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Review

Recent Advances in Zinc Complexes for Stereoselective Ring-Opening Polymerization and Copolymerization

Xia Li [1], Yang Li [2], Gangqiang Zhang [1,*], Yat-Ming So [3] and Yu Pan [1,*]

[1] Institute of Functional Textiles and Advanced Materials, College of Textiles and Clothing, State Key Laboratory of Bio-Fibers and Eco-Textiles, Qingdao University, Qingdao 266071, China
[2] School of Chemical Engineering, Ocean and Life Sciences, Dalian University of Technology, Panjin 124221, China
[3] Department of Chemistry, The Hong Kong University of Science and Technology, Hong Kong 999077, China
* Correspondence: gqzhang@qdu.edu.cn (G.Z.); ypan@qdu.edu.cn (Y.P.)

Abstract: Recent advances in zinc complexes for stereoselective ring-opening polymerization (ROP) and copolymerization (ROCOP) highlight their pivotal role in synthesizing biodegradable aliphatic polyesters and polycarbonates. These materials address the urgent demand for sustainable alternatives to petroleum-based plastics, with stereochemical control directly impacting polymer crystallinity, thermal stability, and degradability. Zinc catalysts, leveraging low toxicity and versatile coordination chemistry, enable precise stereoregulation, whose performance is modulated by ligand steric/electronic effects, coordination geometry, and reaction conditions. This review summarizes the recent developments in zinc complexes for stereoselective ROP and ROCOP, focusing on ligand design strategies to enhance catalytic performance.

Keywords: zinc complexes; ring-opening polymerization; stereoselective; copolymerization; ligand design; biodegradable polymers

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Academic Editor: Alan R. Cabrera

Received: 4 May 2025
Revised: 23 May 2025
Accepted: 3 June 2025
Published: 5 June 2025

Citation: Li, X.; Li, Y.; Zhang, G.; So, Y.-M.; Pan, Y. Recent Advances in Zinc Complexes for Stereoselective Ring-Opening Polymerization and Copolymerization. *Inorganics* **2025**, *13*, 185. https://doi.org/10.3390/inorganics13060185

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1. Introduction

Since industrialization, the large-scale use of traditional petroleum-based polymer materials has been gradually bringing about some problems of greenhouse effect and environmental pollution [1–5]. Therefore, the development of environmentally friendly and degradable high-performance polymer materials has become an important research direction in the field of polymer science [6–8]. Among them, aliphatic polyesters and aliphatic polycarbonates are regarded as ideal candidate materials to replace traditional petroleum-based plastics due to their good biocompatibility and flexible degradable properties [9–13]. It is worth noting that the properties of such materials (including crystallinity, thermal stability, mechanical strength, and degradation rate) are closely related to their stereochemical structures. The controlled ring-opening polymerization (ROP) of lactones and the ring-opening copolymerization (ROCOP) reaction of epoxides with CO_2/cyclic anhydrides by metal catalytic systems are considered classic and efficient methods for producing stereoregular polyesters and polycarbonates [14–19]. This is because they have rapid polymerization kinetics, allow for large-scale polymer production, and offer excellent catalyst tunability and selectivity.

As an essential element for life, zinc not only has the advantages of low cost, low toxicity, and excellent biocompatibility, but the diversity of its coordination chemistry also enables the catalytic system to precisely regulate the electronic structure and steric hindrance of the active center [20–22]. These endow it with some unique advantages in

the precise regulation of stereochemistry, providing innovative strategies for the molecular design and performance optimization of degradable polymer materials (Figure 1) [23–26]. For example, zinc complexes based on the β-diketiminate (BDI) ligands, which had a dimeric structure with an acetate bridge, showed extremely high activity in the alternating ROCOP of cyclohexene oxide (CHO) and CO_2 to obtain a polycarbonate with high molecular weights (M_n up to 31.0 kg/mol) and high carbonate contents (91–96%) [27]. Moreover, BDI-based zinc complexes were employed as initiators for the ROP of *racemic* lactide (*rac*-LA) with high activity to produce highly heterotactic polylactides (PLAs) (P_r up to 0.94 at 0 °C), exhibiting excellent stereocontrol ability [28].

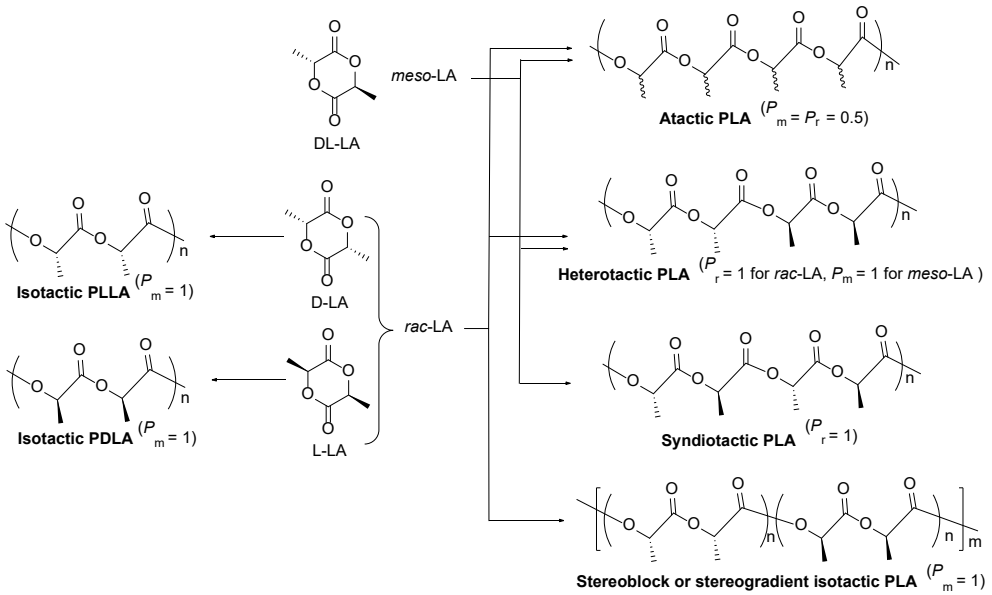

Figure 1. Polylactide with different stereoregularities.

This review focuses on the development of zinc complexes for stereoselective ROP and ROCOP in recent decades, covering their syntheses, structures, and catalytic performances, especially the influence of ligand structures on stereoselectivity. The zinc complexes are grouped according to the types of ligand and coordination modes. It should be noted that, in this review, most of the relevant research papers published in the past decade have been systematically collected, classified, and summarized to elucidate the relationship between the structures of zinc catalysts and their stereoselectivity performance. Nevertheless, it is an inevitable fact that certain literature could have escaped the collection process, presumably as a result of imprecise keyword choices. For more general overviews of transition metal complexes for stereoselective ROP and ROCOP reactions, the reader can refer to a series of recent reviews [29–32].

2. Zinc Complexes Containing Bidentate Ligands

This section reviews the catalytic performance of zinc complexes containing bidentate ligands in stereoselective ROP and ROCOP, which mainly include BDI ligands and their derivatives, as well as 1,2-diamine or 1,2-diimine ligands and others. A summary of the stereoselectivity of zinc complexes containing bidentate ligands, along with other relevant parameters in respective categories such as the feed ratio, polymerization time, polymerization temperature, conversion, and molecular weight distribution, is presented in Table 1. As a kind of famous bidentate ligand, the BDI ligand has been widely used in main group and transition metal chemistry, particularly for the stabilization of low-valent and low-coordinate metal centers [33–35]. A zinc complex ligated with 2,6-diisopropylphenyl-substituted BDI ligand was reported as a single-site catalyst for the ROP of *rac*-LA with

good activity and high heteroselectivity [36]. Moreover, zinc complexes also exhibited high activities in alternating copolymerization of epoxides and CO_2 [37]. Since those studies, BDI-ligated zinc complexes have been greatly developed for ROP [33]. In 2014, the C_1-symmetric BDI zinc complexes (**1** and **2**) were reported by Coates and co-workers (Figure 2) [38]. The optimized complex **1** with an electron-donating substituent showed high isotactic selectivity for copolymerization of CO_2 and *meso* epoxides to produce polycarbonates with units of up to 94% *ee* under mild conditions. Complex **2**, with a *trans*-2-benzyloxycyclohexyl substituent and an electron-withdrawing C_6F_5 substituent, displayed the best performance, combining activity and enantioselectivity. It was found that polymer properties, such as melting temperature and degree of crystallinity, could be adjusted by optimizing the microstructure of the resultant polycarbonate. Moreover, the BDI-ligated zinc complex $BDI^{CF3}-Zn-N(SiMe_3)_2$ (**3**) could initiate terpolymerizations of *racemic* β-butyrolactone (*rac*-BBL), CHO, and CO_2 [39]. Remarkably, it was also found that the type of polymerization could switch between the polymerization of BBL and the copolymerization of CHO and CO_2 by the presence of CO_2 in the reaction mixture, which can be produced from a terpolymer with a statistical composition similar to the exclusive copolymer composed of CHO/CO_2 [40]. However, only the atactic poly(3-hydroxybutyrate) (PHB) fragment was observed using *rac*-BBL as a monomer.

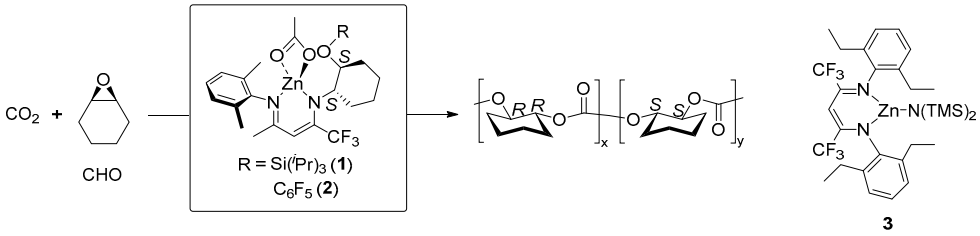

Figure 2. BDI-ligated zinc complexes for the stereoselective ROCOP of CO_2 and CHO.

