydispersities were found in a narrow range (1.06–1.20). The isopropoxy analogue of catalyst **6** (namely **8**) was also shown to promote the reaction albeit requiring longer reaction times (12 h instead of 6 h, Table 13, entry 9). The Cp- and Cp* analogues **9** and **10** were inactive (Table 13, entries 10 and 11). The Te-bridged complexes were also tested in the ROP of δ -valerolactone (δ -VL). Moderate conversions were achieved in the presence of complex **6** both in toluene and under solvent-free conditions (Table 13, entries 12

and 13), while its congener **8** was shown to be active only in the absence of solvent (Table 13, entries 14 and 15). Catalyst **6** was inactive in the ROP of β -propiolactone (β -PL) (Table 13, entry 16), while exhibiting interesting activity in the polymerization of L-lactide (L-LA). In fact, almost complete conversion was achieved after 48 h at 100 °C in anisole, providing a polymer with narrow polydispersity (Table 13, entry 18). The nature of solvent was shown to influence also the structure of the isolated polymers. In fact, the formation of cyclic oligomers arising from backbiting processes was observed in the tests performed in toluene. On the other hand, linear polymers were obtained when anisole and dioxane were employed, suggesting the living nature of the process occurring in such reaction media. This was confirmed by performing a diblock copolymerization of L-LA and ϵ -CL in the presence of **6** in anisole. The pre-polymerization of L-LA was first carried out, followed by progressive addition of the co-monomer. GPC analyses highlighted the linear increase of the copolymer M_n consistent with the amount of co-monomer employed.



Scheme 4. Block polymerization of oxetane and ϵ -caprolactone catalyzed by **40** and **43** [23].

Lately, the same group disclosed the synthesis and catalytic activity of diethylamido complexes bearing sulfur- or methylene-bridged ligands **44** and **45** (Figure 12) [25]. Concerning the polymerization of ϵ -CL, both catalysts prove to be active. However, the reaction proceeded faster in the case of the CH_2 -derivative. In fact, while ca. 90% conversion was achieved in 8 h with **45**, longer reaction times were required in the presence of its sulfur-containing analogue (Table 14, entries 2 and 4). Moreover, the molecular weight of the polymer synthesized with **45** was found to be ca. three times higher than that obtained in the presence of analogue **44** (56 and 19 kDa, respectively). $^1\text{H-NMR}$ spectroscopy analyses on the polymers highlighted the presence of Et_2N -terminal groups, suggesting that the initiation step of the process would be the formal migratory insertion of the monomer in the Ti-NEt_2 bond generating a titanium-alkoxide species. The S-containing complex was also employed in the

ROP of *L*-Lactide (Table 14, entries 5 and 6). High conversion (90%) was achieved after 5 days at 100 °C in toluene affording a polymer with high molecular weight and rather narrow polydispersity (20.4 kDa and 1.23, respectively). The M_n value increased linearly *versus* the polymer yield, suggesting the occurrence of a living process.

Table 13. ROP of cyclic esters catalyzed by titanium-diphenolate complexes [24].

Entry	Complex	Monomer	Solvent	T (°C)	Time (h)	Yield (%)	M_n (10^3)	M_w/M_n
1	1	ϵ -CL	none	100	6	93	62.2	2.07
2	1	ϵ -CL	toluene	100	6	100	72.3	2.28
3 ^a	1	ϵ -CL	anisole	100	6	94	28.1	1.17
4	6	ϵ -CL	none	100	12	55	45.1	1.65
5	6	ϵ -CL	toluene	50	6	<1	-	-
6	6	ϵ -CL	toluene	100	6	88	26.0	1.20
7 ^a	6	ϵ -CL	anisole	100	6	87	11.0	1.09
8 ^a	6	ϵ -CL	dioxane	100	6	90	17.6	1.06
9	8	ϵ -CL	none	100	12	85	37.9	1.43
10	9	ϵ -CL	toluene	100	6	<1	-	-
11	10	ϵ -CL	toluene	100	6	<1	-	-
12	6	δ -VL	none	100	6	51	38.4	1.52
13	6	δ -VL	toluene	100	6	49	24.5	1.29
14	8	δ -VL	none	100	6	82	62.4	1.64
15	8	δ -VL	toluene	100	6	<1	-	-
16	6	β -PL	toluene	100	6	<1	-	-
17 ^a	6	<i>L</i> -LA	anisole	100	8	18	4.9	1.07
18 ^a	6	<i>L</i> -LA	anisole	100	48	98	28.2	1.08

Reaction conditions: $[M]_0/[Ti]_0 = 100$. ^a $[M]_0/[Ti]_0 = 200$. CL = caprolactone; VL = valerolactone, PL = propiolactone, LA = lactide.

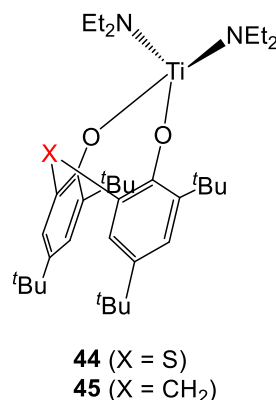


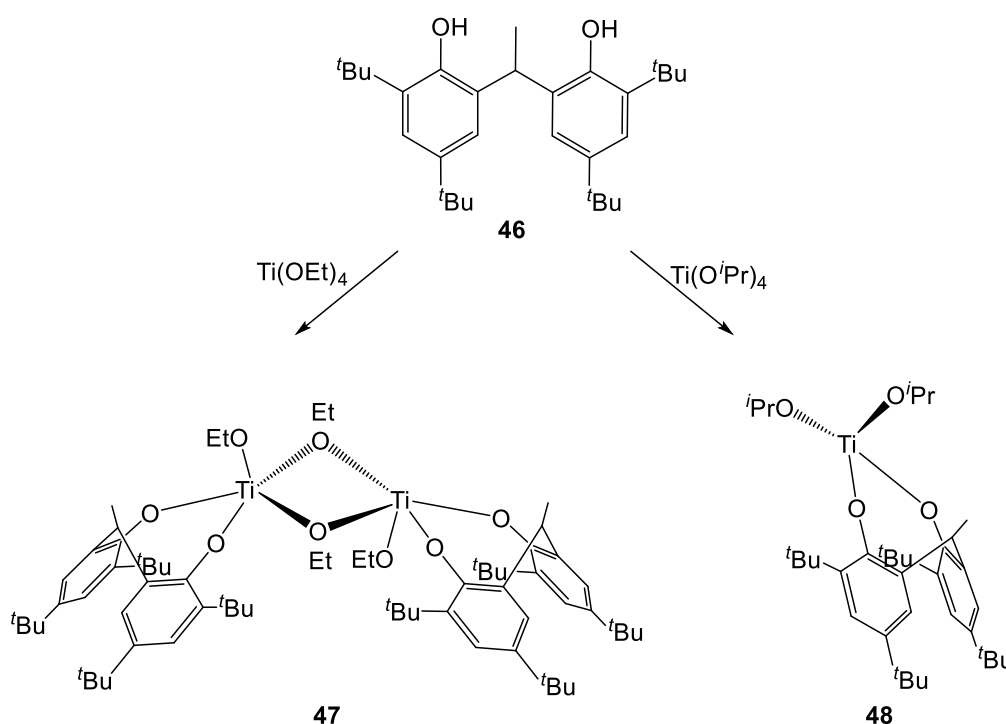
Figure 12. Diethylamido-derivatives of S- and CH₂-bridged diphenolate titanium complexes [25].

