Review

Synthesis of Biodegradable Polymers: A Review on the Use of Schiff-Base Metal Complexes as Catalysts for the Ring Opening Polymerization (ROP) of Cyclic Esters

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Abstract: This review describes the recent advances (from 2008 onwards) in the use of Schiff-base metal complexes as catalysts for the ring opening polymerization (ROP) of cyclic esters. The synthesis and structure of the metal complexes, as well as all aspects concerning the polymerization process and the characteristics of the polymers formed, will be discussed.

Keywords: Schiff-base; biodegradable polymers; polyesters; ROP; cyclic esters; lactones

1. Introduction

Over the past two decades, increasing attention has been dedicated to the development of sustainable polymers that, while retaining all the positive features associated with polyolefins, do not require centuries to biodegrade in the natural environment. In this scenario, polylactones have emerged as suitable candidates, and currently find applications in several fields, spanning from the food and packaging industries to medicinal and pharmaceutical applications [1–5]. Generally, these polymers are synthesized via the metal-catalyzed ring opening polymerization (ROP) of cyclic esters (lactones), with the most common monomers being ε-caprolactone (ε-CL), δ-valerolactone (δ-VL) and lactide (LA) (Figure 1a) [6–8]. In the case of LA, D- and L-isomers, as well as their racemic mixture (rac-lactide, r-LA) can be employed; depending on the stereosequence distribution along the PLA chain, different microstructures are possible (Figure 1b) [9]. Currently, the industrial process for the production of poly-lactones employs tin octoate as a catalyst [10]. Although this complex is known to be toxic, the leaching of tin does not compromise the biocompatibility of the final material, as the metal tends to be used in amounts below the toxicity level. On the other hand, undesired transesterification reactions are promoted by tin octoate, resulting in broad molecular weight distributions. Hence, alternative systems based on different metal/ligand combinations, capable of better control over the polymerization process, have been explored [11–16]. Complexes derived from Schiff-base ligands emerged as efficient catalysts for the polymerization of α-olefins [17–21], and their use in the production of biodegradable polymers has been receiving growing interest. The success of Schiff-base ligands resides in their high tune-ability and availability. In fact, these species are normally synthesized in quantitative yields from (often) commercially available amines/anilines and carbonyl compounds using simple condensation chemistry. In this review, we describe the recent outputs concerning the use of Schiff-base metal complexes as catalysts for the ROP of cyclic esters. The material covered in this contribution is post-2008 and it is categorized via the metal center employed. Most of the research has focused on the development of catalysts based on earth abundant and non-toxic metals such as Al and Zn (Chart 1). This is not surprising, considering the need for cost-effective and more sustainable processes. Aside
from the synthesis and structure of the complexes, all aspects concerning the polymerization process and the characteristics of the polymer forms will be discussed.

![Diagram](https://example.com/diagram.png)

**Figure 1.** General scheme for the Ring Opening Polymerization (ROP) of common cyclic esters (a); possible microstructures of poly-lactide (b).

![Pie Chart](https://example.com/pie_chart.png)

**Chart 1.** Breakdown of the metal centers employed in the ROP of cyclic esters described in this review.

2. Alkaline Metals

In 2012, Chen et al. prepared 12 novel tetrametallic Li- and Na- complexes (six each) by treating pro-ligands 1–6 with LiO\(^\text{tBu}\) or NaH in THF (Scheme 1) [22]. All compounds were tested as catalysts in the ROP of L-lactide in the presence of benzyl alcohol (BnOH) as co-activator in THF (Table 1). The activity of the Li-based complexes was highly dependent on the structure of the ligand present and followed the trend 6-Li > 3-Li > 5-Li > 1-Li > 4-Li > 2-Li. The polydispersity (\(M_w/M_n\)) of the polymers was slightly broad, spanning the range 1.16 to 1.46, while the \(M_n\) values were lower than the expected values in all cases. The sodium complexes proved more active than their Li-congeners, allowing for complete conversion in less than 2 min in almost all cases. Nevertheless, poorer control was observed (polydispersities spanning from 1.3 to 1.8). However, narrower \(M_w/M_n\) values were obtained by decreasing the catalyst loading, in spite of longer reaction times. Interestingly, the reactivity trend was found to be 3-Na > 1-Na ≥ 6-Na > 5-Na > 2-Na > 4-Na, which was different from that of the Li systems. NMR spectroscopic analysis of the polymer prepared with 4-Li showed the presence of the diagnostic signals of the BnO- end group, suggesting that the initiation occurs with the insertion of the co-activator into the monomer. Overall, all complexes proved to be better catalysts than previously reported Li- and Na systems. In particular, 3-Na was found to be more active than a sodium compound...
bearing a salen-type ligand, previously reported by Wu et al., capable of producing mainly cyclic oligomers [23].

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Lately, a series of Li-, Na, and K phenoxo-imine complexes were disclosed by Tabarnero, Cano et al. [24]. In the presence of BnOH as co-activator, all species proved to be very active in the ROP of r-LA, with activity increasing with the size of the metal (K > Na > Li) present. In terms of selectivity, moderate-to-high hetero-enrichment was achieved in the presence of the Li-based species (Pr ~ 80). With respect to tridentate ligation, Chen, Lin et al. reported a family of Li-[25] and Na [26] complexes based on [N,N,O]-type Schiff-bases which were active in the ROP of L-LA. Under similar

| Run | Catalyst | Time (Min) | Conv. (%) | \(M_n(\text{cal.})\) (Da) | \(M_n(\text{GPC})\) (Da) | \(M_w/M_n\) |
|-----|----------|------------|-----------|--------------------------|----------------------------|-------------|
| 1\(d\) | 1-Li | 90 | 52 | 7600 | 4700 | 1.16 |
| 2\(d\) | 2-Li | 90 | 45 | 3300 | 6400 | 1.29 |
| 3\(d\) | 3-Li | 40 | 88 | 6500 | 16,200 | 1.46 |
| 4\(d\) | 4-Li | 90 | 10 | 830 | 2100 | 1.14 |
| 5\(d\) | 5-Li | 90 | 76 | 5600 | 10,000 | 1.33 |
| 6\(d\) | 6-Li | 36 | 90 | 6600 | 15,200 | 1.31 |
| 7\(e\) | 1-Na | 1 | 95 | 13,700 | 14,200 | 1.50 |
| 8\(e\) | 2-Na | 1 | 91 | 13,200 | 9000 | 1.82 |
| 9\(e\) | 3-Na | 0.5 | 99 | 14,400 | 13,400 | 1.68 |
| 10\(e\) | 4-Na | 40 | 93 | 13,500 | 9000 | 1.21 |
| 11\(e\) | 5-Na | 2 | 94 | 13,700 | 12,000 | 1.48 |
| 12\(e\) | 6-Na | 1 | 99 | 14,400 | 13,100 | 1.58 |
| 13\(e\) | 1-Na | 15 | 92 | 26,500 | 16,000 | 1.50 |
| 14\(e\) | 2-Na | 130 | 86 | 25,000 | 13,400 | 1.37 |
| 15\(e\) | 3-Na | 2 | 99 | 28,600 | 23,200 | 1.36 |
| 16\(e\) | 4-Na | 27.5 h | 70 | 20,300 | 11,800 | 1.18 |
| 17\(e\) | 5-Na | 90 | 82 | 23,900 | 14,400 | 1.38 |
| 18\(e\) | 6-Na | 15 | 88 | 25,400 | 15,500 | 1.51 |

\(a\) Obtained from \(^1\)H NMR analysis. \(b\) Calculated from the molecular weight of LA \(\times [\text{LA}]_{0}/[\text{BnOH}]_{0}\) \(\times\) conversion yield + \(M_w(\text{BnOH})\). \(c\) Obtained from Gel Permeation Chromatography (GPC) analysis and calibrated using the polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58. \(d\) Reaction condition: toluene (10 mL), [LA] = 0.5 M, [LA]:[BnOH]:[Cat] = 100:1:0.25. \(e\) Reaction condition: THF (10 mL), [LA] = 0.5 M, [LA]:[BnOH]:[Cat] = 100:1:0.25. \(f\) Reaction condition: THF (10 mL), [LA] = 1 M, [LA]:[BnOH]:[Cat] = 200:1:0.125.
reaction conditions, the Na species proved better performing that the Li analogues; indeed, while full conversion was achieved within minutes in the presence of the former, the latter required up to 21 h. In all cases, good control and polymer $M_n$ matching the expected values were observed. Finally, Wu et al. has recently disclosed six novel Na-Salen complexes [27]. Unlike the previous examples, these species were found to be mononuclear, as observed by Diffusion Ordered Spectroscopy (DOSY). When tested as catalysts in the ROP of r-LA, such compounds proved active even in the absence of exogenous alcohol, albeit with poor control and selectivity. However, undesired side-reactions, including monomer epimerization, were suppressed upon addition of excess BnOH (5 equiv.). For tests performed at low temperature (70 °C), good isoselective bias ($P_{mm} = 0.82$) was observed.

3. Alkaline-Earth Metals

Complexes of alkaline-earth metal (in particular Mg- and Ca) have emerged as a promising class of catalysts for the ROP of cyclic esters. Indeed, these metals are not only earth abundant but also relatively non-toxic, and hence potentially biocompatible [28]. The use of Schiff-base alkaline-earth metal complexes in the ROP of cyclic esters will be only briefly discussed, since these systems (along with many others) have been recently reviewed by Zhang, Solan and Sun et al. [29]

3.1. Magnesium

Omondi et al. recently studied the ROP of several lactones initiated by imino-phenolate Mg complexes [30] For $\varepsilon$-CL, full monomer conversion was achieved within 14–55 h at 110 °C under solvent-free conditions. In all cases, an induction period of 3 h was observed, and $M_n$ lower than expected were achieved. L- and r-LA were also efficiently converted, affording polymers with rather broad polydispersities (ca. 2). However, control was improved ($M_w/M_n \sim 1.4$) upon addition of exogenous alcohol as a co-activator. Furthermore, homolectic Mg complexes bearing $\beta$-ketiminato ligands developed by Wang et al. proved capable of promoting the ROP of $\delta$-VL under living and immortal conditions [31]. The process occurred at 35 °C with monomer:Mg ratios as high as 1000:1 and in the presence of an excess (up to 50 equiv.) of BnOH. Extensive NMR spectroscopy and mass spectrometry studies confirmed that only linear poly-valerolactones (PVLs) were obtained, excluding the formation of cyclic side-products derived from back-biting. With respect to tridentate ligands, a pyrrolyl-pyridylimine complex active in the ROP of $\varepsilon$-CL and L-LA has been reported by Pellecchia et al. in 2017 [32]. In the absence of a co-activator, 200 equiv. of $\varepsilon$-CL were converted within 5 min at 100 °C in toluene. However, the observed $M_n$ values were much higher than the theoretical values, which suggested that only a small fraction of the Mg was active. Indeed, upon introducing BnOH (2 equiv.), higher activity and better control was achieved. Mechanistic investigations proposed the occurrence of an “activated monomer” mechanism. Outstanding performances in the ROP of L- and r-LA were exhibited by the [N,N,O]-based complexes reported by Jones [33]. In particular, they proved active even under industrial relevant conditions, allowing for turnover frequencies up to $10^4$ h$^{-1}$. Interestingly activity was observed with analogues systems bearing bulkier substituents [34]. Finally, tridentate ketoimine-magnesium complexes featuring electron donating groups were disclosed by Fritsch et al. and proved particularly active in the homo- and copolymerization of L-LA and $\varepsilon$-CL [35].

3.2. Calcium

Calcium complexes of tridentate Schiff-base ligands have been extensively employed as catalysts in the homo- and copolymerization of several cyclic esters (Figure 2) [36–38]. In this scenario, Daresbrourgh et al. studied the ROP of L-lactide under solvent-free conditions catalyzed by complexes 7 and 8 [36]. In terms of activity, the former proved better performing than the latter (80% and 64% conversion for 7 and 8, respectively). Moreover, high $M_n$ (up to 110 kDa) and narrow polydispersities were achieved. Kinetic investigations performed with 7 suggested the occurrence of a quasi-living polymerization process. The microstructure of the polymers was also studied. Interestingly, heterotactic PLAs were isolated with 7, while essentially atactic materials were obtained in the presence of 8. Such
different selectivity was thought to be dependent on the steric bulk of the ortho substituent on the ligand framework (tBu and H for 7 and 8, respectively). The catalysts also proved efficient in the ROP of trimethylene carbonate and in its co-polymerization with L-lactide. Lately, Shaver et al. investigated the behavior of 7, 9 and 10 in the ROP of ε-CL and r-LA in toluene at room temperature or 70 °C (Table 2) [37]. Such mild reaction conditions were selected in order to limit undesired transesterification processes. Although good catalyst activity was observed for both monomers, control was poor in the case of ε-CL, with multimodal distribution and broad polydispersities being obtained. Reactions involving r-LA were rather slow, albeit with good control.