BDI Zn amide and alkoxide complexes (**4**) with flexible ligand frameworks bearing N-9-anthrylmethyl and N-benzyl substituents were synthesized (Figure 3) [41]. It was found that zinc alkoxide complex **4b** could initiate the ROP of *rac*-LA with high activity and heterotactic selectivity (P_r = 0.93), and the steric bulkier substituent resulted in higher heterotactic selectivity in comparison to **4c**. The analysis showed that the monomer insertion followed a chain-end control mechanism. Using the asymmetric BDI ligands, it was found that zinc complexes (**5**) could also initiate the ROP of *rac*-LA to produce heterotactic PLAs at room temperature (P_r = 0.79–0.83 in THF) [42]. The steric and electronic characteristics of the ancillary ligands showed significant influence on the polymerization performance of the corresponding zinc complexes. Furthermore, the controlled zinc system can accommodate the polycaprolactone-*block*-poly(L-lactide) (PCL-*b*-PLLA) diblock copolymers via three different copolymerization strategies (one pot polymerization and sequential addition of the two monomers in either order). Remarkably, the sterically differentiated and disymmetric design in the BDI ligand increased the stability and activity of the catalyst. By optimizing the substitutes, the BDI-ligated zinc complexes (**6**) with 2,6-diisopropylphenyl and benzyl groups can initiate the ROP of LA with high turnover frequencies (TOF = 13,950 h^{-1} at 0.1 mol% [Zn] and [LA] = 1.0 M) and low catalyst loadings (down to 0.02 mol%) [43]. The zinc complexes also exhibited excellent controllability to produce PLAs with narrow dispersity, and a wide range of molecular weights with modest to good heteroselectivity. These results suggest low initiation efficiency using a bulkier initiating group, and higher heteroselectivity could be achieved using a zinc complex with bulkier substitutes.

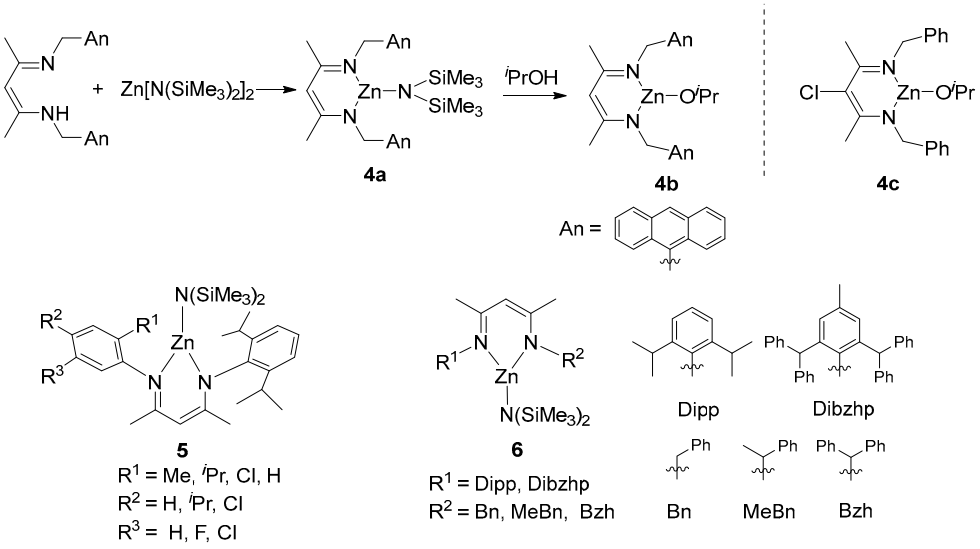

Figure 3. Zinc complexes with BDI ligands for the stereoselective ROP of LA.

An asymmetric BDI-ligated zinc complex with (–)-methyl lactate moiety (**7**) was developed for the controlled ROP of various *O*-carboxyanhydrides (OCAs) without epimerization (Figure 4), generating polymers with controlled molecular weights, narrow molecular weight distributions, and isotactic backbones [44]. The preliminary mechanistic study showed that complex **7** with methyl lactate moiety presented a predominant monomeric form in THF solution that possessed superior catalytic activity for the initiation of ROP in comparison to the analog dimeric complex. Furthermore, complex **7** was also able to produce the block copolymers of OCAs and LA owing to its controllable property, which has potential applications in various biomedical fields. A catalytic system based on BDI-ligated zinc amide complex (**8**) was developed to make use of the CO_2 released from OCAs to prepare copolymers [45]. The tandem copolymerization of OCAs and epoxides was able to produce functionalized poly(ester-*b*-carbonates) with high molecular weights (MWs) (>200 kg/mol) and narrow MW distributions (PDI < 1.1). This is an atom-economical, scalable method to effectively use the released CO_2. The enantiomerically pure OCAs were employed as monomers and no epimerization of the α-methine hydrogen was observed in the resultant polymers. The obtained degradable poly(ester-*b*-carbonates) showed better toughness than their corresponding homopolymers and outperformed some commodity polyolefins.

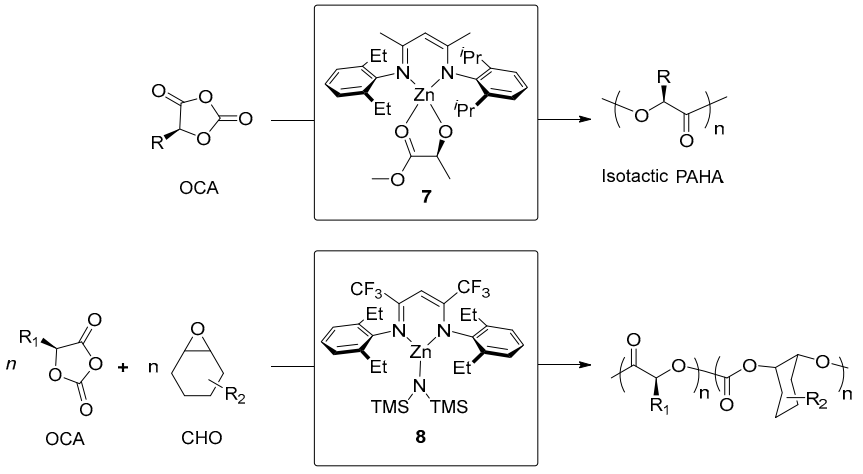

Figure 4. Zinc complexes with BDI ligands for the ROP of OCA.

As a similar structure to the BDI ligand, the 1,5,9-trimesityldipyrromethene (TMP) ligand is also anionic and forms six-numbered chelates when bound to a metal center, but the steric hindrance of TMP to the central metal is greater owing to its pocket structure [46]. The TMP-ligated zinc amido complex **9** and zinc alkoxide complexes **10a** and **11** were synthesized in 2016 (Figure 5) [47]. Thanks to the steric hindrance and coordination mode, complexes **9** and **10a** were monomeric while complex **11** showed a dimeric structure. Zinc alkoxide complex **11** initiated the ROP of both *rac*-LA and ε-caprolactone (ε-CL) to generate heterotactic PLAs and PCL. The reaction solvent influenced the stereoselectivity of the ROP of *rac*-LA (P_r = 0.96 in THF and P_r = 0.75 in CD_2Cl_2/CH_2Cl_2), probably owing to the coordination of the solvent. The TMP-ligated zinc complex **10b** bearing (–)-methyl lactate was used for the highly efficient ROP of enantiopure OCA monomers to generate isotactic polymers without epimerization [48]. Furthermore, the highly isoselective ROP of *rac*-OCA monomers was also achieved by zinc complex **10c** with *rac*-methyl lactate to generate a polymer with P_m = 0.97 at low temperature (−70 °C). The NMR analysis of the resultant polymers showed that the stereoselective mechanism could be attributed to a chain-end control mechanism.

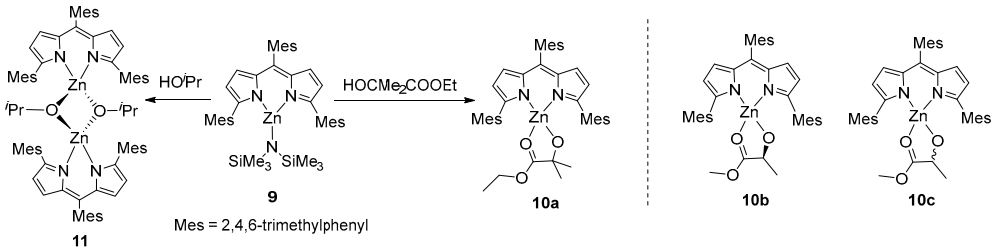

Figure 5. Zinc complexes with TMP ligands for stereoselective ROP.

As the analog of the BDI ligand, salicylaldimine or phenoxy-imine ligands have also been developed in corresponding zinc complexes (**12**), which showed a distorted tetrahedron geometry with coordination of two bidentate NO-ligands to the central metal ion (Figure 6) [49]. The zinc complexes were shown to initiate the ROP of *rac*-LA in solution as well as in bulk with high catalytic activity, controllability, and moderate heterotactic selectivity (P_r = 0.60–0.62), and the steric hindrance and electronic factors showed great influences on the catalytic activity and stereoselectivity. The salicylaldimine-ligated zinc complex with strong electron-withdrawing substitutes was inert to the ROP of LA [50]. Homoleptic zinc complexes (**13**) containing constrained reduced Schiff base ligands based on substituted 7-hydroxy-1-indanone were synthesized, in which the two coordination sites had a larger angle and a more open coordination space [51]. The complexes were well-controlled and exhibited living behavior for the ROP of *rac*-LA with very high activity. The resultant PLA displayed a slight heterotactic-enriched microstructure with P_r = 0.68. The modification of traditional phenoxy-imine ligands by a more robust and donor NNN-trisubstituted amidine function was shown to produce phenoxy-amidine ligands and corresponding zinc complexes (**14** and **15**). Single crystal X-ray diffraction showed a dinuclear complex (**14**) or homoleptic complex (**15**) depending on the applied metal/ligand ratio [52]. Zinc complex **15** was used as an initiator for the ROP of *rac*-LA to generate polylactic acid with narrow molecular weight distribution and heterotactic bias (P_r up to 0.75). Remarkably, zinc complexes (**16**) with chiral amido-oxazolinate ligands showed highly active and isoselective initiators for the ROP of *rac*-LA, yielding isotactic stereoblock PLAs with P_m up to 0.91, which was different from the heteroselectivity of BDI-ligated zinc complexes [53]. All of the zinc complexes showed good control of the polymerization process with narrow molecular weight dispersity. The highest P_m value was obtained by using a zinc complex with strong electron-withdrawing groups of aniline moiety. The chiral

oxazoline moiety played a key role in the stereoselectivity owing to only an atactic PLA, which was produced for the ROP of *rac*-LA by the analogous achiral zinc complex, but the steric hindrance of chiral oxazoline moiety made little difference to the stereoselectivity. The study of polymerization kinetics and the analysis of the microstructures of PLAs showed that both enantiomorphic site control and chain-end control mechanisms are proposed to account for the stereoselectivity in this system.