Subsequently, Sobota et al. synthesized two novel complexes by treating the pro-ligand **46** with a titanium alkoxide precursor (Scheme 5) [26]. Interestingly, a dimeric species was obtained when $[Ti(OEt)_4]$ was employed, while a monomeric complex was isolated in the case of the reaction involving $[Ti(OiPr)_4]$. This was explained by considering the higher steric hindrance of the latter alkoxide ligand over the former. Both complexes were active in the ROP of *L*- and *r*-LA, affording polymers with high molecular weight and narrow polydispersity (18.0 kDa and 1.05, respectively). Nevertheless, higher rates were achieved with the monomeric species **48**. In fact, 98% conversion was achieved in 1 h while longer reaction times (2.5 h) were required by its dimeric analogue to reach similar values.

Table 14. ROP of cyclic esters catalyzed by Ti-diphenolate complexes **47** and **48** [26].

Entry	Complex	Monomer	Time (h)	Yield (%)	M_n (10^3)	M_w/M_n
1	47	ϵ -CL	4	56.9	8.2	1.09
2	47	ϵ -CL	32	90.3	18.8	1.31
3	48	ϵ -CL	2	23.5	15.3	1.16
4	48	ϵ -CL	8	91.8	56.2	1.60
5	47	L-LA	36	24.4	7.6	1.08
6	47	L-LA	120	90.3	20.4	1.23

Reaction conditions: $[M]_0/[Ti]_0 = 200$, toluene, $T = 100\text{ }^\circ\text{C}$. CL = caprolactone; LA = lactide.

**Scheme 5.** Synthesis of complexes **47** and **48** [26].

The M_n increased linearly to the monomer conversion, indicating the living nature of the polymerization. The analysis of the polymer end-groups indicated the presence of terminal ethoxy- or isopropoxy groups, suggesting that the initiation steps involves the insertion of the monomer into the titanium-alkoxo bond. Finally, the NMR spectroscopic analysis of the microstructure of the polymer obtained from *r*-LA highlighted the preference of complexes **47** and **48** for heteroatactic addition.

A series mixed titanium-M (where M = Li, Na, Zn and Mg) heterobimetallic complexes having various substituents on the methylene bridge of the diphenolate ligand were prepared by Lin et al. (Figure 13) [27]. All complexes were tested in the ROP of L-lactide, and their activity was compared to that of the monometallic complex **48** (Table 15). All complexes were shown to be highly active, with good control of molecular weight and narrow molecular weight distributions. Notably, all M_n values were found to be close to the calculated ones. Similar activity values were found for the monometallic complex **48** and for those containing Li and Na (Table 15, entries 1–3). Notably, the rate of the reaction increased in the presence of Ti-Zn bimetallic species **51–53** and **57** (Table 15, entries 4–7 and 13, respectively). Interestingly, a drop of activity was observed when their Mg-containing congeners (complexes **54–56**) were employed (Table 15, entries 8–12). In fact, in order to achieve complete conversion of the monomer, higher temperatures and longer reaction time were required (50 or 70 °C instead of 30 °C and 1–3.5 h instead of 30 min, respectively). The higher activity of the

zinc-containing complexes was explained considering the higher charge density of Mg compared to that of Zn, leading to stronger M-OR bonds which are thus less prone to monomer insertion. Overall, Mg- and Zn-Ti bimetallic complexes were shown to be better performing than their Li- and Na analogues, as well as than the monometallic catalyst **48**. Within the series, the activity followed the trend **56** > **55** > **54** for Mg-Ti species and **53** > **52** > **51** > **57** for the Ti-Zn congeners. This suggested a positive effect conferred by the presence of electron-donating substituent at the *ortho* positions of the ligand.