![Figure 2. Calcium complexes bearing tridentate Schiff-base ligands [36–38].](image)

**Table 2.** ROP of ε-CL and r-LA catalyzed by 7, 9 and 10 [37].

| Run | Monomer | Catalyst | Time (Min) | Conv. (%) | \(M_n\) (Da) | \(M_w/M_n\) | \(M_{niclalc}\)\(^a\) (Da) |
|-----|---------|----------|------------|----------|-------------|--------------|------------------|
| 1   | ε-CL    | 7        | 15         | 68       | 32,841      | 7922         | 1.73             |
| 2   | ε-CL    | 9        | 15         | 81       | 21,544      | 9406         | 1.80             |
| 3   | ε-CL    | 10       | 15         | 72       | 32,583      | 8218         | 1.72             |
| 4   | ε-CL    | 7        | 240        | 54       | 8321        | 7943         | 1.20             |
| 5   | r-LA    | 9        | 240        | 47       | 5987        | 6934         | 1.20             |
| 6   | r-LA    | 10       | 240        | 58       | 8986        | 8520         | 1.12             |

\(^a\) \(M_{niclalc} = \text{Conv.}(%)/\times M_W[ε-CL] \times 100 + M_W[N(SiMe_3)_2]\) for PCL or Conv.(%) × \(M_W[r-LA] \times 200 + M_W[N(SiMe_3)_2]\) for PLA.

Finally, homoleptic complexes 11 and 12 were recently employed by Lin et al. in the ROP of L-LA [38]. The activity of both complexes was quite low in the absence of a co-activator, but it dramatically increased upon addition of 80 equiv. of BnOH, allowing for complete monomer conversion within 30 min at room temperature. The \(M_n\) values determined by GPC and NMR spectroscopy were found to be close to the calculated values with narrow polydispersities, which is compatible with a living and immortal process. Interestingly, 12 was slightly less efficient than its dimethylimino-derivative 11, suggesting that the more donating pyridyl group has a detrimental effect on the catalyst activity.

4. Early Transition Metals

4.1. Titanium

In 2008, Jones et al. disclosed the synthesis of group IV metal complexes bearing chiral Schiff-base ligands and exhibiting chirality-at-metal [39]. The titanium compounds 13 and 14 (Figure 3) were found to be inactive in the ROP of rac-lactide in toluene, while high conversions were obtained in the bulk polymerization with a monomer:Ti ratio of 300 (90% and 95% conversion for 13 and 14, respectively). High molecular weights (up to 26 kDa) and good control were observed by GPC. Interestingly, the PLAs isolated were essentially atactic, as determined by NMR spectroscopy. Lately,
the same group studied the activity of group IV Salalen species [40]. With respect to the titanium complexes 15 and 16, good activity was observed both in the presence and in the absence of the solvent. In particular, 15 allowed for complete monomer conversion within 2 h at 80 °C with a LA:Ti ratio of 100:1. On the other hand, 16 required longer reaction times (24 h) to completely convert the monomer under the same reaction conditions. Interestingly, the opposite activity trend was observed under solvent-free conditions (89% and 95% conversion for 15 and 16, respectively). Regardless of the reaction conditions, both catalysts exhibited poor control, with polydispersities spanning from 1.4 to 1.8. In terms of microstructure, all polymers were found to be atactic. NMR spectroscopic analyses highlighted that all macromolecules were isopropoxy-terminated, suggesting that the polymerization was initiated by the insertion of the alkoxy group into a lactide unit.

![Diagram of complexes 13-16](image)

**Figure 3.** Ti-Schiff-base complexes 13–16 [39,40].

In 2015, Muneeswaran, Velmathi et al. developed the novel tridentate Ti complex 18 by reacting an optical active [ONO] ligand (17) with the metal precursor in alcoholic medium (Scheme 2) [41].

![Diagram of complex 18](image)

**Scheme 2.** Synthesis of complex 18 [41].

The complex was then tested as a catalyst in the ROP of ε-CL under solvent-free conditions (Table 3). No reaction was observed after 24 h in a blank test performed at 150 °C in the absence of the catalyst while complete monomer conversion was achieved upon using a CL:Ti ratio of 650:1 under the same reaction conditions. Polymerization also occurred, albeit to a lower extent, when 18 was replaced by either the pro-ligand 17 or the metal precursor Ti(OiPr)$_4$. Moderate control was observed in all cases and the NMR spectra of the polymer confirmed the presence of both isopropoxy- and –CH$_2$OH chain ends. Finally, the PCLs synthesized with 18 were used in the preparation of novel two-phase polymer nanocomposite with nanocrystalline multiferroic BiFeO$_3$ (BFO NPs).
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Table 3. ROP of ε-CL catalyzed by 18 [41].

| Run | [M]:[C] \(^a\) | Temperature (°C) | Time (h) | \(M_n \times 10^3\) (Da) \(^b\) | \(M_w \times 10^3\) (Da) \(^c\) | Yield (%) \(^d\) | \(M_w/M_n\) |
|------|----------------|-----------------|----------|-------------------------------|-------------------------------|---------------|-------------|
| 1    | -              | 150             | 24       | -                             | -                             | -             | -           |
| 2    | 653:1          | 150             | 24       | 31.66                         | 42.12                         | 96            | 1.33        |
| 3    | 653:1          | 125             | 24       | 22.96                         | 34.55                         | 94            | 1.52        |
| 4    | 1308:1         | 150             | 24       | 27.38                         | 36.00                         | 95            | 1.31        |
| 5    | 2612:1         | 150             | 24       | 14.11                         | 22.71                         | 92            | 1.60        |
| 6    | 3265:1         | 150             | 24       | 9.4                           | 15.15                         | 93            | 1.61        |
| 7    | 366:1\(^e\)    | 150             | 24       | 1.46                          | 1.77                          | 74            | 1.20        |
| 8    | 517:1\(^**\)   | 150             | 24       | 6.31                          | 9.83                          | 84            | 1.55        |
| 9    | 517:1\(^**\)   | 150             | 24       | 1.46                          | 1.77                          | 74            | 1.20        |
| 10   | 517:1          | 150             | 24       | 1.46                          | 1.77                          | 74            | 1.20        |

\(^a\) Molar ratio of monomer/catalyst. \(^b\) Molar ratio of monomer/ligand. \(^c\) Molar ratio of monomer/Ti(OPr)\(_4\). \(^d\) \(M_w\) is the relative weight-average molecular weight. \(^e\) \(M_n\) is the relative number-average molecular weight. \(^*\) Calculated on the basis of the polymer weight.

Interesting activity was also shown by analogue [O,N,O]-based complexes recently reported by Lin, Chen et al. [42]. In fact, these systems allowed for the complete conversion of up to 400 equiv. of ε-CL within 12 h at room temperature with good control. The ROP of L-LA was also achieved, albeit requiring more forcing reaction conditions.

Titanium complexes of Schiff-base ligands derived from ortho-vanillin have been recently synthesized by Williams et al. (Figure 4) [43]. In this species, each metal center is bound to two Schiff-base moieties and two isopropoxy groups derived from the metal precursor. Depending on the steric bulk of the substituent at the N-atom, three coordination types can be adopted. In compounds 19 and 20, having substituents with rather low steric hindrance, the ligands are bound to the Ti center in a N–O:N–O fashion with the imine nitrogen atom in cis to each other.

![Type A-I](image1)

19 (R = Cy)
20 (R = 2,6-Me\(_2\)(C\(_6\)H\(_3\)))

![Type A-II](image2)

21 (R = 2,6-Me\(_2\)(C\(_6\)H\(_3\)))

![Type B](image3)

22 (R = 2,6-Pr\(_2\)(C\(_6\)H\(_3\)))
23 (R = 2-Biphenyl)

![Type C](image4)

24 (R = Adamantyl)
25 (R = 2,4,6-Bu(C\(_6\)H\(_3\)))
26 (R = Trityl)

Figure 4. Binding modes of Ti-based complexes 19–26 [43].
A similar coordination mode is observed in complex 21, however the N-groups are found in a mutually trans geometry. Upon increasing the steric bulk of the ligands, two more modes were observed. For species 22 and 23, bearing a 2,6-Pr(Phenyl)- and a biphenyl-moiety, respectively, the ligands are bound in an N–O–O–O fashion. Finally, an O–O–O–O coordination was found in 25 and 26, featuring the bulkiest substituents in the series. The effect of the binding mode on the activity of these complexes in the ROP of ε-CL and ω-pentadecalactone (ω-PDL) was studied. Interestingly, complexes exhibiting O–O chelation by both ligands were found to be the most active. The occurrence of such binding mode was thought to be due to the increased steric hindrance at the imine nitrogen substituent, favoring the formation of five-membered O–O chelation. In turn, this affects the lability of the ligand around the Ti(IV) active site, hence resulting in faster rates.

Very recently, Li et al. synthesized a dinuclear Ti-Salen catalyst able to promote the ROP of 1800 equiv. of r-LA at 160 °C in 16 h [44]. The system produced a PLA with very high molecular weight (93 kDa) and narrow polydispersity (1.13). Further mechanical and toxicity tests revealed the biocompatibility of the material and its suitability for tissue engineering applications.

Finally, bimetallic Ti complexes of Schiff-bases derived from the condensation of dianinomaleonitrile with salicylaldehyde derivatives have been disclosed by Chakraborty, Chand et al. (Figure 5) [45].

![Figure 5. Cyano-containing Ti-complexes 27–29 [45]](image)

All complexes were tested as catalysts in the ROP of ε-CL and r-LA at 100 and 140 °C, respectively, under solvent-free conditions with a monomer:Ti ratio of 200:1 (Table 4). Conversions higher than 90% were achieved within minutes, highlighting the beneficial effect of a strong electron-withdrawing cyano group on the ligand backbone. For both monomers, the activity trend was found to be 29 > 28 > 27, suggesting that increasing the steric bulk of the substituents on the aromatic ring of the ligand has a positive effect on the polymerization rate.

### Table 4. ROP of ε-CL and r-LA catalyzed by complexes 27–29 [45].

| Entry | Catalyst | Monomer<sup>a</sup> | Time (Min) | Conv. (%)<sup>b</sup> | M<sub>n</sub> (kDa)<sup>c</sup> | M<sub>n(calc.)</sub> (kDa)<sup>d</sup> | M<sub>w</sub>/M<sub>n</sub><sup>e</sup> | P<sub>r</sub><sup>f</sup> |
|-------|----------|---------------------|------------|---------------------|-----------------|-----------------|-----------------|-----------------|
| 1     | 27       | ε-CL                | 10         | 93                  | 20.45           | 22.90           | 1.19            |                 |
| 2     | 28       | ε-CL                | 9          | 96                  | 20.98           | 22.90           | 1.15            |                 |
| 3     | 29       | ε-CL                | 4          | 97                  | 21.18           | 22.90           | 1.12            |                 |
| 4     | 27       | r-LA                | 21         | 92                  | 25.42           | 28.90           | 1.17            | 0.62            |
| 5     | 28       | r-LA                | 15         | 96                  | 25.07           | 28.90           | 1.15            | 0.69            |
| 6     | 29       | r-LA                | 8          | 98                  | 28.15           | 28.90           | 1.14            | 0.68            |

<sup>a</sup> Reaction conditions: [M]₀/[C]₀ = 200:1, 100 °C for ε-CL and 140 °C for rac-LA, solvent-free. <sup>b</sup> Determined from ¹H NMR in CDCl₃ at 25 °C. <sup>c</sup> Measured by GPC at 27 °C in THF relative to polystyrene standard Mark-Houwink corrections for M<sub>n</sub>. <sup>d</sup> M<sub>n(calc.)</sub> = [M]₀/[C]₀ × M<sub>n</sub> (monomer) + M<sub>w</sub> (end-group) at 100% conversion of monomer. <sup>e</sup> P<sub>r</sub> is the probability for heterotactic enrichment calculated from homonuclear decoupled ¹H NMR spectrum in CDCl₃ at 25 °C.
The $M_n$ observed by GPC were in good agreement with the calculated values; good control was generally observed, with polydispersities spanning from 1.1 to 1.2. In terms of microstructure, the PLAs were found to be heterotactic ($P_r$ 0.6–0.7), as observed by homonuclear decoupled $^1$H NMR spectroscopy.

4.2. Zirconium

Jones et al. tested the efficiency of the chiral Schiff-base zirconium complexes 30–35 (Figure 6) as catalysts in the ROP of rac-lactide [39]. By performing the reaction in toluene, moderate yields were achieved at 80 °C in two hours or at room temperature after 1 day. Good control was generally observed, and the GPC data were also in agreement with the formation of only one polymer chain per metal center. Interestingly, all samples were heterotactic, with $P_r$ values found in a very narrow range (0.68–0.71), regardless of the configuration of the optical active catalyst employed. Higher reaction rates were observed under solvent-free conditions, albeit with less control. In fact, broader molecular weight distributions were generally observed. Furthermore, in this case, heterotactic polymers were isolated. Remarkably, all catalysts proved very robust, allowing for the polymerization of rac-lactide even in the presence of water and/or with non-purified monomer.

![Figure 6. Chiral Zr complexes 30–35 [39].](image)

Zirconium complexes, analogues to the tridentate species 15 and 16, were lately investigated by the same group [40]. High conversions and good control were achieved both in solution and in bulk. In terms of microstructure, a slight preference towards forming heterotactic polymers was detected ($P_r \sim 0.69$). Finally, bimetallic Zr complexes bearing cyano-containing Schiff-base ligands were considered as catalysts for the ROP of $\varepsilon$-CL and $r$-LA [45]. Similar to their Ti-analogues 27–29, high molecular weight and good control were generally observed. Similarly, the reaction rate as well as the heterotactic bias increased with the steric bulk of the ligand. Finally, a redox-switchable Salfen Zr species has been successfully employed in the synthesis of bi- and triblock copolymers of $L$-LA and cyclohexene oxide [46].