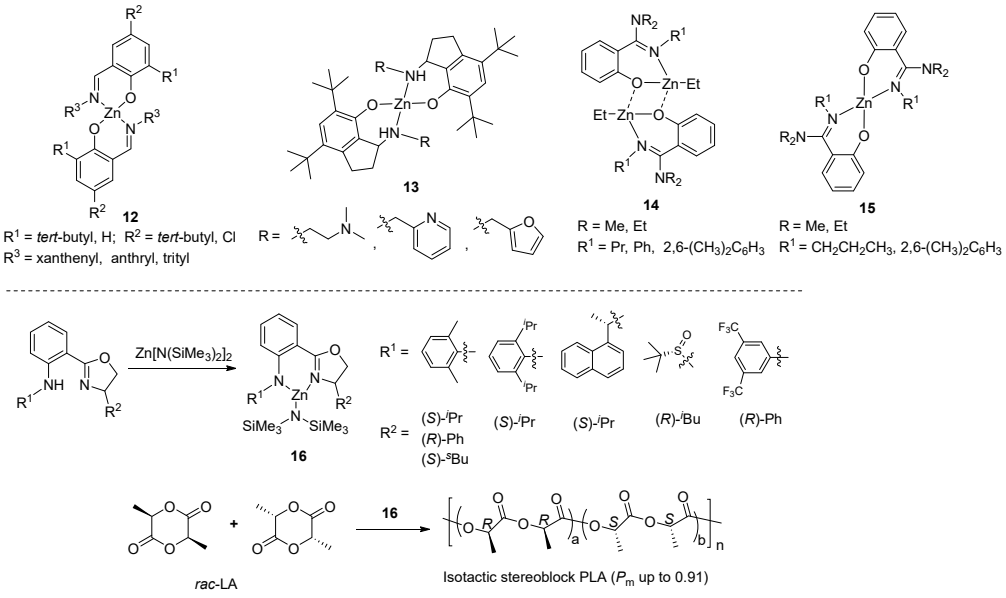

Figure 6. Zinc complexes with salicylaldimine or phenoxy-imine ligands for the stereoselective ROP of LA [53].

Besides the numerous BDI ligands and analogs, 1,2-diamine or 1,2-diimine ligands have also been introduced to support zinc complexes for stereoselective ROP. Zinc dichloride complexes (**17**) based on enantiopure 1,2-diaminocyclohexan-based ligands with furanylmethyl and thiophenylmethyl pendant groups were developed for the ROP of *rac*-LA to generate highly heterotactic PLAs (P_r = 0.80 at −25 °C in THF) (Figure 7) [54]. Zinc complexes (**18**–**20**) ligated by 1,2-diamine with chiral groups and asymmetric structure were highly active in the ROP of *rac*-LA with moderate to high heterotactic selectivity (P_r = 0.58 to 0.90 at room temperature) [55–57]. Furthermore, zinc complexes (**21**–**24**) with enantiopure camphor-substituted 1,2-diamine or iminopyridine ligands were also synthesized, which were found to produce PLAs with heterotactic regularity (P_r = 0.71–0.81 at 25 °C) [58–61]. It was proposed that the generation of a heterotactic-enriched PLA by these zinc catalysts with 1,2-diamine backbone followed a chain-end control mechanism with unclear assistance of the stereogenic centers [57]. *β*-pyridylenolate zinc complexes (**25**) with various *α*,*β*-substituents were synthesized and showed *μ*-O-bridged dimeric structures [62]. These complexes could serve as highly active catalysts for the ROP of *rac*-LA and *ε*-CL to produce slightly heterotactic PLAs, PCL, and their copolymers.

Zn alkoxide complexes (**26** and **27**) of NN-bidentate (benzimidazolylmethyl)amine ligands and NN-bidentate N-(pyridin-2-ylethyl)amine ligands all exhibited *pseudo*-first-order kinetics with respect to monomer concentration in the ROP of lactones, and the resultant PLAs were predominantly heterotactic (P_r = 0.63–0.78) (Figure 8) [63,64]. Zinc complexes (**28**) bearing neutral bidentate ligands with an electron-poor diacylated cyclic guanidine moiety were synthesized [65]. The complexes showed reactivity in the bulk ROP of *rac*-LA with the second-order kinetics, and the resulting polymers had slight heterotactic regularity (P_r = 0.60). In comparison, mononuclear zinc complexes (**29**) ligated by two chiral (*S*)-N-(-2-pyrrolylmethylene)-1-phenylethylamine or (*S*)-N-(2-pyrrolylmethyl)-1-phenylethanamine

ligands were synthesized [66]. All the complexes were applied upon initiating the ROP of *rac*-LA under mild conditions to afford PLAs with predominately isotactic regularity ($P_m \approx 0.70$). Zinc amide complexes (**30**) supported by bulky guanidinate ligands were developed [67]. The complexes were found to be stable at elevated temperatures and exhibited high activity for the ROP of LA, showing activity comparable to that of the commercial Sn catalyst. The resultant PLA showed predominate heterotacticity when *rac*-LA was used as a monomer. In addition, NN-bis(aryl)-substituted formamidine-ligated zinc complexes with trinuclear and dimeric structures were able to initiate the ROP of ε-CL and LA [68]. The resultant PLA showed predominant moderate heterotacticity (P_r of up to 0.65).

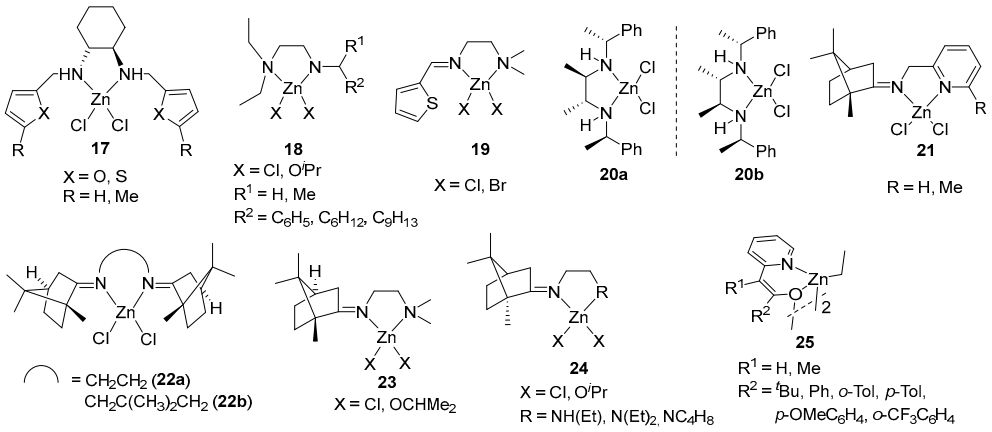

Figure 7. Zinc complexes with 1,2-diamine, 1,2-diimine, or pyridine-based ligands for the stereoselective ROP of LA.

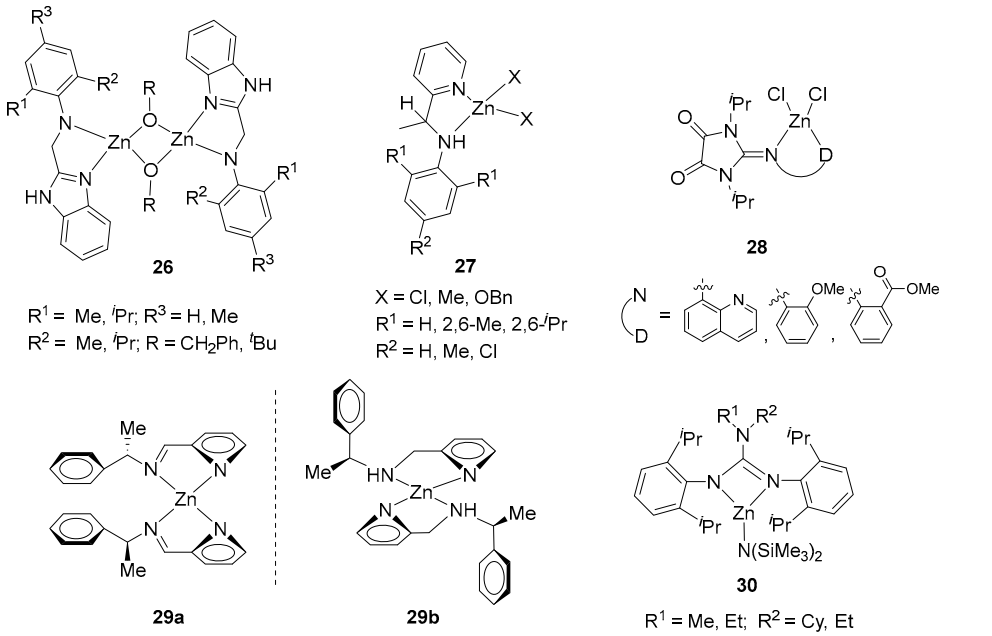

Figure 8. Zinc complexes with NN-bidentate ligands for the stereoselective ROP of LA.

Zinc alkyl complexes (**31**) with NN-bispyrazolyl-based chelating ligands were synthesized and employed as initiators for the ROP of *rac*-LA with moderate to high activities (Figure 9) [69]. The resultant PLA showed high heterotacticity with P_r up to 0.95 at −50 °C. The activities and stereoregularities toward the PLA were influenced by steric and electronic factors. Subsequently, zinc complexes (**32** and **33**) with the NN-bispyrazolyl ligands modified by furan and isopropylbenzene moieties were also developed for the ROP of *rac*-LA with high heterotacticity (P_r of up to ca. 0.94 at −25 °C) [70,71]. The stereoselectivity toward *rac*-LA polymerization was achieved by varying the amine substituents.

