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REVIEW

Living and Immortal Ring-Opening Polymerization of Cyclic Esters

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ABSTRACT

The limited availability of fossil fuels on the Earth has led researchers to develop new materials that are derived from renewable feedstocks. The polymers produced from the ROP of cyclic esters like (LA and ε-CL) are biodegradable, biocompatible, and bioassimilable and thus find major applications in various field. The ROP are catalyzed by the metal-based organometallic catalyst and metal-free organocatalyst. This review exemplifies the living and immortal ROP. The advantage of such polymerization is that they produce polymers with controlled molecular weight distribution. For the immortal ROP, more than one polymer chain grows from the single catalytic site in the presence of chain transfer agents (CTAs), and thus catalyst loading is low, which make the process economically more viable. The nature of CTAs and loading of CTAs with respect to the catalyst is crucial as the catalyst should be effective in the presence of CTAs. The review also discusses functionalized CTAs employed for the polymerization in some instances where functionalized polymers are generated.

KEYWORDS

Ring-opening polymerization, immortal polymerization, living polymerization, chain transfer agents.

INTRODUCTION

Background

The polymers, both natural (cellulose, starch, etc.) and synthetic (polyethylene, polypropene, polyvinyl chloride, polylactide, etc.), find extensive application in our daily life [**1**]. The synthetic polymers derived from petroleum feedstock that once attracted significant interest in academia and industry have been put to limited use in the 21st century due to the limited availability of fossil fuels and growing awareness about environmental issues [**2**]. The synthesis of environmentally benign polymeric materials that could potentially substitute for petroleum-based polymer products is the focus of the present era. The polymerization process involves reactions among the monomer molecules for the formation of macromolecules. There are mainly two pathways by which polymerization reactions occur (chain-growth polymerization and step-growth polymerization) [**3**]. There are three stages (initiation, propagation, and termination) for any polymerization reaction irrespective of the mechanism by which polymerization occurs [**4**]. The polymer chain formation starts with the initiation, followed by the propagation process where the polymer chain grows, and ultimately, the polymer chain's growth is ceased at the termination step [**5**].

The initiation step involves activating the single monomer molecule by the suitable agent that generates the initiating species. The initiating species further reacts with more monomeric molecules to give the growing polymer chain [**6**]. The rate of initiation and the rate of propagation are the two vital parameters that govern the molecular weight distribution of a polymer [**7**]. The molecular weight distribution expresses the relationship between the number of moles of the polymer and the molar mass of the species [**8**]. The narrow molecular weight distribution indicates that each growing polymer chain has approximately the same

number of monomer units. It arises when the rate of initiation is greater than the rate of propagation such that each monomer molecule is activated almost at the same time. On the other hand, when the rate of propagation is greater than the rate of initiation, polymer chains of varying lengths arise that lead to broad molecular weight distribution [**9**] **(Fig. S1)**.

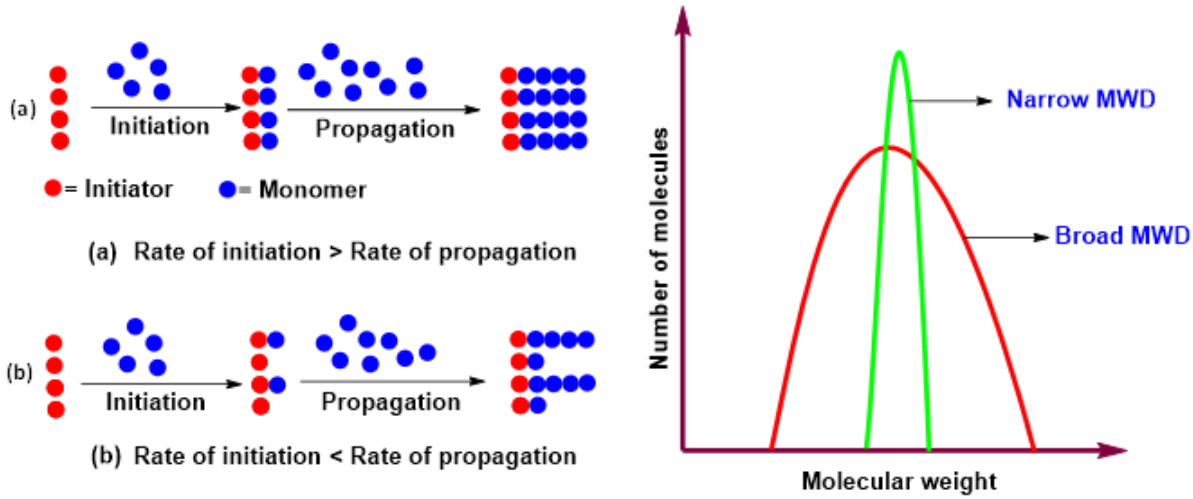

Fig. S1. Schematic diagram showing growth of polymer chain.

Theoretically, the chain propagation continues until all the monomer molecules get consumed. The chain termination stage involves the chemical reactions where the polymer chain ceases to grow due to the irreversible formation of non-propagating species [**10**]. The most common pathways by which chain termination occurs for the growing polymer chain are the recombination of the two reacting species and the disproportionation of the growing polymer chain [**11**]. When the chain termination is absent in the polymerization reaction, the growing polymer chain continues to live for a long time unless the monomer molecules get exhausted. The phenomenon happens in the case of living polymerization, where the polymer chain growth is interrupted by the exhaustion of the monomer, and polymerization resumes once the additional monomer is added [**12**]. The living polymerization reaction is usually characterized by narrow molecular weight distribution of the polymer, linear relationship between number average molecular mass and percentage conversion, the observed molecular mass of the polymer is almost equal to the theoretical molecular mass as predicted by monomer/initiator ratio and the number of growing polymer chain is equal to the number of initiators molecules [**13**]. The living polymerization reaction can be terminated by adding chain-terminating agents, usually protic sources like methanol, externally. The chain-terminating agent reacts with the growing polymer chain end and deactivates the chain end and thus, the growth of the polymer chain is stopped. The main difference between conventional polymerization and living polymerization is that for living polymerization, the termination is solely governed by the experimenter, while for conventional polymerization, it is an unavoidable process [**14**]. The concept of living polymerization was discovered for the first time in 1956 by Michael Swarc for the organo-alkali metal initiated anionic polymerization of styrene [**15**]. The polymerization was initiated by the green coloured complex formed from naphthalene anion and sodium cation. The polymerization starts with the transfer of an electron from a naphthalene radical anion to a monomer molecule. The negatively charged monomer radical ion that is formed undergoes dimerization that acts as an initiator for the polymerization **(Scheme S1)**. The polymerization continues until the monomer molecules are exhausted, or the addition of water terminates the polymerization. The living nature of the polymerization reaction was confirmed when the polymerization resumed after the addition of the second batch of monomer molecules after the first batch of monomer molecules was exhausted.

There is another category of polymerization reaction where the growing polymer chain cannot be killed even by adding the protic sources. The protic sources act as chain-transfer agents and participate in rapid and reversible chain-transfer reactions. Due to the reversibility of the chain transfer reaction, the growing polymer chain never dies completely and becomes dormant for some time. It is referred to as immortal polymerization [**16**]. The immortal polymerization reactions are characterized by polymers with narrow molecular weight distribution, number of polymer chains exceeding the number of initiator molecules and observed molecular weight is less than theoretical molecular weight predicted based on monomer/initiator ratio. For the immortal polymerization on the addition of a chain transfer agent, a fast reversible reaction occurs between a chain transfer agent and growing polymer chain [**17**] **(Fig. S2)**.

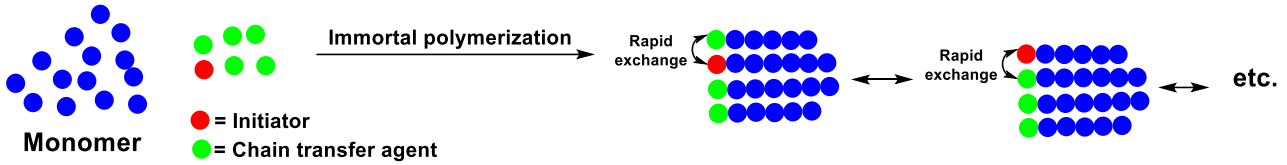

Fig. S2. Schematic representation of immortal polymerization.

The immortal polymerization was pioneered by Inoue *et. al*. in 1985 for the homopolymerization of propylene oxide with aluminium porphyrin-alcohol system [**18**]. It was observed that the polymerization of propylene oxide takes place readily with (tetraphenylporphinato) aluminium chloride in the presence and absence of methanol. It was observed that on the addition of protic source methanol, there was no chain termination as expected. There was a decrease in the average molecular weight of the polymer indicating increase in the number of growing polymer chains and polymers obtained have narrow molecular weight distribution. On addition of methanol, a rapid exchange takes place between aluminium alkoxide (TPP)AlOR and alcohol (R′OH), which is much faster than the propagation (insertion of epoxide into TPPAlOR) **(Scheme S2)**. The new aluminium alkoxide species (TPPAlOR′) and the polymer molecule with hydroxy end group are formed **(Equation 2b)**. From the new aluminium alkoxide species new polymer chain can grow **(Equation 2c)**, and the hydroxy-terminated polymer chain can further revive to growing species due to the reversibility of the reaction indicated in **(Equation 2b)** and thus, the polymer chain never dies. Thus, for controlled immortal ring-opening polymerization reactions rate of chain initiation must be greater than the rate of chain propagation ($k_i >> k_p$), irreversible chain termination reaction must be absent or minimal, and the rate of reversible chain transfer reactions must be greater than chain propagation ($k_{tr} >> k_p$).

The major advantage of immortal polymerization is the high catalytic activity due to which cost of metal catalyst for large volume of polymer production is low and there are less catalytic residues in the resulting polymer [**19**].

Scope

The scope of this review is to survey literature relating to living and immortal ring-opening polymerization (ROP) reactions of cyclic esters (lactide and ε-caprolactone). The review commences with a short discussion on the mechanistic aspect of ROP reactions. The major portion of the review focuses on homogeneous catalytic systems (metal-based and metal-free) for the ROP of lactide, with a few examples been discussed for ROP of caprolactone. Due to its slower biodegradation rate, polycaprolactone (PCL) has been less explored than polylactides (PLA). The most commonly studied metals for the ROP reactions include *s*-block metals (magnesium, calcium, potassium), *p*-block metals (aluminium, indium, tin) and *d*-block metals (titanium, zirconium, copper, zinc, yttrium). The review will mainly focus on complexes of these metals for living and immortal ROP studies. The sections are grouped according to the metals employed. The organocatalysts (metal-free) for the ROP reactions have been discussed briefly toward the end of the review.

GENERAL CONSIDERATIONS

Mechanistic aspect for ROP of cyclic esters

The 'coordination-insertion mechanism' and the 'activated monomer mechanism' are the two mechanisms primarily involved in ROP of cyclic esters. For the ROP of cyclic esters with organometallic catalyst via coordination insertion mechanism, the polymerization starts with coordination of Lewis acidic metal center to the carbonyl oxygen of the monomer. The nucleophilic group attached to the metal center then attacks the electrophilic carbonyl carbon, and the ring-opening of the monomer takes place by acyl-oxygen bond cleavage [**20**] (**Scheme S3 and Scheme S4**). The evidence for the formation of the complex between the initiator and the monomer came from the studies of Kohn for the polymerization of *rac*-lactide with Triisobutylaluminium (TIBA) [**21**]. The original stretching frequency for (C=O) and (C─O) in the IR spectrum for *rac*-lactide was observed at 1775 cm^{-1} and 1235 cm^{-1}. On addition of TIBA, it was observed that there was a shift in the ν(C=O) stretching frequency to longer wavelength and ν(C─O) to shorter wavelength, indicating a weakening of (C=O) and strengthening of (C─O) (**Scheme S4**). For the ROP of cyclic esters that proceeds through the coordination-insertion mechanism, ring-opening of the monomer occurs by the rupture of acyl-oxygen bond. The evidence for the acyl-oxygen bond cleavage came from the studies of Jérôme *et. al*. [**22**], where they carried out the polymerization of *L*-lactide in the presence of aluminium isopropoxide. The complete disappearance of the peak at 935 cm^{-1} in the IR spectrum corresponding to (C─O) stretching indicated that there is a cleavage of the acyl oxygen bond. The chain propagates by the subsequent addition of monomers to the growing polymer chain. The growing polymer chain is terminated by the addition of protic sources like methanol **(Scheme S4)**. In immortal ROP reactions, the growing polymer chain undergoes rapid and reversible exchange reactions with the chain transfer agent (usually protic sources, mainly alcohol) added initially in the reaction medium. The growing polymer chain L_nM─{O---C(O)}OR on reaction with a chain-transfer agent gets converted into a dormant polymer chain (H─Pol─OR), and new metal alkoxide is generated. The hydroxy-terminated dormant polymer chain can further acts

as a chain-transfer agent, and the dormant chain revives back into the growing polymer chain. The rapid growing/dormant polymer chain interconversion occurs during the entire lifetime of the polymerization process.