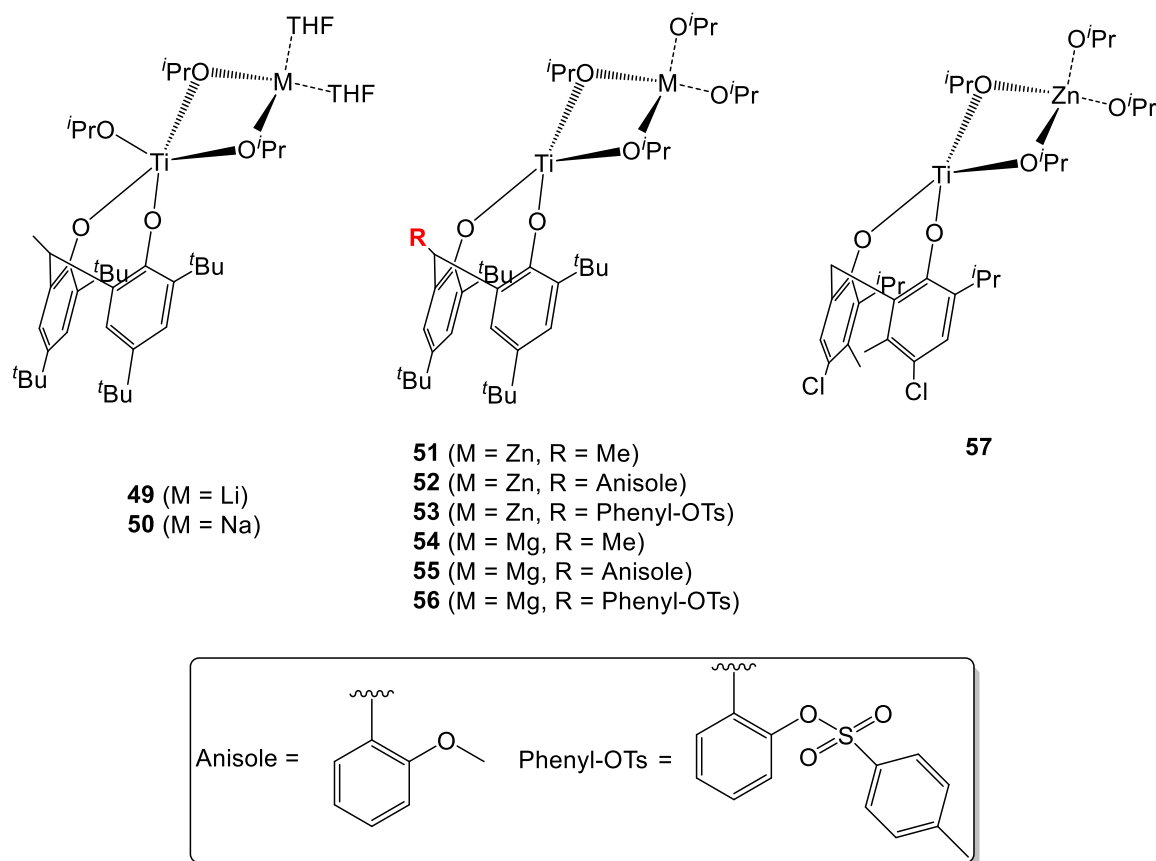


Figure 13. Diphenolate-supported mixed heterobimetallic Ti complexes [27].

Table 15. ROP of *L*-LA catalyzed by bimetallic Ti-diphenolate complexes **48**–**57** [27].

Entry	Complex	[M] ₀ /[Ti] ₀	Time (h)	Conversion ^a (%)	M _n ^{b,c}	M _w /M _n ^b
1	48	100	1.5	76	5400	1.08
2	49	150	1.5	74	5300	1.07
3	50	150	1.5	80	6100	1.05
4	51	100	0.5	91	8800	1.27
5	52	100	0.5	94	7800	1.16
6	52	200	0.5	95	14,800	1.15
7	53	100	0.25	93	6800	1.29
8	54	100	3.5	89	6300	1.28
9 ^d	54	100	1.5	94	7900	1.18
10 ^e	55	100	1	85	8700	1.19
11 ^e	55	200	1	91	16,200	1.12
12 ^e	56	100	1	95	6900	1.29
13	57	100	0.5	94	3800	1.17

Reaction conditions: Toluene 15 mL, complex 0.05 mmol, T = 30 °C. ^a Determined by ¹H-NMR spectroscopy. ^b Determined by GPC. ^c Value corrected considering Mark-Houwink factor (0.58) from PS standard. ^d T = 70 °C. ^e T = 50 °C

Very recently, Chen et al. disclosed the synthesis of a number of dinuclear titanium complexes supported by diphenolate ligands having various substituents on the methyne bridge (Figure 14) [28]. The influence of the nature of the substituents on the ROP of ϵ -CL and L-LA was investigated (Table 16). In the first case, complete conversion of the monomer was achieved within 2–4 h in the presence of all catalysts (Table 16, entries 1–5). The molecular weights determined by GPC were also found to be close to the calculated values.

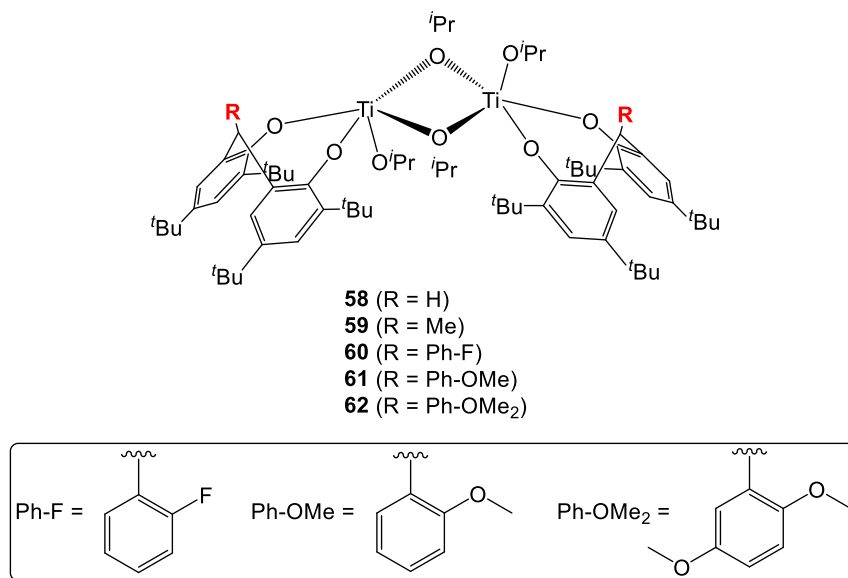


Figure 14. Dinuclear titanium complexes supported by substituted diphenolate ligands [28].

Table 16. ROP of ϵ -CL and L-LA catalyzed by bimetallic titanium complexes 58–62 [28].

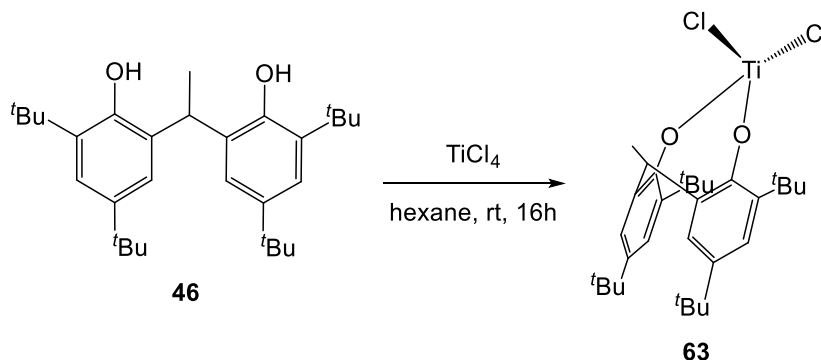
Entry	Complex	Monomer	Time (h)	Conversion ^a (%)	$M_n^{b,c}$	M_w/M_n^b
1	58	ϵ -CL	2.0	>99	4800	1.18
2	59	ϵ -CL	2.5	91	4100	1.11
3	60	ϵ -CL	2.5	88	7100	1.50
4	61	ϵ -CL	3.0	90	7000	1.34
5	62	ϵ -CL	4.5	92	6200	1.47
6	58	L-LA	2.0	91	4600	1.06
7	59	L-LA	2.0	94	5000	1.07
8	60	L-LA	3.7	92	11,000	1.18
9	61	L-LA	5.0	91	8200	1.20
10	62	L-LA	5.0	85	5600	1.12

Reaction conditions: Toluene 5 mL, [monomer] = 2.0 M, [monomer]:[Ti] = 100:1; T = 50 °C for ϵ -CL and 60 °C for L-LA. ^a Determined by ¹H-NMR spectroscopy. ^b Determined by GPC. ^c Value corrected considering Mark-Houwink factor (0.56 for ϵ -CL and 0.58 for L-LA) from PS standard.