It was proposed that the polymerization of *rac*-LA by these NN-bispyrazolyl-based zinc complexes was proceeded by a chain-end mechanism [71].

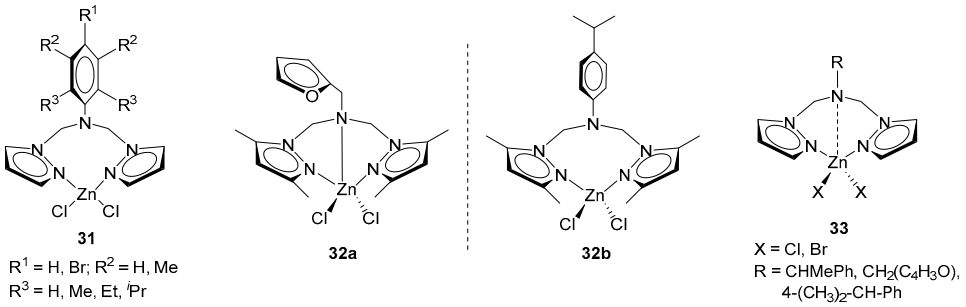

Figure 9. Zinc complexes with NN-bispyrazolyl-based ligands for the stereoselective ROP of LA.

Table 1. Summary of the stereoselectivity of zinc complexes containing bidentate ligands.

Run	Complex	M [1]	[M]:[C] [2]	T (°C)	Time (h)	Conv. (%)	M_n (kg/mol)	PDI	Tacticity	Ref.
1	**4b**	*rac*-LA	300:1	23	6	95	118	1.16	P_r = 0.93	[41]
2	**5**	*rac*-LA	500:1	25	0.42	79	281	1.15	P_r = 0.83	[42]
3	**6**	*rac*-LA	200:1	25	0.33	95	37.90	1.10	P_r = 0.90	[43]
4	**10c**	*rac*-LacOCA	100:1	−70	10	90	6.60	1.25	P_m = 0.97	[48]
5	**12**	*rac*-LA	100:1	130	1	92	10.80	1.16	P_r = 0.62	[49]
6	**13**	*rac*-LA	100:1	30	0.017	98	13.20	1.05	P_r = 0.68	[51]
7	**15**	*rac*-LA	100:1	25	2	72	10.40	1.09	P_r = 0.75	[52]
8	**16**	*rac*-LA	100:1	23	44	96	52.20	1.32	P_m = 0.91	[53]
9	**17**	*rac*-LA	50:1	−25	0.5	>99	5.54	1.31	P_r = 0.80	[54]
10	**18**	*rac*-LA	100:1	25	0.033	100	8.01	1.36	P_r = 0.77	[55]
11	**19**	*rac*-LA	100:1	0	0.33	96.6	6.273	1.25	P_r = 0.74	[56]
12	**20a**	*rac*-LA	100:1	25	0.033	94	7.01	1.33	P_r = 0.90	[57]
13	**21**	*rac*-LA	100:1	25	0.083	100	6.57	1.31	P_r = 0.77	[58]
14	**22**	*rac*-LA	100:1	25	0.33	100	8.42	1.26	P_r = 0.78	[59]
15	**23**	*rac*-LA	100:1	25	0.042	100	7.67	1.26	P_r = 0.80	[60]
16	**24**	*rac*-LA	100:1	25	0.05	100	8	1.21	P_r = 0.81	[61]
17	**25**	*rac*-LA	100:1	70	0.33	78	6.792	1.09	P_r = 0.54	[62]
18	**26**	*rac*-LA	200:1	110	18	98	8.675	1.34	P_r = 0.78	[63]
19	**28**	*rac*-LA	100:1	135	24	100	2.10	1.10	P_r = 0.60	[65]
20	**29a**	*rac*-LA	100:1	70	3	90	9.19	1.49	P_m = 0.71	[66]
21	**31**	*rac*-LA	100:1	−50	12	90	16.20	1.22	P_r = 0.95	[69]
22	**32b**	*rac*-LA	100:1	−25	2	97	7.56	1.16	P_r = 0.94	[70]
23	**33**	*rac*-LA	100:1	−25	2	>99	13.93	1.29	P_r = 0.93	[71]

[1] M indicates monomer. [2] [M]:[C] indicates the ratio of monomer and catalyst.

3. Zinc Complexes Containing Tridentate Ligands

This section reviews the catalytic performance of zinc complexes containing tridentate ligands in stereoselective ROP and ROCOP, which mainly include NNN-, NON-, NNO-, ONO-, OOO-, and ONS-tridentate ligands with pincer or scorpionate structures and so on. A summary of the stereoselectivity of zinc complexes containing tridentate ligands, along with other relevant parameters in respective categories such as the feed ratio, polymerization time, polymerization temperature, conversion, and molecular weight distribution, is presented in Table 2. In comparison to the bidentate ligands, the tridentate ligands for coordination of zinc complexes usually exhibit more diverse coordination characteristics, such as coordination atoms, steric and electronic effects, and chiral induction groups, which determine catalytic performances of the corresponding zinc complexes [72–74]. Achiral heteroscorpionate zwitterionic zinc complexes (**34**) bearing various initiating groups were reported by Cui and co-workers (Figure 10) [75]. For the ROP of *rac*-LA, the zinc benzyloxy complex showed higher activity than the corresponding amido complexes. In

comparison, the zinc alkyl complexes were relatively less active and the chloride analog was completely inert. Remarkably, the achiral zinc complexes exhibited moderate to high isoselectivity for the ROP of *rac*-LA (P_m up to 0.85), and the solvents used in the polymerization affected the stereoregularity of the PLA. A study of the mechanism and the polymer segment showed that the zinc complexes operated stereoselectively via a chain-end control mechanism to generate stereoblock or stereocomplex PLAs. A new enantiopure NNN-heteroscorpionate ligand was developed for the coordination of zinc complexes (**35** and **36**) [76]. Zinc alkyl complex **35** with a chiral substituent group was found to serve as a highly efficient single-component initiator to produce highly enriched isotactic PLAs (P_m up to 0.88) with low to moderate molecular weights, which were slightly higher than the isotacticity achieved by **36** [77]. According to the analysis of the microstructures of PLAs, an inspection of the tetrads resulting from stereoerrors suggested that an enantiomorphic site control mechanism was dominant. In addition, a system based on complex **36** and onium halide salts was found to produce five-membered cyclic carbonates from epoxides and CO_2 with high activity. Scorpionate zinc alkyl or chloride complexes (**37**) were synthesized via the alkyl elimination or transmetalation reaction of NNN-tridentate proligand or its corresponding lithium complex [78]. Zinc alkyl complex (**37a**) behaved as a single-component initiator for the living and immortal ROP of *rac*-LA under mild conditions. The resultant PLAs demonstrated excellent controllability for molecular weights and heteroselectivity (P_r values up to 0.74), which was different from zinc complexes **34** and **35** with other heteroscorpionate ligands [75,76]. Zinc complexes (**38**) supported by chiral tridentate bis(oxazolinylphenyl)amido ligands were synthesized by Wang and co-workers [79]. Asymmetric kinetic resolution polymerization was found in the ROP of *rac*-LA catalyzed by the chiral zinc complexes. The zinc complex with *S*-^{t}Bu groups preferentially initiated D-LA monomer polymerization, while the zinc complex with *R*-^{t}Bu groups preferentially initiated L-LA monomer polymerization. During the polymerization process, the selectivity factor of asymmetric kinetic resolution polymerization remained in the range of 3–5. Kinetic studies and block polymerizations revealed that the stereocontrol mechanism was probably the combination of chain-end control and enantiomorphic site control.

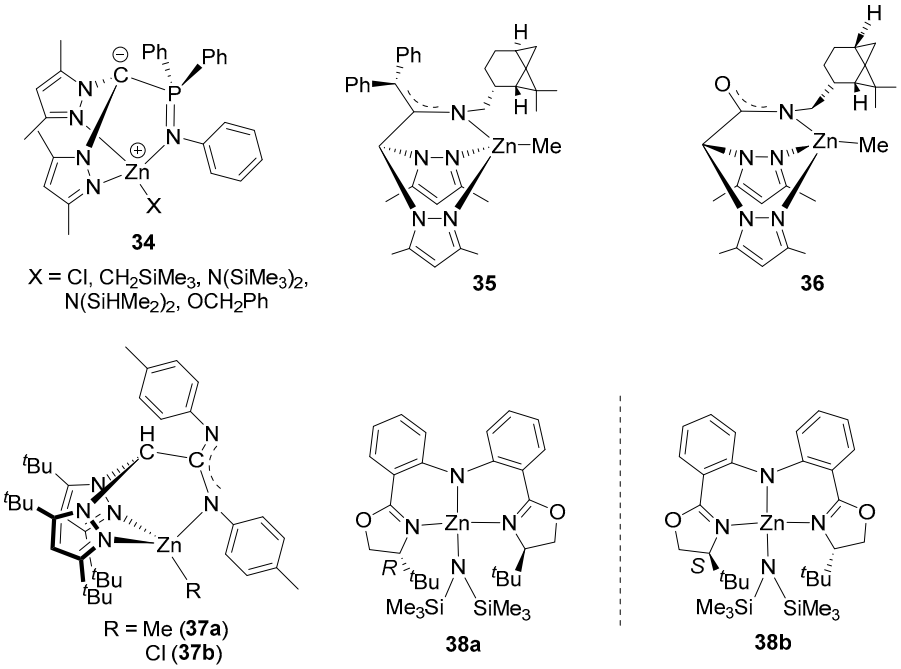

Figure 10. Zinc complexes with NNN-tridentate ligands for the stereoselective ROP of LA.

In comparison to the NNN-tridentate ligands, more NON- or NNO-tridentate ligands were employed to develop zinc complexes for stereoselective ROP. Zinc complexes with enantiopure bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands exhibited mononuclear (**39**) and symmetric binuclear (**40**) structures (Figure 11), both of which were found to initiate the ROP of *rac*-LA in a living mode to generate heterotactic-enriched PLAs with a P_r value of up to 0.77 at mild temperatures [80]. Bis(pyrazol-1-yl)methane-based NNO-donor scorpionate ligands without enantiopure substitutes were also used for complexation to zinc, from which, depending on feed ratios, mononuclear (**41**) and asymmetric binuclear (**42**) complexes were obtained [81]. Binuclear trialkyl complexes (**42**) acted as single-component initiators for the ROP of *rac*-LA with higher activities in comparison to the mononuclear alkyl complexes. Microstructural analysis revealed that the most sterically hindered ligand on the alkoxide fragment exerted a moderate influence on the degree of stereoselectivity, producing heterotactic-enriched PLAs (P_r = 0.68).

