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FULL PAPER

Highly Active and Iso-selective Catalysts for ROP of Cyclic Esters Using Group 2 Metal Initiators

Jayeeta Bhattacharjee,[a] A. Harinath,[a] Hari Pada Nayek,[b] Alok Sarkar,[c] and Tarun K. Panda*[a]

Abstract. A series of alkali and alkaline earth (Ae) metal complexes bearing 1,2 phenylene(bis-diphenylphosphinothioic/selenoic amine) [{$Ph_2P(E)NH$}$_2C_6H_4$] (E = S (**1**-**H2**); Se (**2**-**H2**) ligands are reported. Alkali metal complexes [{$Ph_2P(S)N$}$_2C_6H_4$]$Na(THF)_4$ (**3a**) [{$Ph_2P(Se)N$}$_2C_6H_4$]$Na(THF)_4$ (**3b**), and [{$Ph_2P(Se)N$}$_2C_6H_4$]$K(THF)_5$ (**4b**) were obtained in good yield by treating protic ligand **1**-**H2** or **2**-**H2** with corresponding metal hexamethyldisilazides [$MN(SiMe_3)_2$] (M = Na and K) at ambient temperature. The Ae metal complexes formulated as [{$Ph_2P(E)N$}$_2C_6H_4$]$M(THF)_3$ [E = S, M = Ca (**5a**), Sr (**6a**), Ba (**7a**); E = Se, M = Ca (**5b**), Sr (**6b**), Ba (**7b**)] can be synthesized using two routes. The molecular structures of the free ligand **1**-**H2** and metal complexes **5a**,**b**-**7a**,**b** in their solid states were established. Complexes **3a** and **3b** are isostructural; however, in complex **4b**, an attachment different from ligand **2** was observed. The complexes **5a**,**b**-**7a**,**b** are isostructural and each metal ion exhibits a distorted pentagonal bipyramidal geometry around it. All Ae metal complexes **5a**,**b**-**7a**,**b** were tested for the ring-opening polymerization (ROP) of racemic lactide (rac-LA) and ε- caprolactone (ε-CL) at room temperature. Calcium complexes **5a** and **5b** show excellent iso-selectivity, with a P_i value of 0.78–0.87 at 298 K with a high degree of polymerization control, whereas the corresponding strontium complexes **6a** and **6b** exhibit moderate iso-selectivity, and barium complexes **7a** and **7b** yield only atactic polylactides (PLAs). In all cases catalyst initiates the ROP catalytic cycle in the absence of any external initiator. Kinetics studies of the polymerization reactions indicate the relative order of polymerization rates increases with increase in the size of the metal ion: Ba>Sr>Ca.

Introduction

Various research groups worldwide are working to develop a substance that can efficiently catalyze the ring-opening polymerization (ROP) of biodegradable polyesters such as polylactide[1] (PLA) or polycaprolactone for use in medical applications[2] such as sutures, dental devices, orthopedic fixation devices, drug delivery systems, and tissue engineering.[3] In particular, the focus is on developing a distinct well-defined single-site catalyst that can control the stereochemistry of polyesters,[4] whose mechanical properties and degradation profile may be fine-tuned, and thermal stability and crystallinity may be escalated, to produce a well-regulated molecular weight (M_n) and low polydispersity (PDI) polymer.[5] The polymerization of racemic lactide (rac-LA) may produce either (i) an isotactic or (ii) a heterotactic PLA and atactic PLA, following a homochiral and heterochiral preference, introducing stereo irregularity in PLA.[4] Isotactic PLAs obtained through the ROP of the enantio-pure L-lactide (L-LA) and D-LA have higher melting points (T_m) and modulus than atactic PLAs.[6] The iso-selectivity gained from using rac-LA is especially important and useful because the products—stereo-block/complex PLAs—obtained from rac-LA have superior thermal and mechanical properties when compared to PLAs derived from pure L-LA.[4] For instance, a crystalline-ordered polymer with a high T_m will have better mechanical properties than an isotactic poly-L-lactide (PLLA). In some cases, increase in T_m by as much as 50°C can improve the thermal stability to such an extent that it can enhance the PLA's industrial application as an engineering polymer.[7] Therefore, the stereo-regulated ROP of rac-LA has always been a topic of interest in the field of polymer chemistry. In recent years, the catalytic ROP of cyclic esters such as lactides (LAs) and lactones has been frequently explored by using organocatalysts,[8] as well as discrete metal precursors such as complexes of tin,[9] aluminum,[10] zinc,[11] magnesium,[12] iron,[13] titanium,[14] indium,[15] yttrium,[16] rare-earth metals,[17] and organo-initiators.[18] The main challenge in choosing a catalyst is identifying one that can produce high rates of polymerization with excellent stereo regularity, ideally without the need for expensive chiral auxiliaries or ligands.[19]

Several highly active achiral catalysts are capable of producing amorphous, heterotactic PLAs of low polydispersity values from rac-LA.[20] Generally, there is limited mention of iso-selective achiral catalysts in literature,[21] and most iso-selective ROPs known in literature are based on chiral catalysts.[22] Recently, Kol *et al.* reported a number of chiral aluminum salen complexes as active catalysts.[10] Despite high selectivity, chiral aluminum catalysts suffer from low reactivity and require several hours (sometimes days) at high temperature to achieve higher conversions. Williams *et al.* reported highly active chiral yttrium phosphasalen alkoxide complexes with the best iso-selectivity of P_i = 0.84.[23] Chiral zinc amidooxazolinate complexes yielding a high iso-selectivity (P_i = 0.91) were reported by Du's group recently.[24] Some achiral hetero-scorpionate zwitterionic zinc complexes as catalysts have also been reported (P_i = 0.85).[11b] However, it is highly desirable to develop new complexes that can broaden the range of catalysts for alkali and alkaline earth (Ae) metals for the iso-selective ROP of rac-LA. To overcome hardships, an alternative strategy is proposed. Using this approach, an easily accessible achiral catalyst can promote

[a] *J. Bhattacharjee, A. Harinath, Dr. T. K. Panda*
Department of Chemistry, Indian Institute of Technology Hyderabad
Kandi – 502 285, Sangareddy, Telangana, India.
E-mail: tpanda@iith.ac.in
[b] *Dr. H. P. Nayek*
Department of Applied Chemistry,
Indian Institute of Technology (ISM), Dhanbad,
826004, Jharkhand, India.
[c] *Dr. A. Sarkar*
Momentive Performance Materials Pvt. Ltd.
Survey No. 09, Hosur Road, Electronic City (west)
Bangalore-560100, India

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stereoselective transformations by adopting chirality in the propagating step by chain-end bound to the catalyst in a chain-end controlled mechanism. This strategy is advantageous, as it averts the need for regenerated chiral precursors and rationalizes catalyst modifications to influence stereochemical outcomes.[25]

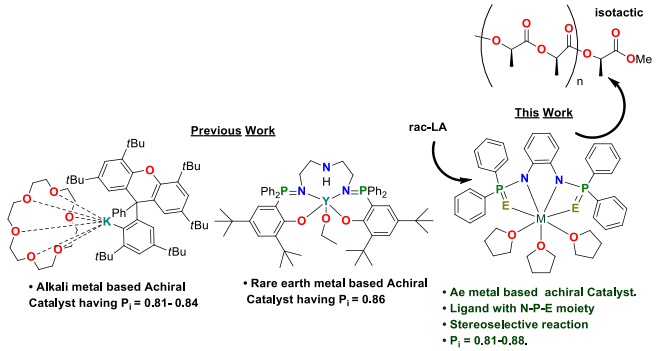


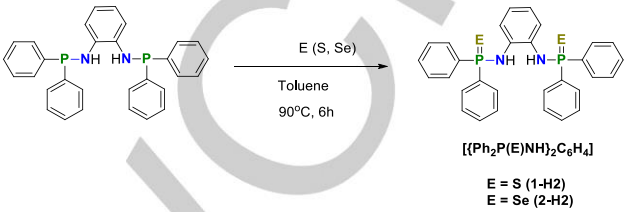
Figure 1. Various achiral catalysts to synthesize stereo regular PLA.