However, slightly broader polydispersities spanning from 1.3 to 1.5 were observed in the case of catalysts 60–62. This was attributed to undesired transesterification reactions. Concerning L-LA, higher temperature and longer reaction times were required (Table 16, entries 6–10). The methyl-substituted complex 59 outperformed its congeners while the methoxyanisole-derivative 62 was shown to be the least performing (Table 16, entries 7 and 10, respectively). Compared to the ROP of ϵ -CL, better control was achieved, with molecular weight distributions found in a narrow range (1.06–1.20). Kinetic studies indicated that the rate of the reaction is in all cases first order dependent on the monomer concentration. The activity trend for ϵ -CL was found to be 58 > 59 > 60 > 61 > 62 and 59 > 58 > 60 > 61 > 62 for L-LA,

suggesting the increasing in the size of the substituent (R) at the bridge has a detrimental effect on the polymerization rate, possible due to higher steric bulk around the metal center.

We have recently synthesized the chlorotitanium diphenolate complex **63**, by treatment of the proligand **46** with an equimolar amount of $[\text{TiCl}_4]$ (Scheme 6) [29].



Scheme 6. Synthesis of the chlorotitanium diphenolate complex **63** [29].

The complex, activated by BnOH, was tested in the ROP of several cyclic esters (Table 17). By conducting the reaction at 80 °C over 24 h, ca. 50 and 35 % conversion was achieved for ϵ -CL and δ -VL (Table 17, entries 1 and 2, respectively). Higher activity was exhibited in the case of *r*-LA at 130 °C. In fact, 80% conversion was observed after 24 h (Table 17, entry 3). Due to possible intramolecular transesterification reactions, M_n lower than the calculated values were obtained in all cases.

Table 17. ROP of cyclic esters catalyzed by **63** [29].

Run	Monomer	M:Ti:BnOH	T (°C)	Conv. (%) ^a	$M_{n(\text{corr})}$ ^{b,c}	$M_{n(\text{calc})}$ ^d	M_w/M_n ^b
1	ϵ -CL	500:1:2	80	53	6390	15,140	1.24
2	δ -VL	500:1:2	80	35	7490	8860	1.15
3	<i>r</i> -LA	500:1:2	130	80	8870	28,900	1.61

Reaction conditions: Toluene 5 mL, [monomer] = 0.9 M, 24 h. ^a Determined by $^1\text{H-NMR}$ spectroscopy on crude reaction mixture based on ϵ -CL. ^b From GPC. ^c M_n values were determined by GPC in THF vs. PS standards and were corrected with a Mark–Houwink factor (0.56 for PCL and 0.58 for PLA). ^d Calculated from $([\text{M}]_0/[\text{OH}]_0 \times \text{Conv.} \times M_{w(\text{monomer})} + M_{w(\text{BnOH})})$.

3.2. Titanocalix[n]arene complexes

Reports using titanocalix[n]arenes in the ROP of cyclic esters are scant. Frediani, Sémeril et al. employed the nitro-containing complex **64** (Figures 15 and 16) under solvent-free conditions, for the well-controlled ROP of L-lactide (Table 17) [30].

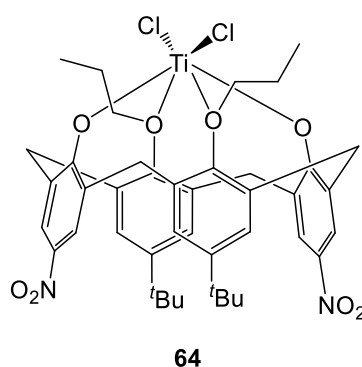


Figure 15. Titanocalix[4]arenes **64** tested in the ROP of L-lactide [30].

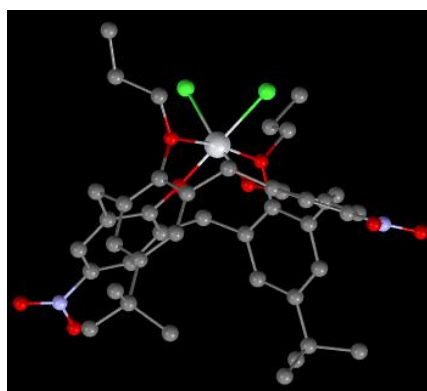


Figure 16. Molecular structure of **64** [30].

By increasing the monomer/catalyst ratio, an enhancement of the productivity and higher molecular weights were obtained (Table 18, entries 1–4). A beneficial effect on the catalyst activity was also achieved by using an alcohol as co-catalyst (Table 18, entry 5). Nevertheless, a drop of the M_n , allegedly caused by alcohol-promoted chain transfer processes, was observed. Number average molecular weights lower than the expected values were obtained in all cases. This was explained by considering intramolecular transesterification reactions taking place during the propagation step. In fact, the complex could be considered as a *dual-site* catalyst, since two polymer chains could independently grow on the same titanium center. The occurrence of transesterification reactions was confirmed by MALDI-TOF analyses. Concerning the microstructure of the polymers, highly isotactic PLA was obtained in all cases, as observed by NMR spectroscopy.

Table 18. Polymerization of L-lactide catalyzed by **64** [30].

Entry	LA:Ti	Activity ($\text{kg}_{\text{PLA}} \times \text{mol}^{-1} \times \text{h}^{-1}$)	T_m ($^{\circ}\text{C}$)	M_n (10^{-3})	M_w/M_n
1	196	9.4	160	11	1.4
2	434	20.6	162	12	1.3
3	864	36.5	161	15	1.2
4	1900	74.5	160	37	1.2
5 ^a	1896	87.8	163	6	1.1
6 ^b	2050	21.1	165	42	1.3
7 ^c	463	20.0	n.d.	52	1.4

Reaction conditions: $[\text{Ti}] = 1.8 \times 10^{-5} \text{M}$, L-lactide, 130°C , 3h. ^a *n*-BuOH 1.35 mmol. ^b 14 h. ^c *L,D*-lactide.

Subsequently, the same research group employed the previously reported complex $[1,3\text{-L}(\text{O})_2(\text{OnPr})_2\text{TiCl}_2]$ (**23**) for the ROP of *rac*-lactide (*r*-LA) [31]. The thermally induced reaction was first investigated (Table 19). As per catalyst **64**, the activity of complex **23** as well as the molecular weight of the polymers were found to be directly proportional to the monomer/Ti ratio. Relatively narrow polydispersity values (1.2–1.3) highlighted the good control of the process. NMR spectroscopic analyses suggested a partial isotactic-stereoblock microstructure of the polymers formed.