4.3. Hafnium

Reports concerning the use of Hf complexes of Schiff base ligands in the ROP of cyclic esters are rather scant. Hf-congeners of the Ti-species 15 and 16 proved to be active in the polymerization of $r$-LA both in solution and in bulk, affording either atactic or isotactic polymers depending on the steric features of the ligand [40]. Finally, the bimetallic complexes 36–38 (Figure 7) proved better performing than their Ti- and Zr- analogues in the ROP of $\varepsilon$-CL and $r$-LA [45]. Furthermore, in this case, both the reaction rate and the syndiotactic bias increased with the steric bulk of the ligand.
4.4. Vanadium

In 2013, our group reported the synthesis of 15 novel V(III) complexes bearing phenoxyimine complexes (Figure 8) [47]. The ability of these species to promote the ROP of ε-CL was investigated (Table 5). In most cases, low to moderate conversions were observed and polymers with $M_n$ much lower than the expected values were obtained. The molecular weight distributions were found in a narrow range (1.2–1.4) in all runs, aside from the test conducted in the presence of the binuclear species 44.

![Figure 7. Cyano-containing bimetallic Hf complexes 36–38 [45].](image)

![Figure 8. V(III) complexes 39–53 employed in the ROP of ε-caprolactone [47].](image)

Based on the results obtained in the ethylene polymerization [48], we have lately explored the ability of tri- and tetradentate vanadium(V) species as catalysts in the ROP of ε-CL [49]. Conversions lower than 50% were achieved after 24 h at 110 °C in the presence of BnOH as a co-activator. The observed $M_n$ were much lower than the calculated values, suggesting a significant deviation from...
a living polymerization. Nevertheless, the process was rather controlled, with polydispersities lower than 1.2. Mass Spec and $^1$H NMR spectroscopy analyses confirmed the presence of the BnO-end group.

### Table 5. ROP of $\varepsilon$-CL promoted by 39–53 [47].

| Run$^a$ | Catalyst | Conv. (%)$^b$ | $M_n$(calc.) (Da) | $M_n$(GPC) (Da)$^c$ | $M_w/M_n$ |
|--------|-----------|--------------|------------------|------------------|-----------|
| 1      | 39        | 57           | 26,024           | 10,751           | 1.4       |
| 2      | 40        | 47           | 21,458           | 8640             | 1.4       |
| 3      | 41        | 24           | 10,960           | 7977             | 1.2       |
| 4      | 42        | 33           | 15,070           | 9249             | 1.2       |
| 5      | 43        | 48           | 21,900           | 10,080           | 1.4       |
| 6      | 44        | 70           | 31,960           | 11,010           | 2.3       |
| 7      | 45        | 72           | 32,870           | 4973             | 1.2       |
| 8      | 46        | 100          | 45,660           | 4060             | 1.1       |
| 9      | 47        | 87           | 39,720           | 13,670           | 1.3       |
| 10     | 48        | 93           | 42,460           | 14,260           | 1.1       |
| 11     | 49        | 97           | 44,290           | 21,340           | 1.1       |
| 12     | 50        | 19           | 8670             | -                | -         |
| 13     | 51        | 93           | 42,460           | 13,290           | 1.2       |
| 14     | 52        | 94           | 42,920           | 4790             | 1.1       |
| 15     | 53        | 3            | 1370             | 4560             | 1.4       |

$^a$ Conditions: toluene (20 mL), [ε-caprolactone] = 2.5 mL, monomer: metal = 400, 1 equivalent of benzyl alcohol (from a 0.97 M solution in toluene). 72 h, 80°C. $^b$ Obtained from $^1$H NMR analysis. $^c$ $M_n$ measured = 0.58 × $M_n$(GPC).

### 4.5. Chromium

Mononuclear- and dinuclear Cr(III)-salphen complexes 54–57 (Figure 9) have been reported by Rieger et al. in 2010 [50]. Next, their efficiency as catalysts in the ROP of β-butyrolactone (β-BL) was investigated (Table 6).

![Figure 9. Mono- and dinuclear Cr(III)-salphen complexes 54–57 [50].](image)

The mononuclear species 54 exhibited rather poor activity, allowing for 6% and 30% conversion after 5 and 24 h, respectively, affording polymers with broad dispersity (2.0–2.6). On the other hand, the bimetallic systems proved more active, exhibiting similar behavior regardless the length of the spacer. The use of 55 allowed for complete monomer conversion within 24 h, while moderate conversions were achieved within 5 h in the presence of 56 and 57. Compared to their mononuclear analogue, 55–57 allowed for higher polymer molecular weights, albeit with broad dispersity.
Table 6. ROP of β-BL catalyzed by 54–57 [50].

| Run | Catalyst | Temperature (°C) | Time (h) | Yield (%) | TOF (h⁻¹) | M_w (kDa) | M_w/M_n |
|-----|----------|------------------|----------|-----------|------------|------------|----------|
| 1   | 55       | 150              | 5        | 6         | 12         | 20         | 2.0      |
| 2   | 55       | 150              | 24       | 30        | 12         | 25         | 2.6      |
| 3   | 56       | 125              | 5        | 35        | 70         | 71         | 1.9      |
| 4   | 56       | 150              | 15       | 86        | 57         | 107        | 1.9      |
| 5   | 56       | 150              | >99      |           | 41         | 108        | 1.9      |
| 6   | 57       | 150              | 5        | 28        | 56         | 68         | 2.2      |
| 7   | 58       | 150              | 5        | 31        | 62         | 70         | 2.1      |

a Determined ¹H NMR spectroscopy. b Turnover frequency calculated per Cr center.

4.6. Manganese

In 2016, our group developed a series of Mn(II) complexes bearing macrocyclic Schiff-base derived ligands [51]. In spite of their interesting structural features, these species proved to be poorly active as catalysts in the ROP of ε-CL in the presence of BnOH as co-activator. Regardless of the reaction conditions, monomer conversion was generally low (10%–14%) and the reaction products were mainly low molecular weight oligomers.

5. Late Transition Metals

5.1. Iron

Similar to the rare-earth metals, iron-based complexes are attractive catalysts for the synthesis of polylactones, given that the metal precursors are both inexpensive and biocompatible [52]. In spite of that, the Fe-catalyzed ROP of cyclic esters still remains rather underexplored. In this scenario, Garden, Shaver et al. recently studied the behavior of half-salen Fe(III) complexes in the ROP of r-LA in the presence of propylene oxide (PO) as co-activator [53]. In most of the cases, low M_n and poor control, accountable to the occurrence of transesterification, were observed. A lack of stereoselectivity was generally observed, with P_i values indicating the formation of atactic PLAs. Nevertheless, these limitations could be overcome upon increasing the amount of co-activator or allowing for the formation of the catalytically active species prior to introduction of the monomer.

Fe(III)-salalen complexes have been recently reported by Jones et al. (Figure 10) [54]. Complex 58 exhibited moderate activity as a catalyst in the ROP of r-LA performed in propylene oxide. In this scenario, PO served both as solvent and co-initiator. Good conversion (80%) was achieved at 40 °C after 7 days, affording an isotactic polymer with a high molecular weight and narrow polydispersity. Increase of activity was observed upon increasing the temperature, albeit with a drop of both stereoselectivity and control. In some cases, a bimodal distribution was detected, suggesting the occurrence of two independent processes. Mass spectrometry analysis of such samples showed the presence of two populations differing from the nature of one end-group. The main distribution was assigned to chloropropanol-capped polymers (derived from the ROP of propylene oxide), while the minor population was attributed to PLAs initiated by propane-1,2-diol, an impurity of PO. Upon using a catalytic amount of BnOH as co-activator, a monomodal distribution was observed by GPC, suggesting the formation of only one active species.

This was confirmed by mass spectrometry showing the presence of only one major population corresponding to BnO-capped polymers. In all cases, a small amount of cyclic oligomers was also obtained. Catalysts 59 and 60 bearing the same ethylene bridge, but less bulky aromatic substituents (H and Cl, respectively) than 58, exhibited higher activity than their t-Bu-containing analogue. In fact, conversions up to 93% were obtained within 4 to 6 h at 60 °C with good control, albeit with slightly lower stereoselectivity. The methyl analogue 61 proved less performing than 59 and 60, requiring up
to 2 days to allow complete monomer conversion. Variation of the backbone in complexes 62–64 led to a drop of activity, possibly due to the reduced flexibility of the catalysts.

Concurrently, Pang, Li et al. disclosed the ROP of \( \varepsilon \)-CL [56]. By performing the reaction in PO as both solvent and co-activator, the activity trend was found to be Salan > Salalen > Salen, which mirrored the order of acidity of the metal center in each complex. Upon introducing bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) as co-activator, no change in the trend was observed, albeit the activity of the catalysts generally improved. Interestingly, 58 proved inactive in the ROP of \( L \)-LA under similar reaction conditions, possibly due to the formation of stable intermediates inhibiting the process.

Lamberti et al. recently compared the activities of 58 and related Salen- and Salan Fe(III) chloride complexes in the ROP of \( \varepsilon \)-CL [55]. By performing the reaction in PO as both solvent and co-activator, the activity trend was found to be Salan > Salalen > Salen, which mirrored the order of acidity of the metal center in each complex. Upon introducing bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) as co-activator, no change in the trend was observed, albeit the activity of the catalysts generally improved. Interestingly, 58 proved inactive in the ROP of \( L \)-LA under similar reaction conditions, possibly due to the formation of stable intermediates inhibiting the process.

Concurrently, Pang, Li et al. disclosed the ROP of \( L \)- and \( rac \)-lactide promoted by four novel Fe(III) salen complexes (Figure 11) [56]. Moreover, in this case, propylene oxide served as solvent as well as co-activator. Complexes 65 and 66 exhibited similar catalytic activity, allowing for complete monomer conversion within 10 h at room temperature. Polymerization also occurred with 67 and 68, albeit with a lower rate. This was attributed to presence of bulky \( \text{Bu} \) groups reducing the accessibility of the metal center. In spite of their lower activity, a better control was achieved with 67 and 68 compared to the runs involving their less sterically hindered congeners. When the \( meso \) monomer was employed, all catalysts exhibited moderate isotactic bias, affording polymers with \( P_m \) values spanning from 0.68 to 0.77.

5.2. Cobalt

Very recently, Sutar et al. described the ROP of \( L \)-lactide catalyzed by the Co(II) salen complex 69 (Figure 12) [57]. Optimization of the reaction conditions revealed that one equiv./Co of BnOH was
required to enable the polymerization. While moderate activity was observed both in toluene and THF, high conversions (86%) were achieved in CH$_2$Cl$_2$ also in the case of monomer:Co ratios as high as 200. The $M_n$ determined by GPC and Vapor Pressure Osmometry were in good agreement with the theoretical values; in addition, narrow polydispersities (between 1.08 and 1.13) were detected. Finally, NMR spectroscopic analysis of the polymers were compatible with α-BnO-ω-CH$_2$OH terminated PLAs. This data suggested the occurrence a living ROP process.

\[ \text{Figure 12. Co(II) salen catalyst for the ROP of L-lactide [57].} \]

5.3. Nickel

In 2016, Sutar, Maharana et al. described the ROP of L-lactide catalyzed by three novel Ni-salen complexes 70–72 (Figure 13) [58]. During the optimization of the reaction conditions performed at room temperature over 24 h in different solvents, CH$_2$Cl$_2$ was found as the most suitable medium. In fact, all catalysts allowed for higher conversions and greater polymer $M_n$ compared to the runs performed in toluene or THF. None of the complexes proved active in the absence of BnOH, while high conversions (90%) were obtained when one equiv./Ni of the co-activator was employed with LA:Ni as high as 200:1, regardless of the catalyst employed. The $M_n$ determined experimentally were in good agreement with the theoretical values and the molecular weight distributions were found in a very narrow range (1.09–1.13). Upon increasing the amount of BnOH (2–4 equiv./Ni), higher reaction rates were observed, albeit with an important decrease of the polymer $M_n$.

\[ \text{Figure 13. Ni salen complexes 70–72 [58].} \]

In 2011, a series of heterobimetallic Ni-Ln(III) (Ln = lanthanide) complexes derived from the compounds 70 and 71 were reported by Bao, Lü et al. (Figure 14) [59–61]. In terms of activity, the bimetallic species proved less performing than their monometallic analogues and required higher temperatures and/or longer reaction times to achieve moderate monomer conversions. On the other hand, higher $M_n$ and better control were generally observed, possibly because of cooperative effects between the two metal centers. For complexes 75–77 and 81–84, the activity trends were 76 > 75 > 77 and 81 > 82 > 83 > 84, respectively. In both cases, the catalyst efficiency decreased with the lengthening of the Ni···Ln intramolecular distance, while the dependency on the lanthanide contraction was observed just for the latter set of complexes.
were observed for the monometallic species, the Nd-containing compound allowed for higher polymerization with the cis species (Figure 16) [63]. Both complexes proved active in the ROP of 1,4-lactide; although higher rates were observed for the trans complex when activated by one equiv./Cu of BnOH in CH2Cl2 or toluene. A significant drop of conversion was observed upon using THF as reaction medium. This was attributed to catalyst deactivation via the solvent coordination to the metal center. By increasing the amount of co-catalyst, an increase of the reaction rate was observed, albeit with a drop of the polymer Mn. Nevertheless, the process was well controlled, and the molecular weights were in agreement with the calculated Mn of its phenyl- and naphthylmoieties.