Although some complexes of Mg and Ca were recently reported as catalyst precursors for lactide polymerization,[26] till date, other group 2 metals have not been exploited in the ROP of cyclic esters.[27] The infrequency of synthesis, stability, and reactivity of such complexes in literature is often attributed to the kinetic lability with Schlenk-type equilibria in solutions of heavier group 2 complexes, which makes it challenging to synthesize these compounds.[28] As the metal residues are difficult to remove from the synthesized polymers, alternative nontoxic metal complexes are encouraged to be active catalysts for the ROP of rac-LA. Calcium and strontium are harmless, abundant elements in the human body, and suitable for the catalytic synthesis of PLAs for use in the medical field. Therefore, exploring the possibility of using Ae metal complexes as catalysts for the ROP of lactides is very valuable.[29]

Recently, we have introduced bis(phosphinoselenoic amine) ligand [{$Ph_2P(Se)NH$}$_2C_2H_4$ in the Ae earth metal coordination sphere to study their structural aspects and catalytic potential in ring opening polymerization of ε-caprolactone.[30] In this paper, we report the synthesis of alkali and Ae metal complexes bearing 1,2 phenylene(bis-diphenylphosphino-chalcogen amine) ligand and their structural aspects. We also demonstrate that the Ae metal complexes show an unparalleled proclivity with site selectivity, high activity, and controlled polymerization at high molecular weights for the ROP of rac-LA and ε-caprolactone (**ε-CL**) to form stereo-block copolymers.

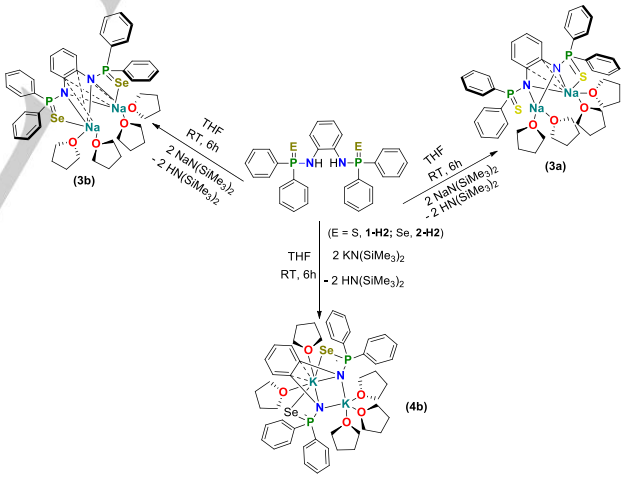
Results and Discussion

Ligand synthesis. Ligands *N,N'*-(1,2-phenylene)bis(P,P-diphenylphosphino-chalcogen amine) [{$Ph_2P(E)NH$}$_2C_6H_4$] (**1-H2** and **2-H2**) were readily prepared according to reported procedure by the reaction between *N,N'*-bis(diphenylphosphino)-benzene-1,2-diamine [$Ph_2PNHC_6H_4NH$-PPh_2] and elemental sulfur or selenium in a 1:2 molar ratio in toluene at 90ºC (Scheme **1**).[31] The spectroscopic data for compound **2-H2** are in full agreement with reported values and are given in the Supporting Information.[31] However, in the ^{1}H NMR spectra of **1-H2**, the 24 phenyl protons attached to the ligand backbone exhibit multiplet resonance signals at δ 8.10–7.10 ppm. The sharp singlet at δ 5.84 ppm can be assigned to both the -NH protons attached to the phosphorus atoms (Figure FS9 in ESI). In the ^{31}P{^{1}H} NMR spectra of **1-H2**, one sharp singlet was observed at δ 56.8 ppm along with two satellite peaks, indicating the coupling of P-Se with the adjacent selenium atom (Figure FS10 in ESI). The molecular structure of compound **1-H2** in the solid state was confirmed by single-crystal x-ray diffraction analysis and given in Figure **FS1** in ESI.



Scheme 1. Syntheses of *N,N'*-(1,2-phenylene)bis(*P,P*-diphenylphosphino-chalcogen amide) ligands (**1-H2** and **2-H2**).

Alkali metal complexes. Sodium and potassium complexes with molecular formulae [{$Ph_2P(S)N$}$_2C_6H_4$]Na(THF)$_5$] (**3a**), [{$Ph_2P(Se)N$}$_2C_6H_4$]-Na(THF)$_4$ (**3b**), and [{$Ph_2P(Se)N$}$_2C_6H_4$]-K(THF)$_5$ (**4b**) were prepared through the reaction between **1-H2** or **2-H2** and [MN(SiMe$_3$)$_2$] (M = Na, K) in THF (Scheme **2**). All three complexes were characterized using spectroscopic and analytical techniques, and the solid-state structures of complexes **3a**, **3b**, and **4b** were confirmed by single-crystal X-ray diffraction analysis.



Scheme 2. Synthesis of alkali metal complexes **3a**, **3b**, and **4b**.

Strong absorption bands for P=S and P=Se bonds appear at 550 cm^{-1} (for complex **3a**) and 552 cm^{-1} and 585 cm^{-1} (for complexes **3b** and **4b** respectively) in the FT-IR spectra, which are in agreement with reported values.[30,32] Both complexes **3b** and **4b** show a sharp signal in the ^{31}P{^{1}H} NMR spectra, δ 52.4 ppm (**3b**) and 52.4 ppm (**4b**), which are in the same region as that of the free ligand **2-H2** (δ53.8 ppm) (Figures FS18, FS21, FS13 in ESI). In the case of complex **3a**, the chemical shift of δ 60.4 ppm indicates a significant low-field shift compared to that of the free ligand **1-H2** (56.8 ppm) (Figures FS15 and FS10 in ESI). The single resonance peak in complexes **3a**, **3b**, and **4b** confirms the chemical equivalence of both phosphorous atoms in solution. All

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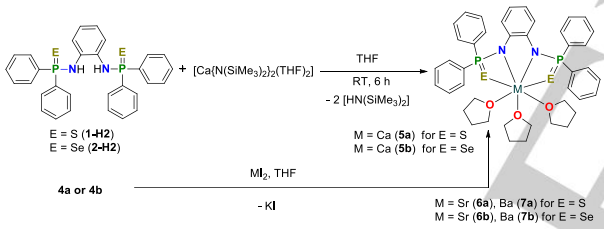
the alkali metal complexes are coordinated to the THF molecules, as evident from the multiplet signals at 3.59–3.56 ppm and 1.43–1.40 ppm (for **3a** and **3b** respectively) and triplet signals centered at 3.50 ppm and 1.36 ppm (for **4b**) observed in the ^{1}H NMR spectra (Figures FS14, FS17, and FS20 in ESI).

Single crystals of complexes **3a**, **3b**, and **4b** were obtained from a mixture of each corresponding complex with THF and pentane solution. The molecular structures of **3b** and **4b** confirm the attachment of ligand **2** to sodium and potassium ions respectively. In complex **3a**, two sodium ions are asymmetrically attached to ligand **1**. The details of the structural parameters are given in Table TS1 in the ESI. The solid-state structures of complexes **3a**, **3b**, and **4b** are shown in Figures **FS2-3**, and **FS4** in ESI respectively.

Ae metal complexes. Ae metal complexes with the general molecular formula [{$Ph_2P(E)N$}$_2C_6H_4$]M(THF)$_3$ [E = S, M = Ca (**5a**), Sr (**6a**), Ba (**7a**); E = Se, M = Ca (**5b**), Sr (**6b**), Ba (**7b**)] can be readily obtained by two different synthetic approaches (Scheme **3**). However, the most convenient method for obtaining all these complexes is a one-pot reaction, in which ligands **1**-**H2** and **2**-**H2** are first reacted with anhydrous [KN(SiMe$_3$)$_2$] in a 1:2 molar ratio in THF to generate *in situ* potassium salts **4a** and **4b**, followed by the addition of anhydrous metal diiodide AeI$_2$ (Ae = Ca, Sr, and Ba) to the reaction mixture (Scheme **3**). The new Ae complexes **5a**,**b**-**7a**,**b** were characterized using multinuclear NMR spectroscopic and combustion analysis techniques. The solid-state structures of complexes **5a**,**b**-**7a**,**b** were confirmed by single crystal X-ray diffraction analysis.



Scheme 3. Synthesis of Ae metal complexes **5a**,**b**-**7a**,**b**.