The ROP of *r*-lactide promoted by microwave irradiation was also explored (Table 20). It was found that an induction time is required by the polymerization. Indeed, only 3% conversion was achieved after 20 min (Table 20, entry 1). However, the conversion increased with the reaction time, reaching 88% after 80 min (Table 20, entry 4). The activity achieved its peak after 60 min (Table 20, entry 3), while longer reaction times led to polymer decomposition.

Table 19. Thermally induced polymerization of *r*-lactide catalyzed by **23** [31].

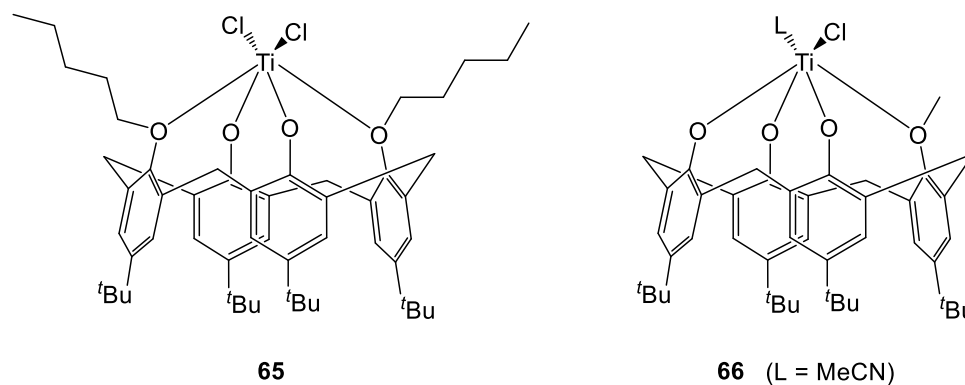
Entry	LA:Ti	Activity (kgPLA · mol _(Ti) ⁻¹ · h ⁻¹)	M _n (10 ⁻³ g mol ⁻¹)	M _w /M _n	T _g (°C)
1	200	9.2	15.0	1.2	53.0
2	500	21.0	14.9	1.3	52.1
3	1000	42.3	22.4	1.2	50.0
4	1994	65.3	36.9	1.2	41.7

Reaction conditions: [Ti] = 1.8 · 10⁻⁵ M, 130 °C, 3 h.**Table 20.** Microwave-assisted polymerization of *r*-lactide catalyzed by **23** [31].

Entry	Time (min)	Conversion ^a (%)	Activity ^b	M _n (10 ⁻³)	M _w /M _n	T _g (°C)
1	20	3	2.9	-	-	-
2	40	38	17.1	-	-	-
3	60	68	19.4	17.4	1.3	46.0
4	80	88	18.9	20.9	1.3	50.1

Reaction conditions: monomer/[Ti] ca. 200, L,D-LA = 1 g, maximal power 200W. ^a Determined by ¹H- NMR spectroscopy; ^b kgPLA · mol_(Ti)⁻¹ · h⁻¹.

Recently, we have reported the isolation of acetonitrile solvates of the known titanocalix[4]arene complexes **24**, **26** (bearing 1,3-methoxy- and propoxy- substituents, respectively) as well as new solvate forms of their analogues **65** and **66** (1,3-pentoxo- and monomethoxy derivative, respectively, Figure 16) [29]. A chloro-bridged compound {[TiL(O)₃(OR)]₂(μ-Cl)₂} (R = *n*-decyl) (**67**) was also synthesized and characterized by X-Ray diffraction studies on single crystals (Figures 17 and 18).

**Figure 17.** Titanium calix[4]arene complexes **65** and **66** (isolated as MeCN solvates) [29].

All complexes were tested as catalysts for the ROP of cyclic esters (Table 21) in the presence of benzyl alcohol. In the case of ϵ -caprolactone, low to moderate conversions were achieved in the presence of **24**, **26** and **65** (32, 33 and 68%, respectively, Table 21 entries 1–3), while complete conversion was obtained when the monomethoxy complex **66** and its dimeric decyl-congener **67** were employed (Table 21, entries 4 and 6, respectively). In all cases, the molecular weights obtained were lower than the expected values, probably due to undesired transesterification reactions. Compared to the reactions catalyzed by **24**, **26** and **65**, higher M_n were achieved in the presence of **66** and **67**.

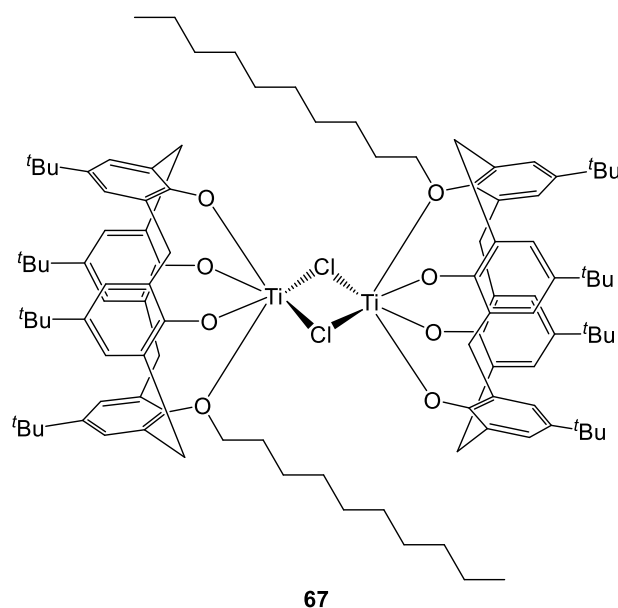


Figure 18. Structure of $\{[\text{TiL}(\text{O})_3(\text{OR})]_2(\mu\text{-Cl})_2\}$ ($\text{R} = n\text{-decyl}$) **67** [29].

Table 21. ROP of cyclic esters catalyzed by **24**, **26**, **65–67** [29].

