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Ring-Opening Polymerization of Lactide by Aluminium Catalyst

Anita Routaray[a], Nibedita Nath[a], Tungabidya Maharana[b*], Alekha Kumar Sutar[a#]

[a]*Catalysis Research Lab, Department of Chemistry, Ravenshaw University, Cuttack-3, Odisha, India*

[b]*Department of Chemistry, National Institute of Technology, Raipur, India*

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* Corresponding author: Dr. T Maharana; Tel-+91-771-2254200; Fax: +91-771-2254600; E-mail: mtungabidya@gmail.com

#Corresponding author: Dr. AK Sutar; Tel - +91-671-2610060; Fax: +91-671-2610304; E-mail: dralekhasutar@gmail.com

Abstract

This review summarizes recent developments in the preparation and use of aluminium catalysts/initiators such as, monometallic aluminium and bimetallic aluminium compounds for the ring opening polymerization of lactide (*L*-lactide and *rac*-lactide). The organoaluminium catalysts/initiators have been synthesized and characterized by different spectroscopic techniques, including X-ray crystal structural studies and NMR data. Lactide polymerization has been analyzed by NMR and GPC methods. The present paper emphasizes on the polymerization kinetics and the control exhibited by the different types of aluminium initiators/catalysts. For the cases, where useful properties, such as high molecular weight, narrow PDI, or stereocontrol, have been observed, a more detailed examination of the catalysts/initiators are provided.

Keywords

Ring-opening polymerization, aluminium catalyst, poly(lacticacid), stereoselective, polydispersity index, living polymerization

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Abbreviation

Nuclear Magnetic Resonance	NMR
Polydispersity Index	PDI
Ring Opening Polymerization	ROP
Polylactic Acid	PLA
Lactide	LA
Turn Over Number	TON
Weight Average Molecular Weight	M_w
Food and Drug Administration	FDA
Poly(hydroxyl alkanoates)	PHAs
poly(ethyele glycol)	PEG
poly(ε- caprolactone)	PCL
poly(ethylene terephthalate)	PET
poly-L-lactic acid	PLLA
Racemic Lactide	*rac*-LA
Oak Ridge Thermal Ellipsoid Plot	ORTEP
Number Average Molecular Weight	M_n

1. Introduction

Since the beginning of concept of macromolecular chemistry, it has been the constant challenge for polymer scientists to search and find new polymeric systems that may lead to the polymers with accurately prepared architectures (controlled molecular weights) and promising properties. Common practice of organic polymer chemists is to adapt the known organic

reactions in such a way that compounds of low molecular weights are converted to polymers of high molecular weights. However, the same approach has been taken in living polymerization, which was first discovered by Szwarc[1-3] and thenafter, Matyjaszewski developed the controlled cationic[4] and radical[5] vinyl polymerizations which was similar to the living polymerizations. Similarly, a number of coordination[6] and metathesis[7] polymerizations, as well as ring opening polymerizations (ROPs) were found to operate in the living polymerization manner. A wide variety of cyclic organic compounds have been investigated, which can be polymerized via ring-opening to achieve the polymers of novel archtitecture. The ROP of cyclic compounds can be a useful method to prepare new polymers, especially microstructure controlled copolymers that are otherwise difficult to achieve by conventional polymerization methods. Thus, the ROP of LA has received renewed attentions in recent years. Many polymer chemists have polymerized LA by using different metal complexes (transition and lanthanide) as catalysts/initiators by different bi-dentate, tri-dentate and tetra-dentate ligands. But group III metal catalysts especially aluminium, was of current interest relative to transition metal coordination networks for ROP. This is true that there are many aluminium compounds of commercial importance. ROP has been reviewed in the past in a few articles and book chapters[8–12]. The present review differs in content and in style from our previous reviews[8, 12] and also from all other previous reviews on ROP. Moreover, the present review is devoted exclusively to ROP of lactide by aluminium catalysts/initiators.

2. Scope

The advances in ROP can be attributed to tremendous efforts by a large number of researchers dedicated for the development of well-defined, functional group tolerant catalysts amenable to ROP. Early catalytic systems were often heterogeneous mixtures and were extremely sensitive to air and moisture, difficult to characterize, and almost impossible to study

systematically and optimize their effect on the reaction. The development of a catalyst with a well-defined structure was essential for ROP to reach its full potential. This was especially true for the progress of living ROP catalysts where knowledge and precise control over polymerization kinetics is critical. It is beyond the scope of this review to give an in-depth study of all the catalysts used in this process, however, this review is concerned with the design of various types of aluminium catalysts/initiators (monometallic alminium and bimetallic alminium catalysts/initiators) and their applications for the ROP of LA for the period of 2005-2014.

The aim of this review is to provide the reader with an appreciation for the origin and progression of this field to insight into how challenges in the future may be addressed. This review describes the essential features of aluminium catalysts and polymers derived from LA rather than to provide a comprehensive list. However, the reader should be able to access a selection from the references given. The aluminium catalysts are categorized on the basis of functional groups attached to it. Consequently, the review begins with a brief description of ROP and poly lactic acid (PLA) and ends with suggestions and concluding remarks. It has also been observed from the literature that the following parameters affect the process of polymerization directly or indirectly: amount of monomer, amount of catalyst, amount of co-catalyst, reaction time, reaction temperature, reaction pressure, rate of reaction and type of aluminium catalysts. However, this review deals mainly with the structures and preparations of the aluminium catalysts for ROP of LA, and descriptions of some of the interesting chemistry using the above parameters and the mechanism of polymerization based on literature review.

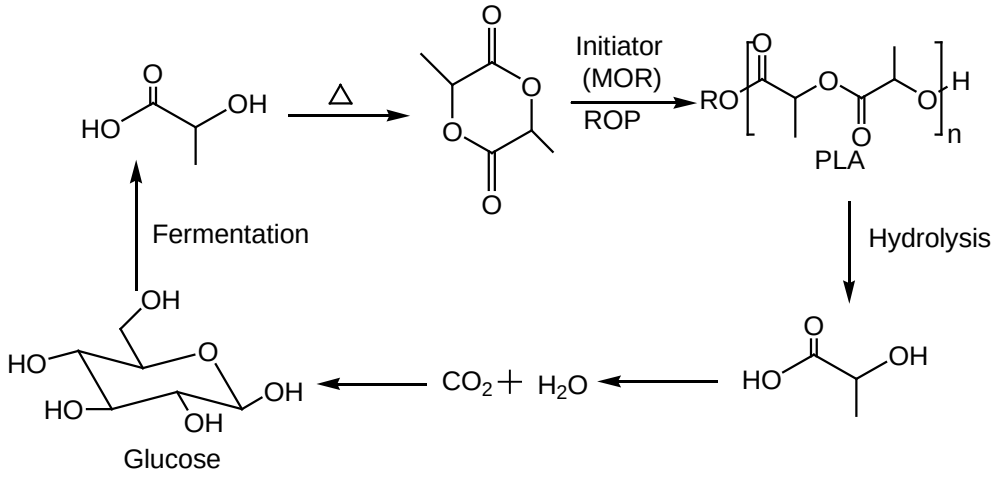
3. Polylactic acid (PLA)

Recently, interest in the synthesis of polymers with well-defined structure and macromolecular architecture has increased substantially.[13] Polymers with unique structures, such as block[14-15], graft[16-17], star[18-19], gradient[20], hyper-branched[21], and comb[22-23] structures, have found applications in colloids stabilization, crystal growth modification, induced micelle formation, and intelligent drug carrier systems.[12, 13] Polymers with unique architectures, such as star polymers, palm-tree-shaped polymers, dumbbell-shaped polymers, and dendritic polymers, were synthesized by conventional radical polymerizations, cationic and anionic polymerizations, ring-opening polymerization, and coordination polymerization.[12] In 1893, Bischoff and Walden published PLA development initiated with the LA and Carothers and coworkers produced low molecular weight PLA in 1932. In 1954, E.I. DuPont de Nemours and Ethicon, Inc. began marketing PLA for medical applications. Shimadzu Corporation and Kanebo Gohsen Ltd., Japan produced PLA fibers by melt spinning in the laboratory in 1992. The commercial production of PLA started by Fiberweb France S.A. under the trade name Deposa in 1997 and in the year 2002 by NatureWorks, USA, which is an independent company invested in by Cargill and PTT Global Chemical[24-25]. The advantages of PLA include, (1) Eco-friendly - as it is derived from renewable resources (e.g., corn, wheat, or rice), and is biodegradable, recyclable, and compostable[26-27] and also production of PLA consumes carbon dioxide.[28] (2) Biocompatibility - PLA has great application in biomedical field as it doesn't produce toxic or carcinogenic effects in local tissues. Further, its degradation products don't interfere with tissue healing.[29-30]. The Food and Drug Administration (FDA) has also approved PLA for direct contacting with biological fluids.[25] (3) Processability - PLA can be processed by injection molding, film extrusion, blow molding, thermoforming, fiber spinning, and film forming and it has better thermal processability as

compared to other biopolymers such as poly(hydroxyl alkanoates) (PHAs), poly(ethyele glycol) (PEG), poly(ε- caprolactone) (PCL), etc.[31] (4) Energy savings - During the production of PLA less energy 25–55% is required than other petroleum-based polymers.[32]

The disadvantages of PLA include, (1) Poor toughness - PLA is a very brittle material[33-34] but its tensile strength and elastic modulus are comparable to poly (ethylene terephthalate) (PET).[31] Poor toughness limits its use in the applications that need plastic deformation at higher stress levels (e.g., screws and fracture fixation plates).[35] (2) Slow degradation rate - the degradation rate of PLA depends on crystallinity, molecular weight, molecular weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content.[36-37] There have been reports of a second surgery almost 3 years after implantation to remove a PLA-based implant.[38-39] (3) Hydrophobicity - PLA is relatively hydrophobic which results in low cell affinity, and can elicit an inflammatory response from the living host upon direct contact with biological fluids.[40-41] (4) Lack of reactive side-chain groups - PLA is chemically inert with no reactive side-chain groups making its surface and bulk modifications a challenging task.

The poly-*L*-lactic acid (PLLA) is extensively used in biomedical and pharmaceutical applications, especially in tissue engineering and drug delivery. PLLA has attracted immense interest because of its favorable properties such as good biocompatibility, biodegradability, and mechanical strength. PLLA has been used to build three-dimensional scaffold for the regeneration of tissue engineered organs and has gained the approval of U.S. Food and Drug Administration (FDA) for a variety of human clinical applications.[42]



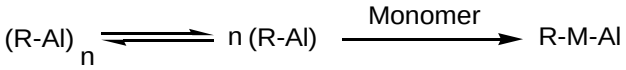
Scheme 1 Synthesis of PLA

Commercially available PLA is generally obtained in bulk via glucose fermentation (Scheme 1).[12] There has been particular emphasis over the past decade on the synthesis of discrete, well-defined complexes that function as active polymerization initiators.[43]

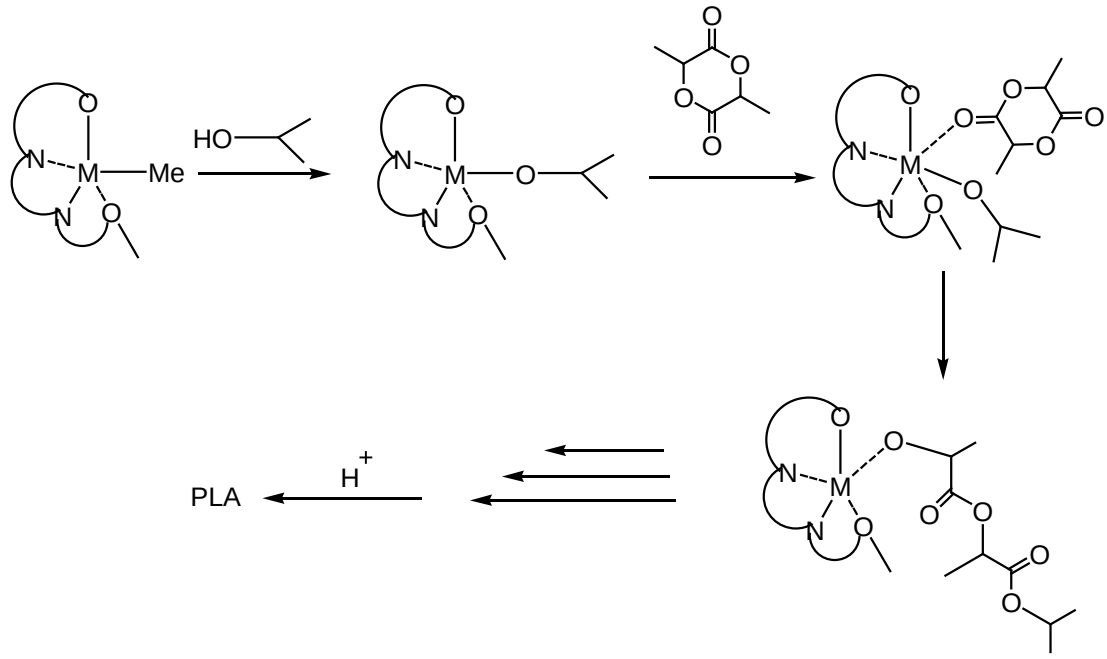
4. Ring Opening Polymerization (ROP)

ROP is a technique to transform stepwise reactions into chain polymerization reactions. By this method, it is possible to control the chemistry of polymerization accurately. The aggregation of organoaluminium (Scheme 2) and thus, the properties, such as molecular weight, molecular weight distribution and architecture of the resulting polymer, can be varied to suit the application. ROP also provides the possibility to achieve desired end groups and copolymerization of various monomers, depending upon the type of catalyst.[44] Generally, ROP has been carried out by solution polymerization, bulk polymerization, melt polymerization and suspension polymerization.[8] The mechanism of polymerization involved (i.e coordination-insertion mechanism or via activated monomer mechanism) in ROP can be ionic-, coordination-

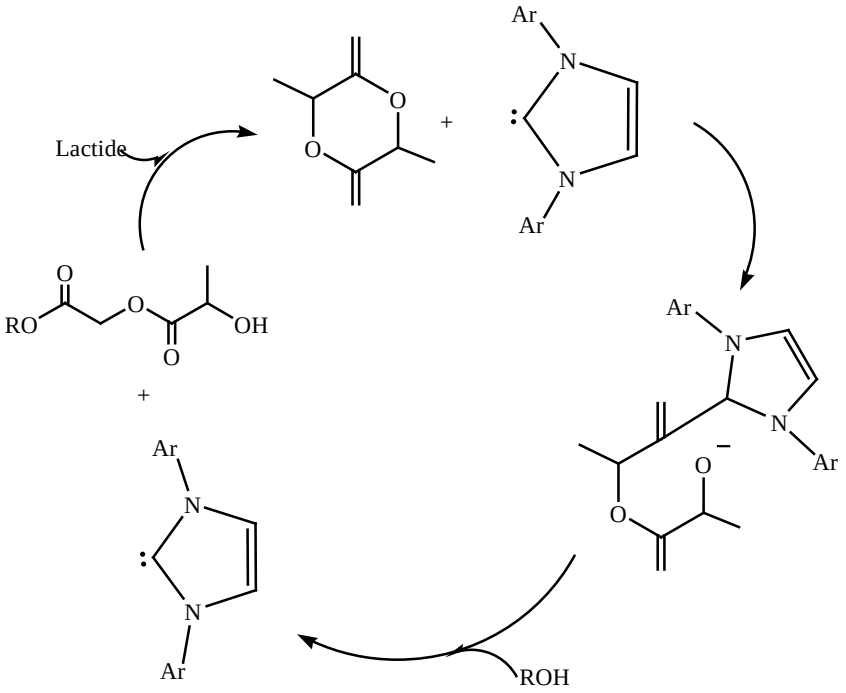
or free radical-type depending on the catalyst used.[12] For example, the block and graft copolymers are obtained mainly by ionic initiators.