On the other hand, for the ROP of cyclic esters by organometallic catalyst via activated monomer mechanism [**23**], the polymerization starts with coordination of Lewis acidic metal center to the carbonyl oxygen of the monomer as same as the coordination-insertion mechanism. The attached ligand then attacks the electrophilic carbonyl carbon, and ring-opening of the monomer takes place by acyl-oxygen bond cleavage. For the next monomer, same cycle is repeated, and the final polyester can be found by hydrolysis reaction [**23**] **(Scheme S5)**.

LIVING AND IMMORTAL RING OPENING POLYMERIZATION REACTIONS

s-block metals

The synthesis of biodegradable aliphatic polyesters has become a vital area of research due to severe environmental issues that is prevalent in our society. The metal-based catalysts are generally used for the ROP of cyclic esters. Nowadays, researchers are focusing on developing catalysts based on bio-metals since metal residues cannot be entirely removed from the final product. Thus, by using bio-metals, the toxicity issues from the final polymer are minimal. The review will focus on *s*-block metals (alkali metals - lithium, potassium) and (alkaline-earth metals-magnesium and calcium) for living and immortal ring-opening polymerization reactions.

Alkali metals

In 2013, Carpentier and Sarazin research group reported a catalytic system based on bio-metals for the ring-opening polymerization of lactides [**24**]. In this regard, the attached ancillary ligand also plays a crucial role, and the choice of ligand framework is vital. The aminophenolates, due to their readily available synthetic pathway, low toxicity, and easy functionalization at the *ortho* position of the aromatic ring, that allows fine tuning in the electron-donating and chelating availability of metal, have drawn considerable attention. Carpentier and co-workers thus synthesized Lithium (Li) and Potassium (K) aminoether-phenolate complexes and investigated their catalytic activity for the ROP of *L*-lactide. The three ligand frameworks differed from each other in the ether linkage attached to aminoether-phenolate moiety **(Fig. S3)**.

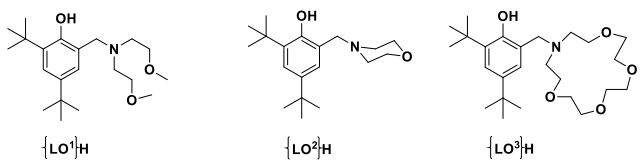

Fig. S3. Three aminoether-phenolate ligands.

The three lithium complexes **(LO^1)Li (a)**, **(LO^2)Li (b)**, and **(LO^3)Li (c)**, were prepared by the reaction of three different ligands and stoichiometric amount of *n*-BuLi in Et_2O **(Scheme 6)**. The ^{7}Li NMR (benzene-d_6) of complex **(LO^1)Li** and complex **(LO^3)Li** gave sharp signals at δ = 0.99 ppm and δ = 0.07 ppm respectively and the value obtained was consistent with the fact that electron density at the metal center is higher in the complex **(LO^3)Li** as compared to the complex **(LO^1)Li**. The complex **(LO^2)Li** was sparingly soluble in hydrocarbon and chlorinated solvent and readily soluble in THF, so its ^{7}Li NMR was recorded in THF-d_8 and that gave δ = 0.86 ppm. The potassium complex **(LO^3)K (d)** was synthesized by the equimolar reaction between potassium hydride (KH) and **(LO^3)H** in THF **(Scheme S6)**. The bimetallic heteroleptic lithium complex **LiN(SiMe$_2$H)$_2$·Li{LO^3} (6e)** was synthesized by reaction of two equivalent of $LiN(SiMe_2H)_2$ with (LO^3)H in diethyl ether **(Scheme S6)**. The ^{1}H NMR (toluene-d_8) recorded at room temperature (298K) showed a broad singlet for the two $SiMe_2H$ and fluxional behaviour for all hydrogen attached to aza-crown-ether moiety. When ^{1}H NMR was recorded at a lower temperature (233K), two different signals were detected for $SiMe_2H$ and fluxionality of hydrogens of aza-crown-ether fragment was completely frozen. The ^{7}Li NMR (benzene-d_6) detected two distinct signals for two lithium centers at δ = 1.14 ppm and δ = – 0.46 ppm in the temperature range (233K-353K) indicating that the two lithium atoms were in different coordination environment and there is no exchange between them at higher temperature upto 353K. Single crystals from all the complexes were obtained by recrystallizing the purified product and subjected to X-ray diffraction studies. The X-ray diffraction studies well elucidated the structure of five complexes in the solid state. The complex **(LO^1)Li** was dimeric with planar a Li_2O_2 core. The two lithium atoms were in a distorted tetrahedral environment with two coordination sites occupied by bridging oxygen atoms coming from phenolate moiety. The third and fourth coordination was completed by the oxygen atom of ether linkage and the nitrogen atom of amine, respectively, of phenolate moiety. The other oxygen atom of the ether arm was free.

The complex **(LO^2)Li** crystallized as a dimeric THF-adduct **((LO^2)Li·THF)$_2$**. One asymmetric unit has two identical molecules which are independent, and each molecule consists of a Li_2O_2 core where two lithium atoms are bridged by an oxygen atom of the phenolate unit. The lithium atoms are in pseudo-tetrahedral coordination environment, with the third coordination satisfied by N atom of morpholine unit attached to one side of phenolate and fourth site is occupied by THF. The Li---N_{amine} bond distance is slightly higher in the structure of **((LO^2)Li·THF)$_2$** (2.25 Å) in comparison to the dimeric structure of **(LO^1)Li** (2.10 Å) due to repulsion between the morpholine rings. The solid-state structure of **(LO^3)Li** has the lithium atom tightly coordinated to the oxygen atom of the phenolate unit (Li---$O_{phenolate}$ = 1.85 Å) and loosely

bound by one nitrogen and four oxygen atom from the aza-crown fragment, and thus, the metal center is six - coordinated. The potassium complex crystallizes in dimeric form with a non-planar K_2O_2 core with two $O_{phenolate}$ bridging two potassium atoms. The potassium atom is further bound to nitrogen and oxygen atoms of the aza-crown moiety, thus making the potassium atom seven coordinated. The potassium atom, due to its large size, does not reside in the pocket of morpholine moiety and lies 1.63Å above the morpholine plane which is in contrast to complex **(LO^3)Li** where lithium atom due to its small size sits inside morpholine cavity. The bimetallic complex **LiN(SiMe$_2$H)$_2$·Li{LO^3}** has two Li atoms bridged by an oxygen atom of the phenolate group. The two lithium atoms are in different coordination environment. One of the lithium atoms is five coordinated with the four sites occupied by nitrogen atom, three oxygen atoms from the aza-crown ether fragment and the fifth site occupied by the bridged oxygen atom of the phenolate group. The geometry around the five-coordinate lithium atom can be described as intermediate between square-pyramidal and trigonal-bipyramidal. The other lithium atom is three-coordinate and adopts trigonal planar geometry with one coordination-site occupied by the oxygen atom of phenolate moiety, the second coordination site occupied by oxygen atom of the aza-crown ether fragment and third site attached to nitrogen atom of -N(SiMe$_2$H)$_2$group. The pulse-gradient spin echo NMR showed that four complexes **(6a-6d)** are monomeric in the solution phase, while for complex **(6e)** the DOSY NMR studies revealed that in the solution phase also the complex retained its heteroleptic bimetallic character. The five complexes were screened for the ROP of *L*-lactide at 30 ˚C in dichloromethane in the presence of one equivalent of benzyl alcohol. It was observed that among the five complexes, the electron-rich and sterically bulky complex **(6c)** gave polymers with narrow molecular weight distribution (PDI = 1.05). The other four complexes though showed high reaction rate, but polymerization was less controlled as indicated by broad molecular weight distribution. The complex **(6c)** was further investigated for the ROP studies in the absence of benzyl alcohol and in the presence of more than one equivalent of benzyl alcohol. It was observed that in the absence of benzyl alcohol, the ROP reaction was controlled as indicated by narrow PDI value (PDI = 1.18) but the reaction rate was very slow (% conversion of monomer = 12). In the presence of one equivalent of benzyl alcohol the molecular weight of the polymer increased linearly with percentage conversion as recorded by carrying out the reaction at different time intervals. When the initial monomer loading was increased to two folds the molecular weight of the polymer doubled (([monomer]: [catalyst]: [benzyl alcohol] = 50:1:1) M_w = 7600) and ([monomer]: [catalyst]: [benzyl alcohol] = 100:1:1 M_w = 16000) which indicated the living nature of the polymerization reactions. In addition, the molecular weight of the polymer diminished proportionally with increase in the amount of benzyl alcohol **(Table S1)**, indicating an increase in the number of growing polymer chains which is a typical characteristic of immortal polymerization. The living and the immortal ROP reaction catalyzed by the binary catalyst **(LO^3)Li** and benzyl alcohol operated by an activated monomer mechanism **(Scheme S7)**. The end group analysis of the polymer in combination with stoichiometric model reactions monitored by ^{1}H NMR showed that the reaction goes by an activated-monomer mechanism. When an equimolar mixture of **(LO^3)Li** and benzyl alcohol was monitored by ^{1}H NMR spectroscopy, it was observed that the spectrum resembled exactly the NMR spectra of **(LO^3)Li** and benzyl alcohol taken separately under the same reaction conditions. This indicated that there was no detectable reaction between **(LO^3)Li** and benzyl alcohol, leading to the formation of free**(LO^3)H** and BnOLi. When the reaction was carried out with 1:1:1 mixture of **(LO^3)Li**, benzyl alcohol and *L*-lactide it was observed that benzyl-2-((2-hydroxyproponyl) oxy) propanoate (**P$_1$**) formed by the quantitative reaction between BnOH and *L*-lactide while **(LO^3)Li** remained intact **(Scheme S7)**. Further when the reaction was carried out with 1:1:2 mixture of **(LO^3)Li**, benzyl alcohol and *L*-lactide it was observed that product **(P$_2$)** formed corresponding to nucleophilic attack of benzyl alcohol on lactide followed by reaction with **(P$_1$) (Scheme S7)**.

Table S1. Polymerization data for ROP of *L*-LA in the presence of varying amount of benzyl alcohol [BnOH].

[*L*-LA]/[Catalyst]/[BnOH]	Time(h)	Yield (%)	M_n (g/mol)
100:1:1	8	90	16000
100:1:2	8	92	7400
100:1:4	8	98	4100

Alkaline-earth metals

Chen and coworkers [**25**] reported inexpensive and convenient ligand-free commercially available dibutylmagnesium, in combination with an alcohol serve as efficient catalytic system for the immortal ROP of *L*-lactide. The metal precursor Mg^{n}Bu$_2$ can alone initiate the ROP of lactide, but the resulting PLA has broad molecular weight distribution (M_w/M_n) = 1.77. Since the metal-alkoxides are generally considered better precursors for the ROP reactions compared to metal alkyls, metal alkoxides were generated *in situ* by the reaction of dibutylmagnesium with different alcohol that differed from each other in steric bulk and acidity. Four different alcohols ^{i}PrOH, PhCH$_2$OH, Ph$_2$CHOH and Ph$_3$COH, were employed for the reaction with Mg^{n}Bu$_2$. It was observed that when the reaction of Mg^{n}Bu$_2$ was carried in the presence of an equimolar amount of alcohol only partial alcoholysis took place. As a result, the PLLA samples isolated showed binodal peaks in size exclusion chromatography traces, indicating the presence of two different initiating species Mg─C (due to metal alkyl) and Mg─O (due to metal-alkoxide). When the alcohol loading was increased to two equivalents, there was slight improvement achieved with respect to molecular weight distribution, but it was still broad. It was observed

that upon increasing the alcohol loading to six equivalents with respect to Mg^{n}Bu$_2$, except in the case of Ph$_2$CHOH, the reaction rate decreased significantly, as indicated by lower conversion of monomer to polymer **(Table S2)**. Thus, further studies were performed with higher loading of Ph$_2$CHOH in the presence of Mg^{n}Bu$_2$. It was observed that the molecular weight of the polymer varied inversely with the amount of Ph$_2$CHOH **(Table S3)**. Hence, with the increase in the amount of Ph$_2$CHOH, the number of growing polymer chains increased leading to a decrease in the molecular weight. The ROP of *L*-lactide thus showed characteristics of immortal polymerization. It was observed that the catalytic system was highly efficient with high conversion of monomer achieved by varying Ph$_2$CHOH from 2 to 300 equivalents and monomer loading upto 3000 equivalents at room temperature within 5-40 minutes.