5.4. Copper

Over the past decade, the ROP of cyclic esters catalyzed by Cu(II) complexes of Schiff-base ligands has obtained increasing attention. Bhaw-Luximon, Mapolie et al. studied the behavior of 7 new copper-phenoxyimino complexes in the ROP of L-lactide (Figure 15) [62]. Compounds 87 and 88 were found to be inactive, even under forcing reaction conditions. This was attributed to the deactivation of the catalysts (through the dimerization of the metal centers) due to the absence of bulky substituents at the phenoxy-moiety. Strangely, complex 89 was also poorly active, albeit containing t-Bu groups both in ortho- and para positions. Concerning the Cl-containing derivatives, low conversion (18%) was obtained with the cis species 91 while no polymerization was observed in the presence of the trans complex 92. Finally, complexes 90 and 93, bearing bulky substituents at both phenoxy- and imino-moieties exhibited moderate to good activity, depending on the solvent employed. The polymers obtained were highly isotactic, as determined by 1H NMR spectroscopy.

Lü, Jin et al. developed the salen-based mono- and heterobimetallic species 94 and 95 (Figure 16) [63]. Both complexes proved active in the ROP of L-lactide; although higher rates were observed for the monometallic species, the Nd-containing compound allowed for higher polymer Mn and better control. An extensive investigation of the catalytic activity of complex 95 and of its phenyl- and propylene-bridged derivatives 96 and 97 was undertaken by the group of Sutar [64–66]. The compounds exhibited similar catalytic behavior in the ROP of L-lactide, allowing for high conversions when activated by one equiv./Cu of BnOH in CH2Cl2 or toluene. A significant drop of conversion was observed upon using THF as reaction medium. This was attributed to catalyst deactivation via the solvent coordination to the metal center. By increasing the amount of co-catalyst, an increase of the reaction rate was observed, albeit with a drop of the polymer Mn. Nevertheless, the process was well controlled, and the molecular weights were in agreement with the calculated Mn.
values in all cases, suggesting the occurrence of a living process. NMR spectroscopic analysis of the polymer confirmed the presence of both BnO- and –CH2OH end-groups.

Figure 16. CuII-[ONNO] complexes active in the ROP of lactide [63–66].

Very recently, Nayab, Lee et al. tested the efficiency of iminomethylpyridine based copper(II) complexes 98–103 (Figure 17) in the ROP of rac-lactide [67]. All compounds proved equally performing, allowing for complete monomer conversion at both room temperature and at −25 °C within 2 h with a monomer:Cu ratio of 100:1 in CH2Cl2. The polymer molecular weights were close to the calculated values while the control was highly dependent on the temperature. In fact, polydispersities ranging from 1.5 to 1.8 were achieved at room temperature, while narrower values (1.25–1.54) were observed for the polymers synthesized at −25 °C. This was attributed to the occurrence of undesired transesterification and/or backbiting processes that are less favored at lower temperature. In terms of microstructure, the isolated polymers were mainly hetero-enriched. Furthermore, in this case, higher selectivity was observed at −25 °C compared to the tests at room temperature.

Figure 17. Cu(II)-iminomethylpyridine complexes 98–103 [67].

In 2011, our group reported the synthesis of bimetallic Cu(II) complexes of acyclic Schiff bases ligands derived from amino acids. In spite of their interesting structural features, these compounds proved inactive in the ROP of ε-CL, even at 80 °C and in the presence of BnOH as co-activator [68]. More recently, we have also synthesized mono-and tetra-nuclear Cu species bearing
were achieved in the presence of the trinuclear analogues. Promising results were also obtained by using a Si-supported derivative. Lately, the same group furtherly explored heterogeneous systems spanning from 1.42 to 1.50), broader polydispersities and moderately heterotactic polymers (ca. 2.0) were observed in all cases. Atactic PLAs were isolated, regardless of the catalyst employed.

5.5. Zinc

Over the past couple of decades, increasing attention has been devoted to the development of Zn-based catalysts for the ROP of lactones. Indeed, the use of this metal is very attractive thanks to its earth-abundance (affordability) and to the potential non-toxicity of resultant complexes [70]. Remarkable results have been achieved in the ROP of L- and r-LA with imino-phenolate Zn species [30,32–34], both in terms of catalyst activity and features (M_n, polydispersity, mechanical properties) of the final materials. More recently, Zn complexes of guanidine-derived Schiff-bases proved to be an outstanding new class of catalysts for the production of PLA under industrially relevant conditions [71]. In this regard, Herres-Pawlis et al. compared the activity of two sets of complexes bearing neutral N-donors, namely imidazolin-2-imine and guanidine, in the ROP of rac-LA (Figure 18) [72]. In terms of monomer conversion, the imidazolin-2-imine derivatives 104 and 105 proved better performing than their guanidine analogues 106 and 107. Complexes containing Cl ancillary ligands 104 and 106 allowed for higher molecular weights than the acetate congeners, while broad polydispersities (ca. 2.0) were observed in all cases. Atactic PLAs were isolated, regardless of the catalyst employed.

![Figure 18. Zn complexes bearing imidazolin-2-imine and guanidine-based ligands [72].](image)

Subsequently, the same group studied the performance of eight Zn complexes derived from the ligands 108–115 (Figure 19) [73]. By performing the ROP of technical grade r-LA in bulk at 150 °C, promising results were observed with complexes 111 and 109 after 6 h (80% and 71% conversion). Compound 112 was the least active, allowing for 63% conversion after 7 h, while similar conversions were achieved in the presence of the other systems after 6 h. In all cases, poor control and M_n much lower than the expected values were observed, possibly because of the harsh reaction conditions and/or the presence of traces of water in the monomer promoting undesired chain-transfer reactions. On the other hand, water served as the actual initiator, as confirmed by NMR spectroscopy and MALDI-TOF studies on the isolated PLAs. In terms of microstructure, atactic polymers were obtained, even in the case of chiral complexes. Since the chirality of these species proved to be retained even at high temperature, the poor stereoselectivity was thought to be due to the lack of steric hindrance. Upon employing purified monomer, both M_n and control improved; the same was observed when BnOH was used as co-activator, independently from the purity of the lactide employed. The polymers isolated in the presence of external alcohol featured the BnO- end group, suggesting that BnOH is the actual initiator of the process.

In 2009, Jones et al. reported novel mono- and trinuclear zinc complexes of variously substituted phenoxyimine ligands [74]. All complexes exhibited good catalytic activity in the ROP of r-LA in melt conditions at 130 °C. While monozinc species afforded atactic PLAs with moderate control (M_w/M_n spanning from 1.42 to 1.50), broader polydispersities and moderately heterotactic polymers were achieved in the presence of the trinuclear analogues. Promising results were also obtained by using a Si-supported derivative. Lately, the same group furtherly explored heterogeneous systems
derived from similar phenoxyimine ligands, which still allowed for good monomer conversions albeit requiring longer reaction times compared to their homogeneous counterparts [75].

Very recently, Zn complexes 116–119, bearing heteroatom-containing [N,O] ligands, were shown to be active in the ROP of L-lactide under industrially relevant conditions (Figure 20) [76]. Conversions ranging between 56% and 66% were achieved with all catalysts within 1 h when using purified L-LA as monomer. The molecular weights were spanning from 48 and 64 kDa, with polydispersity values found in the range 1.3–1.7. The reaction rate followed the trend 119 >> 116 = 117 > 118, as determined by in situ IR spectroscopy. Complex 119 was also employed in combination with technical grade L-lactide with different monomer:catalyst ratios. While 46% conversion was achieved after ca. 1 h with a LA:Zn ratio of 1000:1, a drastic drop of activity was observed by slightly increasing the amount of monomer. However, the productivity improved when BnOH was introduced as co-activator.

Tridentate ligands have also been widely investigated. Chiral Zn complexes of Schiff-bases derived from natural amino-acid proved extremely active in the ROP of rac-lactide (Figure 21) [77]. Complete monomer conversion was achieved after 2 h with LA:Zn ratio as high as 2000:1, affording heterotactic polymers with $M_n$ in agreement with the theoretical values with good control ($M_n/M_w$ ranging between 1.07 and 1.31). By using enantiomerically pure $D$- or L-lactide as monomer, highly syndiotactic PLAs were isolated. However, the configuration of the stereogenic centers on the polymer chain was not influenced by the chirality of the complexes, suggesting that the stereoselectivity of the ROP of r-LA was controlled via a chain-end mechanism.
Zinc complexes of ketoiminate ligands 125–131 (Figure 22) have recently been tested as catalysts in the ROP of L-LA (Table 7) [78]. For the zinc phenoxide complexes, complete conversion was achieved after 3 h with complexes 125, 126, 129 and 130. The lower activity exhibited by 127 and 128 was attributed to the presence of the electron withdrawing groups on the ketoiminate moiety, causing a slower propagation rate. Aside from the test performed with 126, narrow polydispersities and $M_n$ in agreement with the calculated values were achieved. Interestingly, the bis-trimethylsilylamido derivative 131 proved also completely inactive. NMR spectroscopy and MALDI-TOF analyses showed that the polymers prepared with 125–130 and 131 featured 2,6-diisopropylphenoxy- and trimethylsilyl amido-end groups, respectively.

![Figure 21. Amino-acid based Zinc Catalysts 120–124 [77].](image)

![Figure 22. Zn ketoiminate complexes bearing trifluoromethyl substituents [78].](image)

![Table 7. Polymerization of L-LA catalyzed by Zn complexes 125–131 [78].](table)

| Run | Catalyst | Lactide/Zn | Time (h) | Conv. (%) | $M_n$(calc.) (kDa) | $M_n$(obs) (kDa) | $M_w/M_n$ |
|-----|----------|------------|----------|-----------|-------------------|-----------------|------------|
| 1   | 125      | 500        | 3        | 100       | 72.0              | 71.7            | 1.22       |
| 2   | 126      | 500        | 3        | 100       | 72.0              | 55.8            | 1.54       |
| 3   | 127      | 500        | 6        | 60        | 43.2              | 58.7            | 1.27       |
| 4   | 128      | 500        | 6        | 12        | 8.6               | 99.9            | 1.15       |
| 5   | 129      | 500        | 3        | 100       | 72                | 73.4            | 1.08       |
| 6   | 130      | 500        | 3        | 100       | 72                | 105.8           | 1.14       |
| 7   | 131      | 500        | 24       | 5         | 3.6               | 191.4           | 1.08       |

* All reactions were conducted in CH$_2$Cl$_2$ at ambient temperature. * Obtained from $^1$H NMR analysis. * $M_n$(calc.) = (M$_E$)×(Conv.)×($M_w$(lactide)). * $M_n$(obs) values were determined by GPC in THF vs. polystyrene standards and were corrected with a Mark-Houwink = 0.58.

Interesting activity was also exhibited by zinc complexes of dianinocyclohexane-derived ligands (Figure 23) [79]. Compounds 135 and 136 proved the most active of the series, allowing for complete monomer conversion within 1 h, in the presence of BnOH as co-activator. Polymerization was also
observed with the Boc-derivatives 132–134, albeit to a lower extent. MALDI-TOF studies showed the presence of the BnO- end group, as well as a minor population accountable to transesterification-derived chains. All catalysts showed a moderate heterotactic bias, with $P_r$ values spanning 0.56–0.67.

![Figure 23. Zn complexes based on diaminocyclohexane-derived ligands [79].](image)

Zn complexes bearing half-salphen ligands generated by template synthesis from a metal precursor, N1,N1-dimethylbenzene-1,2-diamine and substituted salicylaldehyde have been recently disclosed by Zhu et al. [80]. Different zinc precursors, namely Zn(OAc)$_2$ 2H$_2$O, ZnCl$_2$, Zn(O$_2$CCF$_3$)$_2$ and Zn(O$_3$SCF$_3$)$_2$, were investigated, and the related complexes were tested in the ROP of $\varepsilon$-CL. In the absence of a co-activator, none of the catalysts proved active, while complete conversion of 400 equiv. of monomer was observed within minutes upon addition a 1:1 mixture of BnOH/LiMe, albeit with poor control.

Multinuclear Zn complexes derived from tridentate [NON]-type ligands have been independently reported by us [68] and Jones et al. [72]. Interestingly, these species were found to be inactive in the ROP of cyclic esters ($\varepsilon$-CL and $r$-LA, respectively).

Very recently, González et al. studied the catalytic behavior of the binuclear tridentate complexes 137–139 in the ROP of $r$-LA (Figure 24) [81]. The only difference between compounds 137 and 138 is the nature of the solvent coordinated to the Zn centers (pyridine and DMF, respectively); compared to the 138, the fluorine atom is replaced by a $p$-methoxy substituent in 139. In the absence of an external co-activator, all complexes allowed for complete monomer conversion after 18 h at 130 °C (melt conditions) with LA:Zn ratios as high at 800:1. With respect to the polymer molecular weight, the complexes followed the trend $139 > 137 > 138$ (8.5, 4.6 and 3.9 kDa, respectively). The use of BnOH as a co-activator (20 equiv./Zn) allowed for higher reaction rates but determined a drop of $M_n$. The $^1$H NMR spectra of the polymers prepared in the presence of the alcohol showed the diagnostic resonances of the benzylloxy-terminal group, suggesting that the co-activator is responsible for the ring-opening of the first monomer unit.