Scheme 2 Aggregation of organoaluminium



Scheme 3 Coordination-insertion mechanism of the ROP of lactide



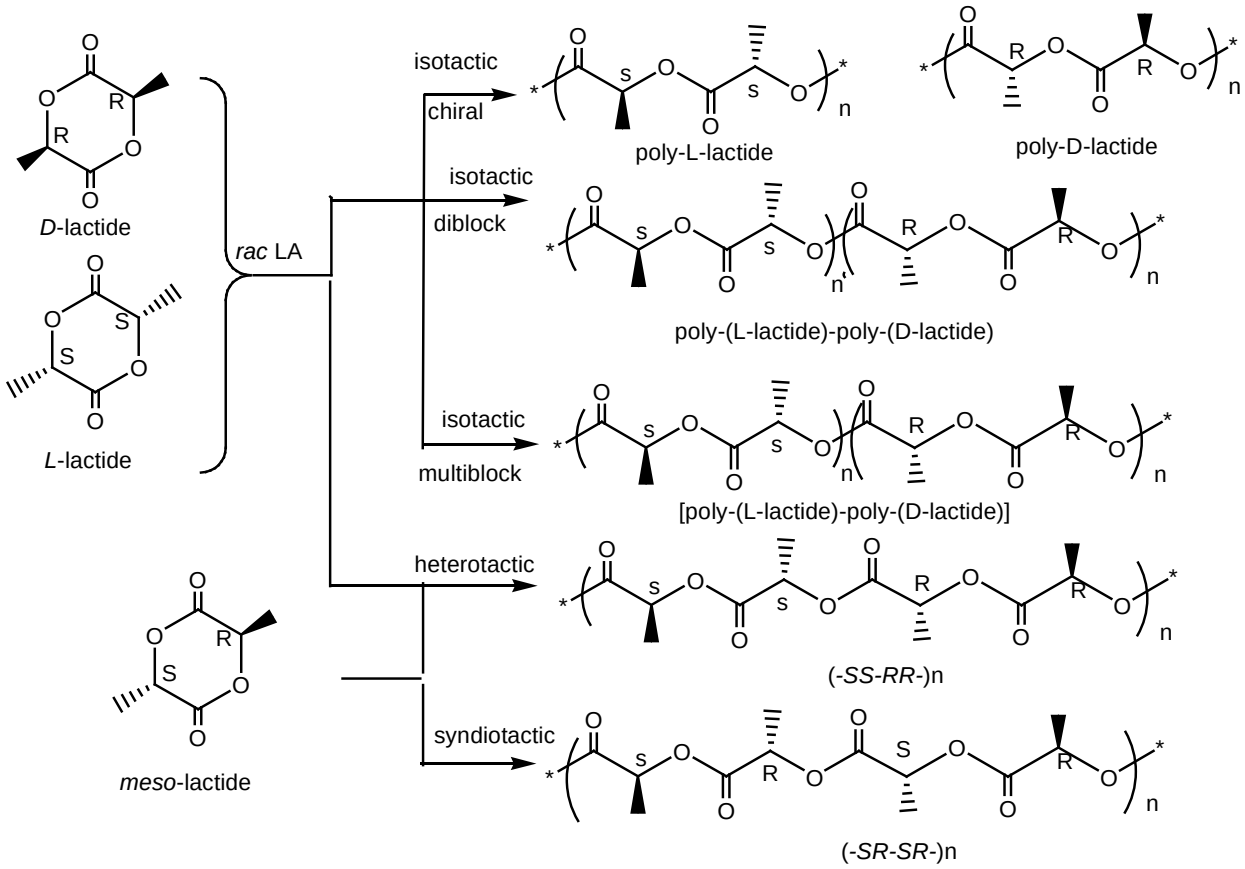
Scheme 4 Activated monomer mechanism of the ROP of lactide

In the coordination-insertion mechanism (Scheme 3), organometallic initiators bearing Lewis-acidic metal centers are used. The metal is ligated by one or more mono- or multidentate ligands, determining electronical and sterical properties of the initiator. Alkoxide or alkyl groups may be used as initiating groups. Lactide coordinates with one carbonyl oxygen to the Lewis acidic metal center, followed by nucleophilic attack of the initiator group at the carbonyl carbon. The lactide ring undergoes acyl-bond cleavage to create a new alkoxide species bonded to the metal center that subsequently attacks another lactide monomer as a nucleophile. Termination by hydrolysis yields hydroxy end capped polymers.[45-48]

In the activated monomer mechanism (Scheme 4), nucleophilic initiator activates lactide by nucleophilic attack. Addition of a protic substrate, i.e. an alcohol, initiates polymerization by generating a ringopened product.[48-49]

5. ROP of lactide by aluminium catalyst

The ROP of LA is a topic of interest in both academic and industrial research, as PLA has application in biomedical, pharmaceutical, and agriculture fields.[44, 50-53] The formation of PLA generally occurs via coordination–insertion mechanism.[11, 43, 54-59] Lactide possesses two stereocenters resulting in three isomers: D-, L- and DL-lactide (*meso*-lactide). Due to these stereocenters, stereocontrolled ROP of lactide monomers can result in a variety of PLA structures (Scheme 5).



Scheme 5 PLA microstructures resulting from stereocontrolled ROP of **A**: *rac*-lactide and **B**: *meso*lactide.

The properties of PLA depend on the stereochemistry of insertion of monomer into the polymer chain and the process can be controlled by the catalyst and the reaction condition. Therefore PLA with desired microstructure [(1) Isotactic PLA featuring all stereocenters along

the polymer chain having the same configuration (*RRRRRR* or *SSSSSS*), (2) Heterotactic PLA evolves from alternating insertion of D- and L- configured monomers out of *rac*-lactide; the stereocenters along the polymer chain doubly alternate (e.g. *SSRRSSRRSS*), (3) syndiotactic PLA featuring the stereocenters alternate along the polymer chain (e.g. *SRSRSRSRSR*), (4) Atactic PLA is formed if no stereocontrol occurs] can be derived from the rac and meso lactide depending on the stereoselectivity of the metal catalysts in the course of polymerisation. Generally, two common methods are well-known : (A) a chain end control, which essentially depends on stereochemistry of the monomer inserted in the growing polymer chain, e.g. if the stereogenic center in the last unit inserted favours a *meso* enchainment, isotactic PLA is obtained from *rac*-Lactide and heterotactic PLA is obtained by using *meso*-LA. However if the stereogenic center in the last unit favours *racemic* enchainment, heterotactic PLA will be produced from *rac*-LA and syndiotactic PLA from *meso*-LA and (B) an enantiomorphic site control which depend on chirality of the catalyst, e.g. in the lactide polymerisation following an enantiomorphic-site control, which depends on chirality of the catalyst, e.g. in the lactide polymerisation following an enantiomorphic-site control mechanism, only isotactic(racemate or stereoblock) or syndiotactic PLA can be obtained from *rac*- or *meso*-LA, respectively. Polymer tacticity is identified by homonuclear decoupled ^{1}H NMR and ^{13}C NMR analysis of tetrad sequences.[60-61] The degree of stereoregularity is quantified as probability of *racemic* or *meso* enrichments along the polymer chain. The probability of forming a new *racemic* diad is referred to as P_r and the probability of forming a new *meso* diad is refered to as P_m. [62-63] According to Bernoullian statistics, PLA derived from rac-LA and meso-LA produces five tetrad sequences in relative ratios, in which the propagating chain end shows a propensy for racemic- [r-dyad] and meso [m-dyad] connectivity of the monomer units. Determination of the stereochemical

microstructures of PLA is achived through inspection of the methine region of homonuclear decoupled ^{1}H NMR spectra of the polymer. Thus although atactic PLA exhibits five resonance in its homodecoupled ^{1}H NMR spectrum perfectly heterotactic PLA is quantified by coefficients P_m and P_r associated with the probability of racemic (r) or meso (m) linkages between monomer units, respectively (P_m=1- P_r). For instance, for determining isotacticity of PLAs, the P_m values are calculated from (area of mmm tetrad)(total area in the methine proton region) obtained from homodecupled ^{1}H NMR spectra of resulting PLA.Isotacticity of PLAs can also be determined from the following relation between P_m and intensity of the tetrads: [*mmm*]= $P_m^{\ 2}$ + (1- P_m) P_m /2, [mmr]=[rmm]= (1- P_m) P_m /2, [rmr]= (1- P_m)^2 /2 and [mrm] = [(1- P_m)^2+ P_m (1- P_m)] /2. A completely atactic polymer features P_r = P_m = 0.50. For ROP of *rac*-lactide, P_r = 1.0 (P_m = 0) describes perfectly heterotactic PLA and P_m = 1.0 (P_r = 0) describes isotactic PLA. For ROP of *meso*lactide, P_r = 1.0 (P_m = 0) describes perfectly syndiotactic PLA while P_m = 1.0 (P_r = 0) describes heterotactic PLA.

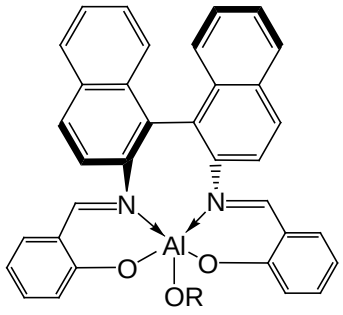
Based on the good control over the polymerization reaction, high lewis acidity and low toxicity, aluminium complexes have received a special attention among all the metal-based initiators but their activity is low.[64-67] Over the past two decades, particular attention has been given to aluminium complexes supported by different ligands, such as Salen[68-73], Salan[64, 74-75] and Salalen[76]. Further, based on coordination insertion mechanism, aluminium catalysts are classified into two categories such as; monometallic aluminium and bimetallic aluminium catalysts. Based on literature, in each experiment, ^{1}H NMR Spectrum is used for the calculation of monomer conversion, gel permeation-chromatography (GPC) calibrated with polystyrene standards in THF and corrected by a factor of 0.58 is used for the determination of M_n (GPC) and PDI, P_m and P_r are determined from the analysis of the methine region of the homonuclear

decoupled ^{1}H NMR spectrum. The theoretical M_n (Theory) can be calculated by using the equation: M_n (Theory) = [([LA]$_0$ / [inititor]) × 144.13 × conversion] + $M_{initiator}$. Where $M_{initiator}$ = 108.14 for BnOH or 60.1 for ^{i}PrOH or 208.26 for AnOH or zero for no use of initiator

5.1 Monometallic aluminium catalyst

In 1959, Kleine had studied the preparation of PLA using metal-based initiators,[77] organometallic compounds have been investigated with regard to their applicability as initiators for the ROP of lactide. Today, numerous homogeneous catalysts have been reported to polymerize lactide monomers. Generally, these complexes consist of a Lewis acidic-metal center M, ancillary ligands Ln and an initiating group R to form complexes of the type [(L$_n$)MR]. Since *rac*-lactide is more easily accessible than *meso*-lactide, many efforts have been made to polymerize *rac*-lactide selectively.[56-57] Most outstanding results for isoselective ROP of *rac*-lactide, were achieved by using aluminum based complexes with Salan or Salen-type ligands. Effects of variations in the ligand backbone or the phenolate moiety were discussed by Dove.[57]

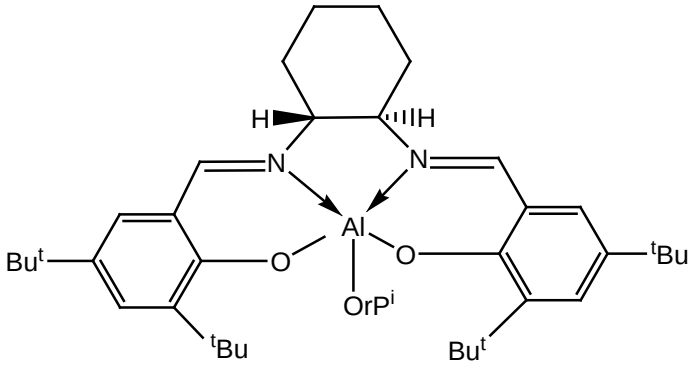
In 1996, Spassky *et al.* first reported formation of highly isotactic and crystalline PLA by ROP of *rac*-lactide using enantiopure (Scheme 6)[78] with less than 50% conversions, mainly poly(D-lactide) is formed while L-lactide remained in solution.



R=Me,O^{i}Pr

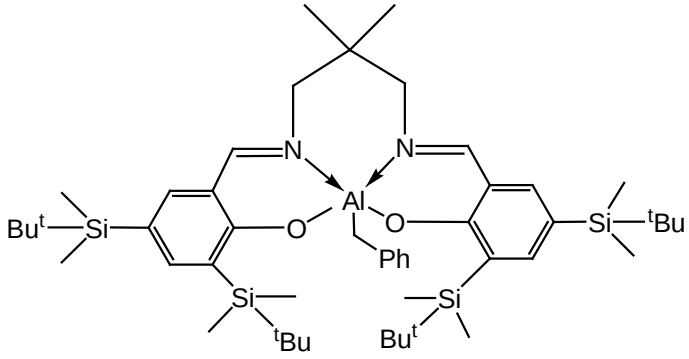
Scheme 6. (R)-SalBinap} Al(OR) [78]

In 2002, Zhong *et al.* reported that enantiopure *RR*-configured aluminum isopropoxide complex with the Jacobsen ligand (Scheme 7) used for ROP of D-lactide ending up with P_m = 0.93 at 85% conversion.[71]



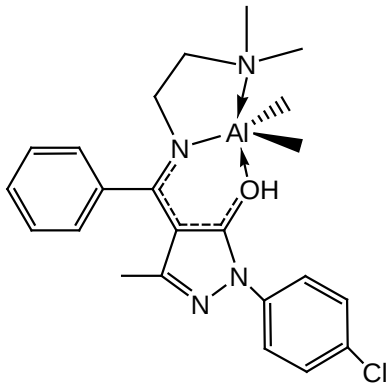
Scheme 7. Al-Salen Complex.[71]

In 2007, Nomura *et al.* prepared isotacic stereoblock PLA with P_m = 0.98 and *T*m = 207 °C using achiral aluminum-Salen complex with a rigid backbone (Scheme 8).[79]



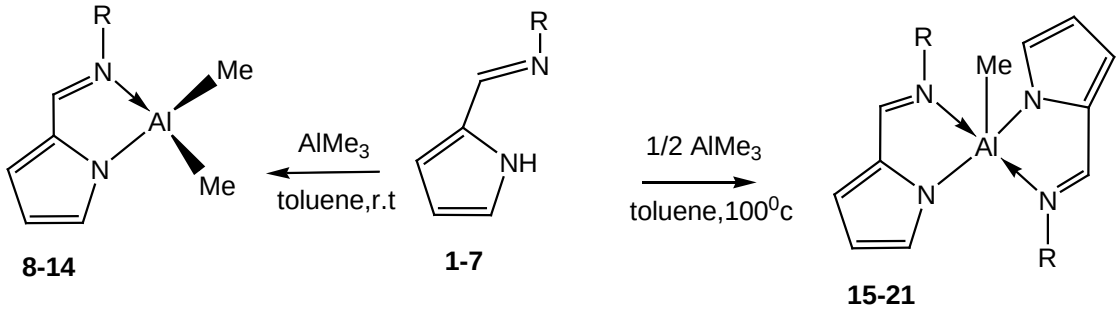
Scheme 8. Al-Salen Complex.[79]

Recently, Lin *et al.* synthesised bulky substituted Aluminum complexes that produce isotactic PLA from *rac*-lactide. (Scheme 9)[80]



Scheme 9. Al-Salen Complex.[80]

Nowadays, salen framework type, anilido–aldimine ligand has been used for the synthesis of dimethylaluminium complexes,[81] and these complexes were used for the controlled ROP of *rac*-LA. The dimethylaluminium complexes stabilized by salicylaldiminate ligands enhance the living as well as controlled polymerization of LA with various polymer microstructures, depending upon the imino substituents of the ligand framework.[12] The pyrrolylaldiminate ligands (**1–7**) were synthesized by reacting pyrrole-2-carboxaldehyde with an equimolar amount of the primary amines in ethanol with a small amount of formic acid as a catalyst, then dimethylaluminium pyrrolylaldiminate complexes (**8-14**) were prepared in good yields (42–89%) by the stoichiometric reaction of the ligands (**1-7**) with one equivalent of $AlMe_3$ in toluene at room temperature.[82] And also the treatment of $AlMe_3$ with the ligands (**1-7**) in the molar ratio 1: 2 in toluene at 100°C resulted in monomethylaluminium pyrrolylaldiminates (**15-21**) in good yields (50–91%) (Scheme 10).[82] Single crystal studies shows that the structure of **17** is distorted trigonal bipyramid geometry of τ value of 0.65.[82]



8-14 **1-7** **15-21**

1, 8, 15: R= C_6H_5
2, 9, 16: R= 4-F-C_6H_4
3, 10, 17: R= 4-Me-C_6H_4
4, 11, 18: R= 4-OMe-C_6H_4
5, 12, 19: R= 2-Me-C_6H_4
6, 13, 20: R= 2-^{t}Bu-C_6H_4
7, 14, 21: R=Adamantyl

Scheme 10 Synthesis of aluminium complexes **8-21**

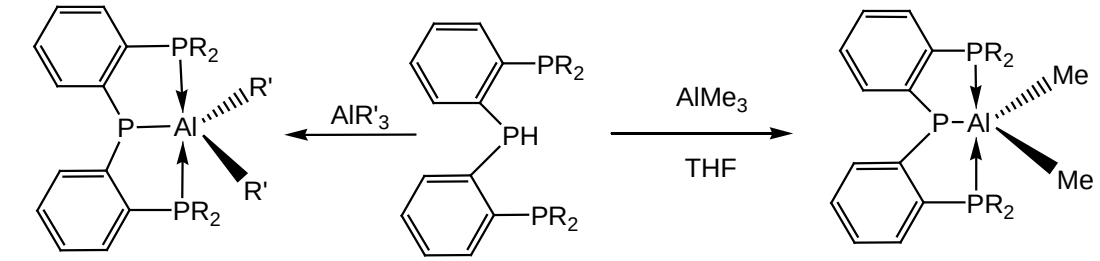
Table 1 Polymerization of *rac*-lactide using complexes **8-21**.

Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_r	P_m
1	**8**	8	86	12500	11500	1.16	0.50	0.50
2	**15**	8	91	13200	12400	1.28	0.47	0.53
3	**9**	8	92	13400	12400	1.24	0.46	0.54
4	**16**	8	86	12500	11700	1.15	0.47	0.53
5	**10**	8	90	13100	11600	1.21	0.46	0.54
6	**17**	8	92	13400	12100	1.16	0.48	0.52
7	**11**	8	90	13100	12100	1.18	0.48	0.52
8	**18**	8	89	12900	11600	1.14	0.47	0.53
9	**12**	8	84	12200	9800	1.19	0.44	0.56
10	**19**	8	92	13400	12100	1.21	0.45	0.55
11	**13**	8	58	8500	6000	1.06	0.58	0.42
12	**20**	8	65	9500	7100	1.12	0.60	0.40
13	**14**	108	91	13200	14400	1.06	0.37	0.63
14	**21**	108	95	13800	13300	1.04	0.26	0.74

Conditions: [*rac*-LA]$_0$/[Al]/ [BnOH] = 100 / 1 /1, [*rac*-LA]$_0$ = 0.83 M, toluene, 70°C.

Polymerizations of *rac*-LA using **8-21** in the presence of 1 equivalent of benzyl alcohol were carried out at 70°C in toluene with the molar ratio of *rac*-LA to initiator was 100 : 1 ($[LA]_0/[Al] = 100$; $[LA]_0 = 0.83$ M; [Al] = 8.33 mM; M_n (theory) = 14400 Da) (Table 1). All of the initiator systems exhibited molecular weights in close agreement with theoretical values and narrow molecular weight distributions in accord with controlled living polymerizations (Table 1). Among all the substituents, adamantyl is the best one producing high molecular weight PLA with PDI ≈ 1.[82] From Table 1, it was clear that atactic PLAs were produced with the P_m = 0.50–0.56 (entries 1–10, Table 1), heterotactic-enriched PLAs (P_r = 0.58- 0.60) were produced with the ortho-tert-butyl substituent on the phenyl ring (entries 11-12, Table 1). And also, the steric hindrance at the ortho-position of aniline affect the stereoselectivity, i.e. by substituting adamantyl group isotacti PLAs were produced with P_m value of 0.63-0.74 (entries 13-14, Table 1)[82] .