Run	Cat.	Mon.	Mon.:Ti:BuOH	T (°C)	Conv. (%) ^a	$M_n^{b,c}$	PDI ^b
1	24	ϵ -CL	500:1:2	80	32	3650	1.10
2	26	ϵ -CL	500:1:2	80	33	650	1.10
3	65	ϵ -CL	500:1:2	80	68	3640	1.10
4	66	ϵ -CL	500:1:2	80	>99	9260	1.48
5	66	ϵ -CL	500:1:1	80	>99	8100	1.40
6	67	ϵ -CL	500:1:2	80	>99	19,030	1.55
7 ^d	24	ϵ -CL	500:1:2	130	>99	3580	1.80
8 ^d	26	ϵ -CL	500:1:2	130	>99	3390	1.40
9 ^d	65	ϵ -CL	500:1:2	130	>99	1630	1.50
10 ^d	66	ϵ -CL	500:1:2	130	>99	4580	2.08
11 ^d	67	ϵ -CL	500:1:2	130	>99	11,770	2.47
12	24	δ -VL	500:1:2	80	50	5310	1.10
13	26	δ -VL	500:1:2	80	45	6090	1.13
14	65	δ -VL	500:1:2	80	44	5700	1.10
15	66	δ -VL	500:1:1	80	81	9550	1.50
16	67	δ -VL	500:1:2	80	78	18,830	1.60
17 ^d	66	δ -VL	500:1:1	130	62	9480	1.45
18	24	<i>r</i> -LA	500:1:2	130	95	13,520	1.68
19	26	<i>r</i> -LA	500:1:2	130	97	11,170	1.94
20	65	<i>r</i> -LA	500:1:2	130	95	15,770	2.09
21	66	<i>r</i> -LA	500:1:1	130	97	28,830	1.94
22	67	<i>r</i> -LA	500:1:2	130	65	22,040	1.04
23 ^d	66	<i>r</i> -LA	500:1:1	130	94	12,200	1.73

Reaction conditions: Toluene 3 mL, 24 h. ^a Determined by ¹H-NMR spectroscopy. ^b Determined by GPC. ^c Values corrected considering Mark–Houwink factor ($M_n \times 0.56$ for PCL, $M_n \times 0.58$ for PLA) from polystyrene standards in THF. ^d Reaction performed in air. CL = caprolactone, VL = valerolactone, LA = lactide.

However, better control was exhibited by the complexes **24**, **26** and **65** (PDI 1.1 *vs.* 1.5, cf. Table 21 entries 1 and 3). The analysis of the terminal groups of the polymer isolated in the presence of **66** was performed by ¹H-NMR spectroscopy. As expected, the presence of the diagnostic resonances for the BuO- and $-\text{CH}_2\text{OH}$ terminations were detected. Further investigations using MALDI-TOF

spectrometry confirmed these results. Nevertheless, a second distribution compatible with cyclic species was also identified. Noteworthy, all catalysts proved also to be active in air, allowing for the complete conversion of the monomer within 24 h at 130 °C (Table 21, entries 7–11). Compared to the runs performed at 80 °C, broader polydispersities were observed in all cases, highlighting the loss of control at these high reaction temperatures. Further structural investigation by MALDI-TOF spectrometry highlighted the presence of only cyclic species for low M_n (20–30 repeating units), while a second distribution accountable to hydroxyl-terminated linear polymer was also detected for higher fractions (>35 repeating units). The formation of such terminations was attributed to the insertion of the first monomer unit in a Ti-OH species arising from the reaction of the pre-catalyst with adventitious water.

The complexes proved to be efficient catalysts also for the ROP of δ -valerolactone (Table 21, entries 12–16). Similarly to the previous case, **66** and **67** were shown to be better performing than their dichloride counterparts. In fact, moderate conversions (*ca.* 50%) were achieved with the chlorides while *ca.* 80% conversion was obtained in the presence of **66/67**. However, in spite of the higher conversions, a loss of control was also observed (PDIs spanning 1.45 to 1.60). Complex **66** was active also under aerobic conditions at 130 °C (Table 21, entry 17).

Compared to the reaction performed under inert atmosphere (Table 21, entry 15), lower conversion was achieved (62 and 81%, respectively). The ROP of *r*-lactide was also investigated (Table 21, entries 18–23), and all catalysts were active at 130 °C with near complete conversion observed in the presence of **24**, **26**, **65** and **66** (Table 21, entries 18–21). Surprisingly, only 65% conversion was obtained when using **67** (Table 21, entry 22). Noteworthy, complete conversion was reached when using **66** under air (Table 21, entry 23). The microstructure of the polymers was studied by means of 2D J-resolved $^1\text{H-NMR}$ spectroscopy [32]. While complexes **24** and **26** afforded almost atactic polymers (P_r 0.46 and 0.42, respectively), isotactic materials were isolated in the case of systems **65–67**.

Complex **66** was also employed in ϵ -CL/ δ -VL co-polymerization leading to a high molecular weight copolymer ($M_n > 23,000$). NMR spectroscopic studies showed the complete conversion of both monomers suggesting the formation of a copolymer with a 1:1 CL/VL ratio. The analysis of the CL-CL, VL-VL, CL-VL and VL-CL dyads by $^{13}\text{C-NMR}$ spectroscopy allowed for the determination of the number-average sequence length that was found to be 2.22 and 1.85 for CL and VL, respectively. These values suggested the formation of random-type co-polymers. Similarly, ϵ -CL/*r*-LA copolymerization was performed, and NMR spectroscopic analyses on the material produced highlighted that only 65% of ϵ -caprolactone had been converted, while full consumption of *r*-lactide was achieved. Differing reactivity of the two co-monomers in ϵ -CL/*r*-LA copolymerization has also been reported elsewhere [33–35]. The co-polymer compositions were investigated by $^{13}\text{C-NMR}$ spectroscopy. By studying the triad distributions in the carbonyl range of the spectrum, the LA/CL ratio was found to be 75:35 and the average sequence length was 3.04 and 2.42 for CL and LA, respectively. Notably, both reactions were performed in air without significant loss of activity and with no effect on the structural features of the isolated copolymers. The monochloride titanocalix[4]arene was tested also in the ROP of the large monomer ω -pentadecalactone [36–40]. However, only 50% conversion was achieved after 24 h at 130 °C when the reaction was performed under an inert atmosphere. Even lower conversion (11%) was observed under air when employing the same reaction conditions.

Furthermore, complex **66** was supported on silica by following a slightly modified reported procedure [41], and tested in the ROP of all monomers previously investigated (Table 22). The catalyst efficiently promoted the polymerization of ϵ -CL, and complete conversion was observed after 24 h at 130 °C, regardless of the use of benzyl alcohol (Table 22, entries 1 and 2).

Notably, higher molecular mass and narrower polydispersity was achieved in the absence of the initiator. Moderate conversions were observed in the tests involving δ -VL and *r*-LA (Table 22, entries 3 and 4). Interestingly, the supported complex was not active in the ROP of the larger monomer ω -pentadecalactone (Table 22, entry 7).

Table 22. Polymerization of cyclic esters catalyzed by Si-supported-66 [29].