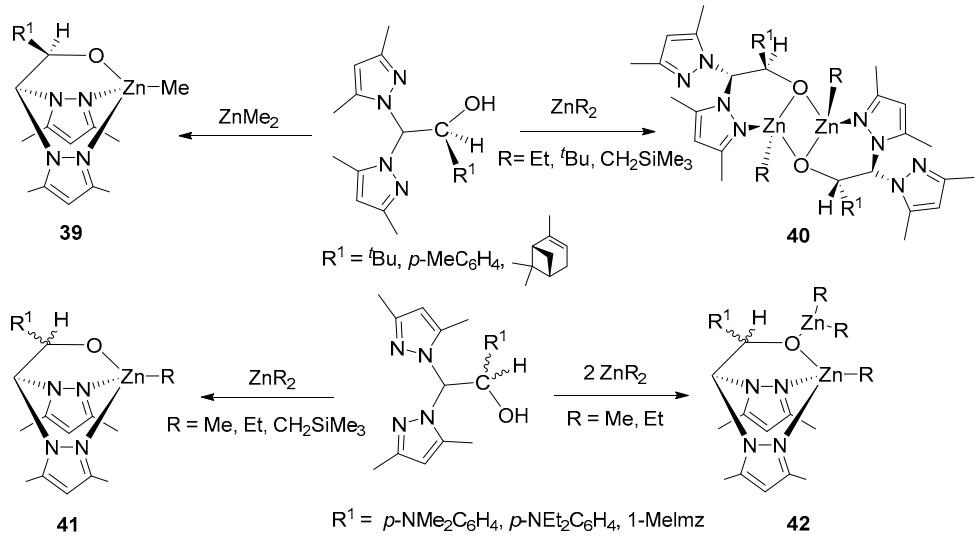

Figure 11. Synthetic routes of zinc complexes with NNO-donor scorpionate ligands.

Zinc complexes (**43**) supported by N,N,O-chelate ligands based on (dimethyl-pyrazol-1-yl)-pyridine were synthesized, which showed binuclear structures [82]. The zinc complexes were found to initiate ROP of CL and *rac*-LA with good molecular weight control and relatively narrow molecular weight distributions. The resultant PLA showed moderate heterotactic regularity with P_r up to 0.73 when polymerization was performed in THF at 0 °C. Zinc phenoxide complexes (**44**) with NNO-tridentate heteroatom-functionalized BDI ligands were developed for the ROP of LA, and it was found that the catalytic activity could be controlled by the electronic and steric properties of the phenoxide group (Figure 12) [83]. The resultant PLAs derived from the ROP of *rac*-LA exhibited an isotactic-enriched microstructure (P_m up to 0.70). In comparison, it was found that zinc alkoxyl complexes (**45**) coordinated by heteroatom-functionalized pyrazolonate-ketiminate ligands could act as single-component initiators for the ROP of *rac*-LA to produce heterotactic-enriched PLAs (P_r up to 0.85) with narrow PDIs [84]. Zn complexes with monophenol diaminocyclohexyl ligands were also developed for the ROP of *rac*-LA [85]. In comparison to the corresponding Al complexes, Zn complexes were found to be more active in generating slightly heterotactic PLAs (P_r up to 0.67). It was found that the monophenol ethylenediamine-based zinc complexes could be conveniently synthesized on a large scale [86]. These complexes were trialed for the ROP of LA under industrially relevant conditions, with high TOF values in excess of 100,000 h^{-1} achieved. Their reactivity has been related to their structure in solution and slightly heterotactic PLAs (P_r = 0.66) were produced. Zinc complexes (**46**) supported by phenoxy-imine ligands bearing nitrogen-containing second coordination

spheres were synthesized to initiate the ROP of *rac*-LA [87]. The *ortho*-substituent in the phenol moiety showed a significant influence on stereoselectivity. It was found that good stereoselectivity for the ROP of *rac*-LA could be achieved by a zinc complex with a bulky triphenylsilyl-substituted ligand to produce highly heterotactic PLAs (P_r = 0.90, at ambient temperature and P_r = 0.94, −30 °C).

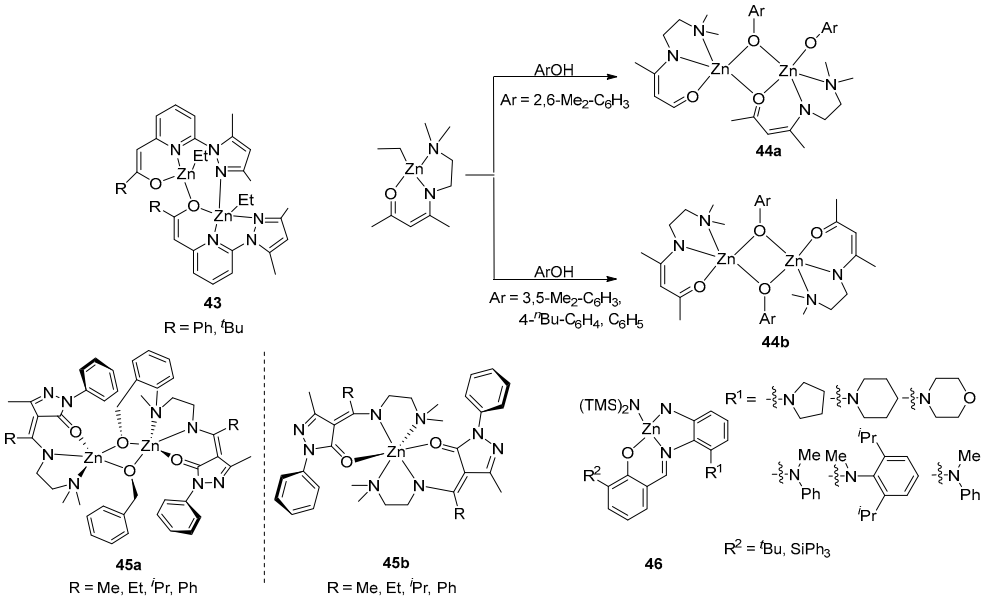

Figure 12. Zinc complexes with NNO-tridentate ligands for the stereoselective ROP of LA.

Zinc complexes (**47**) bearing chiral tridentate N-alkyltetrahydropyrrole-aminophenolate ligands were developed by Ma and co-workers, which were able to initiate the ROP of *rac*-LA with isotactic selectivity (P_m = 0.80) at room temperature (Figure 13) [88]. By investigating model complexes, active species, and polymerization mechanisms, stereoselectivity of the zinc system was proposed according to the cooperation of enantiomorphic site control and chain-end control mechanisms involving three types of active species to generate stereoblock PLAs. Interestingly, the catalytic performance of corresponding magnesium complexes toward *rac*-LA polymerization exhibited significantly different stereoselectivity (heterotactic, P_r = 0.81). Based on their study, Ma and co-workers further investigated the influence of the substituent groups on aminophenolate moiety and tetrahydropyrrole moiety, as well as coordination modes and types of nitrogen-containing moieties [89–93]. Remarkably, the aminophenolate ligands with oxazolinyl groups as nitrogen-containing moieties were able to coordinate zinc complexes (**48**), which showed high isotactic selectivity (P_m = 0.87 at 25 °C; P_m = 0.92 at −20 °C) for the ROP of *rac*-LA to obtain a stereocomplexed PLA [91,92]. Regardless of the presence of any chiral oxazolinyl group on the ligand, it was found that the zinc complexes could afford multiblock isotactic PLAs, which were proven to be formed via a chain-end control mechanism. It was also suggested that the dihedral angle between the phenoxy and oxazolinyl/benzoxazolyl planes in the zinc complexes had a close relation with the isotactic selectivity. A series of benzoimidazolyl-based aminophenolate zinc complexes (**49**) were synthesized and exhibited high activities and high isotactic selectivity (P_m = ca. 0.89) for the ROP of *rac*-LA at ambient temperature [94]. The mechanism and kinetic studies indicated the operation of a chain-end control mechanism. Recently, analog zinc chloride complexes (**50**) with benzoxazolyl-aminophenolate ligands were reported to display excellent activities and stabilities for the ROP of technical grade *rac*-LA [95]. Microstructure analysis of typical PLAs showed that these complexes afforded cyclic PLAs with high molecular weights and narrow to moderate distributions (M_n up to 58.0 kg/mol, PDI = 1.19–1.60), which

possessed high isotacticity (P_m = 0.87 at 25 °C; P_m = 0.93 at −45 °C) and stereoblock microstructures. Zinc complexes derived from *racemic* binaphthyl-based iminophenolate ligands were synthesized by the reaction of proligand and equimolar Zn[N(SiMe$_3$)$_2$]$_2$ [96]. Owing to the steric hindrance of phenol moiety in proligands, the zinc complexes displayed homoleptic and heteroleptic structures, respectively. A heteroleptic zinc silylamido complex (**51**) exhibited heterotactic selectivity for the ROP of *rac*-LA to afford heterotactic PLAs (P_r = 0.80–0.84) in both THF and toluene solvents. Kinetic studies revealed first-order kinetics in both monomer and catalyst concentrations. In addition, zinc complexes with *racemic* biphenyl- or binaphthyl-based aminophenolate ligands were also developed for the ROP of LA, which showed lower heteroleptic selectivity (P_r = 0.45–0.69) [97].