![Figure 24. [ONO]-type Schiff-base zinc complexes 137–139 [81].](image)

The ROP of $L$-lactide promoted by the tetradeinate salen-type zinc complex 140 has been recently disclosed by Sutar et al. (Figure 25) [82]. Similar to its Ni- [58] and Cu- [66] analogues reported by
the same group, the complex proved to be inactive in the absence of a co-activator. Upon using one equiv./Zn of BnOH, good activity was observed in CH$_2$Cl$_2$ (78% conversion) at room temperature after 24 h, while lower conversions were achieved in toluene and THF (60% and 48%, respectively). Further studies conducted in dichloromethane proved 140 was able to efficiently convert the monomer at LA:Zn ratios as high as 200:1, affording polymers with $M_n$ in accordance with the calculated values with good control ($M_w/M_n \approx 1.1$). By increasing the amount of alcohol to 2 and 4 equiv./Zn, faster rates were observed, albeit with a drop of $M_n$. Finally, kinetic studies suggested that the ROP takes place according to a living mechanism.

![Figure 25. Zn-salen complex 140 active in the ROP of L-LA [82].](image)

The use of zinc complexes of macrocyclic Schiff-bases has also been studied. In 2015, Williams, Brooker et al. reported a dinuclear complex based on a bis(anilido)tetraimine macrocycle exhibiting good activity in the ROP of $\varepsilon$-LA in the presence of 1 equiv./Zn of $\Pr$OH in THF (Figure 26, 141) [83]. The $M_n$ of the atactic polymer was in agreement with the calculated value with very narrow polydispersity. NMR spectroscopy and mass spectrometry studies confirmed the presence of the iso-propoxy end-group and confirmed the absence of significant transesterification. Moreover, kinetic investigations proved that an induction time is required, while a linear trend was observed for conversions > 20%. Based on these data, it was postulated that the formation of a catalytically active species featuring a Zn-OPr bond, generated by the alcoholysis of the parental complex 141, takes place during the early stages of the reaction. Lately, the same group further investigated this type of systems, synthesizing the well-defined iso-propoxy- and hexamethyldisilazane (HMDS)-analogues of 141 (142–143 and 144–145, respectively) [84]. All compounds proved extremely active, allowing for complete lactide conversion within 2 min at room temperature. The highest rates were observed for the HMDS-species that showed to be ca. 600 times faster than the alkoxo congener. The efficiency of these dinuclear compounds was also 6 times per metal center higher than that of their corresponding monometallic analogues, suggesting cooperative effects between the two metal centers. Interestingly, a zero-order rate dependence of lactide was found for the HMDS compounds, while 142 and 143 followed the more common pseudo first-order substrate dependence.

![Figure 26. Dizinc(II) complexes of macrocycle Schiff-base ligands [83,84].](image)

Very recently, our group developed mixed Zn/Co heterobimetallic complexes supported by [2+2] Schiff-base macrocycles (146 and 147, Figure 27) [85]. These complexes proved efficient activity in the ROP of $\varepsilon$-CL and $\delta$-VL at 130 °C in the presence of BnOH as co-activator. The $\text{^1}$$\text{Bu}$ derivative 147 outperformed the Me-congener, possibly because of the higher solubility of the former in the reaction

![Figure 27. Dizinc/Co complexes of macrocycle Schiff-base ligands [85].](image)
medium. Kinetic investigations showed a first-order monomer dependence and, interestingly, the ROP of δ-VL proceeded faster than that of ε-CL, with rate constants of 6.10 and 2.12 × 10⁻³ h⁻¹, respectively. Remarkably, the corresponding homo-dinuclear complexes were found to be inactive or poorly active in the ROP of ε-CL and δ-VL, respectively, suggesting the occurrence of cooperative effects between the Co- and Zn centers in the mixed complexes 146 and 147. Preliminary tests proved that the ROP of rac-lactide as well as CL-VL and CL-LA co-polymerization are also possible in the presence of these catalysts.

![Figure 27. Heterobimetallic macrocyclic complexes 146 and 147 [85].](image)

5.6. Cadmium

Cadmium complexes bearing tridentate Schiff-bases of the type [NN’X] (where X = O, N) have been recently shown to promote the ROP of rac-LA (Figure 28) [86]. The tests were performed in dichloromethane at low temperature (−50 or 0 °C) in the presence of MeLi as co-activator. Indeed, the active species was thought to be a Cd-Me containing complexes generated in situ from the interaction of the parental Br-compound with MeLi. All complexes exhibited moderate-to good activity, affording heterotactic PLAs with good control. Although no straightforward structure/activity correlation could be drawn, the activity trend was found to be 151 ~ 153 > 148 > 150 > 149 > 152.

![Figure 28. Cadmium complexes of tridentate Schiff-base ligands [86].](image)

6. Rare Earth Metals

The use of rare-earth (Ln) metal complexes of Schiff-bases as catalysts for the ROP of cyclic esters has been widely investigated. In 2010, Shen et al. tested phenoxylimino complexes 154–158 in
the polymerization of ε-CL (Figure 29) [87]. At 50 °C with a monomer:Ln ratio of 100:1, the Y- and Nd-based complexes allowed for complete monomer conversion with good control, while the La- and Gd-analogues proved less performing, affording PCLs in moderate yields. On the other hand, no reaction was observed in the presence of the Sc compound [88]. Upon increasing the CL:Ln ratio to 200:1, 155 outperformed its Nd-congener. Moreover, the latter exhibited good activity even at lower temperature, albeit with less control. NMR spectroscopic investigations performed on oligomeric species suggested that the ROP of the first monomer unit occurs with the cleavage of the acyl-oxygen bond. Lately, the same group extended the scope of ligands synthesizing La- and Gd-compounds having various substituents and at the imine moiety (159–170, Figure 29) [89].

All complexes proved efficient catalysts for the ROP of ε-CL in toluene at room temperature, with monomer:Ln ratios as high as 300:1. Gd-species outperformed the La-analogues, in terms of both polymer $M_n$ and polymerization control. Amongst the series, complexes bearing electron-donating groups at the para position (165–166 and 167–168) allowed for higher $M_n$ and narrower polydispersities compared to the other systems. Analysis of the polymers by NMR spectroscopy suggested that the reaction is initiated by one phenoxy-group of the catalysts’ Schiff-base moiety. Interesting activity in the ROP of ε-CL was observed also in the case of the dinuclear complex 171–173, bearing a Salen-type ligand (Figure 30) [90]. Good to moderate conversions were achieved in all cases at 70 or 100 °C with CL:Ln ratios as high as 500:1, affording polymers with high $M_n$ (50–90 kDa) and moderate control. The observed reactivity trend was 171 > 172 > 173, which is in agreement with the sequence of the ionic radii of the metal centers involved in the complexes. Kinetic investigations showed a first-order dependence on the substrate concentration and a linear increase of the $M_n$ with the monomer conversion. The $^1$H NMR spectra of oligomers isolated after a short reaction time showed resonances corresponding to the Schiff-base scaffold, suggesting that the ligand could serve as the actual initiator of the polymerization.
The effect of the oxidation state of the metal center on the activity of the catalyst was studied by Cantat, Diaconescu et al. by using the cerium complexes 174 and 175 bearing a salen- and phosphasalen ligand, respectively (Figure 31) [91]. The Ce(III) center could be reversibly oxidized to Ce(IV) upon addition of a suitable reactant; ferrocenium tetrakis(3,5-bis-(trifluoromethyl)phenyl)borate (FcBArF) proved efficient for both catalysts, while I₂ only allowed for the oxidation of 175. In this regard, X-Ray absorption near-edge structure (XANES) and Mössbauer spectroscopic studies confirmed that only the lanthanide was involved in the redox process, while the Fe center retained its +2 oxidation state. When tested in the ROP of L-lactide, the Ce(III) complexes were shown to be more active than their oxidized forms; indeed, the addition of FcBArF completely passivated the catalysts, while oxidation of 175 with iodine led to a drastic reduction of the reaction rate. However, the polymerization could be re-enabled by adding a reducing agent (Cp₂Co) to the reaction mixture, confirming the reversibility of the process. The Ce(III) species were also shown to polymerize 100 equiv. of ε-CL within minutes at room temperature as well as rac-lactide at 0 °C with moderate heterotactic bias. The higher activity of the Ce(III) species over their oxidized analogues was thought to be due to electronic factors (i.e., lower electrophilicity of the metal center) that increase the nucleophilicity of the alkoxide ligand of the growing polymer chain. This hypothesis was confirmed by DFT calculations.

Figure 30. Dinuclear Ln-complexes bearing a tetradentate Schiff-base ligand [90].

Figure 31. Redox switchable Ce-based catalysts [91].

Tetra- and pentadentate phosphasalen complexes have also been considered (Figure 32) [92,93]. The yttrium complexes 176–177 were found extremely active in the ROP of rac-LA at ambient temperature in THF, allowing for complete monomer conversion within seconds, even at very low catalyst loading (0.1 mol%). The pentadentate analogues 178–180 were also highly performing, albeit requiring longer reaction times (20–30 min) to achieve high yields. Interestingly, tetradentate compounds led to heterotactic PLAs while isotactic polymers were isolated in the presence of their pentadentate congeners. In all cases, Mₙ higher than the expected values were achieved; the control was generally good and dependent on the steric bulk of the alkoxide ancillary ligand. In fact, while the polydispersity was 1.34 in the case of complex 178, the value observed with its ethoxy-analogues was narrower. Interestingly, no lactide conversion was obtained upon using Sc-complexes 181 and 182, regardless of the reaction conditions employed. ¹H NMR spectroscopic experiments suggested the formation of a chelate Sc-LA species inactive towards polymerization. However, the catalysts...
were active in the ROP of ε-CL in toluene at ambient temperature; in this case, 182 allowed for higher conversions that its tBu-analogue after 48 h (98% and 84%, respectively). Mn observed were in good agreement with the calculated values and the control was generally good (M_w/M_n ~ 1.05).

Figure 32. Tetra- and pentadentate phosphasalen Y and Sc complexes [92,93].

Rare-earth complexes bearing pentadentate [ONONO]-type salen ligands have also shown notable activity in the ROP of r-LA (Figure 33) [94]. All catalysts completely converted the monomer within 15–20 min at room temperature with LA:Ln ratios as high as 1000:1, proved more active than previously reported tetradentate Y-salen compounds [95]. Heterotactic PLAs were isolated in all cases, with generally high stereoselectivity (P, spanning from 0.7 to 0.9). The observed polymer Mn were close to the calculated values with moderate to good control. The catalytic activity (187 ~ 186 > 185 > 184 >> 183) increased with the ionic radii of the metal center featured in the complexes, while the stereoselectivity followed the reverse trend. A first-order substrate dependence was found in the kinetic investigation while mass-spectrometry on the isolated polymers revealed the presence of the ArO- end group, indicating that the ancillary ligand is responsible for the ring-opening of the first monomer unit.

Figure 33. Rare-earth metal complexes of [ONONO]-type Salen ligands active in the ROP of r-LA [94].

7. Main Group Metals

7.1. Aluminum

Aluminum complexes have been extensively employed as catalysts for the ROP of cyclic esters. This topic has been described in depth in recent reviews, not only from the catalyst design point of view, but also with respect to scope of monomer [96,97]. Early reports mainly concerned chiral- [98–100] and achiral [101–104] Salen complexes, while Salalen [105,106] or related systems [107] have been subsequently introduced. Very recently, a set of Al catalysts bearing a novel Catalen scaffold has been reported by the group of Jones [108]. One of these systems exhibited the highest activity known to date for an Al complex in the melt ROP of r-LA.

Over the past 2 decades, our group have been contributing to the development of the field. Simple arylimino compound 188 (Figure 34) proved inactive in the ROP of ε-CL [109], while the
2,4-tBu-salicylaldehyde derivatives 189–196 exhibited interesting activity towards the polymerization of different monomers [110]. In the presence of BnOH as co-activator, complexes 189 and 195 were the most performing catalysts in the ROP of ε-CL, leading to complete monomer conversion at 80 °C within 3 and 1 h for the former and the latter, respectively. In spite of the higher reaction rate, 195 afforded polymers with lower $M_n$ and broader polydispersities compared to that isolated in the presence of 189. Under the same reaction conditions all other complexes showed moderate to good activity. While increasing the temperature (from 80 to 110 °C) was beneficial, the use of an additional equivalent of BnOH led to a significant drop of polymer molecular weight as well as to a broadening of the molecular weight distribution. Complexes 189–196 proved also capable of promoting the ROP of δ-VL and $r$-LA, although the conversions were somewhat lower than that of ε-caprolactone. In the case of the ε-CL/$r$-LA copolymerization, a good lactide incorporation (up to 63%) was observed. NMR spectroscopy and MALDI-TOF mass spectrometry confirmed the presence of the BnO-end group.