Table S2. Polymerization data for ROP of *L*-LA in the presence of Mg^{n}Bu$_2$ with four different alcohols

ROH	[OH]/[Mg]	Time(min)	Conversion (%)	M_w/M_n
^{i}PrOH	1	5	>99	1.32
^{i}PrOH	2	10	30	1.25
^{i}PrOH	6	10	15	1.27
PhCH$_2$OH	1	5	>99	1.22
PhCH$_2$OH	2	10	60	1.66
PhCH$_2$OH	6	10	18	1.31
Ph$_2$CHOH	1	5	>99	1.32
Ph$_2$CHOH	2	5	>99	1.56
Ph$_2$CHOH	6	5	>99	1.31
Ph$_3$COH	1	5	86	1.53
Ph$_3$COH	2	10	27	1.47

Table S3. Polymerization data for ROP of *L*-LA in the presence of varying amount of [ROH]/[Mg^{n}Bu$_2$].

[*L*-LA]/ [Mg^{n}Bu$_2$]	[ROH]/ [Mg^{n}Bu$_2$]	Time (min)	Conversion (%)	M_n (g/mol)	M_w/M_n
1000:1	5	5	>99	2.90	1.07
1000:1	10	5	>99	1.45	1.09
1000:1	20	5	>99	0.73	1.08
1000:1	40	10	>99	0.38	1.09

The studies were further carried out to understand the mechanistic pathway and active intermediate for the reaction. To get an idea about the active intermediate, stoichiometric reaction between Mg^{n}Bu$_2$ and Ph$_2$CHOH (2 equiv.) was done in a mixed solution of THF and toluene **(Scheme S8)**. The reaction mixture was concentrated and cooled at −35 °C over two days, that afforded colourless crystalline solid. The X-ray diffraction studies and ^{1}H NMR (CDCl$_3$) analysis of complex **(8a)** suggested that the magnesium complex is tetranuclear, having C_2 molecular symmetry. The ^{1}H NMR studies showed that three different signals appeared (δ = 5.89, 5.70, 5.22 ppm), corresponding to the methine proton of diphenylmethanol group (-OPh$_2$CH), indicating that (-OPh$_2$CH) groups are bound to magnesium in three different coordination modes. The molecular structure of the complex **(8a)** showed that the four magnesium atoms are tetracoordinated with two adjacent Mg^{2+} ions being doubly bridged by the diphenylmethanol group. For the outer magnesium atoms, the second coordination site is occupied by the bridging Ph$_2$CHO group, the third coordination site is satisfied by terminal Ph$_2$CHO group and the fourth coordination site is occupied by a THF molecule. The inner magnesium atoms are bound to four bridging Ph$_2$CHO group. The ^{1}H NMR studies in THF-d_8 showed that the complex retained its tetranuclear structure in solution phase indicating that the complex was stable in polymerization medium (since the polymerization was carried in THF). The active intermediate for the polymerization was complex **(8a)**.

The mechanistic study for the polymerization reaction revealed that the reaction follows the coordination-insertion mechanism **(Scheme S9)**. The dibutylmagnesium (Mg^{n}Bu$_2$) reacts with Ph$_2$CHOH to generate tetranuclear magnesium diphenyl methoxide as the preliminary intermediate for the reaction. The tetranuclear magnesium complex is stable in the presence of excess Ph$_2$CHOH, but upon addition of two units of monomer (*L*-lactide) it quickly dissociates to give mononuclear intermediate (A). The monomer molecule that initially coordinates to the metal center subsequently inserts in between Mg─OCHPh$_2$ to give intermediate (B) that quickly transformed into (C). The intermediate (C) further adds two monomer molecules via coordination-insertion mechanism to give polymeric metal-alkoxide species (D). The reaction of Ph$_2$CHOH that acts as chain-transfer agent with intermediate (D) lead to formation of hydroxyl capped dormant polymer (E) and active species (A). The dormant chain can again revive back to growing polymer chain on reaction with other propagating metal-alkoxide species (F) to give (D) and dormant polymeric chain (G). On further addition of monomer, further chain propagation takes place to give active species (H). The end group analysis of the polymer showed signals at δ = 2.60 ppm for hydroxy-capped chain end and δ = 6.81 ppm corresponding to methine proton of ─COOCHPh$_2$ that is formed as a result of *L*-LA insertion into the Mg─OCHPh$_2$ bond. Thus, the end group analysis of the polymer further supports the coordination-insertion mechanism.

Wang and colleagues [**26**] synthesized magnesium complexes supported by phenoxide ligand and investigated their catalytic activities towards the ROP of ε-caprolactone and *rac*-lactide. The magnesium complexes in the presence of benzhydrol as the chain-transfer agent served as an efficient catalyst for the immortal ring-opening polymerization reactions which gave polyesters with well controlled molecular weight and narrow molecular weight distribution. The sterically bulky phenoxide proligands were synthesized by the Friedel-Crafts reaction of substituted phenol derivatives and benzhydrol in the presence of (conc.) HCl and ZnCl$_2$. The magnesium complexes were prepared by reacting respective proligands with half equivalent of dibutylmagnesium (Mg^{n}Bu$_2$) in THF at room temperature **(Scheme S10)**. The coordination of the proligands to the magnesium center was confirmed by the disappearance of signal corresponding to hydroxyl

group (─OH) and the upfield shift in the chemical shift values of the signals in the NMR spectrum. The new signal also appeared in the NMR due to coordinated THF molecule attached to the magnesium center. The X-ray diffraction studies of single crystals of complex **(10b)** and complex **(10c)** showed that the magnesium atoms adopt distorted tetrahedral geometry where the four-coordination site around the magnesium center is satisfied by two oxygen atoms from the phenoxide ligand and two oxygen atoms from coordinated THF. The catalytic activities of the three magnesium complexes for the ROP of cyclic esters (ε-caprolactone and *rac*-lactide) were investigated in the absence and presence of alcohol. The three different alcohols ($PhCH_2OH$, Ph_2CHOH and Ph_3COH) that varied from each other in steric bulkiness were employed for the ROP studies. In the absence of alcohol, the magnesium complexes showed poor catalytic activity. There was a significant improvement in catalytic activity upon the addition of ten equivalents of $PhCH_2OH$ and Ph_2CHOH (% conversion of monomer = 62 and 87 respectively). On increasing the steric bulk of the alcohol (Ph_3COH) the percentage conversion of the monomer was comparable to conversion in the absence of alcohol. This arises because with the increase in the bulkiness of alcohol the active species for the polymerization become sterically congested which hinder the approach of the monomer to the magnesium center. The three magnesium complexes showed highest catalytic activity in the presence of Ph_2CHOH so detailed polymerization studies were done with magnesium complexes in the presence of Ph_2CHOH as coinitiator. Among the three magnesium complexes, the complex **(10a)** showed the lowest catalytic activity due to decreased Lewis's acidity of the metal center. The linear relationship between number average molecular weight and monomer conversion and narrow molecular weight distribution (PDI = 1.05-1.16) gave evidence for the living nature of the polymerization reaction. Further studies were performed with magnesium complex **(10b)** and varying amount of benzhydrol. It was observed that on increasing the loading of Ph_2CHOH from 10 to 100 equivalents, there was gradual decrease in the molecular weight of the polymer indicating an increase in the number of polymer chains. The polymer obtained showed narrow molecular weight distribution (PDI = 1.05-1.15) and experimental and theoretical molecular weights were close to each other which demonstrated immortal behavior of the polymerization reactions. When various benzhydrols that differed from each other in substituent attached to phenyl ring was employed as coinitiator for the polymerization studies different end-functionalized polyesters were obtained as indicated by ^1H NMR studies. Thus, benzhydrol acts as a coinitiator as well as a chain-transfer agent that in the presence of sterically congested magnesium phenoxide complexes, catalyze immortal ring-opening polymerization of cyclic esters (ε-caprolactone and *rac*-lactide).

Feijen and co-workers [**27**] in 2003 reported single-site calcium complexes containing sterically hindered tmhd ligands (H-tmhd: 2,2,6,6-tetramethylheptane-3,5-dione) for the ROP of *L*-lactide. The significant advantage of the tmhd ligand is that side reactions such as transesterification are suppressed to a greater extent due to its bulky nature. The two single-site calcium metal precursors (**11c** and **11d**) were generated *in situ* by the stepwise reaction **(Scheme S11)** starting from (H-tmhd: 2,2,6,6-tetramethylheptane-3,5-dione) and $(THF)_2Ca[N(SiMe_3)]_2$ as reactants. The X-ray crystal structure of the complex **(11c)** showed that the complex is dinuclear, where the calcium atoms are in a distorted octahedral geometry. The two distorted octahedra in the complex are interconnected through a common face. The NMR of complex **(11d)** indicated that the complex has free molecules of $HN(SiMe_3)$ as a contaminant. The calcium complexes were screened for the ROP of *L*-lactide. The complex **(11c)** showed significantly higher catalytic activity for *L*-lactide polymerization, but the experimental molecular weight was much higher than the theoretical molecular weight, and the PDI value was greater than 2. The polymerization reactions carried out with calcium alkoxide complex **(11d)** gave polymers with low PDI value, and experimental and theoretical molecular weight differed slightly as GPC studies indicated. The difference in the two cases may be attributed to the fact that the trimethylsilyl amide group is extremely poor nucleophile compared to the alkoxide group. The catalytic behaviour of the complex **(11c)** was further investigated in the presence of propan-2-ol. The polymer's ^1H NMR analysis showed that the polymer is end-capped with a hydroxyl group and an isopropyl ester group. Thus, the polymerization is initiated by calcium isopropoxide, which is formed *in situ* by the exchange of bis(trimethylsilyl)amide group with propan-2-ol. Besides, the molecular weight of the polymer determined by GPC was close to the theoretically predicted molecular weight. So, for the ROP of *L*-lactide, the complex **(11d)** and the calcium alkoxide complex generated *in situ* by the reaction of complex **(11c)** and propan-2-ol gave polymers with low PDI value , predicted molecular weight, and end-capped with specific end group indicating the living nature of the polymerization reactions.

Based on the studies of Chen [**25**] that a binary catalytic system comprising of dibutylmagnesium (Mg^nBu_2) and alcohol bring immortal ring-opening polymerization of *L*-lactide, Liu [**28**] extended the same catalytic system for the ROP studies of ε-caprolactone. The two magnesium complexes were synthesized by the stoichiometric reaction of dibutylmagnesium (Mg^nBu_2) with diphenylmethanol and triphenylmethanol respectively. As reported earlier the tetranuclear magnesium complex was obtained on reaction with diphenylmethanol and on reaction with triphenylmethanol mononuclear complex formed. In the mononuclear complex the magnesium atom adopts distorted tetrahedral geometry with magnesium being coordinated to two oxygen atoms from THF and two oxygen atoms from triphenylmethoxide ligand **(Scheme S12).** The ring-

opening polymerization of ε-caprolactone was investigated with $Mg_4(Ph_2CHO)_8(THF)_2$ and $Mg(Ph_3CO)_2(THF)_2$ in the absence of alcohol. It was observed that $Mg_4(Ph_2CHO)_8(THF)_2$ polymerized about 500 equivalents of monomer in 5 minutes at room temperature while only 13 % conversion was achieved with $Mg(Ph_3CO)_2(THF)_2$ in 360 minutes. This arises because the more sterically congested triphenylmethoxide group does not allow the monomer to coordinate to the metal center. They next carried out the detailed polymerization studies with $Mg_4(Ph_2CHO)_8(THF)_2$ and in the presence of benzhydrol (Ph_2CHOH). It was observed that the polymerization gave high yield in short reaction time, keeping the [alcohol]/[Mg] constant at 10:1 and varying the monomer loading from 1000 to 8000 equivalents. The polymers obtained have narrow molecular weight distribution (1.16-1.19) and molecular weight of the polymer increased linearly with the increase in monomer loading. This gave evidence for the living nature of the polymerization reactions. Further the polymerization studies were carried with [monomer]/[Mg] = 1000:1 and varying (Ph_2CHOH) from 20 to 100 equivalents. The polymerization was rapid, and the molecular weight of the polymer showed inverse relation with respect to alcohol loading and molecular weight distribution was narrow (1.07-1.13) indicating the immortal nature of the polymerization reaction **(Table S4)**. In the presence of excess amount of alcohol (up to 800 equivalents) the magnesium complex polymerized 8000 equivalents of the monomer at elevated temperature (70 °C) and longer reaction times (120 minutes) which indicated that each magnesium canter produced up to 800 PCL chains giving about 80000% catalytic efficiency. The resulting PCL chains were end-capped with hydroxyl group at one end and Ph_2CO-group at the other end.