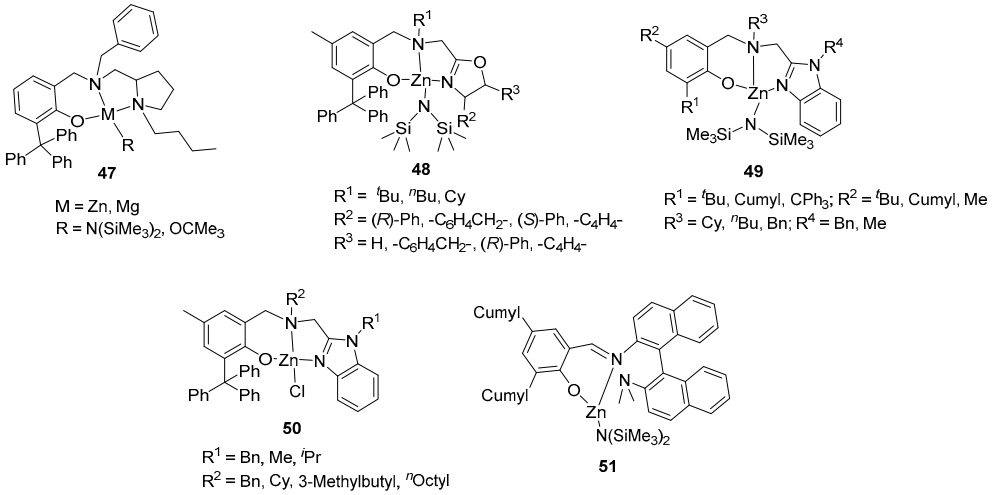

Figure 13. Zinc complexes with chiral NNO-tridentate ligands for the stereoselective ROP of LA.

A series of *racemic* and enantiopure zinc complexes (**52**) supported by substituted diaminophenolate ancillary ligands were developed, which served as excellent catalysts for the controlled living and immortal ROP of *rac*-BBL with high activity (TOF values up to 23,760 h^{-1}) (Figure 14) [98]. The steric hindrance of the ligand was able to influence the stereoselectivity of the zinc complexes. Syndio-rich PHBs with varied syndiotacticity (P_r = 0.57–0.75) and high molecular weight were obtained, which showed good thermal stabilities in the absence of any additives and excellent melt strength. It was found that the diaminophenolate zinc (**53a**) and BDI zinc (**5**) complexes could also catalyze the ROP of *racemic trans*-cyclohexene carbonate (*rac*-CHC) to obtain poly(cyclohexene carbonate) (PCHC) with a slight isotactic bias (P_m = ca. 66%) [99]. Furthermore, it was found that a purely isotactic PCHC could also be prepared via the ROP of enantiopure (*R*,*R*)-CHC, which showed a semicrystalline polycarbonate featuring a high T_g of 130 °C, a crystallization temperature T_c of 162 °C, and T_m of 248 °C. Furthermore, a diaminophenolate zinc isopropoxide complex (**53b**) and a bis(pyrazol-1-yl)-methane-based heteroscorpionate zinc complex (**54a**) were employed for the ROP of 2,3-dimethyl-*β*-propiolactone (DMPL) by Coates and co-workers (Figure 15) [100]. Complex **54a** gave syndiotactic selectivity (P_r = 0.75) for the ROP of *racemic*-DMPL; in comparison, complex **53b** showed slightly lower syndiotactic selectivity (P_r = 0.63). The higher syndiotactic selectivity of complex **54a** might be attributed to the presence of a C_s symmetrical bispyrazole-phenoxide ligand backbone. The resultant *cis*-poly(3-hydroxy-2-methylbutyrates) (*cis*-PHMBs) with syndiotacticity and high T_m (ca. 180–190 °C) exhibited brittleness and strain at break not exceeding 20%. Remarkably, it was found that the toughness of the resultant polymer could be improved by copolymerization of *cis*- and *trans*-DMPL to generate the PHMBs, which showed properties similar to those of polyolefin by tailoring the *cis*/*trans* ratio of the repeating units. Interestingly, with increasing the steric hindrance to phenyl at the C3 position

of pyrazole moiety, it was found that bis(pyrazol-1-yl)-methane-ligated zinc complex **54b** could produce isotactic *cis*-PHMBs (P_m = 0.82) by the ROP of *racemic cis*-DMPL, and the polymer had a high melting point and nearly identical crystal structures [101].

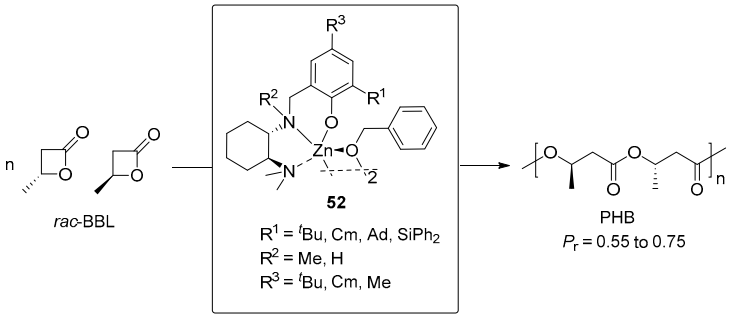

Figure 14. Zinc complexes with chiral NNO-tridentate ligands for the stereoselective ROP of BBL.

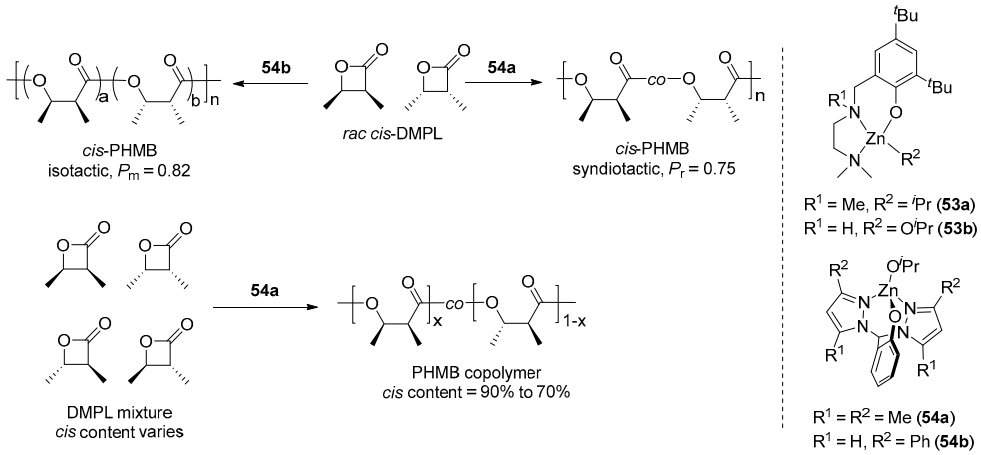

Figure 15. Zinc complexes with NNO-tridentate ligands for the ROP of DMPL [100,101].

For the application of ONO-tridentate ligands, the zinc methyl complexes with a side-arm-modified ketoimine ligand, phenoxide-ketoiminate, were synthesized and showed dimeric structures. It was found that the dimeric methylzinc complexes could initiate the ROP of *rac*-LA, either in the solution state or under melt conditions, to produce a PLA with predominate heterotactic regularity (P_r = 0.53–0.59) and molecular weights (M_n) of up to 100 kg/mol [102]. The bulky *ortho*-Ph_3Si-substituted naphthol-pyridine proligands were reported in the coordination of zinc, aluminum, and group III metal center (Sc, Y, and La) complexes [103]. Zinc complexes with the less bulky ligands exhibited higher activity than the corresponding complexes with bulky ligands. Complexes **55a** and **55b** showed catalytic performance in the ROP of *rac*-BBL (Figure 16). The resultant polymers all had slightly heterotactic-enriched microstructures (P_r = 0.65–0.76). Aminobisphenolate-ligated zinc complexes (**56**) with one molecular coordinated 3-fluoropyridine were developed by Wu and co-workers, in which the central zinc served as a weak Lewis acid and 3-fluoropyridine served as a weak Lewis base [104]. For the ROP of *rac*-OCA derived from mandelic acid, a highly isotactic selectivity was observed by using the weak Lewis pairs of zinc complexes and the 3-fluoropyridine system to generate an isotactic poly(mandelic acid) with the highest P_m value of 0.92, and no obvious epimerization was observed in the polymerization progress. The analysis of the microstructure of the polymer showed that the statistics model was suitable for a chain-end control stereoselective mechanism. Based on this work, OOO-tridentate bis(phenolate) zinc complexes (**57**) were also developed for the ROP of *rac*-OCA derived from mandelic acid with a living mode [105]. The side reaction of racemization was efficiently suppressed by decreasing the basicity of the ligands in zinc complexes, so

the resultant poly(mandelic acid) exhibited high stereoregularity. Furthermore, owing to the living polymerization feature, stereodiblock and stereotriblock copolymers with controllable molecular weights were obtained upon sequential one-pot monomer addition. The stereoblock copolymers exhibited a rapid crystallization behavior and excellent thermal properties (T_m up to 178 °C and T_c up to 120 °C). Mononuclear, dinuclear, and tetranuclear zinc complexes with ONO-tridentate ligands were synthesized via the reaction of proligands with $ZnCl_2$ and $ZnEt_2$, respectively [106]. All the Zn(II) complexes showed high catalytic activities in the ROP of *rac*-LA to produce PLAs with moderate molecular weights (ca. 40 kg/mol) and relatively narrow dispersities (PDI = 1.4–2.1). But, almost atactic regularity (P_r = 0.51–0.58) was observed for the resultant PLAs.

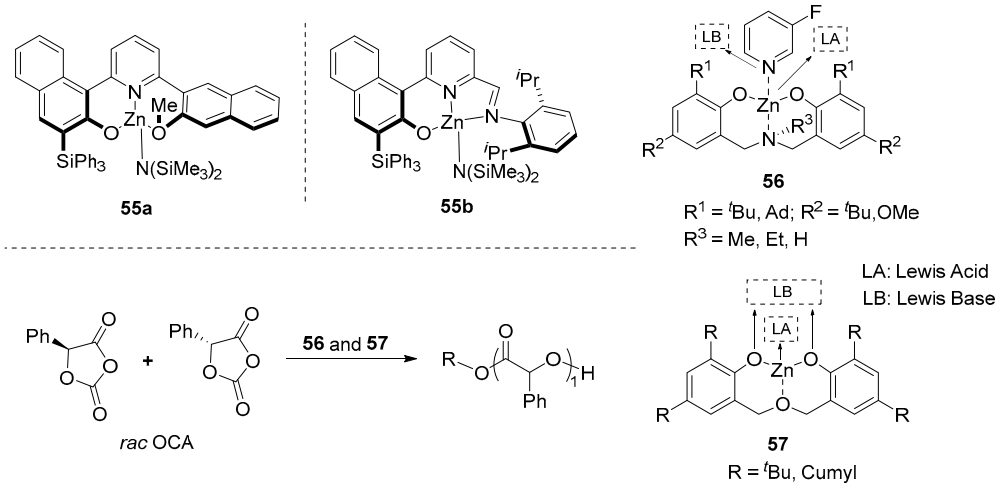

Figure 16. Zinc complexes with ONO- and OOO-tridentate ligands for stereoselective ROP.