Run	Monomer	Monomer:M:SnOH	T (°C)	t (h)	Conv. ^a (%)	M _n ^{b,c}	PDI ^b
1		400:1:0	130	24	>99	9750	2.09
2	ε-CL	400:1:1	130	24	>99	4840	2.77
3	δ-VL	400:1:0	130	24	61	23,260	2.48
4	r-LA	400:1:0	130	24	78	20,340	1.15
5	ω-PDL	400:1:0	130	24	2	-	-

Reaction conditions: monomer 4.5 mmol (400 equiv.), supported catalyst 50 mg, toluene 5 mL, 130 °C, 24 h. ^a Determined by ¹H-NMR spectroscopy on crude reaction mixture. ^b From GPC. ^c M_n values were determined by GPC in THF vs. PS standards and were corrected with a Mark–Houwink factor (M_{n,GPC} × 0.56 for ε-CL, 0.58 for r-LA)

Finally, the activity of the diphenolate complex **63** in the ROP of various cyclic esters was compared to that of the titanocalixarene species **64** and **66** (Table 23); the parent diphenol can be visualized as a ‘half-calix[4]arene’ molecule. In all cases, the monochloride catalyst **66** outperformed the other systems, both in terms of conversion and polymer M_n (Table 23, entries 3, 6, 9). Nevertheless, narrower polydispersities were achieved in the presence of **63** and **64**.

Table 23. Comparison between the activities of various Ti-based ROP catalysts [29].

Run	Catalyst	Monomer	M:Ti:SnOH	T (°C)	Conv. (%) ^a	M _n ^{b,c}	PDI ^b
1	63		500:1:2	80	53	6390	1.24
2	64	ε-CL	500:1:2	80	24	2540	1.13
3	66		500:1:1	80	>99	8100	1.40
4	63		500:1:2	80	35	7490	1.15
5	64	δ-VL	500:1:2	80	33	5700	1.13
6	66		500:1:1	80	81	12,570	1.37
7	63		500:1:2	130	80	8870	1.61
8	64	r-LA	500:1:2	130	77	10,700	1.20
9	66		500:1:1	130	97	28,830	1.94
10	63		500:1:2	130	none	-	-
11	64	ω-PDL	500:1:2	130	12	-	-
12	66		500:1:1	130	53	2835 ^d	nd

Reaction conditions: Toluene 5 mL, [monomer] = 0.9 M, N₂. ^a Determined by ¹H-NMR spectroscopy on crude reaction mixture based on the monomer. ^b From GPC. ^c M_n values were determined by GPC in THF vs. PS standards and were corrected with a Mark–Houwink factor (0.56 for PCL and 0.58 for PLA). ^d Determined by Mass Spectroscopy

Noteworthy, the diphenolate species was found to be inactive in the ROP of the larger pentadecalactone (Table 23, entry 10), while the calixarene-based complexes **64** and **66** afforded polymers in low and moderate conversion (Table 23, entries 11 and 12, respectively).

Interestingly, **63** and **64** turned out to be inactive for the ROP of ε-CL under solvent-free conditions, while the monochloride complex **66** allowed for ca. 50% conversion over 24 h at 130 °C. The inactivity of **63** and **64** was explained by considering the inefficient activation of the dichloride species in the absence of the solvent.

Concerning Ti-based complexes bearing larger calix[*n*]arene ligands, McIntosh et al. recently reported preliminary the synthesis and catalytic activity in the ROP of r-LA of complex [Ti₄L²(O)₈(OnPr)₈(THF)₂] (where L²(OH)₈ = *p*-tert-butylcalix[8]arene, **68**, Figures 19 and 20) [42]. Preliminary polymerization tests were performed in toluene at 130 °C with a monomer/Ti ratio of 100:1, allowing for the complete conversion of the monomer after 16 h. Mass spectrometry revealed that each terminal polymer chain was terminated by an *n*PrO- group. Molecular weights lower than the expected ones were observed, suggesting the occurrence of transesterification reactions. Interestingly, the presence of cyclic oligomers was highlighted by NMR spectroscopy.

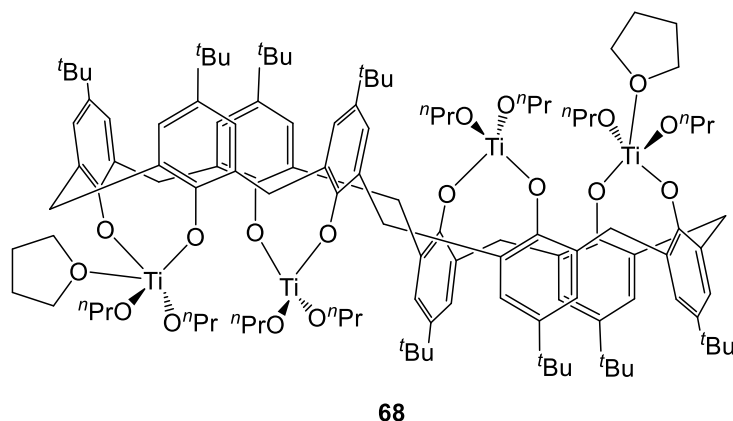


Figure 19. Tetranuclear titanium complex **68** synthesized by McIntosh et al. [42].

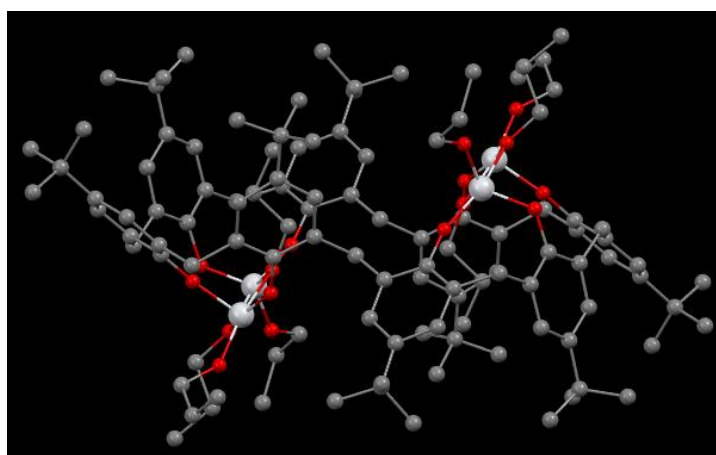


Figure 20. Molecular structure of **60** [42].