Table S4. Polymerization data for ROP of ε-CL in the presence of $Mg_4(Ph_2CHO)_8(THF)_2$ and Ph_2CHOH.

[CL]/[OH]/[Mg]	Temperature (°C)	Time (min)	Conversion (%)	M_n (g/mol)	M_w/M_n
1000/10/1	25	2	100	1.08	1.18
2000/10/1	25	10	100	2.07	1.16
5000/10/1	25	30	96	5.81	1.10
8000/10/1	70	60	93	6.17	1.19
1000/20/1	25	5	100	0.65	1.11
1000/30/1	25	5	100	0.59	1.12
1000/50/1	25	10	100	0.40	1.07
1000/100/1	25	30	100	0.19	1.09

p-block metals

The majority of the elements in the *p*-block are non-metals and, thus a very limited number of metals are available from the *p*-block whose complexes are employed for the ROP studies. This review will highlight the metal complexes of three *p*-block metals (aluminium, tin and indium) as initiators for the living and immortal ROP reactions. '$(Sn(oct)_2)$' or tin (II)(2-ethylhexanoate)$_2$ has been most widely used both in academia and industries for the 'classical' ROP reactions. The advantage of tin (II)(2-ethylhexanoate)$_2$ as the initiator for the polymerization reaction is that it is easy to store and handle. In addition, '$(Sn(oct)_2)$' is soluble in most organic solvents and in the molten state of lactide. The catalyst is highly efficient and versatile under mild reaction conditions. The major drawback of the tin-based complexes is the toxicity associated with them that limit their application in the biomedical research. Hence, tin complexes have been less explored in this review. A major portion of the review will focus on aluminium metal complexes as they have been found to be efficient initiators for the controlled ROP reactions with excellent stereocontrol. The review will also highlight few indium based catalytic systems for the living and immortal ROP reactions of cyclic esters.

Tin complexes

Until 2000 there were no reports of tin-based initiators for the living ROP reactions. In 2000 Gibson and co-workers for the first time reported single-site tin initiators, for the living ROP of lactide [**29**]. The C_s symmetric three-coordinate tin complex was prepared starting from stannous chloride ($SnCl_2$) as the metal precursor **(Scheme S13)**. The tin atom adopts a tripodal geometry with two sites occupied by nitrogen atom from *β*-diketiminate ligand, third site occupied by oxygen atom from isopropoxide moiety and the fourth site have stereochemically active lone pair. The six-membered chelate ring of the *β*-diketiminate ligand adopts a boat conformation. The ROP of *rac*-lactide in dichloromethane under ambient temperature and for 96 h resulted in polymers with narrow molecular weight distribution (PDI = 1.11) and experimental and theoretical molecular weight were close to each other. When the reaction was carried out in toluene at elevated temperature (60 °C) the polymerization was 85% complete in 4h and polymers obtained have low PDI value (1.05). The living nature of the polymerization was exemplified further by linear increase in molecular weight with percentage conversion. The lower activity of the tin catalyst is attributed to poor electrophilicity of tin center and presence of stereochemically active lone pair on tin center that hinder coordination of the monomer.

Aluminium and Indium complexes

Lin et al. in 2001 reported aluminium alkoxide complexes with 2,2'-methylenebis(4,6-di(1-methyl-1-phenylethyl) phenol) as the ligand backbone [**30**]. The ligand was prepared by the reaction of formaldehyde and 2,4-bis(*R*,*R*-dimethylbenzyl)phenol with catalytic amount of benzenesulfonic acid. **(Scheme S14)**. The aluminium complex **(15a)** was prepared by the equimolar reaction of 2,2'-methylenebis(4,6-di(1-methyl-1-phenylethyl) phenol) with trimethylaluminium (Me_3Al) in diethyl ether. The aluminium alkoxide initiator **(15b)** was prepared by the reaction of aluminium complex with benzyl alcohol **(Scheme S15)**. The ^1H NMR ($CDCl_3$) of the aluminium

complex showed disappearance of signal (δ = 5.13, 2H, s) for hydroxyl group of the ligand and appearance of new signal at (δ = –0.99, 3H, s) due to methyl group of trimethylaluminium that confirmed the formation of the complex **(15a)**. Further the NMR studies for complex **(15a)** and **(15b)** revealed the presence of plane of symmetry passing through bridging carbon atom and aluminium atom as only one set of signals were observed for 1-methyl-1-phenylethyl moiety. The two bridgehead hydrogens were magnetically non-equivalent as two different chemical shift values were recorded in the NMR spectrum (complex **(15a)** δ = 3.56 and 3.06 and complex **(15b)** δ = 2.43 and 2.17). The complex **(15a)** crystallises as a mononuclear unit with aluminium atom in distorted tetrahedral geometry. The complex **(15b)** has a dimeric structure with two aluminium atoms bridged by two oxygen atoms of benzylalkoxy group. The complex **(15b)** was employed for the polymerization of ε-caprolactone and *L*-lactide. The polymerization of ε-caprolactone was carried in toluene at 53°C with different [monomer]/[catalyst] ratio. On varying [monomer]/[catalyst] ratio from 25 to 400 the number average molecular weight increased linearly and PDI varied over narrow range (1.04-1.16) indicating living character of polymerization reactions. The living nature of polymerization reactions was further confirmed by resumption of polymerization on addition of monomer for the second time after consumption of monomer that was added first time. It was observed that for [monomer]/[catalyst] = 50, the molecular weight of the polymer increased from 13200 to 22700 on addition of monomer for the second time. The ^{1}H NMR ($CDCl_3$) spectrum of PCL showed an intensity ratio close to 1 for methylene proton attached to benzyl alkoxy chain end and methylene proton attached to hydroxyl end (H_b : H_g = 1) **(Fig. S4)**.Thus the NMR studies revealed that initiation starts with insertion of benzyl alkoxy group to carbonyl carbon of ε-caprolactone resulting in the formation of aluminium alkoxide intermediate that further reacts with the monomer. When the polymerization of ε-caprolactone was carried out in the presence of benzyl alcohol, PCL with narrow PDI value was obtained with the number of polymer molecules exceeding the number of initiator molecules indicating polymerization to be immortal in nature. In addition, the experimental molecular weight of the obtained polymer was less than theoretical molecular weight suggesting that there is growth of more than one polymeric chain per metal center that further give evidence of the immortal polymerization. The complex **(15b)** also initiated ROP of *L*-lactide and PLLA obtained though has narrow molecular weight distribution, but reaction time was longer for appreciable conversion.

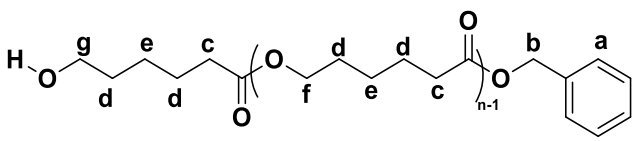

Fig. S4. Polycaprolactone.

The same group synthesised five novel aluminium complexes based on ligand 2,2'-methylenebis(4-chloro-6-isopropyl-3-methylphenol) **(Scheme S16)** and **(Scheme S17)** [**31**]. The X-ray structure of the five complexes revealed distorted tetrahedral geometry around the aluminium atom(s). Further, the X-ray structure for complex **(17b)** showed the complex to be dimeric with Al_2O_2 core where the bridging oxygen atoms are symmetrically bonded to aluminium center. The complex **(17d)** crystallises in dimeric form with Al_2O_2 core where bridging oxygen atoms are unsymmetrically bonded to aluminium atoms. For the complex **(17d)** the aluminium center attached to ligand has more Lewis acidic character than aluminium center attached to methyl group due to electron-withdrawing ability of ligand. Among the five complexes, two complexes **(17b** and **17d)** were screened for ROP of ε-caprolactone. The polymerization was carried in toluene at 50 °C. They carried out extensive studies with complex (**17b)** as initiator and in the presence and absence of isopropanol. The PDI value of the polyesters obtained from ε-caprolactone varied from 1.08 to 1.25 by varying [monomer]/[initiator] ratio from 25:1 to 400:1. In addition to narrow molecular weight distribution linear relationship between [monomer]/[initiator] ratio and number average molecular weight showed the polymerization to be living in nature. The living nature of the polymerization reaction of ε-caprolactone was further confirmed when for [monomer]/[initiator] = 50 after completion of the reaction the polymerization resumed with the further addition of monomer. In the presence of 2-propanol, the polymerization reaction becomes immortal, which is evident from low molecular weight distribution of the polymer and observed experimental molecular weight being less than theoretical molecular weight that indicates from one catalytic site multiple polymer chains grow. The complex **(17d)** also gave polymer with low PDI value.

Lin reported a bisphenol derivative 2,2'-(2-methoxybenzylidene)bis(4-methyl-6-*tert*-butyl phenol) with a bulky group at bridgehead methine carbon **(Scheme S18)** [**32**]. The two aluminium complexes, one monomeric and other dimeric were synthesized using the prepared ligand **(Scheme S18)**. The ^{1}H NMR ($CDCl_3$) studies of the two complexes revealed the two phenyl moieties to be equivalent due to appearance of single peak for *t*-butyl groups attached to two phenyl rings. The single crystal X-ray diffraction studies of complex **(18b)** showed the complex to be monomeric with aluminium atom in distorted tetrahedral geometry. The polymerization of ε-caprolactone was carried out using complex **(18c)** as an initiator in toluene at 50°C. The living character of polymerization reactions carried out by varying [monomer]/[catalyst] ratio was confirmed by the linear relationship between [monomer]/[initiator] and number average molecular weight and narrow molecular weight distribution ranging from 1.07 to 1.21. For [monomer]/[initiator] = 50, further addition of monomer after completion of the reaction resulted in the resumption of the

polymerization indicating a living nature. Mechanistically the reaction proceeds by formation of aluminium alkoxide intermediate through the insertion of benzyl alkoxy group from the initiator to *ε*-caprolactone. This fact is well supported by NMR studies (integral ratio of $H_b/H_g \sim 1$). Thus, the polymer is end-capped with benzyl ester group at one end and hydroxyl group at the other end. **(Fig. S4)**. In the presence of benzyl alcohol, a chain transfer reaction occurs between growing alkoxide chain and alcohol, resulting in new alkoxide that reinitiates the polymerization reaction. Thus, in the presence of benzyl alcohol, the polymerization becomes immortal as the number of polymer molecule exceeds the number of initiator molecules.

Gibson synthesized tetradentate aluminium complexes containing phenoxy amine ligands that showed good stereocontrol for the ROP of *rac*-lactide [**33**]. The main advantage of the catalytic systems from the commercial point of view is that the catalyst are white solids that reduce the cost of decolorization of the catalyst during removal of the catalyst from the polymer. Among the ligands, the substituted phenoxy derivatives were prepared by modified Mannich reaction. The unsubstituted phenoxy derivative were prepared by stepwise condensation of appropriate salicylaldehyde and *N*,*N*-disubstituted ethylenediamine followed by reduction with $NaBH_4$ **(Scheme S19)**. The aluminium complexes were prepared by the reaction of ligand solution in toluene with trimethylaluminium by overnight stirring at 110 °C **(Scheme S20)**. The formation of the complexes was confirmed by the disappearance of broad signal (δ = 10.4-11.6 *ppm*) corresponding to hydroxy group in the ^{1}H NMR spectrum and appearance of new signal in most upfield region due to methyl group attached to aluminium. The X-ray crystal structure of complex **(20c)** showed distorted trigonal bipyramidal geometry around the aluminium center with the equatorial plane occupied by one nitrogen and one oxygen from the ligand and carbon atom from methyl group and the axial positions occupied by remaining nitrogen and oxygen atoms from the ligand. The alkoxide complexes that were used as catalyst for the lactide polymerization were prepared by *in situ* alcoholysis of the aluminium complexes using benzyl alcohol. The polymerizations were carried at 70 °C in toluene. The living character of the polymerization reactions was confirmed by narrow molecular weight distribution and linear relationship between molecular weight and percentage conversion of the monomer. The polymerization rate decreased with the increase in the size of substituent in the phenoxide moiety as it hindered the approach of the monomer to the catalyst.