Among aluminium complexes **22-24** (Scheme 11), complex **22** showed very low conversion of 11% in the absence of alcohol. But by adding isopropyl alcohol, complex **22** has shown better activity in 21 hours (Table 2). Lower activity was observed for complex **23** under the same reaction conditions (Table 2).[83] This may be due to creation of electrophilicity at aluminium center as well as decrease in the bond strength between aluminium and alkoxide group and are favorable for the coordination and insertion of LA monomers. The same effect was also observed for complex **24**.[83]



Scheme 11 Synthesis of complexes **22-24**.

Table 2 Polymerization of *L*-lactide by complexes **22-23**

Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	PDI	P_m / P_r
1	**22**	16	11	3200	1.43	-
2	**22**	21	100	14500	1.12	-
3	**23**	21	91	13200	1.30	-

Conditions: for entry 1 $[LA]_0/[Al]/[^iPrOH] = 200 / 1 /0$ and for entry 2&3 $[LA]_0/[Al]/[^iPrOH] = 200 / 1 /2$, [Al] = 5 mM, toluene, 75°C.

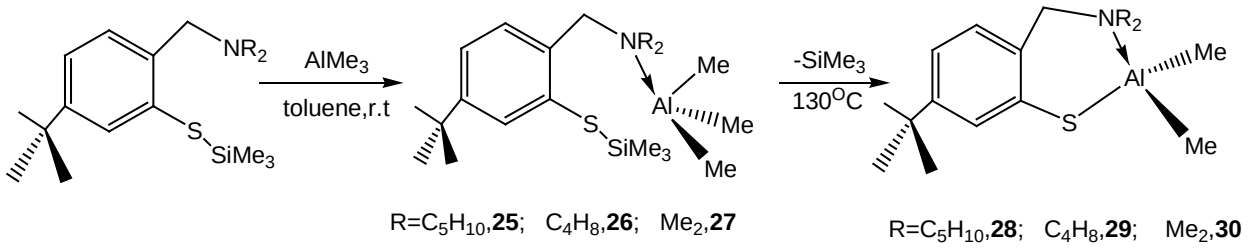
The activity of aluminium species is significantly lower than that of other metals. However, the aluminium species supported by Salen or Salan ancillary ligands; generally exert good control in the ROP of LA.[70, 84-86] Two types of aluminium complexes **25-30** (Scheme 12) can be obtained by reaction of $AlMe_3$ with an equimolar amount of the corresponding trimethylsilyl-protected aminoarenethiolate proligands at room temperature.[87] In the complexes **25-27**, the four-coordinated adduct, with the amine nitrogen coordinated to the aluminium atom, is formed[86] and for the complexes **28-30** the corresponding monomeric dimethyl aluminium complex, which bears a chelating monoanionic aminoarenethiolate ligand, is formed. Single crystals of **28-29** conformed the distorted tetrahedral geometry.[87] The ring-opening polymerization of *L*-LA was carried out in toluene solution at 130°C by using the complexes **28-**

30. All three complexes proved to be significantly active, achieving higher conversions in shorter periods of time than **22-23** (Table 2 & 3).[83, 87]

Table 3 Polymerization of *L*-lactide by complexes **28-30**

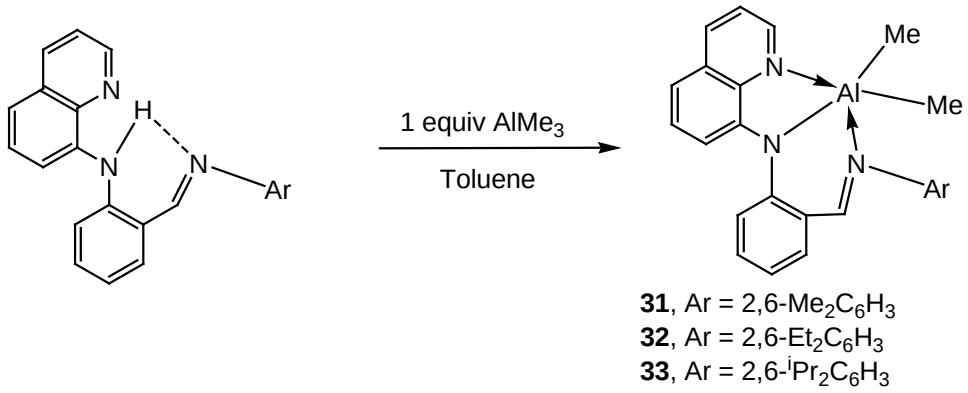
Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**28**	4	85	12240	12100	1.54	-
2	**29**	4	80	11520	13800	2.34	-
3	**30**	4	80	11520	22400	1.29	-

Conditions: [LA]/[Al] = 100, [Al] = 0.031 mmol, toluene, 130°C.



Scheme 12 Synthesis of complexes **25-30**

Based on literature[88], quinolinyl anilido-imine ligand mononuclear aluminium complexes **31-33** were prepared by adding one equiv of $AlMe_3$ to the toluene solution of the ligands at 0°C followed by evaporation of the solvent and recrystallization of the residue with hexane and toluene (Scheme 13). For all complexes, the singlet for NH in free ligands disappeared and the singlet resonances for the HCN proton at 8.14 – 8.16 ppm were observed, which shift to high field with respect to the free ligands. Further, the distorted trigonal bipyramidal geometry of **31** was confirmed by X-ray diffraction analysis.[89]



Scheme 13 Synthesis of complexes **31-33**

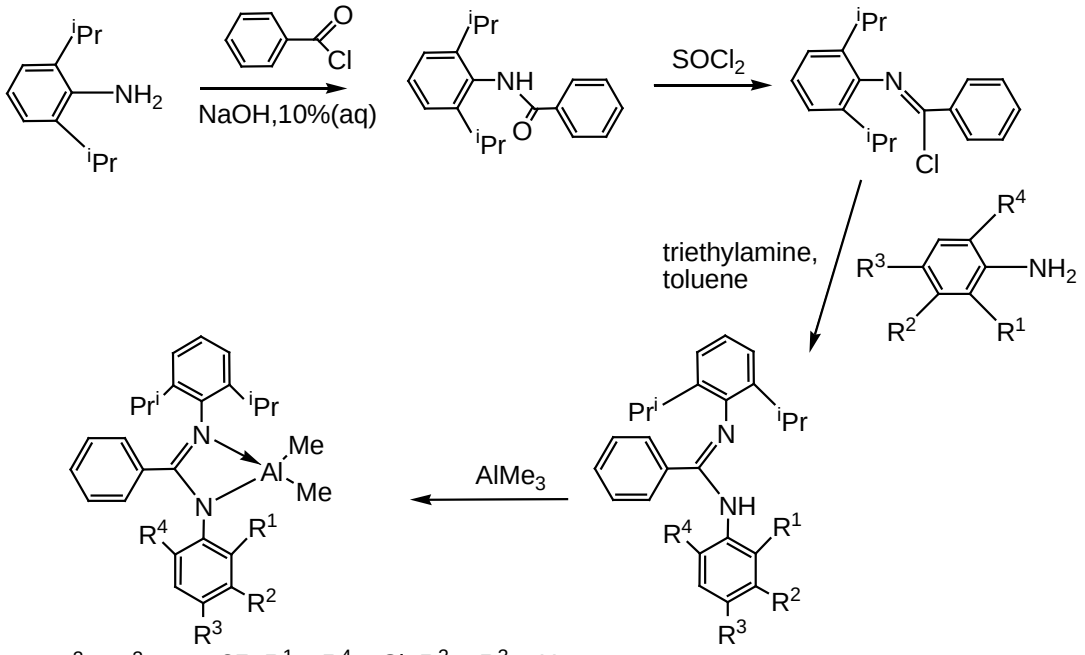
These aluminium complexes **31-33** were investigated for the ROP of *L*-LA in toluene at 70ºC (Table 4). When used as single component, all the aluminium complexes are almost inert for LA polymerization and no polymer was obtained even at high temperature. But in the presence of benzyl alcohol, the activities were improved and about 75–78% conversions were achieved in 24 h.[89]

Table 4 Polymerization of *L*-lactide by complexes **31-33**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**31**	24	77.79	5600	8700	1.13	-
2	**32**	24	75.73	5500	8000	1.14	-
3	**33**	24	76.08	5500	7600	1.12	-

Conditions: $[LA]_0/[Al]/[BnOH] = 100 / 1 /2$, [Al] = 30 μmol, toluene, 70°C.

Benzamidine aluminium complexes were prepared by adding benzoyl chloride to a mixture of 10% NaOH and 2,6-diisopropylaniline, followed by chlorination with thionyl chloride. Further treatment with aryl amine produced the corresponding amidine compounds, which on further reaction with $AlMe_3$ formed **34-39** complexes (Scheme 14). The distorted tetrahedral geometry of **35** was confirmed by X-ray diffraction analysis.[90]



34: $R^1 = R^4 = Me$, $R^2 = R^3 = H$ **35**: $R^1 = R^4 = Cl$, $R^2 = R^3 = H$
36: $R^1 = F$, $R^2 = R^3 = R^4 = H$ **37**: $R^1 = Cl$, $R^2 = R^3 = R^4 = H$
38: $R^1 = Me$, $R^2 = R^3 = R^4 = H$ **39**: $R^1 = R^2 = R^3 = R^4 = H$

Scheme 14 Synthesis of complexes **34-39**

All the aluminium complexes **34-39** were active intiators for ROP of *rac*-LA as shown in Table 5. The electronic nature of the *ortho*-substituents in complexes **34-38** helps in exhibiting superior activities than **39** which is without any substituent on one of the *N*-phenyl groups. And for the same substituent, methyl or chloro, the complex with *ortho*-disubstituted *N*-aryl group exhibits superior activity than the one with *ortho*-monosubstituted *N*-aryl group. That is, complex **34** is more active than **38** and complex **35** is more active than **37**. It is therefore conceived that the introduction of substituent at *ortho*-positions is favorable for the enhancement of catalytic activity and the steric effect may dominate. In general, the introduction of an electron withdrawing group leads to an enhancement of catalytic activity. Thus, complex **35** with *ortho*-dichloro substituents exhibits higher activity than complex **34** with *ortho*-dimethyl substituents. And further, complex **36** with *ortho*-fluoro group on one of the *N*-phenyl groups displays highest activity among complexes **36-38** with *ortho* monosubstitution.[90] From homonuclear decoupled

^{1}HNMR, it is clear that, the predominant *mmm* tetrad peak of the polymer formed by catalyst **34** is slightly isotactic bias enriched (P_m = 0.63) (Table 5).The intensity of *rmr*, *mmr* and *mrm* tetrads relative to the *mmm* tetrad does not change with conversion, indicating a homogeneous distribution of isotactic sequences along the polymer chain.[90]

Table 5 Polymerization of *rac*-lactide by complexes **34-39**

Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	PDI	P_m
1	**34**	12	57	8200	-	0.63
2	**35**	12	94	13500	1.35	0.54
3	**36**	24	85	12200	1.13	0.52
4	**37**	36	82	11800	1.22	0.51
5	**38**	48	88	12700	1.36	0.51
6	**39**	48	64	9200	1.31	-

Conditions: [*rac*-LA]$_0$/[Al] = 100, [*rac*-LA] $_0$ = 1.0 M, toluene, 70°C.

Complexes **40-44** were synthesized by the procedure adopted in the Scheme 15. All the aluminium complexes **40-43** were active initiators for the ROP of *rac*-LA in toluene at 90°C (Table 6). For the series of monoligated complexes **40-42**, with the increase of steric bulkiness of the *ortho*-substituent on the phenoxy moiety, the rate of polymerization decreased. The bisligated complex **43** was unexpectedly more active than the monoligated relatives, with a monomer conversion of 94% being observed in 48 h. This may be attributed to the presence of the electron-withdrawing effect of chloro substituents on the phenoxy unit of the ligand, which increased the electrophilicity of the metal center and thus enhanced the activity of the catalyst by facilitating the coordination of monomer. The more sterically demanding complex **44** slowed down the polymerization to some extent, affording a monomer conversion of 81% within 54 h under the same conditions.[91] From the homonuclear decoupled ^{1}H NMR spectra, the P_r values were calculated by integrating the signals of different triads in the methine region and found taht

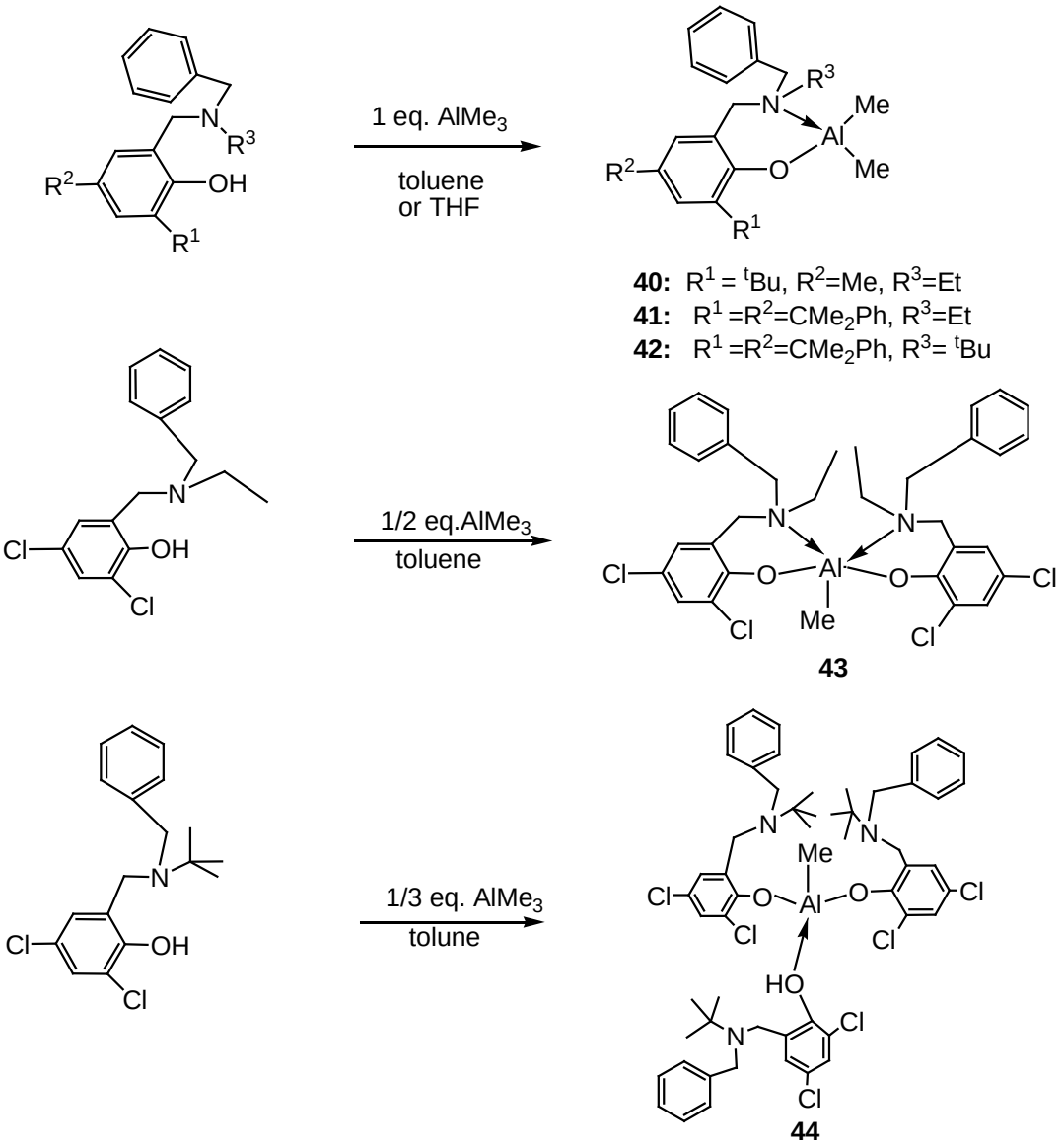
the polymerizations of rac-LA catalyzed by **40-43** produced atactic polymers with P_r values between 0.45-0.53 (Table 6).[91] This P_r values revealed that the substituents on the ligand donot influenced the stereocontrol ability of the active center.

Table 6 Polymerization of *rac*-lactide by complexes **40-44**

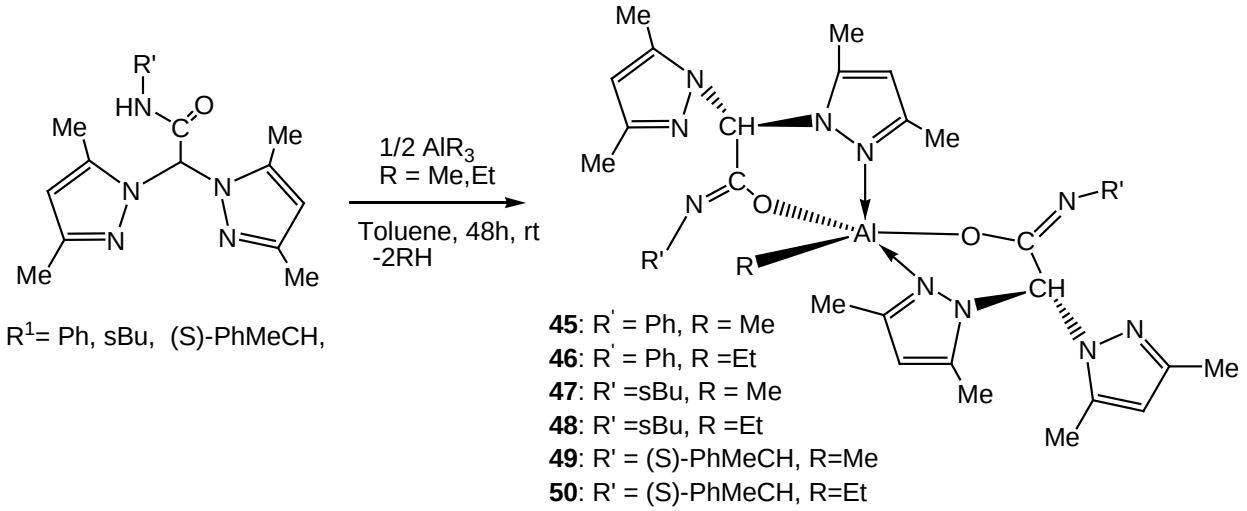
Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_r
1	**40**	60	90	13000	25500	1.32	0.50
2	**41**	240	94	13500	17500	1.80	0.45
3	**42**	48	86	12400	27600	1.69	0.51
4	**43**	48	94	13500	16000	1.25	0.53
5	**44**	54	81	11700	11100	1.79	0.59

Conditions: [*rac*-LA]$_0$/[Al] = 100, [*rac*-LA] $_0$ = 1.0 Ml, toluene, 90°C.