![Catalysts Al-complexes of bidentate Schiff-bases tested in the ROP of cyclic esters](image)

The effect of different substituents at both the phenoxy- and the imino-moiety on the catalytic activity of complexes 197–208 in the ROP of lactides was also studied (Figure 35) [111]. In the case of L-lactide, conversions spanning from 70% to 99% were obtained after 48 h at 100 °C in toluene, with a LA:Al of 250 by using one equiv./Al of BnOH as co-activator. Higher temperatures and/or greater amount of alcohol led to higher reaction rates, albeit with lower $M_n$ and less control. The polydispersities ranged between 1.20 and 1.25 with unimodal distributions, suggesting single site behavior of the catalysts. No clear structure/activity trend was found, although complexes bearing electron-donating groups were found to be more active; moreover, compounds having more soluble alkyl groups displayed enhanced reactivity. Interestingly, all catalysts proved more active upon replacing L-LA with its D-isomer. In addition, higher molecular weights and narrower polydispersities were achieved. Such improved behavior was thought to be dependent on the different coordination modes of the monomers at the catalytically active sites. Finally, poorer control and lower polymer molecular weights were observed upon using $r$-LA as the monomer. The $^{13}$C NMR spectra of the isolated PLAs suggested that BnOH is also involved both in the initiation and in the termination of the polymer chains.
In 2008, Nomura et al. also reported a series of Al-based catalysts for the ROP of several cyclic esters, namely ε-CL, δ-VL and ρ-LA, (Figure 36) [112]. In each catalyst, the 2-tert-butylsalicylaldehyde scaffold is retained while different substituents at the N-atom are featured. Regardless of the monomer, catalysts bearing alkyl groups were found to be poorly active while complexes with aromatic substituents proved more efficient, with catalytic activity increasing with the steric bulk of the N-group. Notably, the C$_6$F$_5$-derivative was the most active species in all cases, suggesting that also electronic effects influence the catalyst behavior. Narrow polydispersities and $M_n$ in agreement with the calculated values, along with kinetic investigations, confirmed the living nature of the polymerization process. In the case of ρ-LA, atactic polymers were isolated. Attempts towards polymerizing smaller lactones such as β-BL and γ-BL were unsuccessful. Lately, the same group investigated the effect of the steric hindrance of the N-substituent on the catalytic activity of binuclear Al-Schiff-base complexes [113].

![Figure 35. Al-aldiminophenolates complexes active in the ROP of lactides [111].](image1)

![Figure 36. Al-Phenoxy-imine catalysts developed by Namura et al. [112,113].](image2)

All complexes, activated by BnOH, were tested in the ROP of ε-CL at 70 °C (Table 8). Under the optimized reaction conditions, compound 218 was completely inactive, possibly because of its poor solubility in the reaction medium. Complete monomer conversion was obtained in the presence of 219 after 10 min. Polymer $M_n$ in agreement with the calculated and the narrow polydispersity suggested the occurrence of a living process; such a hypothesis was confirmed upon performing a two-step polymerization in which an excess of monomer was added after the initial 10-min polymerization. Good activity was also displayed by 220, albeit that a longer reaction time (20 min) was required to completely convert the monomer. The adamantyl-congener 221 was less performing, allowing for 75% conversion after 30 min with less control ($M_n/M_w = 1.67$). Finally, complete conversion was obtained with 222 after the same reaction time, although with a rather broad distribution (1.80). The $^1$H NMR spectra of the isolated polymers displayed the diagnostic resonances of both benzyloxy- and –CH$_2$OH end groups.
Table 8. ROP of ε-CL catalyzed by dinuclear complexes 218–222 [113].

| Run | Catalyst | Al:BnOH:Cl<sup>a</sup> | Time (Min) | Conv. (%) | $M_{n,\text{calc,}b}$<sup>b</sup> $\times 10^4$ | $M_n^{,d}$<sup>c</sup> $\times 10^4$ | $M_w/M_n$<sup>e</sup> |
|-----|----------|--------------------------|------------|-----------|---------------------------------|---------------------------------|---------------|
| 1   | 218      | 1:1:250                  | 30         | Trace     | -                               | -                               | -             |
| 2   | 219      | 1:1:250                  | 10         | 100       | 2.86                            | 3.06                            | 1.16          |
| 6<sup>c</sup> | 219 | 1:1:250                  | 10 + 10    | 100       | 2.01                            | 2.37                            | 1.25          |
| 7   | 220      | 1:1:250                  | 10         | 70        | 2.01                            | 2.37                            | 1.25          |
| 8   | 220      | 1:1:250                  | 30         | 100       | 2.86                            | 3.42                            | 1.28          |
| 9   | 221      | 1:1:250                  | 30         | 75        | 2.15                            | 2.72                            | 1.67          |
| 10  | 222      | 1:1:250                  | 10         | 100       | 2.86                            | 3.74                            | 1.80          |

<sup>a</sup> Conditions: $V_{\text{total}} = 3\text{ mL}$, ε-CL 5 mmol, 70 °C. <sup>b</sup> Calculated using ([CL]₀/[OH]₀) × conv. (%) + BnOH. <sup>c</sup> GPC data in THF vs. polystyrene standards, using a correcting factor of 0.56. <sup>d</sup> Polymerization was conducted for 10 min, ε-CL(5 mmol) was again added, and the polymerization was continued for another 10 min.

Recently, Kirillov, Carpentier et al. reported a series of Al complexes stabilized by phenoxyimine ligands featuring an ortho-triphenylsilyl group at the aryloxy moiety and various N-substituents (Figure 37) [114]. When used in combination with an external alcohol (either iPrOH or BnOH) all complexes were active in the ROP of ε-LA at 100 °C, over a period of time ranging between 2 and 20 h, exhibiting living character. The experimental polymer molecular weights were in good agreement with the expected values with narrow and unimodal polydispersities. Amongst the series, complex 228 bearing a N-benzyl substituent, exhibited the highest activity. Similarly to the previously encountered Zn-macrocycles 144 and 145 [84], kinetic studies highlighted a zero-order dependence on the lactide concentration. The NMR spectra of the isolated PLAs showed signals accountable to alkoxy- (BnO- or iPrO-) terminal groups derived from the insertion of the first monomer unit into the Al-OR bond generated by the reaction of 223–228 with the alcohol employed as co-activator. In terms of polymer microstructure, either iso- or heterotactic PLAs were obtained, depending on the catalyst employed. Indeed, while 225, 228, 230 and 232 exhibited isotactic bias, heterotactic enrichment was observed with 223, 233 and 235. On the other hand, no selectivity was displayed by 224, 227 and 229. The isoselectivity trend was partially rationalized in terms of the bulkiness of the aryl moiety of the N-benzyl substituent; however, the steric hindrance was thought to be only one of the factors influencing the stereoselectivity of the catalysts. In fact, no straightforward correlation could be found in the series of species exhibiting heterotactic bias.
In 2014, Liu et al. disclosed β-ketiminato aluminum complexes active in the homo- and copolymerization of ε-CL and L-LA (Figure 38) [115]. Complex 236, in combination with an equimolar amount of iPrOH, allowed for complete conversion of 100 equiv. of ε-CL within 5 min at 80 °C, while slightly longer reaction times (10 min) were required by its congeners 237 and 238. However, the latter proved to be the best catalyst for the ROP of L-LA, reaching 96% and 99% conversion after 3 and 4 h, respectively. Molecular weights close to the theoretical values and narrow distributions were observed in all cases; in addition, kinetic investigations suggested the occurrence of a living process. This allowed for the synthesis of well-defined block PCL-PLA co-polymers by sequential addition of the two co-monomers. Based on the results obtained in the homo-polymerization tests, species 236 and 238 were employed for the sequential CL-LA and LA-CL co-polymerizations, respectively.

![Figure 38. Cyclic β-ketiminato aluminum complexes 236–238 [115].](image)

Very recently, Nie, Han et al. disclosed diarylhydrazone-based Al complexes displaying good activity in the ROP of ε-CL and r-LA [116]. The four novel complexes proved to be able to completely convert the monomer under mild conditions (70 °C) with good control and $M_n$ in accordance with the calculated values. However, poor stereoselectivity was observed in the case of r-LA, as atactic PLAs ($P_r \sim 0.5$) were obtained in all cases. Interestingly, these complexes were found to be more active than related [N,O]-supported Al complexes. It was suggested that the presence of an extra N-atom at the ligand framework increases the acidity of the metal center, hence enhancing the catalytic activity.

Aluminum complexes of bidentate thiol Schiff bases have shown interesting activity as catalysts in the ROP of ε-CL (Figure 39, Table 9) [117]. In particular, when complex 239 was activated by two equiv./Al of BnOH, almost complete conversion of 100 equiv. of monomer was achieved in 12 min at room temperature, affording a polymer with narrow dispersity and $M_n$ close to the calculated value.

![Figure 39. Five-membered ring Al complexes of N,S-Schiff bases 239–243 [117].](image)

Under the same reaction conditions, lower rates were observed in the presence of the other catalysts, albeit the process resulted to be well controlled in all cases. Upon increasing the amount of co-activator, the reaction resulted to be faster, although with an expected drop of molecular weight and loss of control. Notably, 239 proved efficient even at higher monomer concentrations (up to
350 equiv./Al), allowing for 87% conversion after 3 h at ambient temperature; furthermore, in this case, the polymerization proceeded in a living fashion.

Table 9. ROP of ε-CL catalyzed by 239–243 [117].

| Entry | Catalyst | Time (Min) | Conv. (%) | \(M_n(\text{calc.})\) (Da) | \(M_n(\text{NMR})\) (Da) | \(M_n(\text{GPC})\) (Da) | \(k_{\text{obs}}(\text{error})\) (min\(^{-1}\)) | Induction Period (Min) |
|-------|----------|------------|-----------|------------------------------|-------------------------|-------------------------|----------------------------|------------------------|
| 1     | 239      | 12         | 96        | 5600                         | 4800                    | 5900                    | 1.26                       | 0.284(12)              | 0.8                    |
| 2     | 240      | 12         | 92        | 5400                         | 5600                    | 7800                    | 1.19                       | 0.260(17)               | 1.8                    |
| 3     | 242      | 20         | 92        | 5400                         | 5200                    | 6400                    | 1.23                       | 0.136(4)                | 0.9                    |
| 4     | 243      | 25         | 95        | 5500                         | 7900                    | 8100                    | 1.23                       | 0.115(8)                | 0.8                    |
| 5     | 241      | 25         | 90        | 5200                         | 5500                    | 5200                    | 1.21                       | 0.105(4)                | 2.6                    |

Reaction conditions: Toluene (5 mL), \([M]_0:[\text{Cat}]_0:[\text{BnOH}]_0 = 100:1:2\), \([\text{CL}] = 2.0\) M, at room temperature. \(^a\) Obtained from \(^1\)H NMR analysis. \(^b\) Calculated from the molecular weight of the monomer × \([\text{monomer}]/[\text{BnOH}]\) × conversion yield + \(M_0(\text{BnOH})\). \(^c\) Obtained from GPC analysis and calibration on the basis of the polystyrene standards. \(^d\) Obtained from GPC multiplied by 0.56. \(^e\) The observed \(k_{\text{obs}}\) value is the slope of the first-order kinetic plot of ε-caprolactone polymerization vs. time. The conversion of ε-caprolactone with time was monitored using \(^1\)H NMR.

Recently, dinuclear aluminum complexes supported by bis-iminophenolate ligands have been independently reported by the groups of Wang [118] and Liu [119]. Such systems were highly active in the ROP of rac-lactide, affording high molecular weight polymers with narrow polydispersities. The good performances of these catalysts were attributed to cooperative effects of the two Al-centers.

With respect to tridentate systems, our group reported the mono- and dinuclear species 244 and 245 bearing [NON] scaffold and, lately, the 8-quinolinolates [ONN]-based complexes 246–250 (Figure 40) [109,120]. When used in combination with 1 equiv. of BnOH, 244 and 245 allowed for 50% and 37% conversion, respectively, of 500 equiv. of ε-CL after 11 h at room temperature. The process was well controlled, and the polymer molecular weights matched the expected values. The 8-quinolinolates derivatives were found to be more active at higher temperatures (60–90 °C), exhibiting living behavior. Although the molecular weight distributions were rather narrow and unimodal, a certain degree of transesterification was observed, especially at higher monomer conversion. Interestingly, the transesterification increased according to the trend 248 < 247 < 246 < 249, 250, suggesting that a bulky ortho-substituent reduces the occurrence of the undesired side-process.

![Figure 40](image-url)

Figure 40. Al complexes of tridentate Schiff-base ligands active in the ROP of ε-CL [109,120].

Aluminum complexes of unsymmetrical dinaphthalene-imine derivatives have been disclosed by Pang et al. in 2015 (Scheme 3) [121]. The reaction of either the S- or rac-ligands 251–256 with one
equivalent of trimethylaluminum led to the -AlMe\textsubscript{2} complexes 257–262 (S- or rac, depending on the starting ligand). Upon prolonged heating, these compounds released methane and their mono-methyl analogues 263–268 were isolated. Finally, the bis-Schiff-base species 269–271 (S- or rac) were obtained by treating the corresponding ligands with 0.5 equivalents of the metal precursor.

Scheme 3. Synthesis of Al-based complexes of unsymmetrical dinaphthalene-imine derivatives [121].