Aluminium alkyl complexes containing tetradentate 1,*ω*-dithiaalkanediyl-bridged bisphenol ligand showed good catalytic activity towards the ROP of *rac*-lactide in the presence of isopropanol [**34**]. Among the three aluminium complexes, the two complexes have the same bridged group and differed from each other with respect to alkyl group attached to aluminium center. The third complex resembled one of the two complexes with respect to alkyl group attached to aluminium center but have different bridged group **(Scheme S21)**. The solid-state X-ray crystallographic structure of ethylene bridged aluminium complexes (**21a** and **21b)** showed a distorted trigonal bipyramidal geometry around aluminium with the equatorial sites occupied by one oxygen atom and one sulphur atom from the ligand and one carbon from the alkyl group of alkylaluminium moiety and the axial site occupied by one oxygen and one sulphur atom from the ligand. On the other hand, the *ortho*-xylene bridged aluminium complexes have square-bipyramidal geometry in the solid state. The active aluminium alkoxide complexes for the polymerization were generated by the *in-situ* reaction of the alkyl aluminium complexes with isopropanol. The polymerization of *rac*-lactide with the aluminium alkoxide precursors was carried in toluene at 70 °C. The polymers obtained have a narrow PDI value (1.04-1.07) ,and there was linear increase in molecular weight with conversion that indicated living nature of the polymerization reactions. It was observed that for ethylene bridged aluminium complexes polymerization of *rac*-lactide carried out in the presence of isopropanol gave atactic PLA **(**P_r = 0.50) and the conversion rate was almost similar. For the *ortho*-xylene bridged aluminium complexes, the polymerization rate was slow due to less flexibility of the bridged group that do not allow easy approach of the monomer to the metal center. The polymer obtained with **(complex 21c)** was heterotactic-enriched (P_r = 0.65).

Hormnirun and coworkers reported two series of aluminium complexes (monomethylaluminium and dimethylaluminium) supported by bidentate pyrrolyaldiminate ligand [**35**]. They systematically studied the catalytic activities of the complexes for the ROP of *rac*-lactide. The pyrrolyaldiminate ligands were prepared by the equimolar reaction between pyrrole-2-carboxyaldehyde and corresponding amine in ethanol and in the presence of a small amount of formic acid. The monomethylaluminium and dimethylaluminium complexes were synthesized by the reaction of the ligands with trimethylaluminium in 1:1 and 2:1 ratio in toluene **(Scheme S22)**. The formation of aluminium complexes was confirmed by the disappearance of the imine hydrogen signal and the appearance of new signal upfield to TMS corresponding to methyl group protons attached to aluminium. Further the ^{1}H NMR studies also gave evidence that the monomethylaluminium complex was four-coordinate as the integration ratio of imine proton and the methyl protons was 1:6 while for the dimethylaluminium complexes the integral ratio of imine proton and methyl protons is 2:3 that indicated formation of five-coordinate aluminium complexes. The single crystal X-ray diffraction analysis of complex **(22x)** showed trigonal bipyramidal geometry around the aluminium with the equatorial position occupied by pyrrole nitrogen atoms and carbon of the methyl group and the axial position occupied by the two imine nitrogen atoms. The ROP of *rac*-lactide was carried using the aluminium complexes in the

presence of one equivalent of benzyl alcohol in toluene at 70 °C. The aluminium alkoxide complexes were generated *in situ* by reaction with benzyl alcohol. All the aluminium complexes were effective for the polymerization of *rac*-lactide but there was difference in their catalytic activity. It was observed that the catalytic activity of five coordinate monomethylaluminium complexes were slightly higher than four coordinate dimethylaluminium complexes. This is because aluminium center in five coordinate aluminium complexes is more electrophilic as it is attached to two pyrrole moiety and thus facilitate easy coordination of the monomer to the metal center. In addition, the catalytic activity is influenced by the steric and electronic environment of the imine nitrogen atom. For both monomethylaluminium and dimethylaluminium complexes, it was observed that when the imine nitrogen atom is attached to adamantyl group, the catalytic activity is least as indicated by longer reaction time (**22vii** – 91% conversion in 108h and **22xiv** – 95% in 108h) in comparison to complex where imine nitrogen is attached to the phenyl group. The effect of electronic environment on the polymerization was best exemplified by taking into account the catalytic activities of complexes where imine nitrogen is attached to phenyl ring that have substitution at different position in the ring. It was observed that when the phenyl ring was substituted at the *para* position with different substituent (CH_3, H, F, OCH_3) the order of catalytic activity was *p*-CH_3 > *p*-H ≈ *p*-F > *p*-OCH_3. The higher activity of the fluoro substituted complex in comparison to methoxy substituted complex was due to electron-withdrawing effect of fluorine that decrease the electron density on the metal center and the monomer can more easily coordinate to the metal center. The activity of the fluoro substituted complex was less than the methyl substituted complex because the fluorine in addition to its electron-withdrawing effect can donate its lone pair to the metal center by π-bonding that decreases the electrophilicity at the metal center. When the phenyl ring was substituted at the *ortho* position, the catalytic activity was less than when it was substituted at the *para* position because the substitution at the *ortho* created steric hinderance for the approach of the monomer to the metal center. The substituent at the imine nitrogen atom also influenced the microstructure of the PLA chain. When the phenyl ring attached to the imine nitrogen atom was unsubstituted or *para* -substituted the polymer obtained was atactic with (P_m = 0.50-0.56) and the substitution of the phenyl ring at the *ortho*-position resulted in heterotactically-enriched PLA chain (P_r = 0.58-0.60). The polymers obtained was isotactically-enriched (P_m = 0.63-0.74) when the imine nitrogen atom was attached to sterically bulky adamantly group. Thus, it is well evident that on increasing the steric congestion around the metal center the catalytic activity decreased but the control over tacticity increased. The linear relationship between the number-averaged molecular weight and monomer conversion along with narrow molecular weight distribution of the polymer demonstrated the living nature of the polymerization reactions.

Mehrkhodavandi and coworkers synthesized a series of *para*-functionalized phenoxy-bridged dinuclear indium complexes supported by chiral diaminophenolate ligands [**36**]. They explored the catalytic activities of the complexes towards the ROP of *rac*-lactide and investigated the effect of different *para*-substituents of the phenoxy-bridged moiety towards the ROP reactions. Further, they studied the immortal ROP of *rac*-lactide with a variety of arylated alcohols as chain-transfer agents. The two different synthetic pathways were employed for the synthesis of the dinuclear indium complexes $[(NNO)InCl]_2(\mu\text{-Cl})(\mu\text{-OPh}_R)$ [where R = ((OMe) **(a)**, (Me) **(b)**, (H) **(c)**, NO_2**(d)** and Br **(e))**]. The dinuclear indium complexes were synthesized starting from chiral mononuclear indium complex**(I)** as the metal precursor **(Scheme 23)**. The indium complexes with electron-poor phenoxy substituent favors the formation of mono-phenoxy bridged complexes through pathway**(A)** while with electron-donating phenoxy substituent bis-phenoxy bridged dinuclear indium complexes were obtained. Hence, for the preparation of mono-phenoxy bridged indium complexes with electron-rich phenoxy substituent pathway **(B)** was adopted. The formation of the mono-phenoxy bridged complexes was confirmed by ^1H ($CDCl_3$) NMR studies. The ^1H NMR spectrum showed characteristic signal for the bridging phenolic ring-protons around (6-8 *ppm*) and doublets at 3.7 *ppm* and 4.7 *ppm* corresponding to NH-C**H**$_2$-Ar protons. The molecular structure of the complexes **(b-e)** showed that the complexes are homochiral where each indium atom adopts distorted octahedral geometry asymmetrically bridged by the chloride and the phenoxy ligand. It was observed that with the increase in the electron-withdrawing nature of the *para*-substituent of the phenolate moiety the bridging In─O bond becomes longer and In─Cl bond becomes shorter. The catalytic activities of the indium complexes for the ROP reaction were examined at room temperature in dichloromethane (CH_2Cl_2). It was observed that the catalyst with electron-rich bridging phenolate moiety showed controlled polymerization with narrow PDI value (1.01-1.11) in comparison to catalyst with strong electron-withdrawing group (-NO_2) at the *para*-position of phenolate unit (PDI value: 1.18-1.24). This arises because catalyst with electron-withdrawing group at *para* position of bridging phenolate unit is least nucleophilic among all the complexes. Due to less nucleophilicity of the bridging phenolate unit, the insertion of phenolic oxygen in the ester (C─O) bond of the monomer is hindered. This reduces the concentration of the active catalyst in the solution and polymers obtained have higher than expected molecular mass. The polymerization reaction was living as there was linear increase in the molecular weight of the polymer with the increase in the [monomer]/[catalyst] ratio. Further studies were carried out to demonstrate the behavior of aromatic alcohols as chain transfer agents for the polymerization of *rac*-lactide. The alkoxy-bridged

dinuclear indium complex **(1) (Scheme S23)** was employed for the studies as the phenoxy-bridged complexes were less nucleophilic and thus showed longer initiation period for the polymerization. A variety of aromatic alcohols **(Fig. S5)** were employed as chain transfer agents for the ROP studies at room temperature. The [catalyst]/[chain-transfer agent] was kept fixed at 20 and [monomer]/[catalyst] ratio was varied. Among the various aryl alcohols used as chain-transfer agents for the polymerization it was observed that phenol and 1,5-napthalenediol gave polymers with good control over molecular weight and polydispersity (1.01-1.05). The molecular weight of the polymer increased linearly with respect to the monomer conversion. The MALDI-TOF analysis of the polymer showed that among all the alcohols only phenol and 1,5-napthalenediol was incorporated in the polymer chain as end groups while no other diol was present in the polymer chain indicating that polymerization process was inhibited when other three alcohols (biphenol, dichlorophene and 1,8 naphthalenediol) are used as chain transfer agent. The inability of the three diols to carry out the polymerization reaction can be explained by considering the mechanistic pathway by which the reaction takes place and chelation of the diols to one or both the metal center. Based on computational studies reported by the same group [**37**] it was shown earlier that both the metal centers in complex (1) participate in the polymerization reaction. The reaction of the indium alkoxy complex (1) with two equivalents of dichlorophene led to the formation of dinuclear species where one of the oxygen atoms of deprotonated dichlorophene bridges both the indium centers. The chelation was not possible in 1,5-napthalenediol as the two hydroxy groups were oriented in the opposite direction. Thus, the chelation of the chain transfer agent to the metal center hindered the polymerization activity. This was further confirmed when the polymerization reactions were performed in THF. When THF was used as a solvent for the polymerization there was certain amount of conversion (44 % in 65 h) reported for dichlorophene as chain transfer agent. This is attributed to the fact that in the presence of THF chelation is prevented as THF coordinates to the metal center and blocks the coordination site.

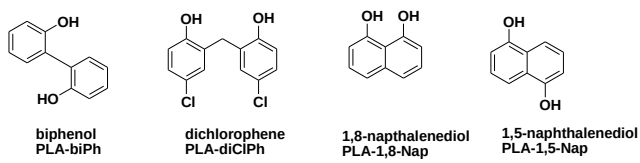

Fig. S5. Aryl alcohols used as a chain transfer agent.