In the ^{1}H NMR spectra of the complexes, the disappearance of signals at δ 5.84 ppm for complexes **5a**, **6a**, and **7a**, as well as the disappearance of the signals at δ 5.92 ppm for complexes **5b**, **6b**, and **7b** assigned for -NH protons indicate the formation of dianionic ligand fragments **1** and **2** in each complex (Figures FS23, FS26, FS29, FS32, FS35, FS38 in ESI). In the ^{31}P{^{1}H} NMR spectra, each complex shows a sharp signal at δ 66.7 ppm (for complex **5b**), 66.7 ppm (for complex **6b**), and 66.6 ppm (for complex **7b**) and the values are significantly low-field shifted in comparison to that of free ligand **2**-**H2** (δ 53.8 ppm) (Figures FS33, FS36, FS39, FS13 in ESI). Similar sharp signals at δ 69.4 ppm (for complex **5a**), 69.6 ppm (for complex **6a**), and 66.6 ppm (for complex **7a**) are also observed and the values are significantly low-field shifted when compared to that of free ligand **1**-**H2** (δ 56.8 ppm) (Figures FS24, FS27, FS30, FS10 in ESI).The appearance of only one resonance signal in each complex indicates the chemical equivalence of both phosphorous atoms present in the ligand moiety **1** and **2**. In addition, two typical multiplet signals, at δ 3.65–3.55 ppm and 1.35–1.33 ppm, indicate the resonance of protons attached to the coordinated THF molecules.

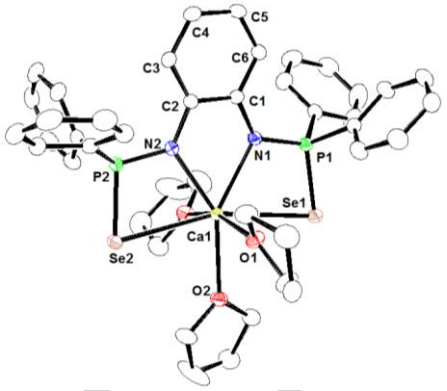


Figure 2. Solid-state structure of compound **5b**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ca1–N1 2.421(17), Ca1–Se1 3.1274(5), Ca1–P1 3.3538(7), Ca1–N2 2.4298(18), Ca1–Se2 3.1179(5), Ca1–P2 3.3500(7), Ca1–O1 2.3815(16), Ca1–O2 2.4915(16), Ca1–O3 2.4008(17), N1–Ca1–Se1 58.71(12), N1–Ca1–N2 63.45(17), Se1–Ca1–Se2 175.44(2), O1–Ca1–O2 74.26(18), O1–Ca1–O3 155.90(19), O2–Ca1–O3 85.91(18), P1–Se1–Ca1 75.90(5), P2–Se2–Ca1 76.91(5).

Crystals of compounds **5**-**7a**, were isolated from a mixture of THF and pentane solution at –35°C, and crystals of compounds **5**-**7b**, were isolated from hot THF solution. The single-crystal x-ray data obtained for complex **7a** was not complete, and therefore poor. A representation of the molecular structure for complex **7a** is available in the ESI. The bond lengths and bond angles of complex **7a** are used for comparison with other complexes only. The calcium, strontium, and barium complexes **5a**, **5b**, **6a**, **6b**, and **7b** crystallize in the triclinic space group *P*-1, with two molecules of compounds **5**, **6**, and **7** in their respective unit cells along with half THF as solvate molecule. The details of the structural and refinement parameters are given in Table TS1 in ESI. The molecular structures of complexes **5b** and **7b** in the solid state are provided in Figures 2 and 3 respectively as representative examples of all Ae complexes, while other structures are given in ESI (Figures FS5-8**)**. Complexes **5a**,**b**-**7a**,**b** are isostructural to each other due to the similar ionic radii of the metal ions (1.00 Å, 1.18 Å, and 1.35 Å respectively) for a coordination number of six.[33]

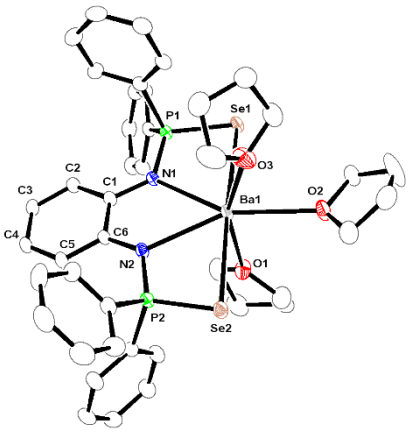


Figure 3. Solid-state structure of compound **7b**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ba1–N1 2.706(4), Ba1–Se1 3.3059(6), Ba1–P1 3.5764(13), Ba1–N2 2.708(4), Ba1–Se2 3.2982(7), Ba1–P2 3.5818(13), Ba1–O1 2.697(4), Ba1–O2 2.774(4), Ba1–O3 2.756(5), N1–Ba1–Se1 60.70(8), N1-Ba-Se2 121.15(9), N1–Ba1–N2 60.53(12), Se1–Ba1–Se2 177.086(17), O1–Ba1–O2 82.86(13), O1–Ba1–O3 158.55(15), O2–Ba1–O3 76.75(15), P1–Se1–Ba1 78.77(4), P2–Se2–Ba1 79.06(4).

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Ligands **1** and **2** are bonded to the Ae metal ion through the chelation of two amido nitrogen atoms and two sulfur atoms (complexes **5a**, **6a**, and **7a**) or two selenium atoms (complexes **5b**, **6b**, and **7b**) attached to the phosphorus atoms. The phosphorus–metal distances (3.365 Å and 3.359 Å for complexes **5a** and **5b** respectively, 3.452 Å and 3.446 Å for complexes **6a** and **6b** respectively, and 3.593 Å and 3.613 Å for complexes **7a** and **7b** respectively) are significantly longer than the sum of the covalent radii of the corresponding metal ion and phosphorus atom, which indicates that there is no interaction between them. Thus, in each case, the central Ae metal ion adopts a distorted pentagonal bi-pyramidal geometry around it, with two selenium atoms, two nitrogen atoms of ligand **1**, along with one oxygen atom from the THF molecule, which are in the basal plane, whereas the two remaining THF molecules occupy the apical positions. The M–N distances, 2.386(8) Å and 2.418(8) Å complexes **5a** and **5b** respectively, 2.517(5) Å and 2.540(5) Å for complexes **6a** and **6b** respectively, and 2.657(5) Å and 2.654(6) Å for complexes **7a** and **7b** respectively, and M–Se distances, 3.252(2) Å and 3.300(2) Å for complexes **5a** and **5b** respectively, 3.2788(1) Å and 3.3259(1) Å for complexes **6a** and **6b** respectively, and 3.4706(9) Å and 3.4071(9) Å for complexes **7a** and **7b** respectively, indicate a slight asymmetrical attachment of the tetra-dentate ligand **1** to the Ae metal ion. Nevertheless, similar M–N distances and M–Se distances were observed in the findings we previously reported for complexes $[(THF)_2M\{Ph_2P(Se)N(CHPh_2)\}_2]$ (M = Ca, Sr, Ba)[31] and Ae metal complexes reported by other groups.[34]

Polymerization of rac-LA. Complexes **5a**,**b-7a**,**b** were tested as initiators for the ROP of rac-LA (Scheme 4). Table **1** summarizes the polymerization result of rac-LA associated with initiators **5b**, **6b**, and **7b**, whereas all the polymerization results initiated by complexes **5a**, **6a**, and **7a** are given in the supporting information (Table TS37 in ESI). All polymerizations were carried out in toluene at room temperature, and the percentage of conversion was monitored through ^{1}H NMR spectroscopy by taking samples from the reaction mixtures at certain time intervals. Reactions conducted using catalysts **5a**,**b-6a**,**b** (1 mM) with 100 equivalents of rac-LA at 25ºC in toluene resulted in 99% conversion in one hour. However, the reaction was very fast and 99% conversion was achieved in only 10 minutes when the corresponding barium complexes **7a** and **7b** were used as initiators (Table 1 and Table TS37 in ESI). Polymerization up to 1000 equivalents of rac-LA with **7b** was completed in less than 10 minutes in toluene (Table 1 and Table TS37 in ESI).