ONS-tridentate ligands and thioether pendant iminophenolate ligands were applied for the coordination of zinc ion [107]. The zinc complexes (**58**) showed high activity and slight heterotactic selectivity for the ROP of *rac*-LA with TOF values up to 250,000 h^{-1} at 180 °C in bulk (Figure 17). In addition, the complexes also possessed the capacity to depolymerize PLA and poly(ethylene terephthalate) (PET) into small molecules under mild conditions. Homoleptic (**59a**) and heteroleptic (**59b**) zinc complexes with thiophene-modified ONS-tridentate ligands showed distinct stereoselectivity in the ROP of *rac*-LA due to their different coordination configurations [108]. Zinc complexes (**59a**) with two ligands showed a distorted square-planar configuration, resulting in a heterotactic-enriched PLA (P_r = 0.67). While zinc chloride complexes (**59b**) with single ligands showed a tetrahedral configuration, producing an isotactic-enriched PLA (P_m = 0.78). Zinc complexes were also active for the ROCOP of CO_2 with CHO and propylene oxide (PO) with tetraphenylphosphonium chloride (TPPCl) as a co-catalyst.

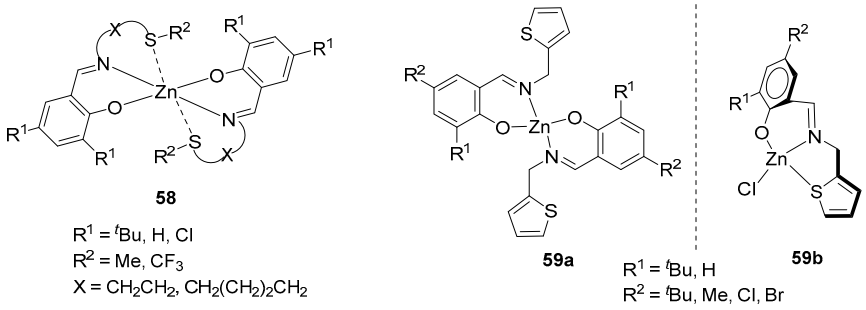

Figure 17. Zinc complexes with ONS-tridentate ligands for stereoselective ROP and ROCOP.

Table 2. Summary of the stereoselectivity of zinc complexes containing tridentate ligands.

Run	Complex	M [1]	[M]:[C] [2]	T (°C)	Time (h)	Conv. (%)	M_n (kg/mol)	PDI	Tacticity	Ref.
1	**34**	*rac*-LA	200:1	30	8	96	5.10	1.37	P_m = 0.85	[75]
2	**35**	*rac*-LA	100:1	50	2.5	37	4.90	1.07	P_m = 0.88	[76]
3	**37a**	*rac*-LA	100:1	50	3.75	95	13	1.13	P_r = 0.74	[78]
4	**40**	*rac*-LA	100:1	50	3.5	73	10.60	1.08	P_r = 0.77	[80]
5	**41**	*rac*-LA	100:1	0	24	37	6.10	1.12	P_r = 0.68	[81]
6	**43**	*rac*-LA	200:1	0	24	58	8.10	1.02	P_r = 0.73	[82]
7	**44a**	*rac*-LA	200:1	25	0.031	93	32	1.4	P_m = 0.70	[83]
8	**45a**	*rac*-LA	100:1	30	12	90	5.10	1.10	P_r = 0.85	[84]
19	**46**	*rac*-LA	200:1	−30	96	33	7.10	1.17	P_r = 0.94	[87]
10	**47**	*rac*-LA	200:1	25	3	84	29.50	1.66	P_m = 0.80	[88]
11	**48**	*rac*-LA	200:1	−20	1.5	88	20.90	1.06	P_m = 0.92	[91]
12	**49**	*rac*-LA	200:1	25	0.93	90	48.40	1.32	P_m = 0.89	[94]
13	**50**	*rac*-LA	200:1	−45	336	96	7.60	1.15	P_m = 0.93	[95]
14	**51**	*rac*-LA	200:1	25	1.5	86	71.60	1.46	P_r = 0.84	[96]
15	**52**	*rac*-BBL	400:1	−30	16	75	21.20	1.34	P_r = 0.75	[98]
16	**53a**	*rac*-CHO	100:1	60	3	91	11.40	1.33	P_m = *ca*.66%	[99]
17	**53b**	*cis*-DMPL	2650:1	25	24	90	202	1.03	P_r = 0.63	[100]
18	**54a**	*cis*-DMPL	2500:1	25	24	92	471	1.06	P_r = 0.75	[100]
19	**54b**	*cis*-DMPL	820:1	50	48	83	62.50	1.09	P_m = 0.82	[101]
20	**55a**	*rac*-LA	500:1	25	0.66	57	40.10	1.88	P_r = 0.76	[103]
21	**56**	*rac*-OCA	50:1	−50	9.5	79	5.30	1.12	P_m = 0.92	[104]
22	**58**	*rac*-LA	10,000:1	180	0.033	83	31.35	1.53	P_m = 0.57	[107]
23	**59a**	*rac*-LA	200:1	70	10	99	30.89	1.20	P_r = 0.67	[108]
24	**59b**	*rac*-LA	200:1	70	18	99	29.98	1.18	P_m = 0.78	[108]

[1] M indicates monomer. [2] [M]:[C] indicates the ratio of monomer and catalyst.

4. Zinc Complexes Containing Tetradentate Ligands and Others

This section reviews the catalytic performance of zinc complexes containing tetradentate and other ligands in stereoselective ROP and ROCOP, which mainly include NNNN-, NNNO-tridentate ligands, and other monodentate or multidentate ligands. A summary of the stereoselectivity of zinc complexes containing tetradentate ligands and others, along with other relevant parameters in respective categories such as the feed ratio, polymerization time, polymerization temperature, conversion, and molecular weight distribution, is presented in Table 3. Based on NNO-tridentate zinc diaminophenolate complexes [109], pyridine moiety was introduced into the ligand design as a side arm group to obtain the NNNO-tetradentate ligands [110]. The corresponding zinc complexes (**60**) were synthesized via the treatment of proligands with $ZnEt_2$, which were shown to produce PLAs with isotactic regularity (P_m = 0.72–0.78) and narrow, low dispersities (PDI = 1.06–1.17) (Figure 18). Interestingly, the electronic effects of ligand substituents were not significant in these zinc complexes (Hammett ρ = +0.3), as evidenced by the similar catalytic activity and isotactic selectivity exhibited by the zinc complexes with different substituents. Mononuclear zinc complexes (**61**) with chiral tetra-azane ligands were synthesized and employed as efficient initiators for the ROP of *rac*-LA to provide PLAs with controllable molecular weights and moderate heterotacticity up to P_r = 0.77 [111]. The substituents on the ligands had an impact on the activities and selectivities of these complexes. N-heterocyclic carbene-based zinc complexes (**62**) were synthesized and shown to be active for the ROP of *rac*-LA [112]. The molecular weights of the resultant PLAs depended on the co-catalysts, and microstructural analysis revealed slightly enriched heterotactic PLAs with P_r values up to 0.66.

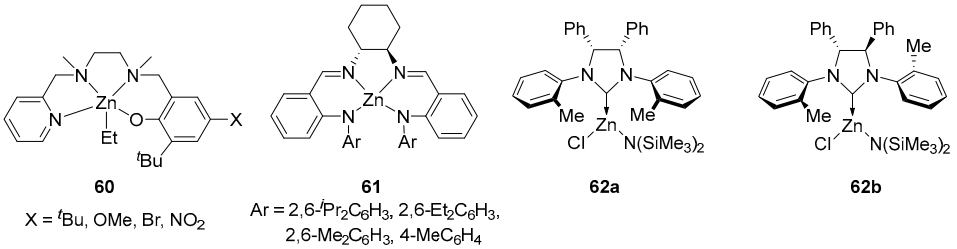

Figure 18. Zinc complexes with tetradentate and N-heterocyclic carbene ligands for the stereoselective ROP of LA.