Carpentier and co-workers [**38**] reported a series of dialkylaluminium and indium complexes supported by the phenoxy-imine ligand backbone $\{ON^R\}^-$ with a variable R imino-substituent [(**a**) to (**m**)] and functionalized by bulky triphenyl silyl group (-$SiPh_3$) at the *ortho*- position in the phenoxy-imine moiety **(Scheme S24)**. The role of the bulky triphenyl silyl group at the *ortho*- position was to introduce sufficient steric hinderance around the metal center and thus diminish the possibility of the catalyst aggregation. The proligands can broadly divided into three categories (i) tridentate (**a**) and (**g**) proligands (ii) bidentate proligands that differed from each other in the bulkiness of the phenyl ring directly attached to nitrogen atom of the imino moiety (**b-e**) and (iii) bidentate proligands that possess N-benzyl-type moiety substituted either at the phenyl ring or at CH_2 unit (**f**, **h**, **k**). The proligands were prepared by the condensation reaction between 2-hydroxy-5-methyl-3-(triphenyl silyl)-benzaldehyde and the primary amine through two different pathways. The dimethylaluminium complexes were prepared by the stoichiometric reaction between the corresponding proligands and trimethylaluminium as the metal precursor in dry toluene at room temperature. For the synthesis of dialkylindium complexes two different metal precursors were employed ($[InMe_3]_n$ generated *in situ* by the reaction between $InCl_3$ and MeLi) and $In(CH_2SiMe_3)_3$). The ^1H NMR (benzene-d_6) spectra of the complexes showed the aluminium and the indium compounds to be monomeric as all single sets of sharp resonance signals were obtained. The solid-state molecular structure of the aluminium complex bonded to tridentate ligand showed that aluminium center is five coordinated and it adopts distorted trigonal bipyramidal geometry. For the I(**a**), I(**m**) where the aluminium atom is coordinated to the bidentate ligand, the aluminium atom is four coordinated and adopts distorted tetrahedral geometry. For the indium complexes (III) where the indium atom is coordinated to the tridentate ligand, the indium atom is five coordinated and the geometry falls in between trigonal bipyramidal and square pyramidal.

They proposed the rate expression for the polymerization $-d[rac\text{-LA}]/dt = k_{app}[LA]^0[Al]^1[^i PrOH]^0$. They combined the $\{ON^R\}AlMe_2$ complexes with alcohol (^{i}PrOH, BnOH), and found a good control over the molecular parameters as well as various microstructures, with different R-imino substituent [(**a**) to (**m**)] for the living (as well as immortal with excess ^{i}PrOH) ROP of *rac*-lactide (*rac*-LA). From the complexes having benzyl-type imino substituents they reported significant isotactic (P_m up to 0.80) PLA. On the other hand $\{ON^R\}InR'_2$ was similarly active for the ROP of *rac*-LA in presence of an external alcohol, but the polymerizations were less controlled. No indium complexes induced stereoselectivity, except III(**a**) (P_m = 0.70). They suggested two different ROP mechanisms operative on the basis of the stoichiometric reactivity depending upon the nature of the metal center. Here they proposed that Al-based complexes proceed through coordination–insertion, while In-based complexes operated through an activated monomer mechanism.

d-block elements

The *d*-block elements constitute a variety of metals that, when combined with a suitable ligand framework, can be employed as efficient organometallic catalysts for the ROP

of cyclic esters. The advantage of *d*-block elements over the main group elements is that their complexes are less sensitive to moisture and air and thus can be handled much more easily. In addition, due to the availability of the *d*-orbitals, the metal complexes have a wide range of possible geometries. The *d*-block metal catalysts have the potential for the synthesis of polyesters required in biomedicine due to low toxicity and low cost of the metal precursors. Among the *d*-block elements, this article will highlight the metal complexes of yttrium, titanium, zirconium, zinc and, copper for the living and immortal ROP reactions. The first breakthrough in the immortal ROP of lactide with the *d*-block metal came in 2007 with Thomas and Carpentier group reporting yttrium amido and alkoxide complexes for the stereoselective polymerization.

Yttrium complexes

Carpentier reported the catalytic activities of amino-alkoxy-*bis*(phenolate) yttrium complexes for the ROP of *rac*-lactide in the presence of 2-propanol [**39**]. The yttrium complexes were highly active and stereoselective for the ROP of *rac*-lactide and *rac*-butyrolactone in the absence of alcohol, as reported earlier by the same group [**40**]. The four different yttrium initiators were synthesized based on two different ligand frameworks. The ligands were synthesised by double Mannich condensation reaction between substituted phenol, formaldehyde and alkoxy-amine **(Scheme S25)**. The two yttrium amido complexes were synthesized by an equimolar reaction of ligand dissolved in toluene and $Y[N(SiHMe_2)_2]_3.(THF)_2$ dissolved in pentane **(Scheme S26)**. The two isopropoxide complexes were generated *in situ* by the reaction of yttrium-amido initiator with propan-2-ol **(Scheme S27)**. The single crystal X-ray diffraction studies of complex **(26a)** and complex **(26b)** revealed that the yttrium atom is in a distorted octahedral environment and six coordination around yttrium is satisfied by three oxygen and one nitrogen atom from the ligand and remaining two sites are occupied by THF and *bis*(dimethylsilyl)amide group. Further, ^1H and ^{13}C NMR (benzene-d_6) data revealed the amido complex to be monomeric with a plane of symmetry present as indicated by single resonance signal for phenolate moiety and silylamido group. The polymerization of *rac*-lactide was carried out with the amido complex in THF at 20 °C in the presence of propan-2-ol. Heterotactic PLA was obtained with complex **(26a)** (P_r = 0.80) and complex **(26b)** (P_r = 0.90). The complex **(26a)** showed higher activity for ROP of *rac*-lactide (conversion of 1000 equivalent of monomer in 40 minutes) in comparison to complex **(26b)** (conversion of 1000 equivalent of monomer in 6h). The high stereoselectivity and less activity of complex **(26b)** may be attributed to presence of more sterically hindered substituent in complex **(26b)**. The ROP of *rac*-lactide with **26 a,b**/2-propanol was carried with different amounts of 2-propanol. The polymerization of *rac*-lactide was found to be immortal in nature with the molecular mass of the polymer increasing linearly with the number of propan-2-ol molecules added and narrow PDI value (1.06-1.17) obtained. The two complexes showed almost same productivity with the only difference being with complex **(26a)** about 50 equivalents of propan-2-ol can be used effectively resulting in polymer whose experimental and calculated molecular weight are in good agreement with each other while for complex **(26b)** upto 20 equivalents of propan-2-ol can produce good results. In case of the isopropoxide complexes generated *in situ*, the excess alcohol that remains after formation of the complexes acts as chain transfer agent that undergoes rapid exchange with growing alkoxide species. The exchange reaction competes with the chain propagation but the narrow PDI value (1.07-1.16) and conversion of large number of monomers with a small amount of catalyst indicate that exchange between alkoxide growing species and free alcohol is much faster than chain propagation.

Chen and coworkers [**41**] reported air and moisture stable dinuclear yttrium phenoxide complexes that catalyzes the immortal and stereoselective ROP of *rac*-lactide with just use of *ppm* level of the catalyst **(Scheme S28)**. The yttrium complexes were based on three tridentate ligands of *bis*(2-hydroxyphenyl)methanone with different substitution in the phenyl ring. The yttrium complexes were prepared with $Y[N(SiMe_3)_2]_3$ as the metal precursor. The binuclear yttrium complexes have D_3 symmetry as confirmed by ^1H and ^{13}C NMR studies. In order to confirm the air/moisture stability of the complexes they performed NMR titration experiments with complex **(28a)** with water in $CDCl_3$. It was observed that upon addition of one equivalent of water complex **(28a)** was stable. Upon addition of 10-500 equivalents of water in $CDCl_3$ a new species formed **(28b)**. The X-ray crystal structure of the complex **(28b)** revealed that the complex is partial hydrolysed product of complex **(28a)** where the two tridentate ligands acquire protons from two water molecule and change its coordination mode from tridentate to bidentate and additional two water molecules coordinate to the yttrium center. The partial hydrolysis product exists in the dimerized form due to the high basicity of the hydroxyl group. It was observed that complex **(28b)** can be fully converted to complex **(28a)** by heating at 120 °C in deuterated *o*-xylene-d_{10} solution indicating that the complexes are thermally switchable. The ROP studies with complex **(28a)** and benzyl alcohol as the initiator was carried out in THF, toluene and dichloromethane at room temperature. It was observed that the polymerization proceeded smoothly at room temperature to yield polymers with desirable molecular weight (**Table 5**, entries 1, 2, 3). It was observed that when the polymerization reactions were carried out under melt condition at 130 ˚C and in the presence of more than one equivalent of benzyl alcohol, the reaction rates were faster and the molecular weight distribution became narrow. The immortal feature of the polymerization reaction was well highlighted by the fact that polymers with controlled molecular weight can be obtained with upto 1000 equivalents of benzyl alcohol

indicating, that 1000 polymer chains grow from single catalyst unit. Further, the polymerization reactions were carried with complex **(28b)**. It was observed that in the absence of benzyl alcohol, both complex **(28a)** and complex **(28b)** were inactive for the polymerization and in the presence of same amount of benzyl alcohol the catalytic activity of complex **(28a)** was more than complex **(28b)** at room temperature. When alcohol was replaced with water as an initiator the initiation efficiency decreased. This was further proved when polymerization reactions were carried out in mixture of water and alcohol. The MALDI-TOF spectrum of the final polymer showed major peaks corresponding to the benzyl ester group rather than the carboxyl group indicating mainly benzyl alcohol initiated the polymerization reaction. The catalyst showed some degree of heteroselectivity for the polymerization of *rac*-lactide.

Table S5. *rac*-lactide polymerization data with complex **(28a)** in air.

Entry	Catalyst	[*rac*-LA]/[Cat]/[BnOH]	Temp. (°C)	Time	Conv (%)	M_n (Exp.) g/mol	M_w (Theo) g/mol	PDI	P_r
1	28a	100:1:1 (THF)	RT	48 h	82	10800	11900	1.25	0.69
2	28a	100:1:1 (toluene)	RT	48 h	85	10200	12300	1.36	0.68
3	28a	100:1:1 (DCM)	RT	48 h	98	12900	14200	1.26	0.72
4	28a	100:1:2 (DCM)	RT	3 h	70	4900	5100	1.05	0.72
5	28a	100:1:4 (DCM)	RT	2 h	85	2700	3200	1.05	0.69
6	28a	10000:1:20	130	12 h	85	56800	61300	1.25	0.62
7	28a	10000:1:50	130	5 h	78	24300	22600	1.26	0.62
8	28a	10000:1:100	130	80 min	94	12800	13600	1.26	0.61
9	28a	10000:1:1000	130	40 min	92	1100	1400	1.30	0.60
10	28a	20000:1:200	130	5 h	76	9800	11100	1.26	0.61
11	28a	40000:1:400	130	10 h	70	9900	10200	1.28	0.60

Titanium and zirconium complexes

Novel titanium complexes based on three different benzotriazole phenoxide ligand were reported by Ko [**42**]. The three benzotriazole phenoxide ligands differed from each other in the substitution in the phenoxide ring and substitution in the benzotriazole moiety. The four titanium alkoxide complexes were synthesized taking titanium isopropoxide as the metal precursor and varying the ratio of the ligand with respect to the metal precursor **(Scheme S29)**. Among the four complexes, the one which was formed by the equimolar reaction between the metal precursor and the ligand was dimeric with a Ti_2O_2 core where each Ti center adopts distorted octahedral geometry. The two coordination sites are occupied by the two 14ridge atoms from two different units of benzotriazole phenoxide ligand. The third coordination site is satisfied by one nitrogen atom from the benzotriazole phenoxide ligand and remaining three sites are occupied by three oxygen atoms from the isopropoxide moiety. The other three complexes were monomeric where the titanium atom adopts a distorted octahedral geometry with two coordination sites occupied by the two nitrogen atoms and the other two-coordination site occupied by two oxygen atoms coming from two different benzotriazole phenoxide ligand. The fifth and sixth coordination site is occupied by two oxygen atoms from the isopropoxide moiety. The ROP studies were carried with the titanium complexes with ε-caprolactone as the monomer. Among the four titanium complexes, the monoadduct complex with less sterically hindered titanium center showed the highest catalytic activity with about 99% conversion achieved at 30 °C in 6 hours. With the *bis*-adducts, the reaction occurred at higher temperature (80 °C) as the approach of the monomer was difficult due to steric congestion around the metal center. Among the *bis*-adduct complexes, the catalytic activity decreased with the increase in the bulkiness of the substituent on the phenolate moiety of the benzotriazole phenoxide ligand. The catalytic activity of the monoadduct complex **(29a)** and the *bis*-adduct complex **(29b)** was further investigated for the living nature of the ROP. The living nature of the polymerization reaction was exemplified by the linear increase in the number-average molecular weight of the polymer with the increase monomer/initiator ratio and the close proximity between theoretical and experimental molecular weight. It was further observed that the polymerization resumed on addition of the second batch of monomer after the first portion has gone to completion that further supported the living character of the polymerization reaction. The molecular weight of the polymer when the second batch of monomer has gone to completion was almost the same when the reaction was done alone with double equivalent of the monomer that was used in the first batch**.** The polymerization reaction was also done in the presence of isopropyl alcohol as the chain-transfer agent and monomer/initiator/isopropyl alcohol = 300/1/9. It was observed that the molecular weight of the polymer was similar to the polymer when monomer/initiator was 75/1. This indicated the immortal behavior of the ROP whereby due to chain-transfer reactions more than one active polymer chain grows from the single metal center. The monoadduct complex **(29a)** was further employed for the ROP studies of *L*-lactide. The polymerization reactions were done at (80 °C) in toluene. The polymerization reactions were studied with different monomer/initiator ratio and the studies indicated polymerization is living in nature. In addition, the reactions done in the presence of

isopropyl alcohol indicted the immortal nature of the polymerization reaction.