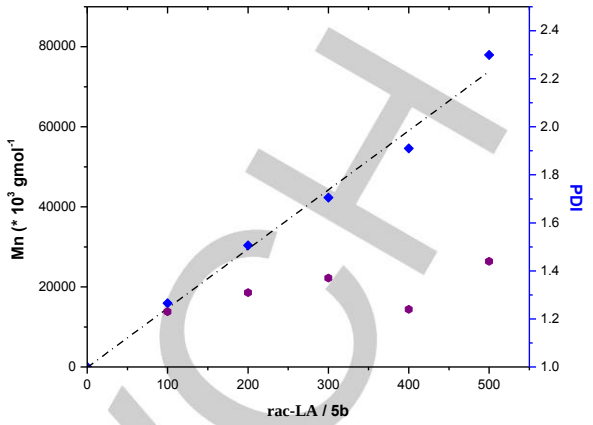
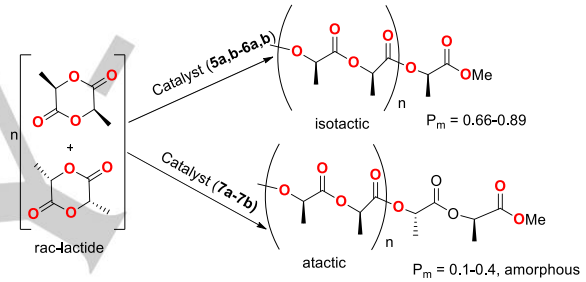


Figure 4. Plot of observed (M_n) and molecular weight distribution of PLA as functions of added rac-LA with respect to catalyst **5b** (M_n = number averaged molecular weight, PDI = polydispersity index). The line indicates calculated M_n values based on the LA: initiator ratio. All reactions were carried out at room temperature in toluene, and conversion to polymer samples was >90%.



Scheme 4. ROP of rac-LA catalyzed by Ae metal complexes **5a**, **5b**, **6a**, **6b**, **7a**, and **7b**.

Despite the high overall rates of polymerization, the polymerizations time required to accomplish the complete conversion of rac-LA into PLA, the order of activity decreased as Ba>Sr>Ca. In addition, they followed very well controlled manner. In general, there was close agreement between the theoretical and observed molecular weights, as well as the narrow polydispersity index (PDI) (PDI<1.6) (Figure 4). It is noteworthy that the polymerization of rac-LA in the presence of the catalysts (**5a**,**b-7a**,**b**) was a living process, with a linear increase of M_n values and low molecular weight distributions for monomer: initiator (M/I) ratios up to 500 (Tables 1 and Table TS37 in ESI and Figure 4 and Figures FS103–FS105 in ESI). Depending upon the Ae metal coordination is changed from sulfur (**5-7a**) to selenium (**5-7b**), we also noticed a significant enhancement in the order of activity. To quantify these observations, the polymerization kinetics was thoroughly monitored and the data are given in ESI (Table 2 and Tables TS2–TS11, Tables TS19–TS25).

To explore the reaction order with respect to the monomer and catalyst, a typical kinetics study was conducted.[35] For this study, rac-LA (0.228 g, 2.0 mmol) was added to a solution of catalysts (**5a**,**b-7a**,**b**) (0.01, 0.02, 0.03, 0.04, 0.06 M respectively) in $CDCl_3$ (1 mL), at room temperature. The solution was placed in the NMR tube at 25ºC and at the indicated time intervals, the tube was analyzed by ^{1}H NMR. As expected, plots of $[LA]_0/[LA]$ versus time for a wide range of $[\{Ph_2P(Se)N\}_2C_6H_4Ca(THF)_3]$ are linear, indicating the usual first order dependence on monomer

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concentration (Figure **5**).Thus, the rate expression can be written as follows: $-d[LA]/dt = K_{app}[LA]^1[\{Ph_2P(Se)N\}_2C_6H_4Ca(THF)_3]^x = K_{obs}[LA]^1$, where $K_{obs} = K_{app}[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3]^x$. A plot of $\ln(k_{obs})$ versus $\ln[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3]$ (Figure **5**) is linear, indicating the order of $[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3]$ is x = 0.999. A similar observation was also made in the case of other catalysts **6b** and **7b** and **5a**, **6a**, and **7a** (Figures FS44–FS50 and Figures FS66–FS74 in ESI). The polymerizations with respect to all catalysts followed first-order kinetics, indicating that there is only one initiating species for all complexes, and gives an overall second-order rate law. Therefore, the polymerization of rac-LA in the presence of all catalysts followed the following overall rate equation:

rate = $-d[LA]/dt = \mathbf{k_p[catalyst]^1[LA]^1}$.

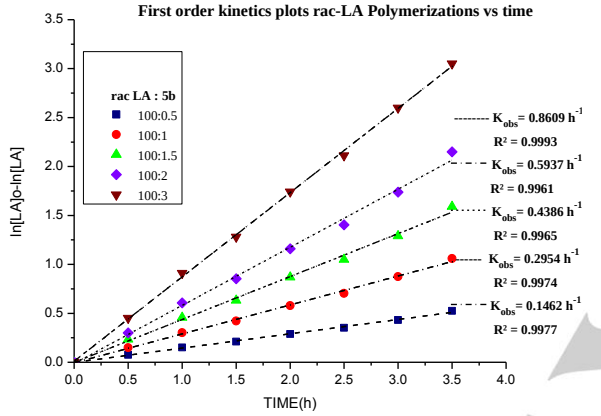

Figure 5. First-order kinetics plots for rac-LA polymerizations (with time) in $CDCl_3$ (1 mL) with different concentrations of complex **5b**.

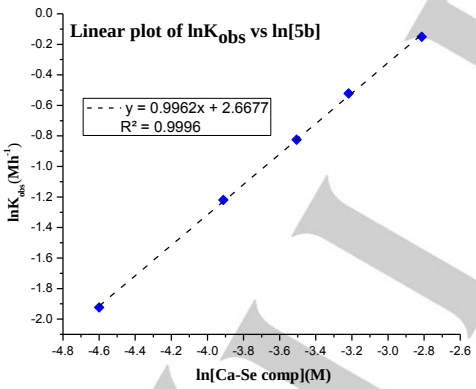

Figure 6. Kinetics plots of K_{obs} versus in $[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3]$ for the polymerization of rac-LA with [LA] = 2.0 M in $CDCl_3$ (1 mL) at 25°C.

Table **2** summarizes the rate constants for the concentration of catalyst versus time for the ROP of rac-LA catalyzed by complexes (**5-7b**). This allows us to directly compare K_{obs} values for all the six catalysts used in the ROP of rac-LA. The K_{obs} values for the barium complexes (K_{obs} = 0.839 $M^{-1}h^{-1}$ for complex **7a**, 0.906 $M^{-1}h^{-1}$ for complex **7b**) are relatively higher than those for the calcium and strontium complexes (K_{obs}= 0.137 $M^{-1}h^{-1}$ for complex **5a**, 0.146 $M^{-1}h^{-1}$ for complex **5b**, 0.149 $M^{-1}h^{-1}$ for complex **6a**, and 0.147 $M^{-1}h^{-1}$ for complex **6b**) (Table 2 and Table TS25 in ESI). On the basis of our study, the enhanced K_{obs} of the barium complex can be attributed to the larger size of the barium ion compared to the other Ae metal ions.[36] Due to greater size of barium ion, the availability of free space in the complex increases, favoring initiator−LA interactions, which eventually enhances the ring-opening of LA and drives the propagation step. Notably, the calcium (**5a** and **5b**) and strontium (**6a** and **6b**) complexes have nearly identical rates, within error, due to the smaller difference of ion size between them. Additionally, the order of rates correlates with the metal–selenide bond lengths, as determined by single-crystal X-ray diffraction analysis experiments. The barium–selenide bond is significantly longer than the calcium–selenide and strontium–selenide bonds [M–Se: 2.196(4) Å, 2.060(3) Å, and 2.069(6) Å in complex **7** (Ba), complex **6** (Sr), and complex **5** (Ca) respectively], which also determines the requirements for efficient polymerization, that is, the need for sufficient Lewis acidity to ensure rapid coordination.