Binuclear zinc alkoxide complexes (**63**) with a bis-salalen multidentate ligand were synthesized and developed for the ROP of *rac*-LA, affording partially isotactic PLAs (P_m value of 0.59) with narrow polydispersities and desirable molecular weights (Figure 19) [113]. Interestingly, the polymerization mechanism showed a coordination–insertion mechanism at a high temperature of 130 °C and an "activated monomer" mechanism at a low temperature. A dinuclear zinc complex (**64**) supported by bis(iminopyrrolide) ligand was synthesized and showed good control over the molecular weights for the ROP of *rac*-LA, generating PLAs with moderate heterotactic regularity (P_r up to 0.7) [114]. Zinc bimetallic complexes (**65**) supported by hexadentate ligands bearing imine and pyridine nitrogen neutral donors with a binaphthol backbone were synthesized by direct reaction of the enantiomerically pure and *racemic* ligands with two equivalents of zinc amide precursor [115]. Both complexes were highly active in the ROP of LA under several reaction conditions, even for a technical grade melted LA monomer. All the resultant PLAs showed isotactic-enriched microstructures with P_m up to 0.72. However, similar stereoselectivity probably indicated that the chirality of the binaphthol backbone lacked influence on stereoselectivity. An alkoxide-bridged zinc complex (**66**) supported by a chiral bis(diamino)-phenolate ligand platform showed higher selectivity (P_r = 0.64) but lower activity as a catalyst for the ROP of *rac*-LA [116] in comparison to analogous dinucleating zinc complexes with achiral ethylenediamine skeletons [109,117]. Owing to the lesser influence of the chirality of the complexes on stereoselectivity, a chain-end control mechanism was postulated for the complex **66** system. Zinc alkyl, alkoxide, acetate, and amide complexes containing imine- and amine-based dinucleating ligands bearing a bisphenol backbone were synthesized [118]. The amine-based complexes were more reactive than the imine-based analogs, such as the higher activity of **67** than that of **68**. Furthermore, complex **67** also showed more activity than dinucleating alkoxy zinc complex **66**. Heterotactic-enriched PLAs with P_r values of 0.67 were generated by complex **68**. It was found that the binuclear zinc alkyl complex (**69**) activated by benzyl alcohol could initiate the ROP of *rac*-LA to produce PLAs with relatively narrow molecular weight distributions (PDI $\leq$ 1.23) and heterotactic-enriched microstructures (P_r up to 0.67) [119]. Zinc/rare-earth heterometallic complexes (**70**) containing both alkoxy-amino-bis(phenolato) and chiral salen ligands were synthesized from the reactions of alkoxy-amino-bis(phenolato) rare-earth complexes with chiral salen zinc complexes via ligand redistribution and THF disassociation [120]. The zinc/samarium and zinc/dysprosium heterometallic complexes were highly efficient catalysts for the copolymerization of CO_2 with CHO. In comparison, the individual corresponding samarium and zinc complex exhibited low activity or was inert. However, the resultant polycarbonates were atactic according to the analysis of ^{13}C NMR spectra. Furthermore, a heteronuclear zinc/yttrium complex (**71**) was developed in which it was found that the BDI zinc moiety could initiate the ROCOP of CO_2 and CHO and the yttrium metallocene catalyzed the rare-earth metal-mediated group-transfer polymerization of the polar vinyl monomers [121]. Regarding the ROCOP by dinuclear zinc complexes, Williams and co-workers have made great achievements. For example, a chemoselective control mechanism was developed

based on a binuclear zinc complex, which was found to induce both the ROP of lactones and the ROCOP of epoxides and CO_2 by the addition of exogenous switch reagents [122]. The mixture of CL, CHO, and CO_2 allowed the selective preparation of either polyesters, polycarbonates, or copoly(ester-carbonates) by this method. Other important research works have recently been well reviewed by Williams and her co-workers [123,124]. In relation to the design of catalysts, the relationship between the structure and performance of catalysts, and the properties of polymers, readers can refer to the aforementioned reviews.

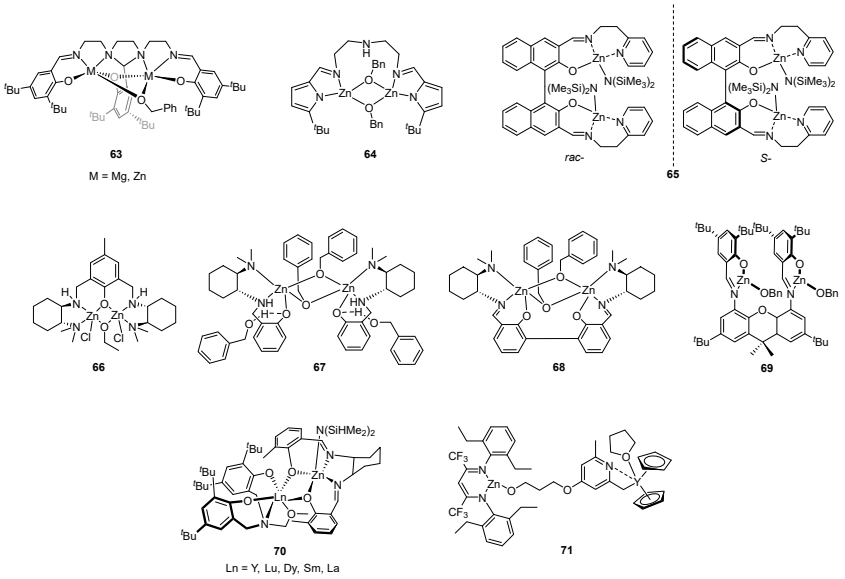

Figure 19. Zinc complexes featuring homometallic and heterometallic dinuclear structures.

Inspired by the coordination catalysis of OCAs by BDI-based zinc complexes, Tong and co-workers developed a ternary catalytic system that combined photoredox Ni/Ir catalysis with the use of $Zn[N(SiMe_3)_2]_2$ for the ROP of OCAs [125]. The isotactic polyesters with expected molecular weights (>140 kg/mol) and narrow molecular weight distributions (PDI < 1.1) were produced by the ROP of enantiopure OCA monomers. Instead of $Zn[N(SiMe_3)_2]_2$, the ternary catalytic system composed of photoredox Ni/Ir complexes and zinc complexes (**72**) with NNO-aminophenolate-based ligands was able to synthesize stereoblock polyesters by the stereoselective ROP of *racemic* OCAs (Figure 20) [126]. The stereoblock copolymers are highly isotactic with high molecular weights (>70 kg/mol) and narrow molecular weight distributions (PDI < 1.1). A chain-end control mechanism was postulated for the stereoselective polymerization of *racemic* OCAs by this system. In addition, the visible-light photoredox catalytic systems derived from manganese or cobalt compounds with a zinc complex were also developed for the ROP of OCAs [127–129].

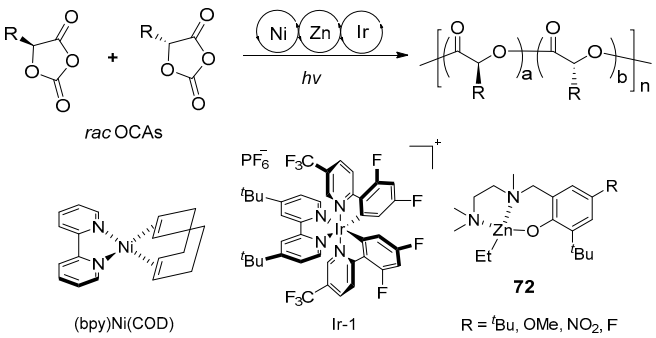

Figure 20. Ternary catalytic system with a zinc complex for the stereoselective ROP of OCAs via visible-light photoredox catalysis [126].

Table 3. Summary of the stereoselectivity of zinc complexes containing tetradentate ligands and others.

Run	Complex	M [1]	[M]:[C] [2]	T (°C)	Time (h)	Conv. (%)	M_n (kg/mol)	PDI	Tacticity	Ref.
1	**60**	*rac*-LA	300:1	25	0.5	>95	35.50	1.15	P_m = 0.78	[110]
2	**61**	*rac*-LA	100:1	0	24	94	13.10	1.11	P_r = 0.77	[111]
3	**62b**	*rac*-LA	100:1	25	1.2	95	35.874	1.35	P_r = 0.66	[112]
4	**63**	*rac*-LA	100:1	80	12	97	6.90	1.09	P_m = 0.59	[113]
5	**64**	*rac*-LA	200:1	35	24	55	0.55	1.18	P_r = 0.70	[114]
6	**65**	*rac*-LA	200:1	25	1.5	75	37.70	1.76	P_m = 0.72	[115]
7	**66**	*rac*-LA	200:1	25	120	95	24.29	1.04	P_r = 0.64	[116]
8	**68**	*rac*-LA	600:1	25	24	95	22.37	1.10	P_r = 0.67	[117]
9	**69**	*rac*-LA	600:1	25	24	86	23.43	1.23	P_r = 0.67	[118]
10	**72**	*rac*-OCA	150:1	−15	4	100	45.70	1.06	P_m = 0.97	[126]

[1] M indicates monomer. [2] [M]:[C] indicates the ratio of monomer and catalyst.

5. Conclusions

In summary, after devoting considerable efforts to the development of zinc complexes for ROP and ROCOP, the design and optimization of the coordination mode, as well as the steric and electronic effects of the ligands, have been regarded as the most effective approaches to achieve good stereoselectivity and even enable a switch in stereoselectivity. Most zinc complexes applied in the ROP of lactones generate heterotactic or heterotactic-enriched polymers, which usually follow a chain-end control mechanism. Generally speaking, tridentate or multidentate ligands with more coordination sites can effectively coordinate and regulate the stereochemical environment around the central zinc ion, which is beneficial to improving the stereoselectivity of the complex. Moreover, introducing chiral groups or increasing steric hindrance in the complex is also conducive to enhancing its stereoselectivity. It is worth noting that although some catalytic systems follow the enantiomorphic site control mechanism, due to the presence of transesterifications during the ROP of lactones, their stereoselectivity usually accounts for both enantiomorphic site control and chain-end control. Furthermore, through the use of well-designed and precisely controlled zinc catalytic systems, polymers with unique microstructures have been synthesized via ROP and/or ROCOP reactions, which exhibited special thermal and mechanical properties. Given the achievements in the past, it is reasonable to anticipate that the development of zinc complexes with diverse bidentate and multidentate ligands in stereoselective polymerization is bound to thrive.

Author Contributions: Conceptualization, Y.P. and Y.L.; resources, X.L.; data curation, X.L. writing—original draft preparation, Y.P. and X.L.; writing—review and editing, Y.P., X.L. and Y.-M.S.; supervision, Y.P., Y.L. and G.Z.; funding acquisition, G.Z. and Y.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China, grant number 2021YFB3801901; the Taishan Scholars Project of Shandong Province, grant number tsqnz20230611; and the National Natural Science Foundation of China, grant number 21971029.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: We gratefully acknowledge Kaitao Zhang for his assistance and contributions to discussions.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

ROP	Ring-opening polymerization
ROCOP	Ring-opening copolymerization
BDI	β-diketiminate
LA	Lactide
PLA	Polylactide
ε-CL	ε-caprolactone
PCL	Polycaprolactone
rac	*Racemic*
PHB	Poly(3-hydroxybutyrate)
CHO	Cyclohexene oxide
BBL	β-butyrolactone
OCA	*O*-carboxyanhydride
TMP	1,5,9-trimesityldipyrromethene
CHC	Cyclohexene carbonate
PCHC	Poly(cyclohexene carbonate)
DMPL	2,3-dimethyl-β-propiolactone
PHMB	Poly(3-hydroxy-2-methylbutyrate)
PET	Poly(ethylene terephthalate)
PO	Propylene oxide
TPPCl	Tetraphenylphosphonium chloride

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