4. Conclusions

In this review, we have described the use of titanium complexes bearing bridged-diphenolate or calix[*n*]arene ligands as pre-catalysts for either α -olefin polymerization or ROP of cyclic esters. It was shown that the structure of the complex can dramatically influence the outcome of the transformation, both in terms of activity of the catalytic system and the properties of the polymer obtained. A comparison between the performances of selected catalysts in the ethylene polymerization is shown in Table 24. In the case of diphenolate-containing complexes, both the nature of the bridging unit and the labile ligands proved to affect the polymerization process; for the former aspect, the catalyst activity was shown to follow the trend $S > CH_2 > Te$ (**1**, **2** > **4** > **6**, **8**). This could be due to the higher flexibility of the system provided by the S-bridging unit compared to that of the CH_2 -group; the lower activity of the Te-containing congener was explained considering the possible Te- Al_{MAO} exchange leading to early catalyst decomposition. Notably, systems containing Ti-Cl proved to be better performing than Ti-OR congeners. In fact, both in the case of S- and Te-bridged systems, the activity of the chloride derivatives are ca. 2-fold higher than that of their *iso*-propoxy analogues (**1** > **2** and **6** > **8**, respectively). This could be ascribed to the faster activation of the chloride pre-catalysts. However, in the presence of the propoxide analogues, the molecular weights of the isolated polymers were higher, albeit with slightly broader polydispersities, suggesting the formation of multiple active species which were allegedly more robust than those generate from their Cl-congeners. On the other hand, titanocalix[*n*]arenes proved to be less active than diphenolate systems by 10-15 times to several orders of magnitude. The accessibility of the metal center proved to be crucial for the catalyst activity. In fact, the 1,2-depleted complex **29** was shown to be better performing than dialkoxy titanocalix[4]arenes **28**

and **24**. The size of the calixarene also proved to affect the catalyst performance. In fact, the activity for titanocalix[*n*]arenes was found to follow the trend $n = 8 > n = 6 > n = 4$ (**34**, **33** and **32**, respectively), which perhaps reflects the increased conformational flexibility of the larger ring system. Finally, systems having thiacalixarene ligands (namely **36** and **37**) exhibited activities similar to those achieved in the presence of 1,2-dialkoxy calixarenes. Nevertheless, the broad and bimodal molecular weight distributions for such thiacalixarene systems suggest an uncontrolled process and/or the formation of multiple active sites.

Table 24. Comparison between titanium catalysts for ethylene polymerization.

Complex	Co-catalyst	Conditions	Activity (kgPE/mol _{Ti} ·h·atm)	<i>M_w</i> (10 ⁻⁴)	<i>M_w</i> / <i>M_n</i>	Reference
1	MAO (1000 equiv.)	25 °C, 1 h 1 atm	220	0.8	2.2	8
2	MAO (4700 equiv.)	20 °C, 20 s, 1 atm	120	420	2.5	6
4	MAO (500 equiv.)	20 °C, 15 min, 3 atm	60	nd	nd	7
6	MAO	25 °C, 1 h, 1 atm	70	1.5	3.2	8
8	(1000 equiv.)		29	2.5	4.1	
24	MAO	50 °C, 2 h, 30 atm	0.47	290	2.7	15
28	(500 equiv.)		6.2	260	3.3	
29			11.7	140	5.4	
32			1.4×10^{-4}	120	nd	
33	MAO	40 °C, 30 min, 10 atm	1.8×10^{-4}	500	nd	16
34	(500 equiv.)		2.0×10^{-4}	170	nd	
36	MAO		4.7	1.1	41.3	
37	(1000 equiv.)	50 °C, 2 h, 1 atm	4.3	1.5	41.2	21

Similar conclusions could be drawn by comparing the activity of titanium diphenolate catalysts in the ROP of cyclic esters (Table 25). S-bridged complexes were shown to be better performing than Te-containing analogues (**1** > **6** and **8**). Unlike for ethylene polymerization, methylene-bridged complexes outperformed the other systems in the ROP of ε-CL (**45** > **44**), suggesting that a lower bridge flexibility is beneficial for the ROP process. With respect to the polymerization of L-lactide, bimetallic species (**49**–**51** and **54**) proved to be better performing than monometallic analogues.

Table 25. Comparison between titanium diphenolate catalysts in the ROP of ε-CL and L-LA.

Complex	Monomer	Conditions	Conversion	<i>M_n</i>	<i>M_w</i> / <i>M_n</i>	Ref
1		Toluene, 100 °C, 6 h	100	7230	2.28	22
6			88	2600	1.20	
8	ε-CL	Neat, 100 °C, 12 h	85	3790	1.43	25
44		Toluene, 100 °C, 32 h	90	1880	1.31	
45		Toluene, 100 °C, 8 h	92	5620	1.60	22
6		Anisole, 100 °C, 48 h	98	2820	1.08	
49		Toluene, 30 °C, 1.5 h	74	5300	1.07	27
50			80	6100	1.05	
51	L-LA	Toluene, 30 °C, 0.5 h	91	8800	1.27	28
54		Toluene, 30 °C, 3.5 h	89	6300	1.28	
58		Toluene, 50 °C, 2 h	91	4600	1.06	28
62		Toluene, 50 °C, 5 h	85	5600	1.12	

In particular, the highest activity was shown by the mixed heterobimetallic Ti-Zn complex. This was ascribed to a cooperative effect between the two metal centers. The higher activity of the Zn-adduct complexes was attributed to the lower charge density of Zn compared to that of the other metals investigated (ie. Mg), leading to weaker M-OR bonds, which are more prone to form M-lactide adducts via monomer insertion. Bulky substituents at the bridging unit of the diphenolate ligand were

also shown to negatively influence the performance of the catalytic systems (**58** > **62**), possibly because of reduced accessibility at the metal center.

Reports concerning the use of titanocalix[*n*]arenes as catalysts for the ROP of cyclic ester are still scarce. After the seminal work by Frediani et al., the research field has remained widely unexplored. We have recently disclosed the synthesis of new complexes based on calix[4]arenes which exhibited interesting activity in the ROP of the most common cyclic esters such as ϵ -CL, δ -VL and *r*-LA, as well as the more challenging substrate ω -pentadecalactone. The highest activities were observed in the presence of complexes **64** and **66**, suggesting that an electron-withdrawing group (NO₂) at the lower rim or a labile ligand (MeCN) at the metal center are beneficial for the ROP process. Moreover, these species proved to be better performing than their biphenolate counterparts, highlighting the positive effect of the calixarene moiety.

Whilst the results described in this review indicate that titanocalix[4]arenes and related species can perform well on a laboratory scale, their potential to deliver useful polymeric materials on a bulk scale is the next challenge. In the case of biodegradable polymers, future studies will also need to evaluate the impact and fate of any chemicals released upon decomposition. Such studies are on-going in our laboratories.

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