The alkyl-aluminium complexes **45-50** were synthesized in a straightforward way by an alkane elimination route, with 0.5 equiv. of the corresponding AlR_3 (Scheme 16). The reactions were carried out in toluene and, the complexes were isolated in good yield (85%) as colourless solids. Complexes **45-48** were isolated as racemic chiral compounds and **49-50** were obtained as enantiopure compounds. The complexes are stable in air for several days and remain in solid state at room temperature.[92]



Scheme 15 Synthesis of complexes **40**-**44**



Scheme 16 Synthesis of complexes **45-50**

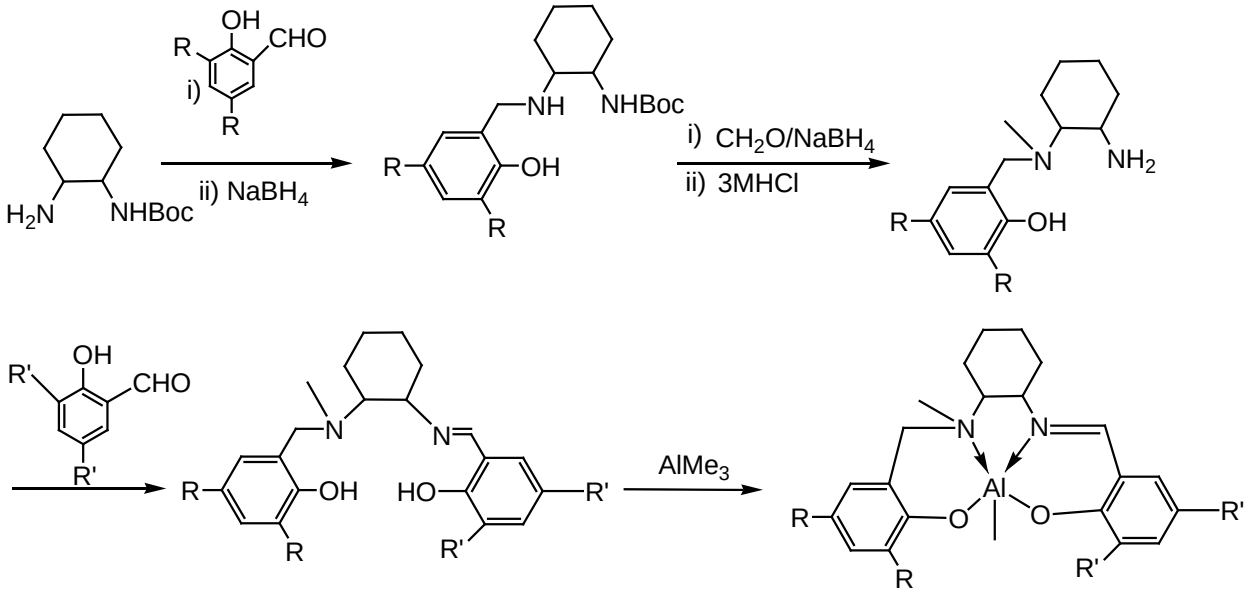
Table 7 Polymerization of *rac*-lactide by complexes **45-50**

Entry	Complex	Time (h)	Conversion[a] (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**45**	16	90	26000	27220	1.18	-
2	**46**	16	76	22000	24230	1.21	-
3	**47**	16	70	20100	23220	1.22	-
4	**48**	16	70	20100	24170	1.16	-
5	**49**	16	83	24000	25540	1.15	-
6	**50**	16	82	23600	24780	1.15	-

Conditions: [*rac*-LA]$_0$/[Al] = 200, [Al]$_0$ = 90 μmol, toluene, 110°C.
[a] Percentage conversion of the monomer [(weight of polymer recovered/weight of monomer) × 100].

The polymerization of *rac*-LA by **45-50** showed negligible activity in toluene at 25°C; however, at 110°C with a [LA]:[Al] ratio of 200, around 80% monomer conversion was achieved in 16 hours (Table 7). All polymers thus produced, exhibit unimodal and narrow PDI in the range 1.15–1.22 for the experiments carried out at 110°C, a finding that indicates the single-site nature of these catalysts in ROP.[92] The alkyl aluminium complexes **51-55** were derived from the amine

ligands, prepared by modifying the 1,2-diaminocyclohexane which was initially mono-protected and treated with an equivalent amount of an aldehyde and subsequent reduction generated an amine. This was treated with another equivalent of aldehyde to form the salalen ligand (Scheme 17). The alkyl aluminium complexes **51-55** were utilised as the initiators for synthesis of PLA, with narrow PDIs range from 1.06–1.35 and PLA could be isolated with moderate degrees of tacticity (P_r range from 0.49 to 0.65) (Table 8).[93]



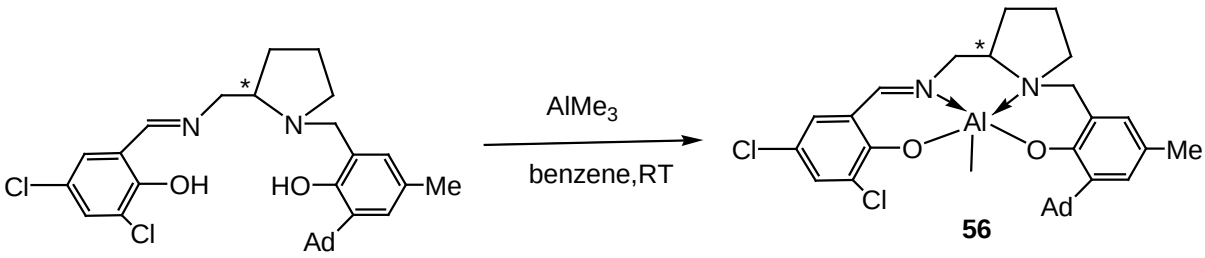
Scheme 17 Synthesis of complexes **51-55**.

Table 8 Polymerization of *rac*-lactide by complexes **51-55**

Entry	Complex	Time (days)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_r
1	**51**	4	42	6000	8950	1.06	0.49
2	**52**	4	71	10200	12200	1.07	0.65
3	**53**	4	97	14000	17150	1.35	0.60
4	**54**	4	83	12000	7700	1.06	0.57
5	**55**	4	61	8800	7100	1.07	0.54

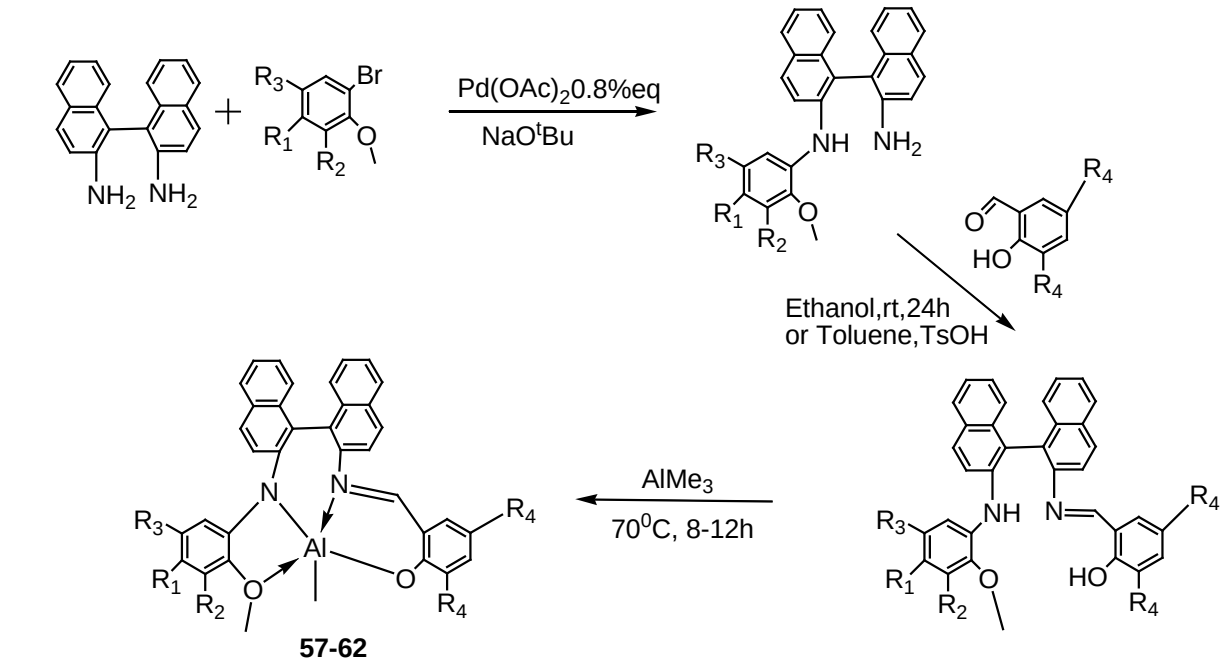
Conditions: [*rac*-LA]$_0$/[Al] /[BnOH] = 100 /1 /1, toluene, 80°C.

The salalen aluminium complex **56** was prepared by the treatment of –ONNO- type ligand with equimolar amounts of $AlMe_3$ in benzene (Scheme 18). The PLA obtained by using catalyst **56**, has narrow molecular weight distribution (PDI = 1.09).[94]



Scheme 18 Synthesis of complex **56**

Aluminium complexes **57-62** were synthesized easily in high yields under mild conditions by combining 1.0 equivalent of trimethylaluminium and the corresponding ligands under an inert atmosphere. The complexes were isolated as yellow or orange precipitates from toluene in 80-93% conversion (Scheme 19).[95] For complex **59**, the τ value is 0.44, which indicates it is close to square pyramidal geometry (τ value is 0.49).[95]



57: R_1=R_2=R_3= R_4=H; **58**: R_1=R_2=R_3=H, R_4 = ^{t}Bu;
59: R_1=R_2=R_3=H,R_4 = Cl; **60**: R_1= F,R_2=R_3= R_4 = H;
61: R_1= H,R_2=R_3=^{t}Bu, R_4 = Cl; **62**: R_1= F,R_2=R_3=H, R_4 = Cl;

Scheme 19 Synthesis of complexes **57-62**

All aluminium complexes were investigated as catalysts for the ROP of *L*-LA and *rac*-LA (Table 9). These aluminium complexes showed moderate to high activities (81.6−93.0% conversion) with the cocatalyst 2-propanol at 70°C. It is worth noting that the activities of these complexes decreased with the increase in substituent size on the benzene rings, while electron-withdrawing substituent enhances the polymerization rate.[95]

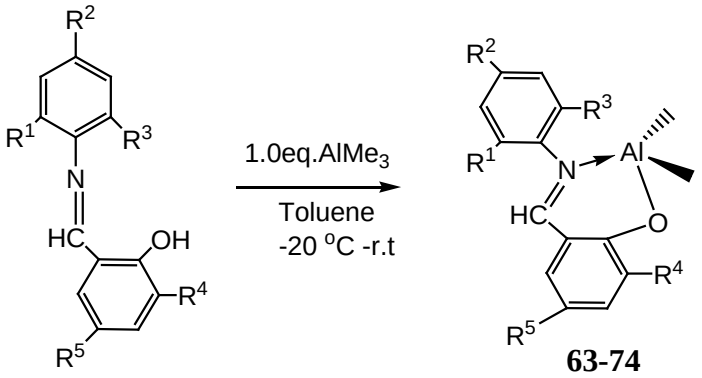
The ^{1}H NMR spectra of the PLA oligomers revealed that the integral ratio of the two peaks at 1.24 ppm (methyl protons from the isopropoxycarbonyl end group) and 4.35 ppm (methine proton adjacent to the hydroxyl end group) approximates to 6:1, signifying that the aggregating chains were end-capped with an isopropyl ester and a hydroxyl group. In other words, the alkyl aluminium compound has been converted into an isopropoxy aluminium species at the origin of the aggregation, so the actual initiator is the isopropoxy aluminium species.[95] The

homonuclear decoupled ^{1}H NMR spectrum of the methane region stated that the P_m selectivities increased from 0.50 to 0.57 with the increase in the size of the substituents on salicylaldehyde parts from hydrogen atoms to tert-butyls on the benzene ring (Table 9, entry 7,8) and from 0.50 to 0.55 with an increase in the size of the substituents at anisole groups from hydrogen atoms to tert-butyls (Table 9, entry 7,11). [95]

Table 9 Polymerization of lactide by complexes **57-62**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m
1	**57**	36	85.2	12300	20400	1.09	1.0
2	**58**	46	82.9	12000	20100	1.04	1.0
3	**59**	32	85.0	12300	20800	1.08	1.0
4	**60**	32	87.1	12600	21400	1.09	1.0
5	**61**	45	84.7	12200	21300	1.08	1.0
6	**62**	29	93.0	13400	23400	1.09	1.0
7	**57**	36	84.0	12100	22900	1.08	0.50
8	**58**	46	80.5	11600	21100	1.09	0.57
9	**59**	32	82.9	12000	22400	1.12	0.50
10	**60**	32	84.0	12100	22200	1.12	0.52
11	**61**	45	85.0	12300	21300	1.11	0.55
12	**62**	24	84.7	12200	22100	1.09	0.50

Conditions: $[LA]_0/[Al]/[^{i}PrOH]$ = 100 /1 /1, [Al] = 0.5 molL^{-1}, toluene, 70°C. Entry 1-6 for *L*-LA and entry 7-12 for *rac*-LA

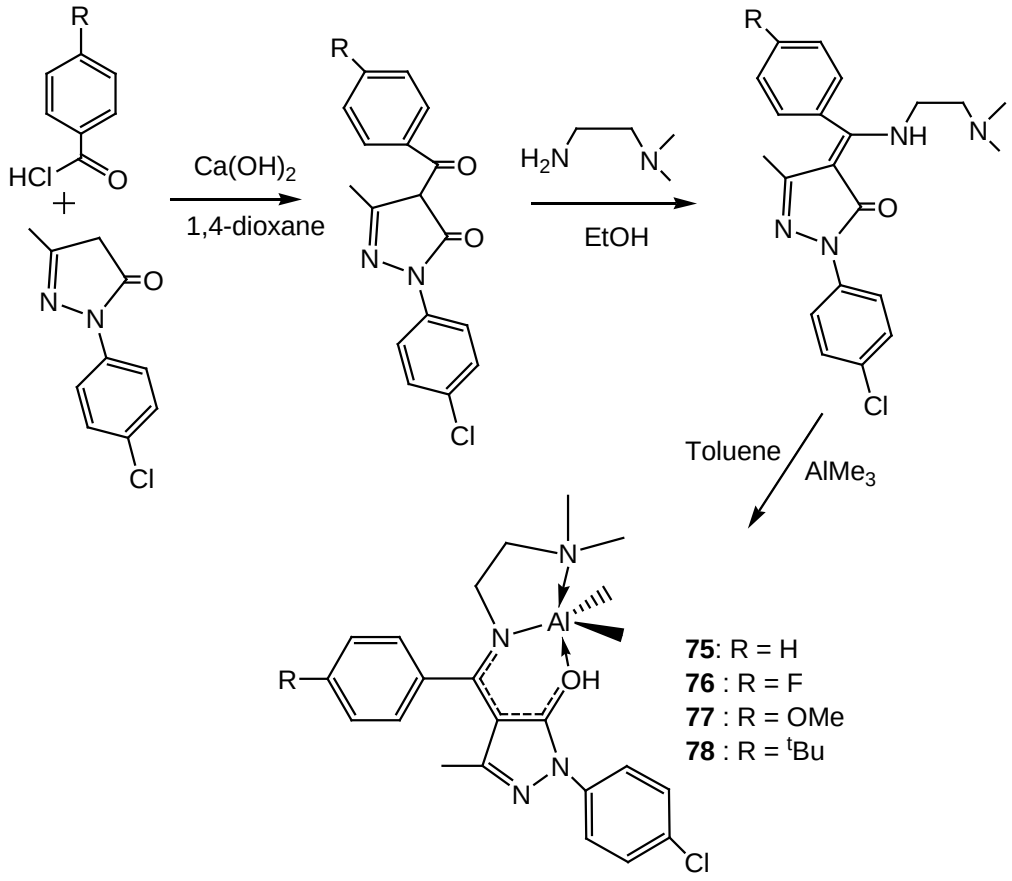


63-74

	63	**64**	**65**	**66**	**67**	**68**	**69**	**70**	**71**	**72**	**73**	**74**
R^1	Φ	Φ	Me	^{i}Pr	Φ	Φ	Me	Me	Me	^{i}Pr	^{i}Pr	^{i}Pr
R^2	^{i}Pr	Cl	Φ	Φ	^{i}Pr	Me	Φ	Me	H	H	H	H
R^3	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Φ	Me	^{i}Pr	^{i}Pr	^{i}Pr
R^4	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Φ	L	^{t}Bu	H
R^5	^{t}Bu	^{t}Bu	^{t}Bu	^{t}Bu	Me	Me	Me	Me	Me	L	^{t}Bu	H

Scheme 20 Synthesis of complexes **63-74**

The aluminium phenolate complexes **63-74** were prepared by reaction of the corresponding phenolate ligand with one equivalent of $AlMe_3$ in toluene at −20°C (Scheme 20).[96] All the complexes are significant initiators in the presence of benzyl alcohol for the ROP of *rac*-LA and follow the same mechanism as described earlier. The obtained polymers exhibited broader molecular weight distributions (PDI: 1.32-1.69) suggesting that there was less control and more transesterification occuring.[96] The ketiminate aluminium complexes **75-78** (Scheme 21) are also efficient catalyst for ROP of *L*-LA in the presence of benzyl alcohol. The distorted trigonal–bipyramidal geometry of **76-77** was confirmed by single crystal analysiss.[80]



Scheme 21 Synthesis of complexes **75-78**

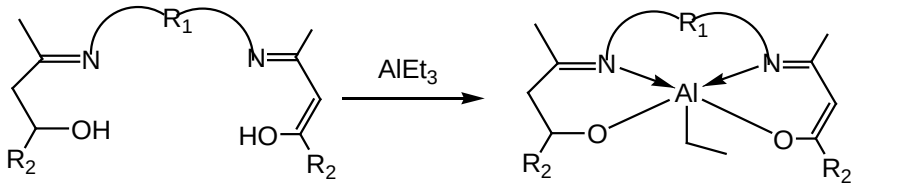
It was found that a great catalytic activity and a "controlled" character were achieved with a Al : BnOH molar ratio of 1:2 in toluene at 110°C. All the complexes have shown greater "controlled" character and as a result, "living" character was observed (Table 10).[80]

Table 10 Polymerization of *L*-lactide by complexes **75-78**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**75**	14	93	6800	7400	1.16	-
2	**76**	14	91	6600	6300	1.16	-
3	**77**	14	91	6700	6200	1.20	-
4	**78**	14	90	6600	6100	1.15	-

Conditions: $[LA]_0/[Al]/[BnOH] = 100/1/2$, [Al] = 0.1 mmol, toluene, 110°C.