Next, the ability of these complexes to polymerize L- and rac-lactide was investigated. Moderate to high activity was displayed at 70 °C in the presence of isopropanol as co-activator. The optical active complexes were found better performing than their racemic analogues, both in terms of activity and stereoselectivity. Noteworthy, is the fact that the conversions improved upon increasing the steric bulk of the substituents on the phenyl moiety. All polymers were isotactic and the isoselectivity increased with the steric hindrance of the groups at the salicylaldehyde part. Kinetic studies showed that the $M_n$ linearly increased with the monomer conversion while the polydispersity remained constant throughout the reaction, proving the occurrence of a living polymerization. The presence of the isopropoxy end group was observed in the \textsuperscript{1}H NMR spectrum of the isolated polymers, suggesting that the active species features an Al-O\textsubscript{iPr} bond arising from the reaction of the pre-catalysts with the co-activator. The whole process proceeds according to a coordination–insertion mechanism.

Tridentate complexes with different N-side arms were recently studied by Zhang et al. (Figure 41) [122]. When used as catalysts in the ROP of $\varepsilon$-CL and $\delta$-VL in the absence of a co-activator, random polymerization and low control was observed, while the addition of 1 equiv./Al of BnOH led the generation of systems displaying moderate to high activity depending on the side-arm of the starting complex. In fact, the reactivity trend was found to be 272 > 273 > 274. Systems based on 272–273/BnOH proved efficient also under immortal conditions, affording high molecular weight
polymer with narrow polydispersities (as low as 1.2). NMR spectroscopy and mass spectrometry studies confirmed the presence of the benzylxoy-end group as well as showing the formation of cyclic oligomers generated by intramolecular back-biting. Controlled block CL/VL co-polymers were obtained by sequential monomer addition in the presence of the 273/BnOH system, both at room temperature and at higher temperature. On the other hand, the catalysts based on the other two Al-complexes allowed for good control only at low temperature, while undesired transesterification was observed under more forcing conditions.

**Figure 41.** Tridentate Al-based catalysts 272–274 active in the homo- and co-polymerization of ε-CL and δ-VL [122].

Aluminum catalysts supported by half-salen ligands were reported derived from natural products have been reported by Darenbourg and Karroonirun (Figure 42) [123]. The backbone of the dinuclear complexes 275–278 and 279–282 derived from modified chiral- and aliphatic amino-alcohols, respectively, while the monometallic species 283 and 284 were based on amino-acids. All complexes were tested as catalysts in the ROP of rac-LA both in deuterated chloroform and in toluene at 60 °C, with a monomer to Al ratio of 50:1. Compound 275 proved inactive in the chlorinated solvent at room temperature, while moderate conversion was achieved after 66 h in toluene at 70 °C. Within the same set of complexes, bulky or electron-donating substituents had a detrimental effect on the polymerization, both in terms of conversion and iso-selectivity. In fact, while the PLA isolated in the presence of 275 displayed a $P_m$ value of 0.7, lower values (< 0.5) were observed for the polymers obtained with 276 and 277. The catalysts derived from the aliphatic amino-alcohols, except for 282, exhibited higher rates than their chiral counterparts, albeit with similar isoselectivity ($P_m > 0.7$). The amino acid-based compounds were found as active as 275–278 although exhibiting higher stereoselectivity. In all cases, the polymer molecular weights were in accordance with the expected values with narrow polydispersities spanning from 1.03 to 1.08. Complexes 274–282 were found capable to promote, to a certain extent, the epimerization of D- or L-lactide of the racemic mixture of the monomer into its meso form prior to polymerization, as observed by $^1$H NMR spectroscopy (appearance of a diagnostic signal at 1.70 ppm).

**Figure 42.** Half-salen aluminum complexes active in the ROP of rac-LA [123].

With respect to tetradeinate complexes, an Al-isopropoxy species supported by the racemic CF$_3$/phenoxy-diimino ligand reported by Carpentier et al. exhibited moderate activity in the ROP
of rac-LA [95]. The process occurred in a living fashion affording isotactic PLAs with good control. The same group also disclosed a series of chiral Salen-Al complexes bearing alkyl- or alkoxy ancillary ligands [124]. When tested in the ROP of r-LA, exogenous alcohol was required by the former, while the well-defined isopropoxy-derivatives acted as single-component catalysts. Enhanced reactivity was observed for the complexes bearing either electron-withdrawing (NO$_2$) or non sterically demanding (H) substituents. High isoselectivity was generally observed in such systems.

Later, salalen-type complexes active in the ROP of lactide were studied by the group of Jones. (Figure 43) [125,126]. Upon activation with BnOH, the ethylene-bridged species 284, 286, 288 and 290 showed a slight isotactic bias, whereas heterotactic PLAs were isolated in the presence of 285, 287 and 289. The BnO-derivatives of complexes 291–299 were screened in bulk conditions with a monomer to Al ratio of 300 at 130 °C. While almost complete conversions were achieved with 296 and 298 within 2 h, the other systems required longer reaction time to allow for low- to moderate conversions. The rather broad polydispersities observed in the runs involving 292–293 and 297–298 (spanning from 1.5 to 1.7) suggested the occurrence of undesired transesterification. Concerning the polymer microstructure, 294 and 297 exhibited isotactic bias while slightly hetero-enriched PLAs were isolated in the presence of the other catalysts.

![Figure 43. Salalen complexes active in the ROP of rac-lactide [125,126].](image)

The polymerization was then performed in solution by employing both the well-defined BnO-derivatives as well as their parental methyl analogues activated in situ with 1 equiv. of BnOH (Table 10). The Al-Me compounds were found to be less active in all cases, aside from 294 and 297, for which their Al-OBn congeners allowed for much higher conversions. Control was generally better than for the solvent-free tests, although broad polydispersity was observed in the run involving 298-OBn (1.67). Interestingly, the polymer $M_n$ are higher than the expected values, suggesting that in solution not all Al-centers initiate the polymerization.

Al complexes of aminopiperidine-based Salalen and half-Salalen ligands have been recently studied by Mahon, Jones et al. [127]. These species, activated by BnOH, proved active in the ROP of r-LA under relatively mild conditions, allowing for moderate- to high conversions and good control ($M_n/M_w < 1.1$). In terms of stereocntrol, heterotactic enrichment was generally observed. The occurrence of transesterification, albeit to a small extent, was confirmed by mass spectrometry.

Methyl- and benzyloxy Al complexes bearing salphen ligands (Figure 44) were also found active in the ROP of rac-lactide (Table 11) [128]. In the case of compound 300, the active species was generated in situ upon addition of an equimolar amount of BnOH; however, the $M_n$ of the isolated polymer was higher than the calculated value, indicating only a partial activation. On the other hand, higher conversions and narrower distributions were obtained with the BnO-derivatives 301–303. Moreover, the observed polymer $M_n$ were in perfect agreement with the theoretical values. Interestingly, the presence of bulky ortho substituents positively affected the reaction rate, albeit playing a detrimental effect on the stereoselectivity.
Catalysts considering the polymerization following a chain-end control mechanism. Exhibited higher activity than its Me- and Ph-analogues, possibly because of the presence of the electron-withdrawing group (CF<sub>3</sub>). Being all non-chiral catalysts, the isoselectivity was explained considering the polymerization following a chain-end control mechanism.

Interestingly, the presence of bulky substituents positively affected the reaction rate, albeit helping the cleavage of Al-OR bond during the catalysis, proved also beneficial. Compound <sup>306</sup> ethylene-bridge analogues. In turn, the presence of the germinal methyl groups on higher flexibility, species bearing a C3 backbone (<sup>307</sup> and <sup>308</sup>) were more active than their ethylene-bridge analogues. Due to their higher flexibility, species bearing a C3 backbone (<sup>307</sup> and <sup>308</sup>) were more active than their ethylene-bridge analogues. In turn, the presence of the germinal methyl groups on <sup>308</sup>, allegedly helping the cleavage of Al-OR bond during the catalysis, proved also beneficial. Compound <sup>306</sup> exhibited higher activity than its Me- and Ph-analogues, possibly because of the presence of the electron-withdrawing group (CF<sub>3</sub>). Being all non-chiral catalysts, the isoselectivity was explained considering the polymerization following a chain-end control mechanism.

Table 10. ROP of rac-LA catalyzed by 291–299 (Me- and BnO-derivatives) [126].

| Run | Catalyst | Time (Days) | Conv. (%)<sup>a</sup> | <i>M</i><sub>n</i> | <i>M<sub>n</sub>/M<sub>0</sub></i> | <i>P</i><sup>c</sup> |
|-----|----------|-------------|------------------------|----------------|----------------------|----------------|
| 1   | 291-Me   | 4           | 42                     | 8950           | 1.06                 | 0.49           |
| 2   | 291-OBn  | 4           | 26                     | 3750           | 1.08                 | 0.54           |
| 3   | 292-Me   | 4           | 71                     | 12,200         | 1.07                 | 0.65           |
| 4   | 292-OBn  | 4           | 91                     | 19,550         | 1.12                 | 0.61           |
| 5   | 293-Me   | 4           | 97                     | 17,150         | 1.35                 | 0.60           |
| 6   | 293-OBn  | 4           | 99                     | 17,000         | 1.18                 | 0.69           |
| 7   | 294-Me   | 4           | 83                     | 7700           | 1.06                 | 0.57           |
| 8   | 294-OBn  | 10          | 40                     | 6400           | 1.08                 | 0.42           |
| 9   | 295-OBn  | 4           | 96                     | 24,600         | 1.12                 | 0.56           |
| 10  | 296-OBn  | 4           | 96                     | 19,900         | 1.27                 | 0.54           |
| 11  | 297-Me   | 4           | 61                     | 7100           | 1.07                 | 0.54           |
| 12  | 297-OBn  | 10          | 49                     | 8300           | 1.06                 | 0.31           |
| 13  | 298-OBn  | 4           | 96                     | 14,600         | 1.67                 | 0.54           |
| 14  | 299-OBn  | 4           | 99                     | 19,350         | 1.15                 | 0.73           |

Reaction conditions: monomer: initiator ratio 100:1 (: 1 BnOH if required) solvent toluene, T = 80 °C. Obtained from <sup>1</sup>H NMR analysis. Determined from GPC analysis using THF as the solvent and reference to polystyrene standards. Determined from the analysis of the methane region of the <sup>1</sup>H homonuclear decoupled NMR spectrum.

Table 11. ROP of rac-lactide catalyzed by 300–303 [128].

| Entry | Catalyst | Time (h) | Conv. (%)<sup>a</sup> | <i>M</i><sub>n</i> | <i>M<sub>n</sub>/M<sub>0</sub></i> | <i>P</i><sup>c</sup> |
|-------|----------|----------|------------------------|----------------|----------------------|----------------|
| 1     | 300<sup>c</sup> | 24       | 75                     | 9200           | 5500                 | 1.24           | 78            |
| 2     | 301      | 12       | 95                     | 6700           | 6900                 | 1.12           | 77            |
| 3     | 302      | 24       | 85                     | 6800           | 6200                 | 1.13           | 79            |
| 4     | 303      | 12       | 95                     | 6800           | 6900                 | 1.12           | 68            |

Reaction conditions: 20 µmol of Al, LA/Al = 50, 2 mL of toluene solution, 110 °C. Obtained from <sup>1</sup>H NMR spectroscopic analysis. GPC data in THF vs. polystyrene standards, using a correcting factor of 0.58. <sup>c</sup> Mn(cal.) = M(LA) × ([LA]/[Al]) × conversion +<sup>1</sup>H NMR spectroscopy. Determined from the analysis of the methane region of the<sup>1</sup>H homonuclear decoupled NMR spectrum. 20 µmol of BnOH was added.

Similar to phenoxyimine-based compounds, Al complexes of enolic Schiff-bases 304–310 proved interesting activity as catalysts for the isoselective ROP of rac-lactide (Figure 45) [129]. Due to their higher flexibility, species bearing a C3 backbone (<sup>307</sup> and <sup>308</sup>) were more active than their ethylene-bridge analogues. In turn, the presence of the germinal methyl groups on <sup>308</sup>, allegedly helping the cleavage of Al-OR bond during the catalysis, proved also beneficial. Compound <sup>306</sup> exhibited higher activity than its Me- and Ph-analogues, possibly because of the presence of the electron-withdrawing group (CF<sub>3</sub>). Being all non-chiral catalysts, the isoselectivity was explained considering the polymerization following a chain-end control mechanism.
Recently, salen-aluminum complexes bearing cyclic β-ketoiminato ligands reported by Wang et al. proved promising activity in the ROP of larger lactones, such as ω-pentadecalactone, ambrettolide and ethylene brassylate [130]. The complexes, activated by BnOH, were able to completely convert such monomers within 3 h at 130–150 °C, with a monomer:Al ratio as high as 1000. However, poor control (M_w/M_n spanning from 1.5–1.8) was generally obtained, and the observed M_n were lower than the calculated values. Mass spectrometry analyses indicated the formation of linear macromolecules and, to a lower extent, cyclic oligomers. Finally, the complexes proved extremely active in the ROP of smaller lactones (ε-CL and lactides). Indeed, the monomers were fully converted at room temperature within 1 h, with good control and M_n matching the expected values. High isoselective bias (P_m = 0.88) was observed in the case of r-LA.