In addition, for a given Ae metal, the rate of polymerization increases when the donor atom of the ligand changes from sulfur to selenium (K_{obs} = 0.906 $M^{-1}h^{-1}$ for **7b**, 0.839 $M^{-1}h^{-1}$ for **7a**) (Table 2 and Table TS25 in ESI). This clearly indicates that not only the metal ion, but also the nature of the ligand plays an important role in the ROP of rac-LA. The increased size of selenium compared to sulfur presumably aids in providing an additional free space around the metal ion, causing the metal chalcogen bond to be more labile in the initiation step.

Table 1. Polymerization of rac-LA in the presence of Ae metal complexes bearing the bis-phosphinamine selenoid ligand.

Entry	M:1	Catalyst	Time (h:m)	conversion[b]	M_{ntheo} (KDa)	M_{nexp}[c] GPC (KDa)	PDI	Pm[d]
1	100	**5b**	00.30	99	14.3	16.7	1.53	0.83
2	200	**5b**	01.00	99	28.5	29	1.50	0.80
3	300	**5b**	01.30	95	41	40.3	1.47	0.79
4	400	**5b**	01.30	95	51.8	50.5	1.44	0.78
5	500	**5b**	02.00	99	67	70.8	1.34	0.81
6	100	**6b**	00.30	99	14.3	22.1	1.35	0.75
7	200	**6b**	00.30	99	28.5	33.2	1.37	0.69
8	300	**6b**	01.00	95	41	40.6	1.38	0.72
9	400	**6b**	01.00	95	54.7	56.5	1.50	0.71
10	500	**6b**	01.30	97	69.8	68.2	1.52	0.68
11	100	**7b**	00:03	99	14.3	15.9	1.21	0.52
12	200	**7b**	00:05	99	28.5	28.8	1.41	0.48
13	300	**7b**	00:08	99	42.8	42.3	1.40	0.41
14	400	**7b**	00:10	99	57.1	54.6	1.42	0.42
15	500	**7b**	00:15	99	71.3	78	1.51	0.47

In toluene at 25°C, [Catalyst] = 1 mM. [b]Conversions were determined by ^{1}H NMR spectroscopy. $M_n$theo = molecular weight of chain-end + 144 $gmol^{-1}$ × (M:1) × conversion. [c]In THF (2 mg mL^{-1}) and molecular weights were determined by GPC-LLS (flow rate ¼ 0.5 mL min^{-1}). Universal calibration was carried out with polystyrene standards, laser light scattering detector data, and concentration detector. Each experiment was duplicated to ensure precision. [d]Calculated according to using the relative integrals of rmr and rmm resonance.

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Table 2. Rate constants for polymerization of rac-LA with various concentrations of complexes **2**, **3**, and **4** as a catalyst.

Entry	Catalyst	rac-lac: catalyst	K_{obs} in ($M^{-1}h^{-1}$)
1	$[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3$	100:0.5	0.1462
2	$[\{Ph_2P(Se)N\}_2C_6H_4]Sr(THF)_3$	100:0.5	0.1467
3	$[\{Ph_2P(Se)N\}_2C_6H_4]Ba(THF)_3$	100:0.5	0.906
4	$[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3$	100:1	0.2954
5	$[\{Ph_2P(Se)N\}_2C_6H_4]Sr(THF)_3$	100:1	0.2291
6	$[\{Ph_2P(Se)N\}_2C_6H_4]Ba(THF)_3$	100:1	1.362
7	$[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3$	100:1.5	0.4386
8	$[\{Ph_2P(Se)N\}_2C_6H_4]Sr(THF)_3$	100:1.5	0.4418
9	$[\{Ph_2P(Se)N\}_2C_6H_4]Ba(THF)_3$	100:1.5	1.758
10	$[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3$	100:2	0.5937
11	$[\{Ph_2P(Se)N\}_2C_6H_4]Sr(THF)_3$	100:2	0.5958
12	$[\{Ph_2P(Se)N\}_2C_6H_4]Ba(THF)_3$	100:2	2.262
13	$[\{Ph_2P(Se)N\}_2C_6H_4]Ca(THF)_3$	100:3	0.8609
14	$[\{Ph_2P(Se)N\}_2C_6H_4]Sr(THF)_3$	100:3	0.8673
15	$[\{Ph_2P(Se)N\}_2C_6H_4]Ba(THF)_3$	100:3	2.67

Activation parameters for the ROP of rac-LA catalyzed by Ae complexes in $CDCl_3$ were found to be $\Delta H^{\ddagger}$ 22.27 (3) kJ/mol, $\Delta S^{\ddagger}$ -172.76 (7) J/mol K, $\Delta H^{\ddagger}$ 13.23 (4) kJ/mol, $\Delta S^{\ddagger}$ -200.65 (3) J/mol K, $\Delta H^{\ddagger}$ 17.58 (1) kJ/mol, and $\Delta S^{\ddagger}$ -182.07 (4) J/mol K for (**5**-**7b**) (Figures FS51-FS65 and Table TS12-TS18 in ESI) whereas in case of (**5**-**7a**) values are $\Delta H^{\ddagger}$ 23.76 (4) kJ/mol, $\Delta S^{\ddagger}$-169.10 (7) J/mol K, $\Delta H^{\ddagger}$ 15.22 (3) kJ/mol, $\Delta S^{\ddagger}$ -195.46 (5) J/mol K, $\Delta H^{\ddagger}$ 20.57 (5) kJ/mol, and $\Delta S^{\ddagger}$ -173.34 (8) J/mol K respectively. (Figures FS75-FS82 and Tables TS26-TS29 in ESI).These values were calculated from the temperature-dependent second-order rate constants determined from K_{obs} divided by temperature values as provided in Table TS30 in ESI. The Eyring plot (Figure 7) indicates similar ordered transition states in a coordination insertion mechanism.[37] $\Delta G^{\ddagger}$ values were calculated for the ROP of rac-LA catalyzed at 25°C. (Table TS30 in ESI).

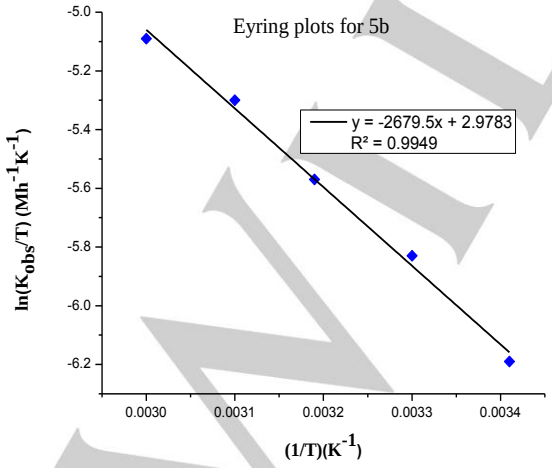

Figure 7. Eyring plots of ln(K_{obs}/T) versus (1/T) for ln[{$Ph_2P(Se)N\}_2C_6H_4Ca(THF)_3$] catalyst for the polymerization of rac-LA (0.01M) with [LA] = 2.0 M in $CDCl_3$ (1 mL). $\Delta H^{\ddagger}$ = 22(3) kJ mol^{-1} $\Delta S^{\ddagger}$ = –172(7) J $mol^{-1}K^{-1}$ ($CDCl_3$).

The tacticity of the PLA obtained from catalysts (**5a**,**b**-**7a**,**b**) was determined with the help of a homonuclear-decoupled ^{1}H NMR spectrum of the methine region (Figures FS97–FS102 in ESI).[38] It was observed that the PLA obtained from catalysts **5a**, **5b**, **6a**, and **6b** at 298 K were highly isotactic in nature, whereas the PLAs formed by catalysts **7a** and **7b** at 298 K were atactic in nature. The significant steric bulk of the phosphimino ligands (**1** and **2**), along with the achiral nature of the Ae metal complexes induce stereo selectivity in the PLA through a chain-end control mechanism. The degree of isotacticity (P_i) values were determined by the (normalized) integration of the homonuclear-decoupled NMR spectra and comparison with the values predicted by Bernoullian statistics (Figures FS97-FS102 in ESI). The PLA obtained from calcium complex **5a** showed excellent iso-selectivity (P_i = 0.87–0.78) at 298 K, which is the highest value obtained so far by an Ae initiator. In addition, when the strontium complex **6a** was substituted for the calcium complex **5a**, the degree of iso-selectivity dropped (P_i = 0.75–0.63) (Figures FS97-FS102 in ESI). It is surprising to note that the PLA obtained through barium catalysts (**7a** and **7b**) exhibited atacticity (Pi < 0.50) (Figure FS84 in ESI). It can be rationalized that atacticity is observed since the larger metal center (Ba) provides a more open coordination geometry on the metal ion, whereas iso-selectivity is induced due to the steric congestion around the metal center as we move towards the smaller Ae metals. This is expected, as a gradual decrease in stereo control on decreasing steric shielding is usual and well-reported in literature.[23] However, when we change the ligand from sulfur to selenium, the degree of iso-selectivity dropped (P_i = 0.87 complex **5a**, versus P_i = 0.82 for complex **5b**), presumably because of some scrambling of stereochemistry during chain transfer. A similar observation was made in case of strontium complexes where PLA exhibits isotacticity but the degree of iso-selectivity of complex **6b** (P_i = 0.71) was lower, compared to complex **6a** (P_i = 0.75). In contrast, the barium complex of bisphosphinoamide selenoid ligand produced an atactic PLA (P_i < 0.50).