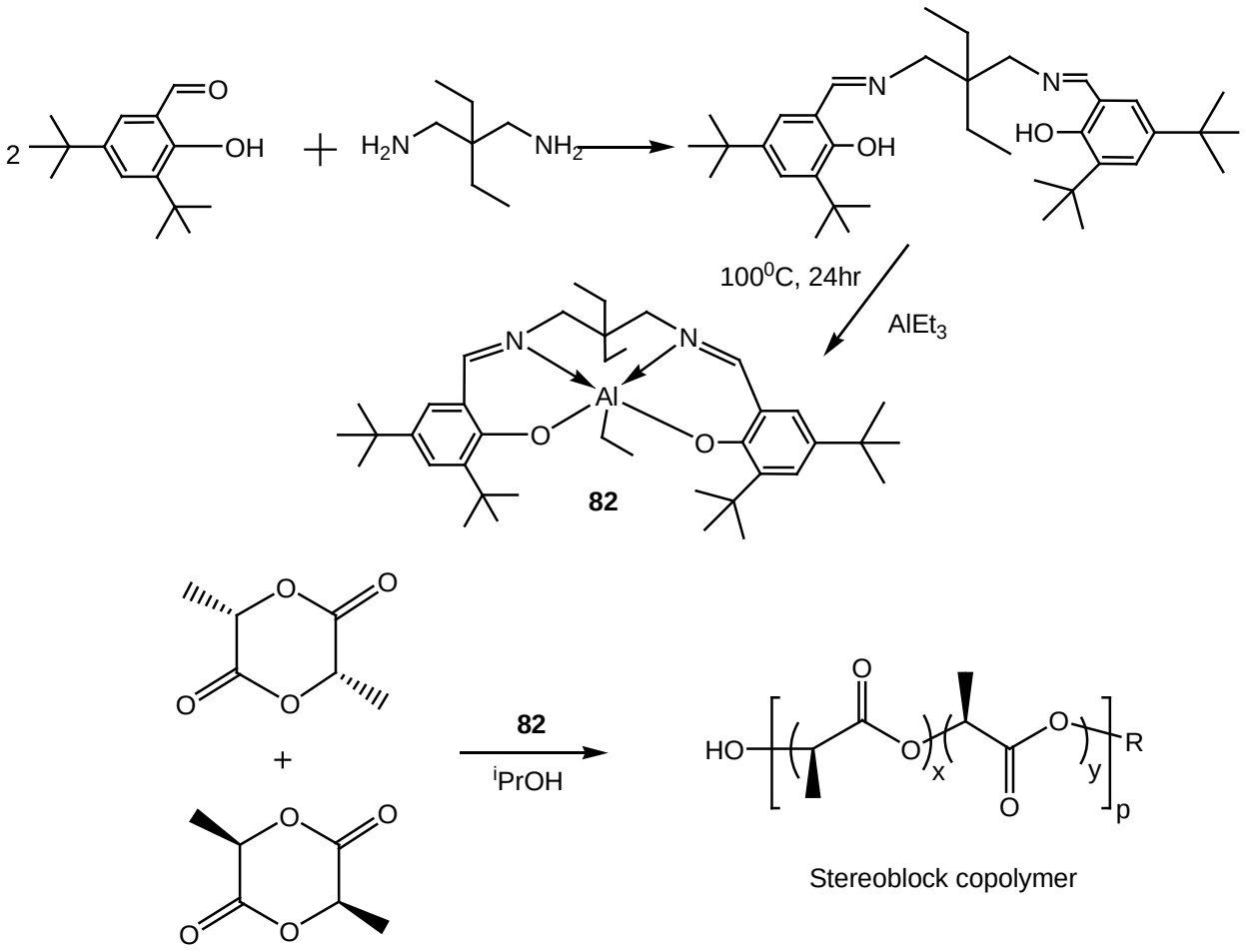
The aluminium complexes **79-81** (Scheme 22) were used for ROP of *rac*-LA in the presence of iso-propyl alcohol to examine the influence of different diimine bridging parts and enol substituents on their catalytic performance, respectively. It was observed that complex **79** in the presence of alcohol gives highest conversion.[97]



79: R_1= -$CH(CH_3)CH_2$-, R_2 = Ph:
80: R_1= -$CH(CH_3)CH_2$-, R_2 = CH_3:
81: R_1= -$CH(CH_2)_4CH_2$-, R_2 = Ph.

Scheme 22 Synthesis of complexes **79-81**

The aluminium complex **82** was synthesized by the condensation of 2, 2-diethyl-propane-1,3-diamine and 3,5-di-*tert*-butyl-salicylaldehyde and then treatment with $AlEt_3$ in toluene and heptane at 100°C for 24 h (Scheme 23). This aluminium complex in the presence of isopropanol acts as intitiator to produce PLA with narrow PDI (Table 11).[98] The homonuclear decoupled ^{1}H-NMR spectrum of the methane region of poly(*rac*-LA) showed, the mmm tetrad was the predominant peak, which indicated that the poly(*rac*-LA) was dominantly isotatic and also in addition to the major mmm signal, there were three small rmm, mmr, and mrm tetrads with approximately equal intensity and an almost negligible rmr resonance indicating the formation of a stereoblock-type PLA (Scheme 23). The degree of stereoselectivity (P_m) was 0.84 based on the chain-end control polymerization mechanism, indiating stereoblocks contained an average of 12 units. [98]

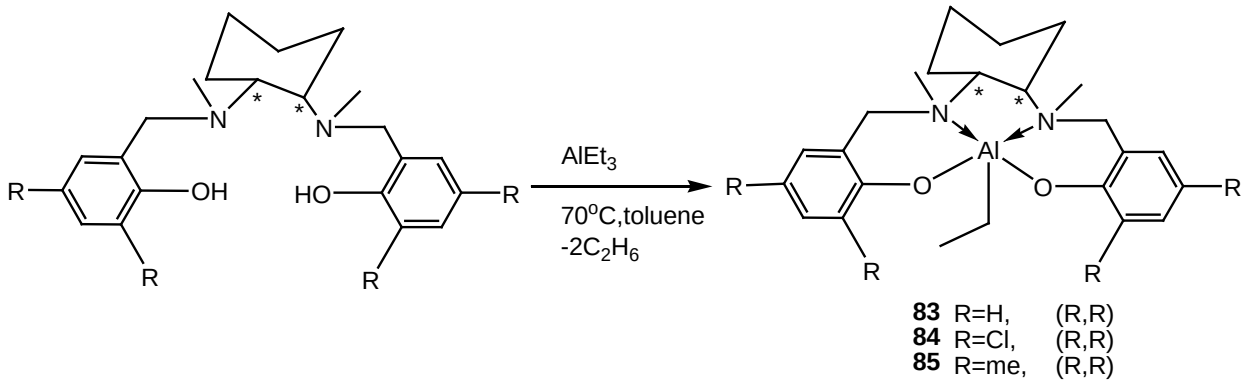


Scheme 23 Synthesis of stereospecific polymerization of *rac*-LA by complex **82**

Table 11 Polymerization of *rac*-lactide by complex **82**

Entry	Time (min)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m
1	38	8.76	1300	1900	1.05	-
2	89	25.05	3600	3600	1.08	81.6
3	119	35.12	5100	4500	1.08	81.8
4	160	47.02	6800	6500	1.07	82.1
5	211	59.75	8600	8400	1.08	82.0
6	276	70.8	10200	10500	1.07	81.9
7	337	77.39	11200	11700	1.08	82.7

Conditions: [*rac*-LA]$_0$/[Al] /[^{i}PrOH] = 100 /1 /1, toluene, 100°C.



Scheme 24 Synthesis of complexes **83-85**

The corresponding salan aluminium ethyl complexes **83-85** were prepared by reacting equimolar amounts of salan and $AlEt_3$ in toluene at 70°C (Scheme 24). The presence of two species in each case was clearly revealed by ^{1}H NMR spectroscopic data. One species (a) gives a dissymmetric resonance pattern, whereas the other (b) gives a symmetric resonance pattern. The complexes **83-85** were treated with propan-2-ol (1 equiv) to generate the active isopropoxide initiators for the ROP of *rac*- or *meso*-LA in situ in toluene at 70°C, and the furnished PLAs have narrow molecular weight distributions, indicating well-controlled polymerization (Table 12).[64] From homonuclear decoupled ^{1}H NMR spectra it was clear that, complex **83** polymerized rac-LA to form isotactically biased polymers with P_m values of 0.66. Whereas, complex **85**, with methyl substituents at the ortho and para positions of their phenolic groups, furnished atactic PLA from rac-LA with P_r values of 0.55. Interestingly, **84** afforded heterotactically biased PLAs with a P_r value of 0.64. Heterotactic PLAs cannot be obtained from *rac*-LA through a site control mechanism (SCM) with use of an enantiomeric pure complex, so this reveals the existence of a chain-end control mechanism (CEM) with use of **84** in the *rac*-LA polymerization. The **83, 84** and **85** complexes produced syndiotactically biased PLAs from *meso*-LA with P_r

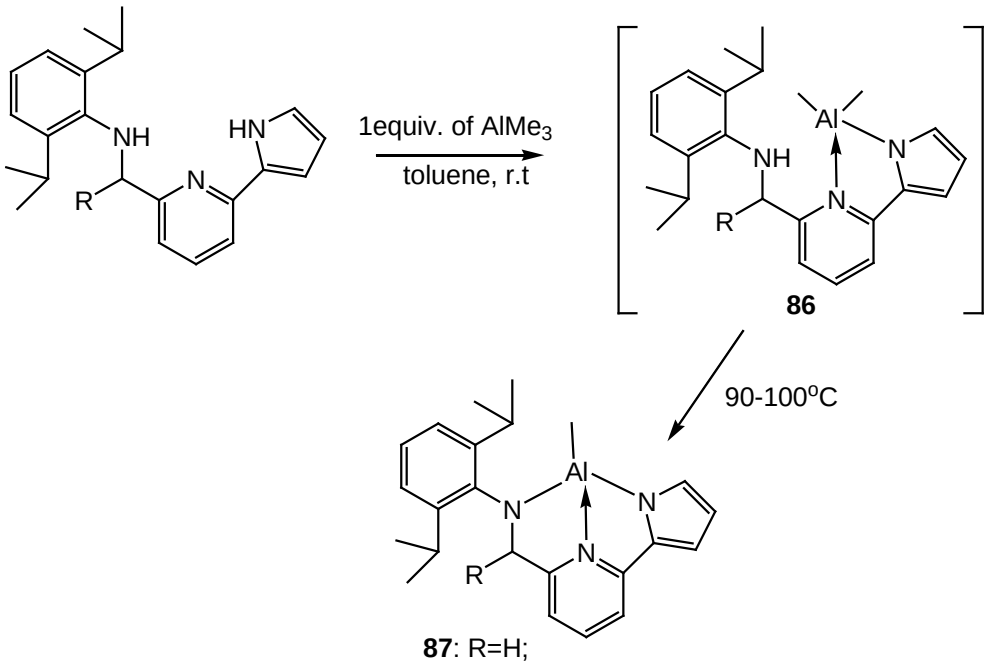
values of 0.64, 0.70, and 0.69, respectively. This clearly confirms the operation of a SCM in *meso*-LA polymerization with use of these chiral complexes.[64]

Table 12 Polymerization of lactide by complexes **83-85**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_r	P_m
1	**83**	10	70.7	5000	5800	1.09	-	0.66
2	**84**	57	87.6	6300	7000	1.10	0.64	-
3	**85**	69	87.0	6200	6000	1.10	0.55	-
4	**83**	23	97.3	7000	6600	1.12	0.64	-
5	**84**	27	83.1	6000	5100	1.09	0.70	-
6	**85**	27	93.5	6700	6900	1.10	0.69	-

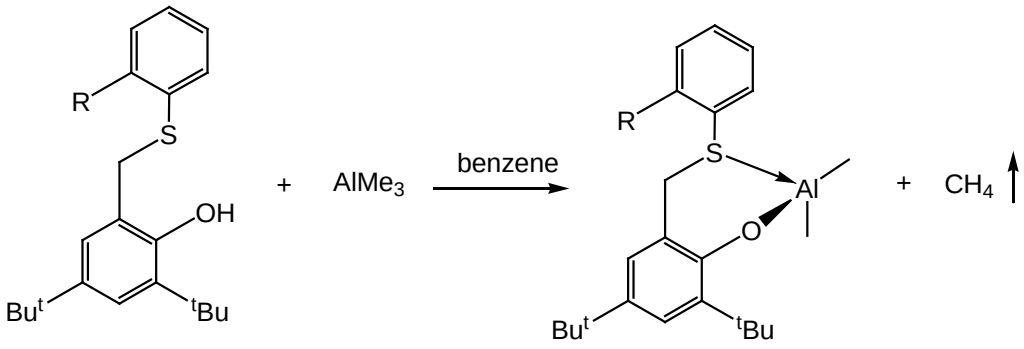
Conditions: $[LA]_0$ = 0.534M, [Al] = 10.7mM, toluene, 70ºC. Entry 1-3 for *rac*-LA and entry 4-6 for *meso*-LA

Complexes **87-88** were synthesized in toluene by the alkane elimination reaction between the corresponding ligands and $AlMe_3$, with the dimethyl compounds **86** as intermediate (Scheme 25). Further, these complexes **87-88** were tested for the ROP of LA, in toluene solution at 70°C in the presence of 1 equiv of 2-propanol (Table 13). Complex **87** was able to polymerize *L*-LA and *D, L*-LA with the same activity and a good control of the molecular weight. But, compound **88** showed a relatively lower activity in the polymerization of *D, L*-LA, which may be attributed to steric effect.[65] The homonuclear decoupled ^{1}H NMR analysis of the stereosequences distributions of the obtained polylactide samples produced by both **87-88** showed tetrads, in agreement with an "enantiomorphic sites" mechanism of the steric control. Both the complexes **87-88** able to polymerize *D, L*-LA to isotactic-enriched PLAs with slightly higher P_m values for encumbered catalyst **88**.[65]



87: R=H;
88: R=2-^{i}PrC$_6$H$_4$

Scheme 25 Synthesis of complexes **87-88**



89: R = H **90**: R = Br
91: R = CH_3 **92**: R = CF_3

Scheme 26 Synthesis of complexes **89-92**

Table 13 Polymerization of lactide by complexes **87-88**

Entry	Complex	Time (days)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m
1	**87**	3	88	12700	15900	1.15	-
2	**87**	3	85	12300	11100	1.11	0.71
3	**87**	3	74	21300	16400	1.17	-
4	**87**	4	82	23600	19700	1.12	0.68
5	**88**	4	61	17600	8900	1.33	0.73
6	**88**[d]	4	54	15600	8600	1.30	0.76

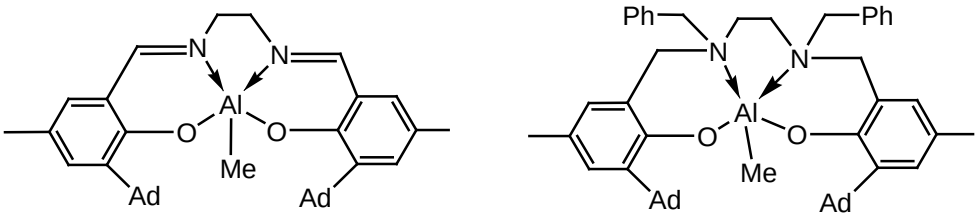
Conditions: $[LA]_0/[Al]/[^iPrOH] = 100/1/1$, [Al] = 10μmol, toluene, 70°C. Entry 1 for *L*-LA and entry 2-6 for *D,L*-LA, for entry 6 $[LA]_0/[Al]/[BnOH] = 100/1/1$

Table 14 Polymerization of *L*-lactide by complexes **89-92**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**89**	48	77	11100	11600	1.14	-
2	**90**	48	54	7800	8700	1.12	-
3	**91**	48	57	8200	7300	1.14	-
4	**92**	48	38	5500	4000	1.16	-

Conditions: $[LA]_0/[Al]/[^iPrOH] = 100/1/1$, [Al] = 12.5 μmol, toluene, 80°C.