Bimetallic species 311–314, activated with ¹PrOH, proved efficient catalysts in the ROP of ε-CL and rac-lactide (Figure 46) [131]. For both monomers, the increase of steric bulk at the ortho substituent resulted in a drop of activity. Nevertheless, good control (M_w/M_n ranging between 1.09 and 1.22) and M_n matching the expected values were obtained in all cases, regardless of the monomer. With respect to the polymerization of r-LA, all catalysts displayed isotactic bias and the stereoselectivity increased in accordance with the steric hindrance of the ortho substituents at the ligand. Kinetic experiments showed a first-order dependence on the monomer concentration and confirmed the occurrence of a living polymerization according to a coordination/insertion mechanism.

Figure 45. Enolic Schiff-base aluminum complexes 304–310 [129].

Figure 46. Bimetallic Al-salen complexes 311–314 [131].
Complexes 315–317, activated by four equivalents of 1PrOH proved capable of polymerizing r-LA under relatively mild conditions (Figure 47) [132]. The length of the backbone linker significantly influenced both the activity and the stereoaselectivity of these species. In fact, 315 was found to be more active than its larger congeners, allowing for complete monomer conversion within 12 h, affording polymers whose molecular weights were close to the predicted values with good control and high isoselectivity (up to 82%). Longer reaction times were required in the case of 316 and 317 and the observed molecular masses were ca. half of the expected, suggesting that polymerization takes place only at one Al-center. A lower isotactic bias (56%–59%) was also observed, possibly due to the greater flexibility of the catalysts compared to 315. The highest performances of the latter were attributed to possible cooperative effects between the two metal centers in close proximity due to the shorter backbone. The complex also proved as an efficient catalyst for the homo- and copolymerization of other cyclic esters (L-LA, ε-CL and β-BL), epoxides and anhydrides [133].

![Figure 47. Bimetallic Al-complexes active in the ROP of lactones, epoxides and anhydrides [132,133].](image)

High activity was also observed upon using compounds 318–320 as catalysts in the ROP of rac-lactide (Figure 48) [134]. While long reaction times were required in the absence of a co-activator, faster rates were achieved upon introducing one to four equivalents of 1PrOH. Interestingly, the racemic compound 318 exhibited the same activity as its chiral version 320; instead, complex 319 proved slightly more active. This was attributed to the effect of the electron-withdrawing Br-substituents. Good control was observed in all runs and atactic PLAs were isolated regardless of the catalyst employed (racemic or chiral). Finally, 318 proved efficient also in the polymerization of ε-CL and β-BL as well as in the copolymerization of phthalic anhydride with cyclohexene oxide and limonene oxide and in the terpolymerization of such monomers with lactide affording di-block polyesters. Moreover, in this case, the high activity of these catalysts was attributed to the cooperative effects of the two metal centers favored by the rigidity of the ligand.

![Figure 48. Bimetallic Al complexes supported by binaphthyl- Schiff-base ligands [134].](image)

Functionalized aliphatic polyesters could be directly accessed via the ROP of “alternative” monomers, such as α-X-ε-caprolactones (X = Cl, Br, I) [135–137]. In this scenario, the polymerization of α-Cl-ε-CL, catalyzed by previously reported Al-salen complexes [103,138], has been recently studied by Dagorne et al. [139]. The reaction was tested both in solution and under solvent-free conditions; in both case, good conversions were obtained, although thermal degradation was observed in the latter
case. This was thought to be due to the cleavage of C-Cl bonds occurring under the forcing reaction conditions. When an excess of alcohol was introduced in the reaction mixture (immortal process), complete conversion and good control were achieved. Furthermore, such an approach was employed for the synthesis of poly-α-Cl-CL and PLA diblock co-polymers with interesting thermal features.

Reports concerning the use of macrocyclic AI systems are scant. Our group reported complexes based on the [2 + 2] macrocyclic ligands 321–322 and 323–325, bearing ethylene- and oxo bridges, respectively (Figure 49) [109,140]. Di- and tetramet allic species were obtained upon treating these ligands with the corresponding amount of AlR₃ (R = Me or Et) in either toluene or hexane at reflux. Ethylene-bridged complexes were active in the ROP of ε-CL and beneficial cooperative effects were observed for multimetallic systems not displaying an aluminoxane-type bonding (Al-O-Al). While oxo-bridged complexes outperformed their ethylene-analogues in both the ROP of r-LA and ε-CL, no evidence of cooperative effects was observed with these systems.

Figure 49. Ethylene- and oxo-bridged [2 + 2] macrocyclic Schiff-base ligands [109,140].

7.2. Gallium

Unlike their Al counterparts, Ga(III) catalysts for the ROP of cyclic esters remain widely unexplored. Mononuclear Salen complexes 326–331 (Figure 50) proved active in the ROP of r-LA, both in toluene and in bulk [141]. Regardless of the reaction conditions, the activity trend was found to be 331 ~ 326 > 330 > 328 > 329 > 327, suggesting that less sterically demanding substituents and flexible linkers are beneficial. In terms of stereoselectivity, while isotactic PLAs were isolated with 326–328 and 330–331, hetero-enrichment was observed with 329. In particular, the highest isoselectivity (Pᵢ = 0.77) was achieved with 331, bearing electron-withdrawing Cl groups. Compound 326 also proved to be efficient in the ROP of ε-CL and in the CL/LA copolymerization. Similar Salen-based complexes exhibiting poor activity were concomitantly reported by Mehrkhodavandi et al. [142]. With respect to bimetallic complexes, species 332–334 proved able to catalyze the ROP of r-LA at 70–100 °C, albeit with poor stereocontrol [124].

Finally, compounds 335–338 and the salt 339 (Figure 51) were found to be capable of acting as catalysts in the ROP of 200 equiv. of r- or L-LA at 140 °C under solvent-free conditions [143]. Complex 335 proved the most active, requiring 9 h to fully convert the monomer, while longer reaction times were necessary in the case of 336–338 (14–20 h). In all cases, Mₙ values in agreement with the theoretical values and good control were achieved. Moreover, high isotactic bias was observed (Pᵢ 0.79–0.84). On the other hand, 339 was the least performing, requiring 50 h to completely convert the monomer and affording atactic PLAs with Mₙ lower than the expected values, albeit with narrow polydispersities.
While no reaction was observed in the absence of exogenous alcohol, no significant improvement with analogous phenoxy-imine-In complexes reported by the same group \[114\]. The catalytic activity followed the trend 342 >> 340 > 341, indicating that electron-withdrawing and/or electron-donating substituents are beneficial. Concerning the diiminophenolate species 342–346, behavior similar to that of their Ga-analogues was observed \[143\].

Recently, the use of In(III)-based systems for the production of biodegradable polymers has been drawing increasing attention \[144\]. Carpentier et al. disclosed Salen complexes 340–342 (Figure 52) active in the ROP of r-LA at 100 °C in the presence of BnOH as co-activator, affording atactic PLAs \[124\]. While no reaction was observed in the absence of exogenous alcohol, no significant improvement of the reaction rate was detected under living conditions (excess BnOH). It was proposed that the polymerization occurred according to an activated monomer mechanism, as previously observed with analogous phenoxy-imine-In complexes reported by the same group \[114\]. The catalytic activity followed the trend 342 >> 340 > 341, indicating that electron-withdrawing and/or less sterically demanding substituents are beneficial. Concerning the diiminophenolate species 343–346, behavior similar to that of their Ga-analogues was observed \[143\].

![Ga-based catalyst](image1)

**Figure 50.** Ga-based catalyst 326–334 \[124,141\].

![Bis(imino)phenoxide-based Ga complexes](image2)

**Figure 51.** Bis(imino)phenoxide-based Ga complexes \[143\].

### 7.3. Indium

Recently, the use of In(III)-based systems for the production of biodegradable polymers has been drawing increasing attention \[144\]. Carpentier et al. disclosed Salen complexes 340–342 (Figure 52) active in the ROP of r-LA at 100 °C in the presence of BnOH as co-activator, affording atactic PLAs \[124\]. While no reaction was observed in the absence of exogenous alcohol, no significant improvement of the reaction rate was detected under living conditions (excess BnOH). It was proposed that the polymerization occurred according to an activated monomer mechanism, as previously observed with analogous phenoxy-imine-In complexes reported by the same group \[114\]. The catalytic activity followed the trend 342 >> 340 > 341, indicating that electron-withdrawing and/or less sterically demanding substituents are beneficial. Concerning the diiminophenolate species 343–346, behavior similar to that of their Ga-analogues was observed \[143\].
Highly isoselective Salen-In catalysts have been studied by the group of Mehrkhodavandi (Figure 53). Preliminary tests revealed that rac-347 is capable of converting up to 1000 equiv. of r-LA at room temperature within 4 h or under 10 min, in CH$_2$Cl$_2$ or bulk, respectively [145]. Upon using the optical active version of the complex, namely (R,R)-347, high isoselectivity ($P_m = 0.77$) was obtained. The catalysts proved site-selective, exhibiting higher preference towards L-LA than D-LA; hence, upon feeding the racemic monomer, stereo-block PLLA-b-PDLA with high crystallinity was isolated. The effect of the steric encumbrance of the ortho substituents was next investigated [146]. All dinuclear complexes 348–351 allowed for complete r-LA conversion at room temperature; however, catalysts bearing bulky substituents (i.e., 349 and 350) exhibited lower propagation rates than that of smaller congeners. On the other hand, isoselectivity increased with the steric hindrance of the ortho groups. The mononuclear analogues 352–354 showed faster rates albeit with lower stereoselectivity. In all cases, $M_n$ values lower than the expected values were observed, suggesting the occurrence of transesterification. Finally, the same group disclosed a set of cationic hemi-Salen indium complexes bearing hemilabile thiophenyl, furfuryl or pyridyl pendant arms [147]. Amongst the series, the pyridyl-derivative proved active in the ROP of r-LA in the absence of a co-activator, producing high molecular weight polymers with narrow polydispersity.

**Figure 53.** Salen-In catalysts for the isoselective ROP of rac-Lactide [145,146].

### 7.4. Tin

Reports describing the use of Schiff-base tin complexes as catalysts for the ROP of cyclic esters are scant. Sn(II) species bearing bi- and tridentate ligands have been recently disclosed by Phomphrai et al. and tested in the polymerization of lactide and $\varepsilon$-CL (Figure 54) [148,149]. Cyclic PLAs were obtained in the melt polymerization of L-LA with 355–362 in the absence of a co-activator, while linear polymers were isolated upon introducing BnOH. The activity trend was strongly influenced by the
nature of the ortho-substituents. Indeed, while high activity was observed with 358 and 362, bulky and/or electron-withdrawing groups had a detrimental effect. No racemization of the stereocenter of the poly-(L-lactide) was observed in all cases. When rac-lactide was used as monomer, atactic PLAs with a slight hetero-enrichment were isolated. The tridentate compounds 363, 364 and 365 were also found to be active in the melt polymerization of L-LA; no monomer conversion was observed with 365. Cyclic polyesters were isolated in the case of 363, while its congeners afforded linear macromolecules, albeit with poor control. This indicated that for 364 and 366, intermolecular transesterification occurs at a faster rate than the intramolecular process that would lead to cyclic species. This was attributed to the longer alkoxy-chains (compared to shorted ethylene bridge of 363) keeping the ester group of the growing chain away from the metal center, hence suppressing the cyclization. In the case of ε-CL, cyclic polymers were isolated with all catalysts for long reaction time (4 to 48 h) runs, while a mixture of linear- and cyclic products were observed after 2, 10 and 30 min. This suggested that the cyclization competes with the chain propagation during the early stages of the polymerization and becomes the main event throughout the process.

![Figure 54](image_url)

**Figure 54.** Schiff-based SnII complexes active in the ROP of ε-CL and lactides [148,149].

### 8. Conclusions

Schiff-base metal complexes have emerged as an interesting class of catalysts for the ROP of cyclic esters showing, in many cases, remarkable performances even at low loadings and under mild conditions. The majority of the reports herein described focused on the production of poly-lactides, while other monomers (i.e., ε-CL and/or δ-VL) have been considered less. This could be justified considering the extensive use of PLAs in the daily life, compared to the rather limited applications of other biodegradable polyesters. With respect to the type of ligands, the use of bi-, tri- and tetradeutate Schiff-bases has been well documented, while contributions concerning multidentate and macrocyclic scaffolds are still scant (Chart 2).

![Chart 2](image_url)

**Chart 2.** Breakdown of the denticity of the Schiff-base ligands reported in the review.

Given the need for cost-effective and environmentally friendly processes, the development of catalysts based on abundant and non-toxic metals is proposed as a valuable solution. In this regard, systems based on alkaline-earth metals, as well as zinc and iron are highly attractive and, as demonstrated in this review, are drawing increasing attention. Nevertheless, only limited examples [71,78,108] are capable
of affording polymers with sufficiently high $M_n$ to be industrially relevant. The use of such benign metals in combination with multidentate or macrocyclic ligands can access new families of homo- and hetero-multinuclear species showing enhanced performances due to cooperative effects [109,140]. The design of ligand frameworks based on or inspired by biomolecules (i.e., amino acids) could also be envisioned. Indeed, this would lead to optical active catalysts with (potential) high stereoselectivity and, possibly, low toxicity [150].

Overall, the ease of synthesis of this class of ligand set, together with the facile modification, means that Schiff-bases are likely to attract continued interest as ancillary ligands in the metal-based ROP of cyclic esters.

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