All the catalysts, (**5a**,**b**-**7a**,**b**), showed excellent catalytic activities. Control over polymerization and degree of stereo control were found to be inversely proportional to each other during PLA formation. For instance, larger Ae metal ions resulted in a higher observed rate of polymerization (Ba>Sr>Ca), whereas for the same set of metal complexes the highest stereo selectivity was achieved with the smaller Ae ions (Ca>Sr>Ba). The smaller metal ion of calcium gave the PLA with the highest iso-selectivity, while barium led to the formation of PLA with atacticity. Similar observations were noted while switching from a sulfur-based to a selenium-based ligand. In the case of the complexes based on selenium ligand (**5b**, **6b**, and **7b**), an increased rate of polymerization was seen, when compared to the corresponding complexes of sulfur-based ligand (**5a**, **6a**, and **7a**). However, as far as stereo selectivity is concerned, a different mode with higher stereo selectivity was achieved just by switching from a selenium-based (**5b**, **6b**, and **7b**), to a sulfur-based ligand (**5a**, **6a**, and **7a**). Thus, from a single catalytic system it is possible to achieve two different modes of stereo control, either by changing the metal or nature of the ligand system.

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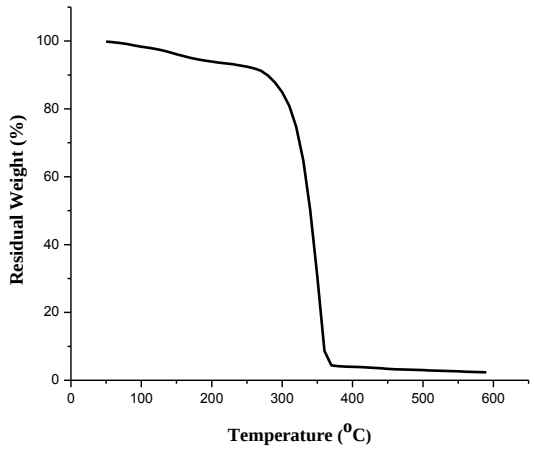


Figure 8. Thermogravimetric analysis (TGA) curves for the PLA catalyzed by complex **5a**.

Polymer melting point often serves as strong evidence to determine the degree of stereo selectivity in PLAs. In our study, the PLAs obtained from rac-LA catalyzed by barium complexes were amorphous in nature with a Tg value <55°C (Figure FS110 in ESI), indicating its atacticity. However, the PLAs obtained from the calcium and strontium complexes were found to be highly crystalline in nature, with the T_m values being >170°C, which is indicative of its high iso-selectivity, similar to the optically pure L-LA (based on the DSC curve in Figure **9**).[39] All the polymers obtained from catalysts (**5a,b-7a,b**), are stable up to more than 280°C (based on the TGA curve in Figure **8** and Figures FS106–108 in ESI), illustrating very high level of polymer purity.

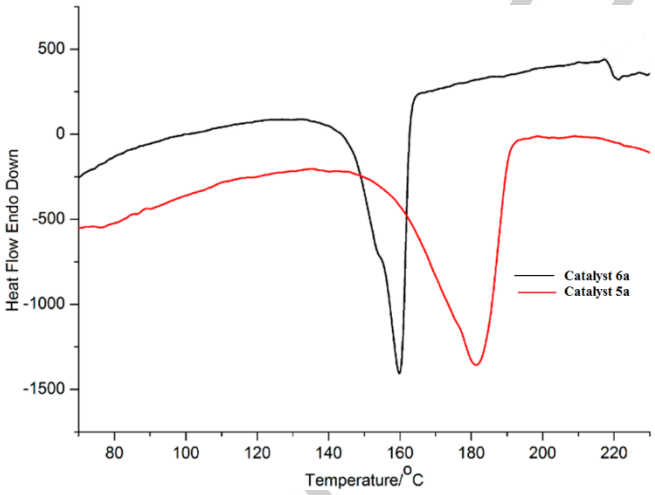
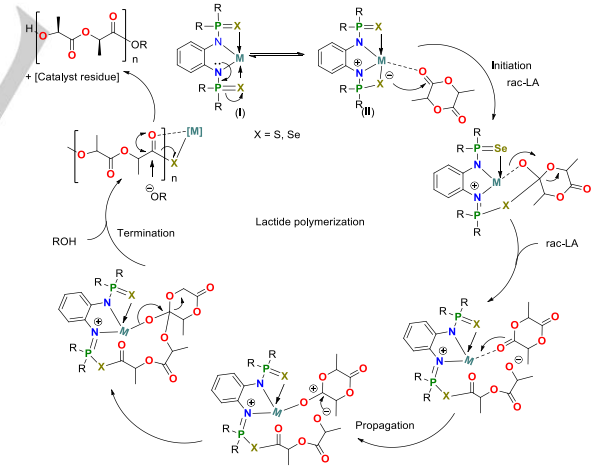


Figure 9. DSC curves for the PLA catalyzed by complexes **5b** and **6b**.

A typical kinetics study was conducted to establish that the ROP of rac-LA occurs without the presence of any external initiator and the phosphorus chalcogen bond of catalysts **5a**,**b**-**7a**,**b** acts as an initiator for the reaction. From the kinetics study it is observed that the rate of polymerization catalyzed by **5b** remain same even in presence of external initiator such as benzyl alcohol. (Figures FS83 - 85 in ESI). Several reactions were attempted with a range of concentrations of benzyl alcohol (0.02-0.2 M) with constant concentration of **5b** (0.02 M) and rac-LA (0.228 g, 2.0 mmol), however K_{obs} remained unchanged. Thus the lack of dependence of benzyl alcohol concentration confirms its zero-order contribution to the rate law (Figure FS87/88). So kinetics study proved that the polymerization reaction does not depend on external initiator and the Ae catalysts **5a**,**b-7a**,**b** themselves act as initiator for ROP of rac-LA. In addition to investigate the mechanism of initiation we have carried out reactions of 5:1 and 10:1 loadings of monomer: catalyst, and analyzed the reaction mixture by ^{1}H NMR, ^{31}P and ^{13}C spectra. The ^{1}H NMR spectra using 10:1 (as well as 5:1) loadings of monomer:catalyst showed that the catalyst is present in the (expected) ratio with the PLA (Figures FS91 - 96 in ESI). Moreover, we have also observed two sharp resonance peaks in the ^{31}P{^{1}H} NMR spectra, at δ 61.5 and 56.5 ppm for **7a** (FS 92 in ESI) at δ 60.2 and 52.6 ppm for **5b** (FS 95 in ESI). The resonance peaks at δ 61.5 (for **7a**) and 60.2 (for **5b**) indicated the chemically non-equivalence nature of two phosphorus atoms during the polymerization process. Based on these study, a mechanism of stereo-controlled polymerization of rac-LA is proposed in Scheme **5**. In the initiation step of the polymerization, in the presence of the lactide molecule, the phosphorus–chalcogen (S, Se) double bond of the complex [{$Ph_2P(Se)N$}$_2C_6H_4M(THF)_3$] could be converted into a single bond to form a zwitterionic species (Scheme **5**). The equilibrium between the first and second (**I** and **II**) forms of the catalysts could be dictated by the steric bulk around the metal centers and is directly related to the size of the metal ion. The larger the metal size, greater the possibility of the metal-lactide interaction period.[37] The steric crowding enhances the initiation of the selenoid to monomer by releasing the unstable energy of repulsion.