Complexes **89-92** were synthesized (Scheme 26) and were used in ROP of *L*- LA in toluene at 80°C, in the presence of MeOH. The polymerization data may suggest that the catalytic activity decreases with the increase of steric hindrance offered by the *ortho* substituent on the aromatic ring of the sulfur donor (Table 14).[67]



93 **94**

Scheme 27 Structure of complexes **93-94**

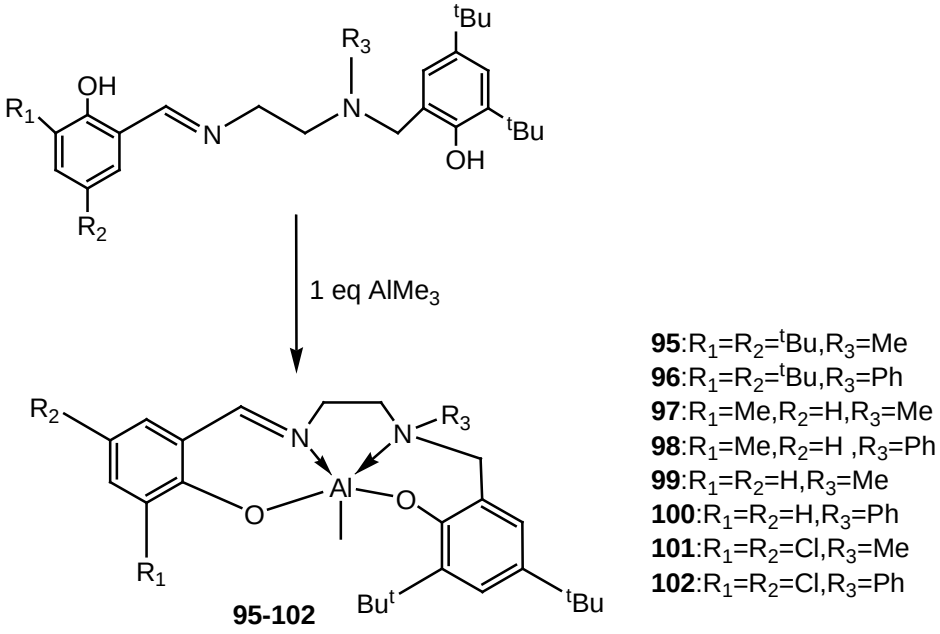
The complexes **93-94** (Scheme 27) were used for the living ROP of *rac*-LA and were examined at 70°C in toluene (Table 15). From the results, it has been found that, only trace amounts of PLA oligomers is isolated after 24 h at 70°C in toluene using **94**. In contrast, complex **93** was effective in mediating the living ROP of *rac*-LA. This may be due to bulky dialkyl-substituted Al-salan complexes. And also these complexes produced highly isotactic PLAs with P_m ranges 0.88 to 0.89.[75]

Table 15 Polymerization of *rac*-lactide by complexes **93-94**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**93**	12	49	7000	6100	1.07	0.88(m)
2	**93**[d]	18	78	28200	26200	1.04	0.89(m)
3	**93**[e]	24	56	40000	33600	1.04	0.88(m)
4	**94**	24	<5	-	-	-	-

Conditions: [*rac*-LA]$_0$/[Al] /[BnOH] = 100 /1 /1, toluene, 70°C, for entry 2: [LA]$_0$/[Al] /[BnOH] = 250 /1 /1, for entry 3: [LA]$_0$/[Al] /[BnOH] = 500 /1 /1

A series of aluminium salalen complexes **95-102** (Scheme 28) have been prepared and tested for the ROP of *rac*-LA (Table 16). All complexes were shown to be active for the polymerisation of *rac*-LA with the addition of 1 equivalent of BnOH. Relatively narrow PDI were observed, except with the polymers formed with complex **98**. The probability of heterotactic linkages (P_r ranging from 0.39 to 0.74) were determined by the homonuclear decoupled ^{1}H NMR spectra. [76]



Scheme 28 Synthesis of complexes **95-102**

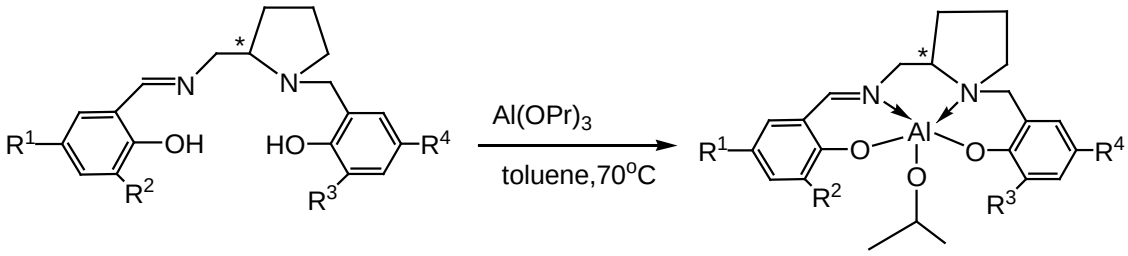
Table 16 Polymerization of *rac*-lactide by complexes **95-102**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_r
1	**95**	36	73	11900	10600	1.05	0.39
2	**96**	46	96	11900	13900	1.11	0.43
3	**97**	32	26	7400	3800	1.04	0.54
4	**98**	32	96	10400	13900	1.65	0.42
5	**99**	45	86	6600	12500	1.07	0.74
6	**100**	29	98	9000	14200	1.39	0.45
7	**101**	36	96	8600	13900	1.10	0.63
8	**102**	46	98	12500	14200	1.12	0.40

Conditions: [*rac*-LA]$_0$/[Al] /[BnOH] = 100 /1 /1, [Al] = 0.5 molL^{-1}, toluene, 80°C.

The aluminium complexes bearing nitrogen-based bidentate or tridentate ligands have recently attracted much attention in fine chemical synthesis and even more in polymerization reactions.[99-106] The synthesis of polyesters by alkoxy aluminium catalyst is attracting a considerable current interest. The salalen aluminium complexes **103-106** of the type

[{ONNO}Al(O^{i}Pr)] were prepared by the treatment of –ONNO- type ligands with equimolar amount of Al(O^{i}Pr)$_3$ (Scheme 29).[94] The molecular weights of the obtained PLAs were in good agreement with the calculated values, and the molecular weight distributions were narrow (PDI<1.1), supporting a well-controlled polymerization with stereoselection derived from their specific substitution pattern (Table 17). The homodecoupled ^{1}H NMR spectra of PLAs showed a clear relationship between the ligand substitution pattern and the PLA stereoregularity. The complex **103** which have chloro substituents on the imine-side phenol and bulky alkyl groups on the amine-side phenol gave PLAs of a heterotactic nature (Table 17, Entry 1). Whereas, all other complexes **104-106** with the opposite phenolate substitution pattern, i.e. bulky alkyl substituents on the imine-side phenol and halo groups on the amine-side phenol produce isotactic PLAs (Table 17).



103-106

103: R_1 =R_2 =Cl,R_3 = Ad,R_4= Me
104: R_1 = Me,R_2 = Ad,R_3=R_4= Cl
105: R_1 =R_2 =^{t}Bu ,R_3 = R_4= Cl
106: R_1 =R_2 =^{t}Bu,R_3 = R_4= I

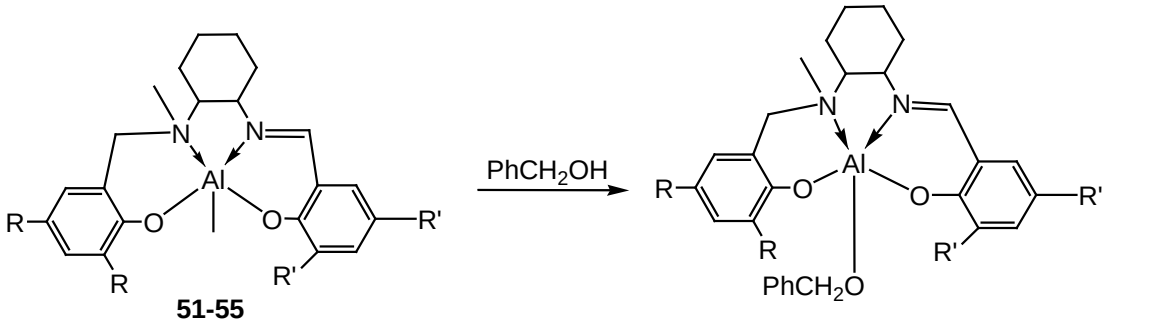
Scheme 29 Synthesis of complexes **103-106**

Table 17 Polymerization of *rac*-lactide by complexes **103-106**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m
1	**103**	24	75	10800	8500	1.07	0.24
2	**104**	24	42	6100	6800	1.05	0.82
3	**105**	24	78	11200	9000	1.07	0.82
4	**106**	24	91	13100	9700	1.07	0.59

Conditions: [*rac*-LA]$_0$/[Al] = 100, [*rac*-LA] $_0$ = 20 μmol toluene, 80°C.

The alkoxy aluminium complexes **107-111** were derived from the aluminium complexes **51-55** as given in the Scheme 30. And these complexes **107-111** were utilised as the initiators for ROP of *L*-LA and produced PLA with relatively controlled M_n values and low PDIs (Table 18). [93] The difference in stereoselectivity is conceivably an effect of the enhanced flexibility about the amine bond. And also complex **109** with a chloro group on the imine fragment of the salalen produce PLA with a heterotactic bias under melt conditions (Table 18).[93]



51-55 **107-111**

107: R = ^{t}Bu, R' = ^{t}Bu **108**: R = ^{t}Bu R' =H
109: R = ^{t}Bu R' =Cl **110**: R =H R' = ^{t}Bu
111: R =Cl R' = ^{t}Bu

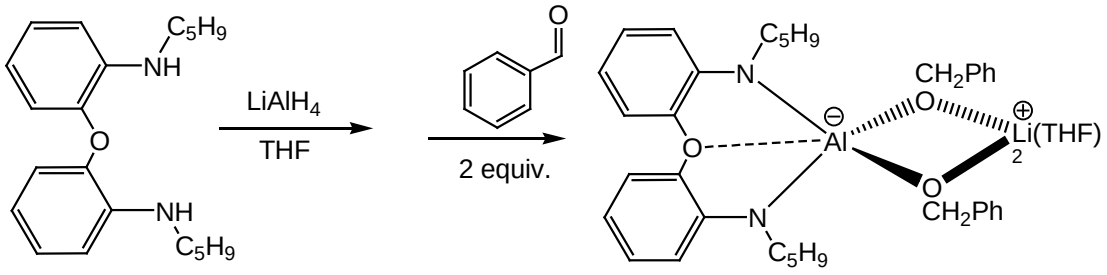
Scheme 30 Synthesis of complexes **107-111**

Table 18 Polymerization of *L*-lactide by complexes **107-111**

Entry	Complex	Time (days)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_r
1	**107**	4	26	3800	3750	1.08	0.54
2	**108**	4	91	13200	19550	1.12	0.61
3	**109**	4	99	14400	17000	1.18	0.69
4	**110**	10	40	5900	6400	1.08	0.42
5	**111**	10	49	7200	8300	1.06	0.31

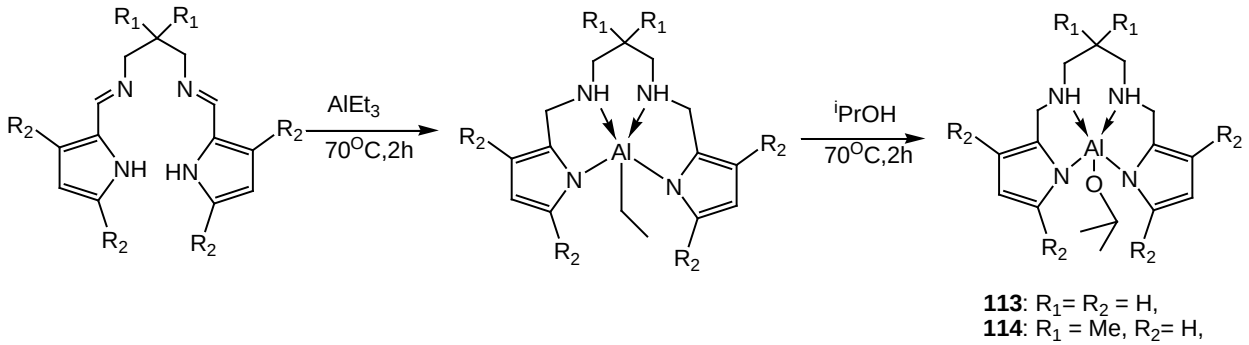
Conditions: $[LA]_0/[Al]/[BnOH] = 100/1/1$, toluene, 80°C.

The aluminium complex **112** was readily synthesized as mentioned in the Scheme 31. The bis-alkoxide aluminium species **112** maintained a well-controlled ROP process of *rac*-LA; and PLA with a narrow PDI (1.03) and molecular weight 8060 Da was obtained at 16hrs.[107] The alkoxy aluminium complex **113-114** were prepared by the reaction of the ligands with $AlEt_3$ in anhydrous toluene at 70°C (Scheme 32). Both the complexes were active catalyst for ROP of *rac*-LA but complex **113** was proven to be more active in comparison to **114. (**Table 19**)** This may be due to the presence of 'H' atom in place of methyl group.[108]



112

Scheme 31 Synthesis of complex **112**

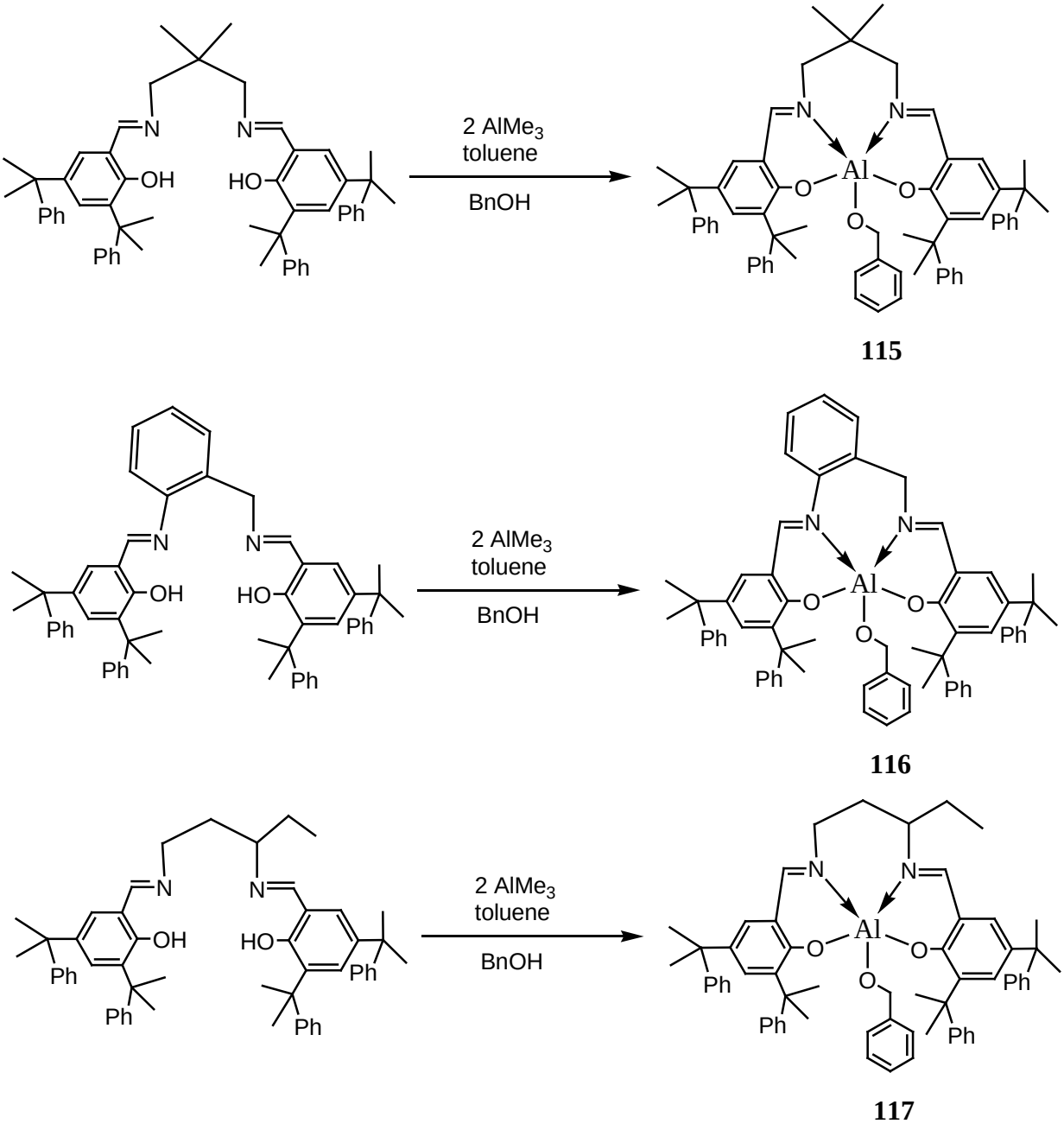


Scheme 32 Synthesis of complexes **113-114**

Table 19 Polymerization of *rac*-lactide by complexes **113-114**

Entry	Complex	Time (min)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**113**	90	96.2	13300	32900	1.24	-
2	**114**	120	87.6	12100	20000	1.05	-

Conditions: [*rac*-LA]$_0$/[Al] /[BnOH] = 99 /1 /1, [*rac*-LA]$_0$=0.474 mol.L^{-1}, toluene, 110°C.