Wang and coworkers [**43**] synthesized titanium and zirconium complexes based on symmetrical amino-*bis*(phenolate) ligands and systematically examined their catalytic activities towards ROP of *L*-lactide and *rac*-lactide. The zirconium complexes were synthesized by the reaction between ligand and zirconium isopropoxide as the metal precursor in 2:1 ratio in toluene at room temperature while the titanium complexes were synthesized by the equimolar reaction between titanium isopropoxide and the ligands **(Scheme S30).** The single crystal X-ray diffraction studies of zirconium complex revealed that the complex is monomeric where the zirconium atom adopts distorted octahedral geometry. The four coordination sites are occupied by four phenolate oxygen atoms coming from two ligands and the remaining two axial sites are occupied by nitrogen atoms. On the other hand, in the titanium complex, the titanium center is six coordinated where the three-coordination site is occupied by two oxygen atoms and one nitrogen atom coming from the ligand, two sites occupied by two oxygen atoms coming from the isopropoxide group and the sixth site is occupied by oxygen atom of morpholinyl unit of the ligand which is bound to other titanium center. All the four complexes were screened for the ROP of *L*-lactide and *rac*-lactide under solvent-free condition at 140 ˚C and 160 ˚C respectively. Among all the complexes, the zirconium complex **(30b)** showed the highest catalytic activity and productivity with upto 200000 equivalent of *rac*-lactide loading and % conversion = 57 achieved in 46h at 160 ˚C. The zirconium complexes were further employed for the immortal ROP studies of *rac*-lactide and *L*-lactide in the presence of benzyl alcohol under melt condition. It was observed that for the polymerization of *rac*-lactide with the zirconium complexes and benzyl alcohol varying from 10 to 120 under solvent-free conditions at 160 °C, the monomer loading upto 150000 was achieved with TOF 6593 h^{-1} at [monomer]/[catalyst]/[BnOH] = 150000/1/100. The polymers produced showed relatively low molecular weight distribution (1.19 -1.58) and there was linear increase in the molecular weight of the polymer with percentage conversion. The MALDI-TOF mass spectrum of the oligomer showed that one end of the polymer chain is capped with hydroxyl group and the other end of the polymer chain is capped with benzyloxy group indicating that the benzylalkoxy group act as initiator for the polymerization reaction.

Dagorne and coworkers [**44**], reported novel *bis*-aryloxide NHC zirconium alkoxide complexes for the ROP of *rac*-lactide. They synthesized tridentate *bis*-aryloxide-NHC ligands where the NHC moiety acts as central two electron donor and flanked on each side by an aryloxide moiety. The NHC proligand 1,3-*bis*(3,5-di-*tert*-butyl-2-hydroxyphenyl)imidazolium chloride was prepared from *N,N'-bis*(3,5-di-*tert*-2-hydroxyphenyl)-ethylenediamine **(Scheme S31).** The metal precursor for the polymerization was obtained by the reaction of NHC proligand with zirconium isopropoxide in THF **(Scheme S32).** The X-ray crystal structure of Zr-NHC isopropoxide complex revealed that the Zr atom adopts a distorted octahedral geometry with the NHC ligand binding to the zirconium center in *mer*-fashion. The Zr-NHC isopropoxide complex was screened for the polymerization of *rac*-lactide both under solvent free condition and in the presence of dichloromethane and THF. It was observed that when the polymerization was carried in the presence of solvent it was much better controlled (PDI = 1.06-1.10) than when it was carried under solvent free condition (PDI = 1.20-1.25). This can be explained by considering the fact that in the presence of solvent, the solution is homogeneous and also due to dilution, the reaction occurs slowly and thus control over monomer insertion is better. The polymers obtained were heterotactic with P_r = 0.95. The degree of stereocontrol was less under solvent free conditions as is evident from P_r = 0.82. The polymerization was living in nature as the molecular weight increased linearly with percentage conversion of the monomer.

Zinc complex

Different zinc phenoxide complexes supported by a *β*-diketiminato ligand were used for the ROP of *L*-lactide [**45**]. The *β*-diketiminato ligand was synthesized and the ethyl zinc complex **(Scheme S33)** was then prepared by the reaction of one equivalent of ligand and one equivalent of Et_2Zn. The single crystal X-ray diffraction studies of the zinc complex revealed that the zinc complex crystallized as dimer in centrosymmetric environment with each zinc atom in distorted tetrahedral geometry and coordinated to two nitrogen atoms from one ligand, one nitrogen atom from another ligand and fourth coordination satisfied by an ethyl group. The formation of dimer is favoured over the monomer as monomer would lead to almost planar four coordinated configuration which is less stable than four coordinate tetrahedron configuration. The different *β*-diketiminato zinc phenoxide complexes were prepared by the reaction of zinc complex with different substituted phenols in dichloromethane. Among the seven complexes four complexes **(33a-d)** were isolated in good yield but remaining three complexes **(33e-g)** were obtained as mixtures as indicated by ^{1}H NMR studies. The purification of three complexes was difficult due to increased lability of complexes as less steric hinderance is provided by the substituted phenol moiety. The single-crystal structure of complexes **(33a)** and **(33b)** showed similar structural features with zinc atom in distorted tetrahedral geometry and shorter bond distance between zinc ion and pyridine nitrogen in comparison to complex indicating slightly stronger interactions in *β*-diketiminato zinc phenoxide complexes. The interaction between zinc and phenoxide is slightly strong in complex **(33b)** than complex **(33a)** as indicated by Zn−O bond distance (**33a**: 1.925 Å and **33b**: 1.896 Å) due to greater electron-donating nature of isopropyl group than methyl group. For the complex **(33c)** for which single crystals were not obtained a detailed DFT

study indicated weak interaction between Zn and phenoxide (Zn−O bond distance = 1.958 Å) due to strong electron-withdrawing nature of nitro group. The four complexes **(33a-d)** were systematically screened for the ROP of *L*-lactide in dichloromethane. For [monomer]: [catalyst] = 100:1 almost complete conversion to polymer was achieved for complexes **(33a)** and **(33b)** in 40 minutes and for complexes **(33c)** and **(33d)** in 720 minutes indicating presence of electron-withdrawing groups in the phenol moiety decrease the activity of the catalyst. The polymerization was uncontrolled with wide difference between experimental and theoretical molecular mass and broad PDI values (1.20-1.38). The addition of one equivalent of benzyl alcohol and using different solvents (toluene and THF) did not bring about much control over the molecular weight. The addition of 10 equivalents of benzyl alcohol as co-initiator brought about good control over the molecular weight with calculated molecular weight in good agreement with experimental molecular weight and narrow PDI values (1.03-1.13) were obtained. For the [monomer : catalyst : benzyl alcohol] = 250:1:10 the conversion of monomer for the four complexes were (complex **(33a)** : 96 % in 40 minutes , complex **(33b)** : 73% in 40 minutes complex **(33c)** : 70 % in 720 minutes and complex **(3d)** : 66 % in 720 minutes). The lesser conversion with complex **(33b)** in comparison to complex **(33a)** was due to two sterically crowded isopropyl group (^{i}Pr) in the phenoxide moiety that inhibits coordination of monomer. The longer reaction time and less conversion with complex **(33c)** and complex **(33d)** may be attributed to less basicity of the phenoxide due to electron-withdrawing nitro group present. On carrying out the polymerization reactions with complex **(33a)** and different [monomer]/[benzyl alcohol] ratio, the molecular weight of the polymer increased linearly with increase in the ratio of [monomer]/[benzyl alcohol] which gave evidence for living nature of polymerization reactions. The resumption of polymerization on addition of monomer for the second time after first reaction has gone to completion supports the living nature of polymerization reaction **(Scheme S34)**. The complex **(33a)** in the presence of 10 equivalent of benzyl alcohol polymerizes upto 5000 units of monomer in 40 minutes with 82% conversion producing polymer with controlled molecular weight and low PDI value (1.06). This highlights the immortal nature of the ROP. The ESI-MS spectrum of PLLA obtained by ROP of *L*-lactide with [monomer : catalyst : benzyl alcohol] = 100:1:10 showed major peaks at 108 +144*n* + 23/39 that was assigned to BnOH + n($C_6H_4O_8$) + Na^+/K^+. In addition, a series of identical peaks separated by molecular mass of 144 Da that correspond to repeating unit of lactide was obtained indicating there was practically no transesterification reactions.

Copper complex

Lin *et al*. reported [**46**] air and moisture-stable copper complexes supported by commercially available *N,O*-bidentate benzotriazole substituted phenol. The three copper complexes were synthesized by the reaction of $Cu(OAc)_2 \cdot H_2O$ as the metal precursor and three different ligands [2-(2H-benzotriazol-2-yl)-4,6-*bis*(1-methyl-1-phenylethyl)phenol (**^{CMe2Ph}BTP-H**) , 2-(2H-benzotriazol-2-yl)-4,6-di-*t*-butylphenol(**$^{t\text{-}Bu}$BTP-H)** and 2-*t*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (**^{TMCl}BTP-H**) in 1:2 molar ratio in ethanol under reflux for 24 h. The fourth complex **(^{TMCl}BTP)$_2$Cu(Me$_2$CO))** was synthesized by the reaction of copper complex **[(^{TMCl}BTP)$_2$Cu]** with acetone for 16h at 25 °C **(Scheme S35)**. The attempt to synthesize acetone adduct of Cu-complexes (**^{CMe2Ph}BTP-H**) and (**$^{t\text{-}Bu}$BTP-H)** was unsuccessful, probably because for the Cu-complex **[(^{TMCl}BTP)$_2$Cu]**, the electron-withdrawing nature of chlorine increases the Lewis acidity of Cu-center which in turn facilitated weak bonding between copper atom and oxygen atom of acetone moiety. The single-crystal X-ray diffraction studies of the Cu-complexes (**^{CMe2Ph}BTP-H**) and (**$^{t\text{-}Bu}$BTP-H)** showed that the two were isostructural differing only in the substituent attached to phenoxide ring. Both the complexes are monomeric with Cu atom bonded to two nitrogen and two oxygen atoms coming from two bidentate ligands and Cu atom adopts distorted square planar geometry as two sets of bond angles are recorded around the Cu center (89.43-92.85^{o}) and (158.07-167.95^{o}). For the complex **(^{TMCl}BTP)$_2$Cu(Me$_2$CO)** (acetone adduct of complex **[(^{TMCl}BTP)$_2$Cu]**, the crystal structure showed the complex to be monomeric with the copper center in a distorted square-pyramidal geometry which is coordinated to two oxygen atoms and two nitrogen atoms from two ligands and the fifth coordination satisfied by oxygen atom from acetone moiety. The benzotriazole nitrogen atoms and aryloxy oxygen atoms form the basal plane of square - pyramid and copper atom is located about 0.0790 Å above the basal plane. The three copper complexes **[(^{CMe2Ph}BTP)$_2$Cu], [($^{t\text{-}Bu}$BTP)$_2$Cu]** and **[(^{TMCl}BTP)$_2$Cu]** were screened for the ROP of *L*-lactide in the presence of 9-anthracenemethanol in toluene at 110 °C. It was observed that for (monomer : catalyst : alcohol) = (200:1:2) among the three copper complexes **[(^{TMCl}BTP)$_2$Cu]** was most active catalyst for the ROP of *L*-lactide with 93% conversion achieved in 6 h with PDI value 1.13. Further polymerization reactions were carried with **[(^{TMCl}BTP)$_2$Cu]** and varying [monomer]/[alcohol] ratio from 25 to 200. The polymers obtained have narrow PDI value varying in the range 1.11 to 1.19 and molecular mass of the polymer increased linearly with increase in [monomer]/ [alcohol] ratio. The close agreement between experimental and calculated molecular weight further gave evidence for living character of polymerization reactions. It was observed that upto 16 equivalent of 9-anthracenemethanol can be used effectively as chain transfer agent in the presence of 1 equivalent of metal catalyst to polymerize 400 units of monomer which suggested that at very low catalyst loading large number of monomers can be easily polymerized which indicates that

the ROP is immortal in nature. The end-group analysis of the polymer with [monomer]/[alcohol] = 25 showed polymer to be end-capped by anthracenemethyl at one end and hydroxyl group at the other end with integral ratio of H_a : H_b : H_d : H_e = 9:2:1:1 **(Fig. S6)**. The polymerization thus goes by an activated monomer mechanism where *L*-lactide is first activated by Cu-complex **[(^{TMCl}BTP)$_2$Cu]** and then 9-anthracenemethanol inserts in the carbonyl carbon of the lactide followed by ring opening of monomer and subsequent cleavage of the catalyst from the monomer. Furthermore, ROP of *L*-lactide was investigated with different multifunctional alcohols 2, 2'-(hexadecylimino) diethanol ($NC_{16}H_{33}$-2ROH), *tert*-butyl *bis*(2-hydroxyethyl) carbamate (BOC-2ROH), and triethanolamine (TEA-3ROH) to give two arm PLLA with ($NC_{16}H_{33}$-2ROH) and (BOC-2ROH) and star-shaped three arm PLLA with (TEA-3ROH).The formation of star-shaped PLLA was further confirmed by ^{1}H NMR ($CDCl_3$) spectral data with triethanolamine core and three HOCH(Me)CO chain ends having integral ratio of hydrogen ≈ 2:1 **(Fig. S7)**.