Scheme 5. Proposed mechanism of lactide polymerization initiated by complexes **5a**,**b–7a,b**.

End-group analysis of the polymer was performed by ^{1}H and ^{13}C NMR quenched by benzyl alcohol (Figures FS90 and FS111 in ESI). It was revealed that the presence of two peaks at δ 5.20 ppm (benzyl protons on the benzyl ester end-group) and δ 4.34 ppm (methine proton connected to the hydroxyl end-group) in the ^{1}H NMR of the proposed propagation species (Figures FS90 and FS111 in ESI). These results are indicative of the fact that the aggregating chains were end-capped by benzyl ester and hydroxyl groups (Figures FS90 and FS111 in ESI).

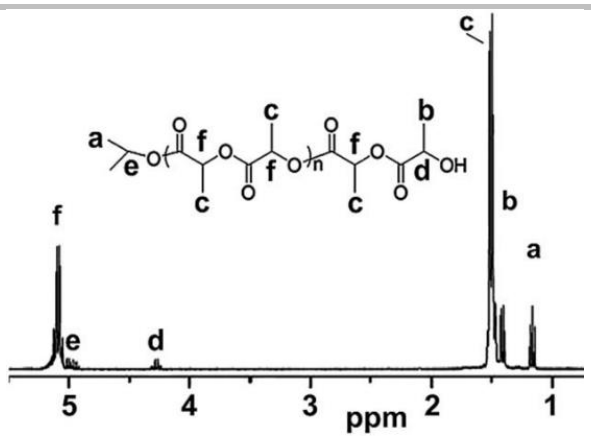
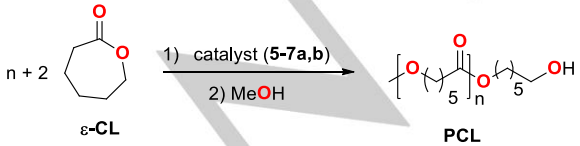


Figure 10.[1]H NMR spectrum of PLA synthesized by the complex **5a**.

End-group analysis was also extended to understand the polymerization reaction of the lactide, initiated by the present catalytic system. Therefore, a controlled experiment was performed where the polymerization of rac-LA in the presence of catalyst **7b** was quenched by isopropanol and the product obtained was characterized using ^{1}H NMR (Figure 10). The presence of the two peaks at δ 1.34 ppm (methyl protons on the isopropoxy end-group) and δ 4.34 ppm (methine proton connected to the hydroxyl end-group) is clear evidence that the aggregating chains were end-capped by an isopropyl ester and a hydroxyl group.

Polymerization of ε-CL. Compounds (**5a,b-7a,b**) were tested as initiators for the ROP of ε-CL. Tables TS38 and TS39 in ESI summarize the polymerization results of ε-CL using the initiators (**5a**,**b-7a**,**b**). Polymerization studies were typically conducted in toluene, with various monomer/catalyst ratios at 25°C. The reaction between catalysts (**5a**,**b-6a**,**b**) (1 mM) with 100 equivalents of ε-CL at 25ºC in toluene resulted in 99% conversion in five minutes, whereas when barium complexes **7a** and **7b** were used as initiators the reaction was very fast and 99% conversion was achieved in only one minute (Table TS38-TS39 in ESI).Polymerization up to 1000 equivalents of ε-CL with complexes **7a** and **7b** was completed within one minute in toluene (Tables TS38 and TS39 in ESI). Given the large ionic radius of the barium atom, it was expected that complexes **7a** and **7b** would show the highest reactivity towards the ROP of ε-CL, similar to what was observed in some previously reported studies using other barium complexes.[31,40] The overall control over the ROP process was good, affording PCLs, featuring a considerable match between the observed (as determined by GPC) and calculated molar mass values, while maintaining narrow polydispersity with a PDI up to 1.18 (Table TS38-TS39 in ESI).



Scheme 6. ROP of ε-caprolactone in toluene with barium complexes (**5a,b-7a,b**).

The Ae metal complexes (**5a,b-7a,b**) as pre- catalysts were extremely fast initiators, enabling almost complete conversion of 1000 equivalents of ε-CL in less than 30 seconds (Table 38 and 39 in ESI). Therefore, no further kinetics studies were undertaken for these polymerization reactions of ε-CL.

Conclusions

To conclude, we have demonstrated the synthesis and catalytic applications of a series of alkali and Ae metal complexes of bis-phosphinimino-chalcogen amide ligand. All the Ae metal complexes (**5a**,**b-7a,b**) are found to serve as superior initiators of the ROP of rac-LA. The relative order of the rate of polymerization increases with an increase in the ionic radius of the metal center (Ba>Sr>Ca) and size of the chalcogen atom in the ligand moieties. Calcium complexes **5a** and **5b** proved to be highly iso-selective initiators of the ROP of rac-LA. The sulfide complex **5a** shows a Pi value of 0.87, and the selenide complex exhibited a Pi value of 0.81 at 298 K, The strontium complexes exhibit moderate iso-selectivity, whereas the barium complex induces only actacticity in the PLA stereochemistry. Thus, the smaller metal center of calcium promotes a high degree of iso-selectivity, while the more open-coordination geometry of the relatively larger barium ions leads to atacticity. Thus, the choice of Ae metal center and the chalcogen atom in the ligand backbone provides an attractive route to obtain a high yield of PLA with excellent control over iso-selectivity.

Experimental Section

General considerations

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out under argon using the standard Schlenk technique or argon-filled glove box. Hydrocarbon solvents (*n*-pentane, toluene) were distilled under nitrogen from $LiAlH_4$ and stored in the glove box. CH_2Cl_2 was dried over P_2O_5 and distilled under reflux condition. THF was dried and deoxygenated by distillation over sodium benzophenone ketyl under argon and then distilled and dried over CaH_2 prior to being stored in the glove box. C_6D_6 was dried over Na/K, distilled, and stored in the glove box. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz), and ^{11}B{^{1}H} (128.3 MHz) spectra were measured on a BRUKER AVANCE III-400 spectrometer. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. All the polymer samples were analyzed using Shimadzu LC solution GPC at Osaka University. Ligand **2-H2** was prepared according to procedures prescribed in literature[29] and ligand **1-H2** was synthesized in a modified protocol described in literature.[29] [Li{$N(SiMe_3)_2$}], [Na{$N(SiMe_3)_2$}], [K{$N(SiMe_3)_2$}], MI_2 were purchased from Alfa aesar India. [M{$N(SiMe_3)_2$}$_2$(THF)$_2$] (M = Ca, Sr, Ba) were prepared according to the procedures given in literature, by using the respective metal diiodides and [$KN(SiMe_3)_2$].[41]

Synthesis of [{$Ph_2P(S)NH$}$_2C_6H_4$] (1-H2) [29]

In a 100 mL Schlenk flask, one equivalent (616 mg, 5.57 mmol) of 1,2-phenylenediamine, two equivalents of triethylamine (1.56 ml, 11.4 mmol), and two equivalents of chlorodiphenylphosphine (2 ml, 11.4 mmol) were mixed together with 30 mL of CH_2Cl_2 and THF mixture (2:1) and the reaction mixture was stirred for 12 hours. After that, two equivalents of elemental sulfur powder (365 mg, 11.4 mmol) were added and the mixture was stirred for another 20 hours at 90ºC. The solution was then evaporated under reduced pressure and THF (10 mL) was added to the solution. Unreacted excess sulfur was filtered through a G4 frit and the filtrate was

collected. After evaporation of the solvent from filtrate *in vacuo*, a light yellow solid residue was obtained. The colorless residue was further purified by washing with *n*-pentane or *n*-hexane.

Yield: 2.76 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99–7.94 (m, 8H, Ar*H*), 7.52-7.43 (m, 12H, Ar*H*), 6.80-6.52 (m, 4H, Ar*H*), 5.84 (bs, 2H, N*H*) ppm. ^{13}C-{^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.8 (P attached ArC), 132.4 (P attached *o*-ArC), 131.9 (P attached *o*-ArC), 131.7 (P attached *p*-ArC), 128.5 (P attached *m*-ArC), 127.3 (P attached *m*-ArC) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, $CDCl_3$): δ 56.8 ppm. ($C_{30}H_{26}N_2P_2S_2$) Calc. C 66.65, H 4.85, N 5.18; found C 66.33 H 4.61, N 4.88.