Scheme 33 Synthesis of complexes **115-117**

The complexes **115-117** synthesized by Scheme 33 perform the ROP of *rac*-LA (Table 20). Complexes **115** and **116** exhibit very high isotactic selectivity, estimated from a homodecoupled ^{1}H NMR, with conversion >90% at 70°C in toluene. The slight selectivity

difference between **115** and **116** might be due to more flexibility of 2,2-dimethyl-1,3-diamine than 2-(aminomethyl)aniline.[85]

Table 20 Polymerization of *rac*-lactide by complexes **115-117**

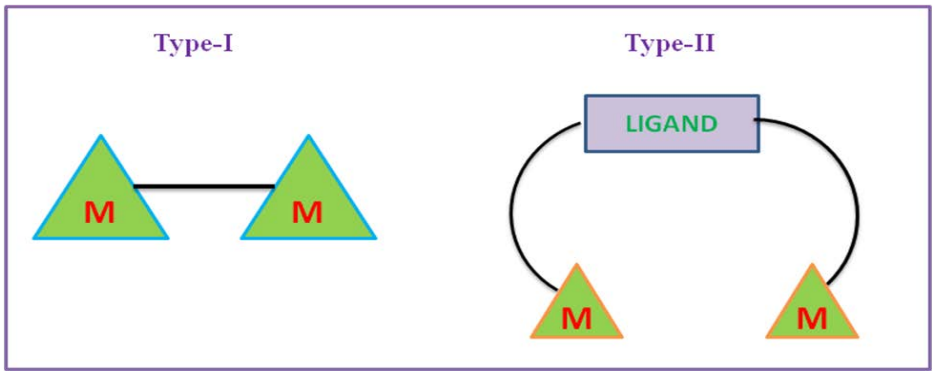
Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**115**	12	96	14000	13900	1.10	-
2	**116**	12	97	14000	14600	1.09	-
3	**117**	12	72	10500	10900	1.06	-

Conditions: [*rac*-LA]$_0$/[Al] /[^{i}PrOH] = 100 /1 /1, [Al] = 0.5 molL^{-1}, toluene, 70°C.

5.2 Bimetallic aluminium catalyst

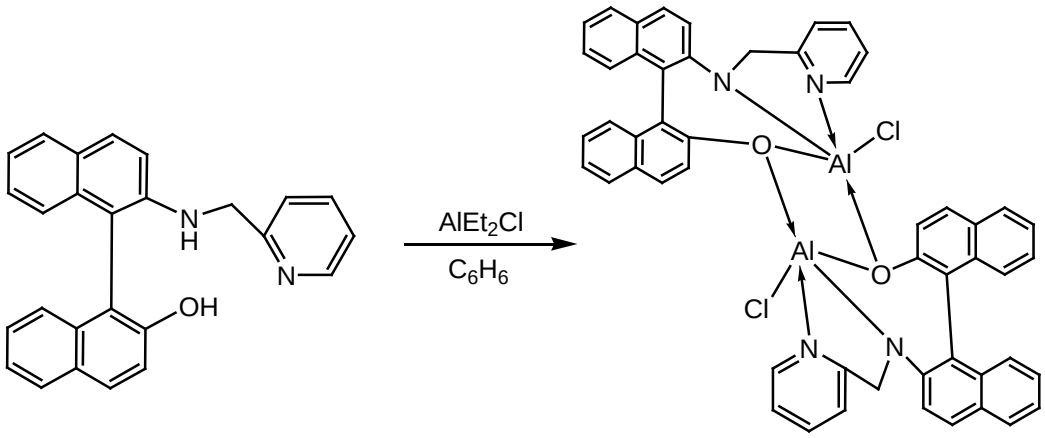
Since the beginning of concept of catalysis, it has been the constant challenge for chemist to search and find new design catalytic systems for fine-chemicals.[109] The activation of an organic functionality by two catalytic centers, is of great importance in the industrial processes and are playing a key role in the understanding of surface catalysis.[110] Bimetallic catalysts started to gain considerable commercial interest in 1960s because they displayed activities unlike those of the monometallic catalysts. The findings of these unexpected properties of bimetallic catalysts have inspired many extensive investigations on their possible applications. The relative ability of the metals to make a σ- or a π-complex with appropriate substrates is useful in making the choice of catalysts for the desired organic transformations. In bimetallic catalysts, the introduction of a second metal to a monometallic catalyst can influence the catalytic properties, including factors such as catalytic activity, stability and selectivity.[111-114] In this regard, homobimetallic catalysis constitutes an important subarea within the broader domain of multimetallic catalysis. In homobimetallic catalysis, the two metals are linked together by a metal - metal bond or via a

ligand and directly or indirectly the two metals participate in substrate activation (Scheme 34).[115- 116]



Scheme 34 Schematic representation of intramolecular homobimetallic Catalysts

Nowadays, binuclear aluminium complexes have great importance in the polymerization of LA. The binuclear aluminium chloride complex **118** is readily prepared by alkane elimination of diethylaluminium chloride with protic ligands (Scheme 35).[117]



118

Scheme 35 Synthesis of complex **118**

From the polymerization data, it is evident that complex **118** can initiate the ROP of *rac*-LA under the conditions given in Table 21. Complete conversion of 500 equiv of *rac*-LA occurs

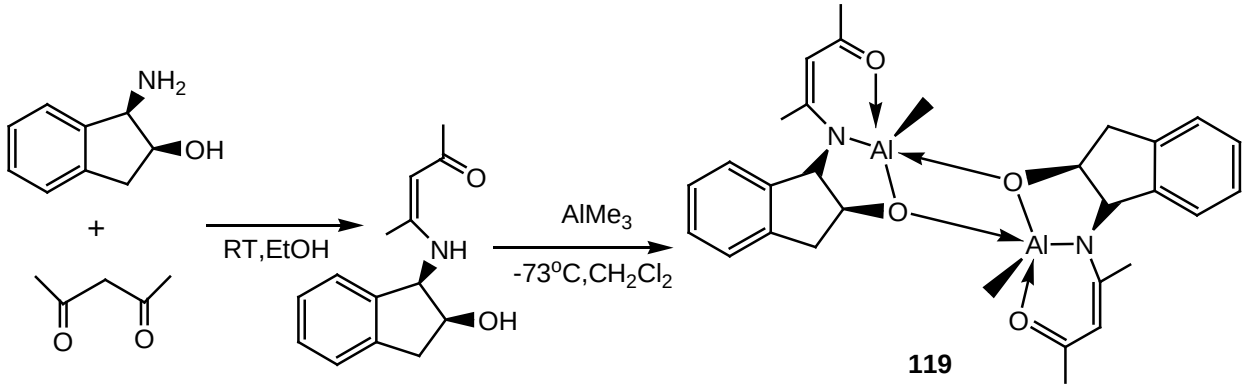
within 48 h at 70°C in toluene at [*rac*-LA] = 0.5 mol L^{-1}, and the molecular weight distribution is very narrow (1.13) leading to the heterotactic-rich polylactides (Table 21).[117]

Table 21 Polymerization of of *rac*-Lactide complex **118**

Entry	Solvent	Conversion(%)	M_n (NMR) (g mol^{-1})	PDI	P_r(%)
1	Toluene	100	36200	1.13	0.72
2	THF	62	22100	1.17	0.68

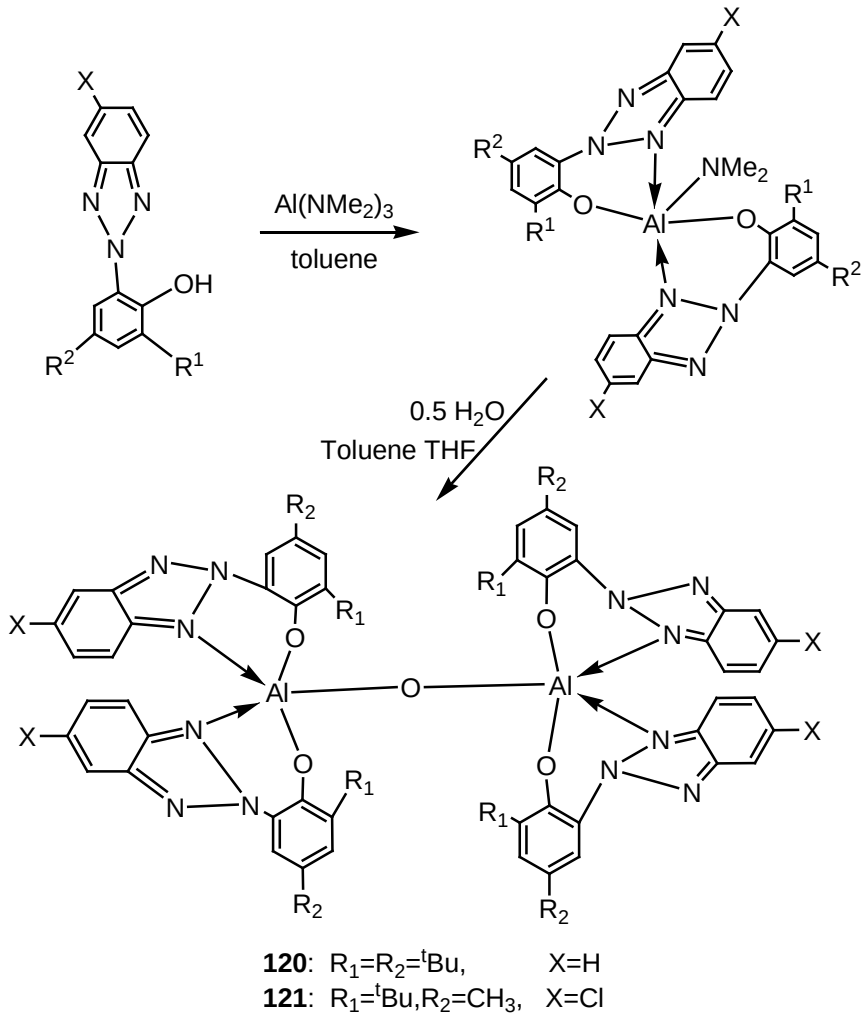
Conditions: [*rac*-LA]$_0$/[Al] / Propylene oxide = 500 /1/2, 48 hrs, 70°C.

A new ONO-type tridentate dianionic chelating ligand, binuclear aluminium complex **119** was synthesized by the reaction of 2,4-pentanedione with (1S,2R)-(−)-cis-amino-2-indanol and then recting with $AlMe_3$ (Scheme 36), which was characterized by NMR spectroscopy, mass spectrometry and elemental analysis.[118]



Scheme 36 Synthesis of complex **119**

Methyl aluminium complex **119** has been tested as a catalyst for ROP of LA in the presence of iso-propyl alcohol as an initiator and narrow PDI (1.01) PLA was obtained.[118] The binuclear aluminium complexes **120-121** coordinated with sterically hindered benzotriazole phenoxide ligands are illustrated in Scheme 37.[119]



Scheme 37 Synthesis of complexes of **120-121**

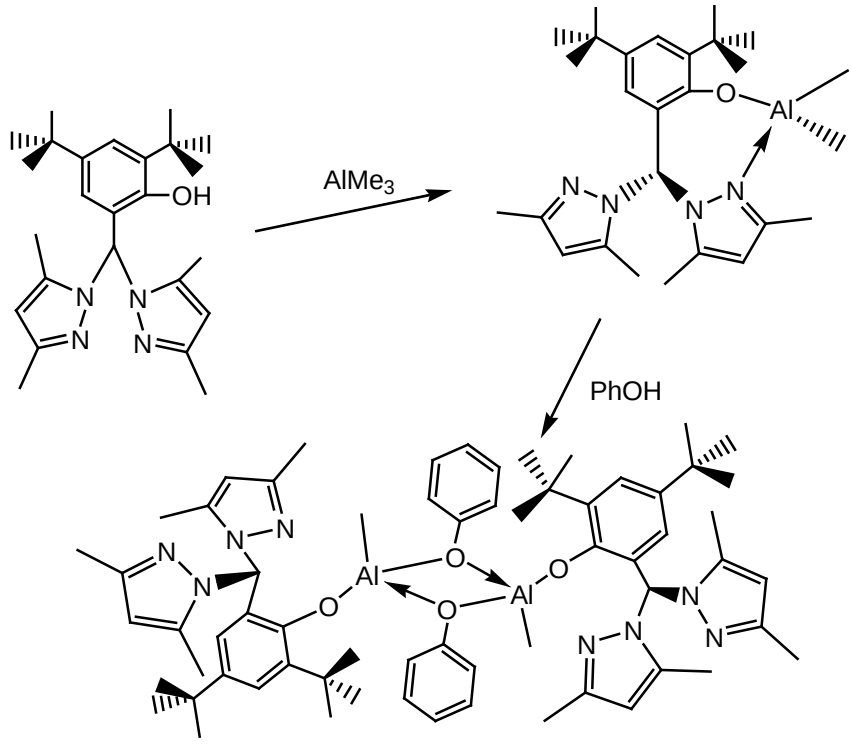
Further, the addition of two equivalents of 9-anthracenemethanol (9-AnOH) and Al catalyst (5 mM) in toluene (10 mL), aluminium complexes **120-121** exhibited good catalytic activity towards ROP of *L*-LA at 110°C. (Table 22) Moreover, **120-121**/9-anthracenemethanol catalytic systems were able to give polymers with the expected molecular weights and narrow molecular weight distributions (PDI < 1.25).[119]

Table 22 Polymerization of *L*-Lactide complexes **120-121**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**120**	24	92	13500	13500	1.22	-
2	**121**	11	92	13500	13100	1.16	-

Conditions: $[LA]_0/[Al]$ /[AnOH] = 100 /1 /1, toluene, 110°C. [Al]= 0.05 mmol

The bimetallic aluminium complex **122** was synthesized as described in the Scheme 38. This aluminium complex **122** was assessed in the polymerization of *L*-LA in toluene at 70 ^{0}C with a prescribed equivalent molar ratio of initiator and monomer (1: 200) and found a trace amount of PLA i.e. complex **122** was inactive under the used polymerization conditions.[120]



122

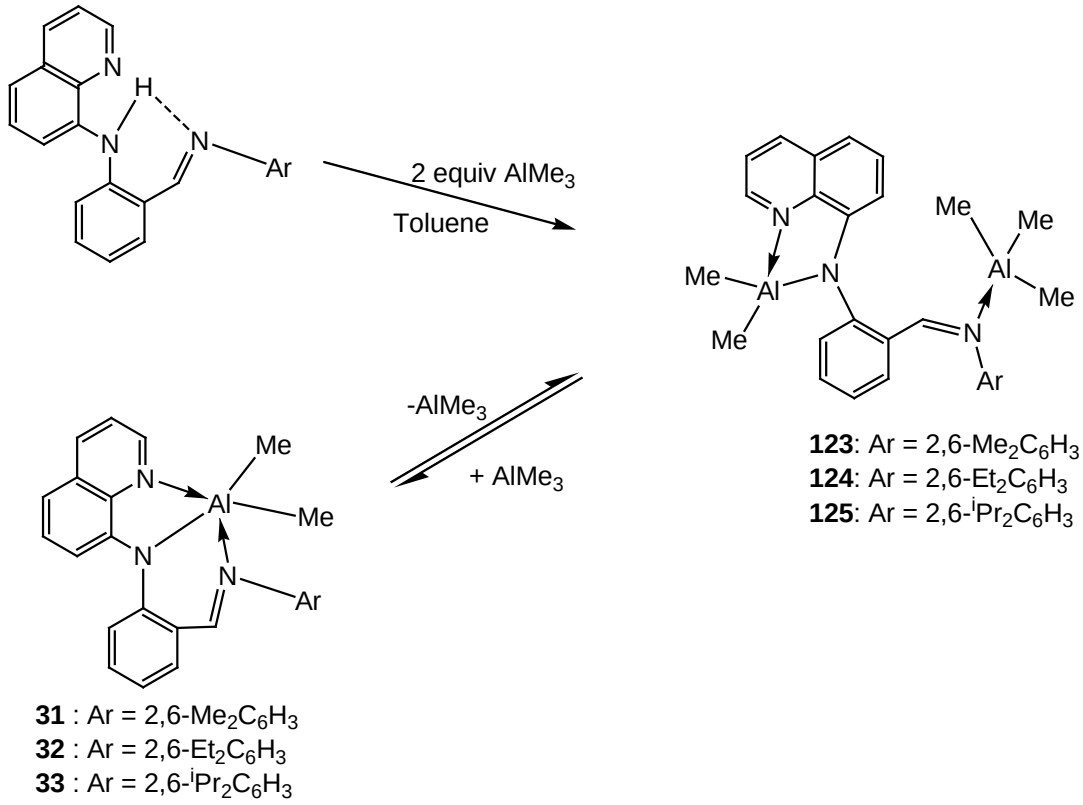
Scheme 38 Synthesis of aluminium complex **122**

The aluminium complexes **123-125** (Scheme 39) were investigated as initiators for the ROP of *L*-LA in toluene at 70°C (Table 23). When used as single component, all the aluminium complexes are almost inert for LA polymerization and no polymer was obtained even at high temperature. While when activated with benzyl alcohol, the activities were improved and about 90–95% conversions were achieved in 24 h.[89]

Table 23 Polymerization of *L*-lactide by complexes **123-125**

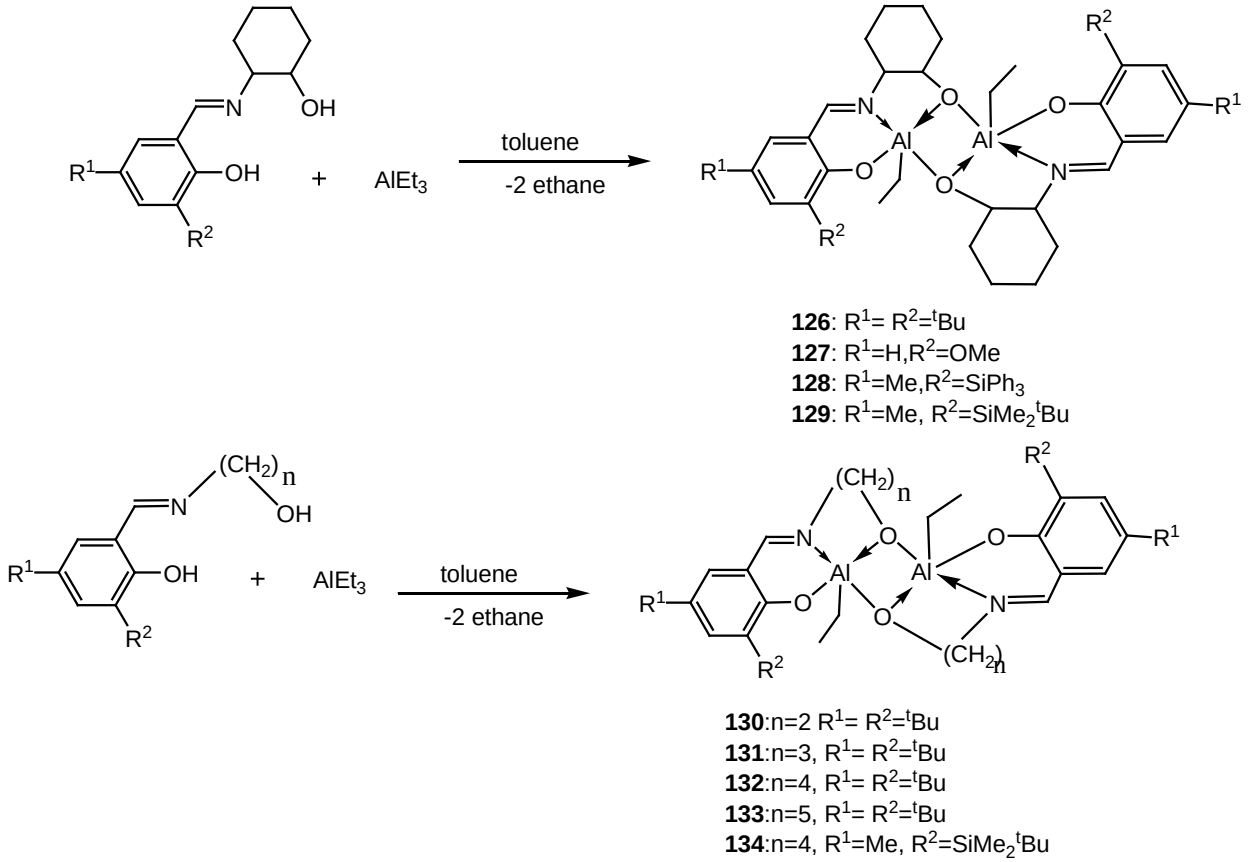
Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**123**	24	90.60	2600	2700	1.13	-
2	**124**	24	94.68	2700	3900	1.21	-
3	**125**	24	94.62	2700	3800	1.23	-

Conditions: $[LA]_0/[Al]/[BnOH] = 100 / 1 / 5$, [Al] = 30 μmol, toluene, 70°C.