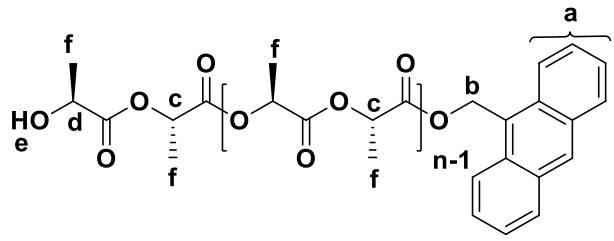

Fig. S6. End group in PLLA.

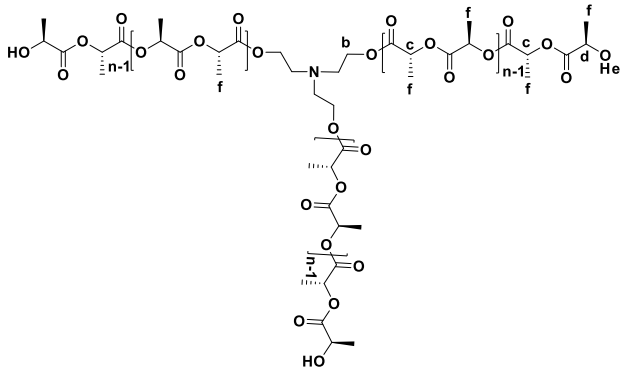

Fig. S7. Star shaped PLLA.

Metal-free catalytic system for the ROP of lactide

The metal-free catalyst systems or the organocatalysts serve as the alternate route for the ring-opening polymerization of lactide over the traditional metal catalytic systems. The organocatalyst relies on the use of organic molecules for catalytic activity. The major advantage of using organocatalyst is that it produces polymers that are free from metallic residues and thus find wide applications in the biomedicine. In addition, low lost and easy availability of the catalyst, and mild reaction conditions give them an added advantage. The lower activity of the catalyst and longer reaction time limits the application of organocatalyst on an industrial scale for ROP [**47**]. The organocatalyst mainly constitutes of (nucleophilic or non-nucleophilic) organic bases [**48**] like pyridine, guanidine, amidine, *N*-heterocyclic carbene, phosphazene, a biocomponent system consisting of organic base and acid[51] and bifunctional system composed of H-bond donor and H-bond acceptor [**49**].

The first report for the living organocatalytic ROP of the lactide came in 2001 when Hedrick and coworkers reported the use of 4-(Dimethylamino)pyridine (DMAP) as efficient catalyst for the ROP of lactide. They studied the catalytic behaviour of DMAP in the presence of alcohol as the initiator under solvent free condition (135 °C) and in the presence of dichloromethane as the solvent at 35 °C [**50**]. The three alcohols used were ethanol, benzyl alcohol and isopropanol and the ratio of DMAP was varied upto 4.0 equivalents with respect to alcohol. It was observed that in the absence of alcohol there was no polymerization observed after prolonged reaction time. At low concentration of DMAP (0.1 equiv.) there was negligible polymerization observed and at higher concentration of DMAP (4 equivalents) almost 100% conversion was observed with polymer having narrow PDI (1.10) (**Table S6**). The living nature of the polymerization was well exemplified by the linear increase in the molecular weight of the polymer with percentage conversion and extremely low PDI values. The polymerization proceeds with an activated monomer mechanism as when the reaction was done in the presence of ethanol the ^{1}H NMR of the product isolated showed peaks for ethoxy ester and hydroxyl end groups.

Table S6. Polymerization data with different ratio of DMAP and varying the initiator

Entry	Catalyst (equiv.)	Initiator	Temp (°C)	Time	[M]:[C]	Degree of polymerization	PDI
1	DMAP (0.1)	EtOH	35	96 h	30	5	
2	DMAP (1.0)	EtOH	35	60 h	30	29	1.13
3	DMAP (2.0)	EtOH	35	36 h	30	29	1.13
4	DMAP (4.0)	EtOH	35	24 h	30	29	1.08
5	DMAP (2.0)	EtOH	35	24 h	15	17	1.12
6	DMAP (2.0)	EtOH	35	36 h	30	29	1.13
7	DMAP (2.0)	EtOH	35	50 h	60	62	1.10
8	DMAP (4.0)	EtOH	35	64 h	100	78	1.10
9	DMAP (2.0)	$PhCH_2OH$	35	30 h	30	43	1.08
10	DMAP (2.0)	$PhCH_2OH$	135	5 min	30	29	1.10
11	DMAP (2.0)	$PhCH_2OH$	135	10 min	60	42	1.09
12	DMAP (4.0)	$PhCH_2OH$	135	20 min	100	77	1.19
13	DMAP (2.0)	$PhCH_2OH$	135	20 min	140	120	1.14
14	DMAP (2.0)	$(CH_3)_2CHOH$	35	48 h	30	35	1.12

Li *et. al*. in 2004 for the first time reported organic guanidine salt as a metal-free initiator for the ROP of lactide [**51**]. The hexabutyl guanidinium acetate (HBG·OAc) was used as the precursor for the polymerization. The hexabutyl guanidium acetate was synthesized in the stepwise process starting from tetrabutylurea and phosphorus oxychloride **(Scheme S36)**. The bulk ROP of *L*-lactide and *rac*-lactide was carried out at the temperature range of (110 ˚C - 130 ˚C). The kinetics study of the polymerization reaction carried out with *L*-lactide showed the reaction to be first-order with respect to the monomer. The polymers obtained have narrow PDI value and the molecular weight of the polymer increased linearly with percentage conversion that gave evidence for the living nature of ROP.

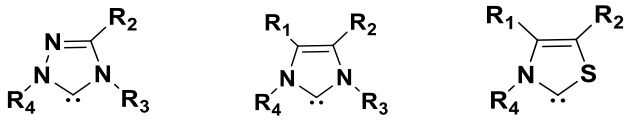

Fig. S8. Structural variation of *N*-heterocyclic carbene.

The catalytic activity of *N*-heterocyclic carbenes as metal-free organocatalyst for the living ROP of lactide was explored [**52**]. The main advantage of the heterocyclic carbenes is that they show diverse structural variations depending upon the groups attached to different position in the ring and heteroatom present in the ring **(Fig. S8)**. The carbene complexes were generated *in situ* in order to avoid difficulty associated with the isolation of the sensitive carbene complexes. The *N*-heterocyclic carbenes **(Fig. S9)** were synthesised by the reaction of respective imidazolium and imidazolinium chloride salts and potassium *tert*-butoxide in THF. The reaction mixture was stirred for ten minutes. The resulting yellow solution was filtered and carbene that act as catalyst for the reaction was isolated. For the polymerization reaction benzyl alcohol that act as initiator for the reaction was added to the solution followed by the addition of solution of *L*-lactide in THF. The polymerization reaction was quenched with carbon disulphide (CS_2) and the polymer was precipitated by the addition of cold methanol.

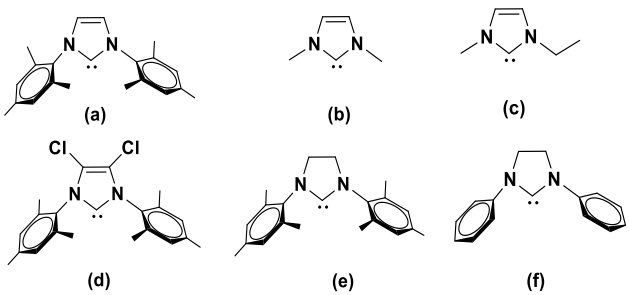

Fig. S9. *N*-heterocyclic carbenes.

The ROP reactions were investigated with the *N*-heterocyclic carbenes with [monomer]/[initiator]/[catalyst] = 200/1/1.5. It was observed that when 1 and 3 position of the *N*-heterocyclic carbene was substituted with sterically bulky substituent the polymerization was faster as the approach of monomer molecule to the nucleophilic center was easier. The polymerization with the bulky substituent at 1,3 positions of the carbene was slow but it was more controlled. This is well evident from the percentage conversion of the monomer and the PDI value of the polymer obtained using carbene (9a) [% conversion = 85 and PDI = 1.18) and (9b) [% conversion = 97 and PDI = 1.31) as catalyst for the polymerization reaction. Further it was observed that the introduction of the electron-withdrawing substituent at 4,5 positions of the carbene i.e. (9d) decreased the activity of catalyst to a significant extent due to increase in the stability of the carbene. The living nature of the polymerization reactions was confirmed from narrow PDI value of the polymer and linear increase in molecular weight with conversion of the monomer.

CONCLUSION & FUTURE PROSPECTIVE

In the present scenario, the biodegradable thermoplastics derived from renewable feedstocks have drawn considerable interest as a suitable alternative for sustainable development. The most efficient method for synthesizing biodegradable polyesters is the ROP reactions catalyzed by organometallic, organic or enzyme catalysts. The major drawback of the classical ROP is low catalyst efficiency and high catalyst loading. Researchers across the globe aim to develop catalytic systems with high catalytic activity and good control over the molecular weight, molecular weight distribution, and microstructure of the polymer. In this regard, the concept of living and immortal polymerization has gained considerable research interest. The major advantage of the immortal ROP is the low catalyst loading due to which the polymer's production cost is reduced, and the metal residues in the final polymer are greatly diminished.

The success of the immortal ROP reactions mainly depends on rapid and reversible reactions between the growing polymer chain and the chain transfer agent that eventually leads to the growth of multiple polymeric chains from a single catalytic site as compared to conventional living polymerization reactions where from a single catalytic site only one polymeric chain grows. In most of the reports, the chain-transfer agents (CTAs) are the aliphatic or the aryl alcohols. Thus, along with the catalyst framework, the loading of CTAs with respect to the catalyst and the steric and electronic environment of the CTAs play a crucial role in governing the fate of immortal polymerization reactions. The steric bulkiness of the alcohol must be suitable, which allows easy approach of the monomer to the catalytic site. When the CTAs used are very small, it might lead to random formation of the clusters that

would make the ROP reaction uncontrolled and polymers obtained will have broad molecular weight distribution. When more sterically bulky alcohol is used, the coordination of monomers to the active catalyst site becomes difficult.

Additionally, the CTAs must be suitably substituted by electron-donating and electron-withdrawing groups, making chain-transfer reaction easily feasible. The orientation of the group in the CTAs that facilitate the chain-transfer must be such that it does not form a stable adduct with the active catalytic site. The stoichiometry of the CTAs added with respect to the active catalyst should be monitored so that the active catalyst does not undergo any dissociation in the presence of CTAs. Recently the major aspect of immortal ROP reactions that have withdrawn considerable interest from researchers is the use of various end-functionalized CTAs that would generate functionalized end-capped polymers with a novel framework that would have diverse applications.

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CONFLICTS OF INTEREST

There are no conflicts to declare.

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