Scheme 39 Synthesis of complexes **123-125**

The aluminium complexes **126-134** were synthesized as described in Scheme 40, by the reaction of triethylaluminium and chiral amino alcohols or aliphatic amino alcohols. These complexes were used in the ROP of *rac*-LA in solution (Table 24). Although complex **126** was not efficient at catalyzing *rac*-LA in $CDCl_3$ after an extended period of time at 60°C; over the same time period a 57% conversion to PLA was noted in toluene at 70°C. In the series of aluminium complexes **126-129** when the substituents (R^2) on the phenoxide portion of the Schiff base ligand increased in size (R^2 = $SiPh_3$) or is more electron donating (R^2 = OMe), the rate of polymerization decreased. This may be due to steric effect.[66] Complex **126** afforded a moderately isotactic polylactide with a P_m value of 0.70, whereas, complexes **127** & **128** produced atactic polylactide with P_m values less than 0.50. The aluminum complexes **130**, **132**, **133** & **134** were observed to polymerize rac-lactide at faster rates than complex **126** to provide isotactic polymers with P_m values of 0.62, 0.76, 0.73, and 0.82, respectively. And also it was shown that when the substituents on the phenoxide (R^2) of the half-salen ligand in the complexes **132** & **134** increased in size from ^{t}Bu to $SiMe_2{}^t$Bu, the percent of isotacticity of the polymer increased from 0.76 to 0.82.[66]



126: R^1= R^2=^{t}Bu
127: R^1=H,R^2=OMe
128: R^1=Me,R^2=$SiPh_3$
129: R^1=Me, R^2=$SiMe_2{}^t$Bu

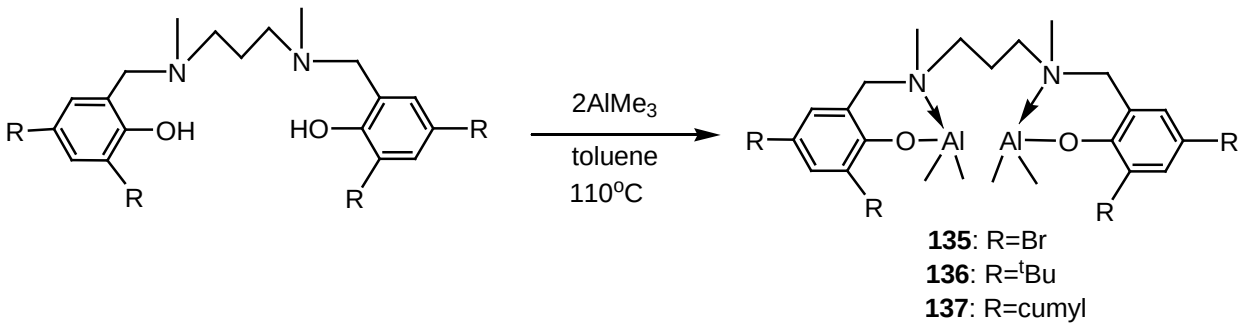
130:n=2 R^1= R^2=^{t}Bu
131:n=3, R^1= R^2=^{t}Bu
132:n=4, R^1= R^2=^{t}Bu
133:n=5, R^1= R^2=^{t}Bu
134:n=4, R^1=Me, R^2=$SiMe_2{}^t$Bu

Scheme 40 Synthesis of complexes **126-134**

Table 24 Polymerization of *rac*-lactide by complexes **126-134**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m (%)
1	**126**	66	57	4100	7900	1.05	70
2	**127**	69	43	3200	3800	1.08	<50
3	**128**	168	45	3200	4900	1.09	<50
4	**129**	15	0	-	-	-	-
5	**130**	15	64	4600	7000	1.04	62
6	**131**	15	0	-	-	-	-
7	**132**	15	34	2400	2400	1.07	76
8	**133**	15	50	-	-	-	73
9	**134**	15	21	-	-	-	82

Conditions: $[rac\text{-LA}]_0/[Al]$ = 50 /1 , [Al] = 0.5 $molL^{-1}$, toluene, 70°C.



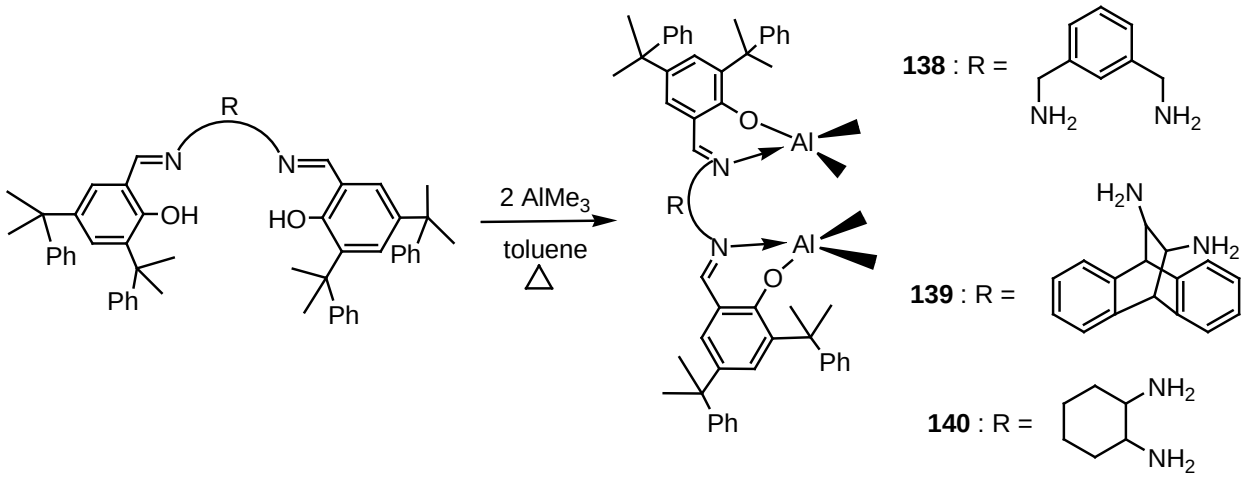
Scheme 41 Synthesis of complexes **135-137**

Dinuclear aluminium complexes **135-137** (Scheme 41) were active catalysts for the ROP of *rac*-LA at 70°C in toluene, and the molar ratio of 2-propanol to aluminium complex had a significant influence on the catalytic efficiency of polymerization. For all aluminium complexes, a relatively long time was required for polymerization with the addition of 2 equiv. of 2-propanol. Apparently enhanced activity could be observed in the presence of 4 equiv. of 2-propanol. The introduction of substituents such as tert-butyl and cumyl groups on ligands resulted in a remarkable decrease of the polymerization rate (Table 25).[84]

Table 25 Polymerization of *rac*-lactide by complexes **135-137**

Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m
1	**135**	18	88	6300	6900	1.10	0.57
2	**136**	96	86	6200	5700	1.13	0.62
3	**137**	96	83	6000	5600	1.12	0.62

Conditions: [*rac*-LA]$_0$/[Al]/ [^{i}PrOH] = 100 /1/2, [*rac*-LA]$_0$ = 1.0 mol L^{-1} , toluene, 70°C.



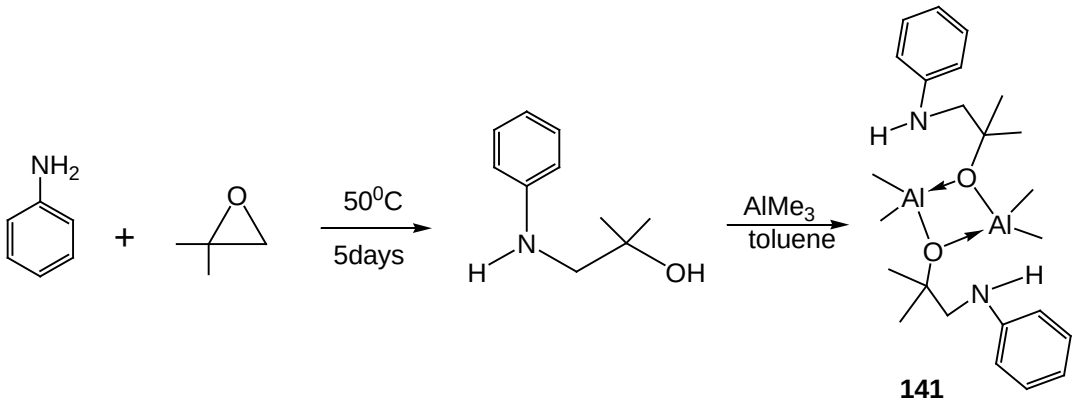
Scheme 42 Synthesis of complexes **138-140**

The bimetallic complexes **138-140** were synthesized following the procedure given in Scheme 42. Aluminium methyl complexes **138** and **139** for *L*-LA polymerization in the presence of benzyl alcohol have good molecular weight control but unfortunately do not have selectivity in the reaction. In addition, complex **140** exhibits >90% conversion at 70°C in toluene with a low isotactic selectivity (Table 26).[85] The less catalytic activity of **138-139** in comparision to **140** is probably due to the presence of sterically bulky substituent on the diamine which is responsible for retarding the reaction rate.[85]

Table 26 Polymerization of *L*-lactide by complexes **138-140**

Entry	Complex	Time (h)	Conversion (%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**138**	12	57	4200	3700	1.08	-
2	**139**	12	61	4400	4200	1.08	-
3	**140**	8	99	7200	8000	1.25	-

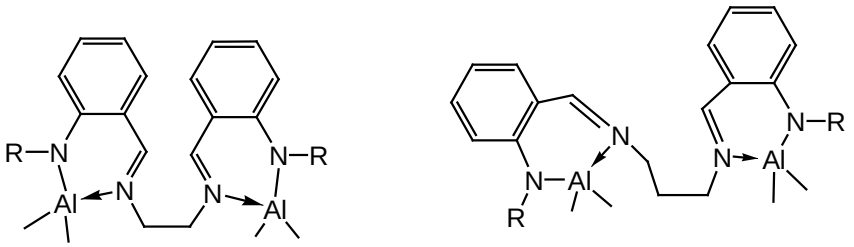
Conditions: $[LA]_0/[Al]/[BnOH]$ = 100 /1/4, [Al] = 5mM, toluene, 70°C.



141

Scheme 43 Synthesis of complex **141**

The dinuclear aluminium complex **141** was synthesized via simple exchange reaction by reacting $AlMe_3$ with the ligand 2-methyl-1-(phenylamino)propan-2-ol (Scheme 43). This complex was tested for ROP of *L*-LA in toluene at 70ºC in the presence of 9-hydroxyfluorene. Rapid polymerization was observed and monomer conversion up to 100% could be reached within 6 h. However, very little conversion was observed for the complex in the absence of 9-hydroxyfluorene. It is reasonable to assume that the dimethylaluminium compound reacts with 9-hydroxyfluorene, giving rise to methane.[121]



142: R = 2,6-$^{i}Pr_2C_6H_3$
144: R = C_6H_{11}
146: R = Me

143: R = 2,6-$^{i}Pr_2C_6H_3$
145: R = C_6H_{11}
147: R = Me

Scheme 44 Bimetallic aluminium complexes **142-147**

The polymerizations of *rac*-LA catalyzed by **142-147** (Scheme 44) are rapid but lack of control. High polydispersities and molecular weights are indicative of poor catalyst stability and

activity at high temperature 120°C. However, the same catalysts offer good control in toluene at 70ºC, reaching moderate to high conversions in 16 h. For these catalysts higher conversions led to catalyst degradation and transesterification of the polymer (Table 27).[81]

Table 27 Polymerization of *rac*-lactide by complexes **142-147**

Entry	Complex	Time (h)	Conversion(%)	M_n (Theory) (g mol^{-1})	M_n (GPC) (g mol^{-1})	PDI	P_m / P_r
1	**142**	16	67	9594	9010	1.17	-
2	**143**	16	60	8592	9123	1.25	-
3	**144**	16	82	11724	11244	1.23	-
4	**145**	16	65	9308	9034	1.37	-
5	**146**	16	66	9322	7324	1.07	-
6	**147**	16	58	8701	6780	1.07	-
7	**142**	3	82	9447	18626	1.59	-
8	**143**	3	85	9724	30539	1.64	-
9	**144**	3	86	9908	16132	1.47	-
10	**145**	3	78	8986	26507	1.49	-
11	**146**	3	81	11416	11834	1.58	-
12	**147**	3	91	13590	10175	1.56	-

Conditions: [*rac*-LA]$_0$/[Al]/ [BnOH] = 200 /1/2, [Al] = 0.5 molL^{-1}, toluene, for entry 1-6 temp is 70 ^{0}C and for entry 7-12 temp is 120°C

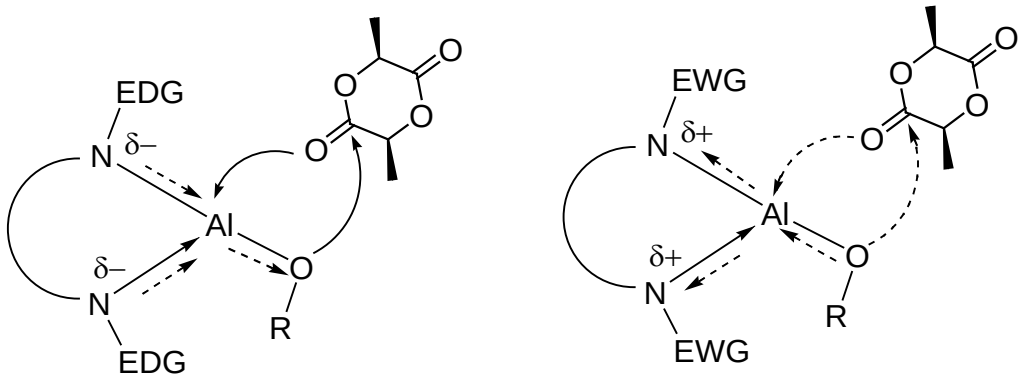
6. Concluding remarks

After reviewing the reported examples for ROP using aluminium catalysts/initiators, it can be safely concluded that, production of ecofriendly high molecular weight biodegradable and biocompatible PLA with high yield can be achieved by ROP using aluminium catalyst. Further, the production cost of different polymer depends upon the catalyst. As described above, great progress in the ROP of lactide by aluminium catalysts/initiators have been achieved in the past few decades as they are very economic and almost non-toxic reagents. The methodologies

described have clearly opened up new avenues for a major growth in the area of ROP of LA by aluminium catalyst.

Aluminium catalysts/initiators such as monometallic aluminium and bimetallic (homo metal) aluminium compounds are used in the ROP of lactide. All of these processes have their relative advantages and disadvantages. Based on the analysis, it can be concluded that aluminium compound with alcohol group or alkoxy aluminium compound are used for ROP of LA, and changing the ancillary ligand of an organoaluminium complex is obviously an important strategy for the modification of the catalyst performance. The control of the composition and microstructure of the resulting PLA, for example, high molecular weight PLLA can be synthesized by the monometallic aluminium and bimetallic aluminium system with narrow PDI and high yield (>99).

The mononuclear complexes have higher selectivity than dinuclear aluminium complexes, probably because the mononuclear complex can provide a special geometry space for the monomer LA to enter and react with the active metal center. And also the electron-donating substituents at the phenyl rings decrease the electrophilicity of the aluminium center as well as decrease the bond strength between aluminium and alkoxide group, (Scheme 45) and are favorable for the coordination and insertion of LA monomers, whereas the electron withdrawing group gives the adverse effect. Therefore, future challenges in this area will include the development of more active mononuclear catalyst systems with electron-donating substituents at the phenyl rings which can efficiently be used for ROP of LA in a controllable fashion, to produce polymers with desired physical, mechanical and optical properties. Undoubtedly, synthesis of new organoaluminium complexes with various sophisticatedly controlled ligands will continue to play an important role in these endeavors.



a b

Scheme 45 Generalized mechanism for ROP of LA by aluminium catalyst (EDG = Electron Donating Group and EWG = Electron Withdrawing group)

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