Synthesis of [{$Ph_2P(S)N$}$_2C_6H_4$]Na(THF)$_2$ (3a)

In a 10 mL sample vial, one equivalent (50 mg, 0.093 mmol) of **1-H2** and two equivalents of [NaN($SiMe_3$)$_2$] (34 mg, 0.185 mmol) were mixed together with 5 mL of THF. After six hours, a small amount of THF (2 mL) and *n*-pentane (2 mL) were added and kept at −35ºC. Colorless crystals of **3a** were obtained after one day.

Yield: 80 mg (91%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.25–8.20 (m, 8H, Ar*H*), 7.06–7.92 (m, 12H, Ar*H*), 6.38–6.36 (m, 4H, Ar*H*), 3.43–3.40 (m, THF), 1.30-1.23 (m, THF) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 131.8 (P attached ArC), 131.7 (P attached *o*-ArC), 128.4 (P attached *o*-ArC), 128.3 (P attached *p*-ArC), 128.2 (P attached *m*-ArC), 127.9 (P attached *m*-ArC), 67.8 (THF), 25.6 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 60.4 ppm. ($C_{50}H_{64}N_2Na_2O_5P_2S_2$) (945.07) Calc. C 63.54, H 6.83, N 2.96; found C 63.19 H 6.47, N 2.58.

Synthesis of [{$Ph_2P(Se)N$}$_2C_6H_4$]Na(THF)$_4$ (3b)

In a 10 mL sample vial, one equivalent (50 mg, 0.078 mmol) of **2-H2** and two equivalents of [NaN($SiMe_3$)$_2$] amide (27 mg, 0.157 mmol) were mixed together with 5 mL of THF. After six hours, a small amount of THF (2 mL) and *n*-pentane (2 mL) were added and kept at −35ºC. Colorless crystals of **3b** were obtained after one day.

Yield: 75 mg (92%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.39–8.32 (m, 8H, Ar*H*), 7.05–7.00 (m, 16H, Ar*H*), 3.53-3.52 (m, THF), 1.51–1.37 (m, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 131.8 (P attached ArC), 130.8 (P attached *o*-ArC), 128.4 (P attached *o*-ArC), 127.9 (P attached *p*-ArC), 127.6 (P attached *m*-ArC), 127.1 (P attached *m*-ArC), 67.7 (THF), 25.6 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 52.4 ppm. ($C_{50}H_{64}N_2Na_2O_5P_2Se_2$) (1038.87). Calc. C 57.80, H 6.21, N 2.70; found C 67.38 H 5.93, N 2.50.

Synthesis of [{$Ph_2P(Se)N$}$_2C_6H_4$]K(THF)$_5$ (4b)

In a 10 mL sample vial, one equivalent (50 mg, 0.078 mmol) of **1-H2** and two equivalents of [K($N(SiMe_3)_2$] (32 mg, 0.157 mmol) were mixed together with 5 mL of THF. After six hours, a small amount of THF (2 mL) and *n*-pentane (2 mL) were added and kept at −35 ºC. Colorless crystals of **4b** were obtained after one day.

Yield: 78 mg (93%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.37–8.20 (d, 8H, Ar*H*), 7.16–6.92 (m, 16H, Ar*H*), 3.51–3.50 (m, THF), 1.51–1.36 (m, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 131.8 (P attached ArC), 130.8 (P attached *o*-ArC), 128.5 (P attached *o*-ArC), 128.2 (P attached *p*-ArC), 127.9 (P attached *m*-ArC), 127.6 (P attached *m*-ArC), 67.8 (THF), 25.5 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 52.4 ppm. ($C_{50}H_{64}K_2N_2O_5P_2Se_2$) (1071.1). Calc. C 56.07, H 6.02, N 2.62; found C 55.81 H 5.78, N 2.44.

General preparation of [{$Ph_2P(S)N$}$_2C_6H_4$]M(THF)$_3$ [M = Ca (5a), Sr (6a), Ba (7a)]

Route 1. In a 10 mL sample vial, one equivalent (100 mg, 0.185 mmol) of **1-H2** and one equivalent of the corresponding metal precursor [M{$N(SiMe_3)_2$}$_2$(THF)$_2$] (M = Ca, Sr, Ba) were mixed together with 5 mL of THF. After six hours of stirring at room temperature, another 2 mL of THF and *n*-pentane (2 mL) were added and the resulting mixture was kept at −35 °C. Light yellow-colored crystals were obtained after one day.

Route 2. In a 25 mL pre-dried Schlenk flask, potassium salt of **1-H2** (100 mg, 0.177 mmol) (which was prepared like **4a**) was mixed with corresponding metal diiodides (0.177 mmol) in 10 mL of THF solvent at ambient temperature and the reaction mixture was stirred for 12 hours. The white precipitate of KI was filtered and the filtrate was evaporated under reduced pressure. The resulting white compound was further purified by washing with pentane and was recrystallized from THF–pentane (1:2 ratio) mixture at −35 °C.

M = Ca (**5a**). Yield: 140 mg (91%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.23–8.18 (m, 8H, Ar*H*), 7.10–6.94 (m, 12H, Ar*H*), 6.61-6.59 (d, 4H, Ar*H*) 3.72 (bs, THF), 1.36 (bs, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 132.3 (P attached ArC), 132.1 (P attached *o*-ArC), 132.0 (P attached *o*-ArC), 129.9 (P attached *p*-ArC), 128.2 (P attached *p*-ArC), 127.9 (P attached *m*-ArC), 127.7 (P attached *m*-ArC), 68.6 (THF), 25.4 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 69.4 ppm. ($C_{44}H_{52}CaN_2O_{3.50}P_2S_2$) (831, **5a. 1/2THF**). Calc. C 63.59, H 6.61, N 3.37; found C 62.98 H 6.37, N 3.22.

M = Sr (**6a**). Yield: 150 mg (92%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.14–8.12 (m, 8H, Ar*H*), 7.02 (bs, 12H, Ar*H*), 6.56–6.53 (m, 4H, Ar*H*), 3.64 (bs, THF), 1.37 (bs, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 132.3 (P attached ArC), 132.1 (P attached *o*-ArC), 128.3 (P attached *o*-ArC), 128.1 (P attached *p*-ArC), 128.0 (P attached *p*-ArC), 127.9 (P attached *m*-ArC), 127.8 (P attached *m*-ArC), 68.2 (THF), 25.7 (THF). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 69.6 ppm. ($C_{44}H_{52}N_2O_{3.50}P_2S_2Sr$) (878.5, **6a.1/2THF**). Calc. C 60.15, H 5.97, N 3.19; found C 59.73 H 5.49, N 2.97.

M = Ba (**7a**). Yield: 165 mg (96%).^{1}H NMR (400 MHz, C_6D_6): δ 8.24–8.04 (d, 8H, Ar*H*), 7.16–6.96 (m, 12H, Ar*H*), 6.56–6.54 (m, 4H, Ar*H*), 3.56 (bs, THF) 1.40 (bs, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 132.3 (P attached ArC), 132.1 (P attached *o*-ArC), 128.3 (P attached *o*-ArC), 128.1 (P attached *p*-ArC), 128.0 (P attached *p*-ArC), 127.9 (P attached *m*-ArC), 127.8 (P attached *m*-ArC), 68.2 (THF), 25.7 (THF). ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 66.6 ppm. ($C_{44}H_{52}BaN_2O_{3.50}P_2S_2$) (928.3, **7a.1/2THF**). Calc. C 56.93, H 5.65, N 3.02; found C 56.59 H 5.43, N 2.86.

General preparation of [{$Ph_2P(Se)N$}$_2C_6H_4$]M(THF)$_3$ [M = Ca (5b), Sr (6b), Ba (7b)]

Route 1. In a 10 ml sample vial, one equivalent (100 mg, 0.158 mmol) of **2-H2** and one equivalent of the corresponding metal precursor [M{$N(SiMe_3)_2$}$_2$(THF)$_2$] (M = Ca, Sr, Ba) were mixed together with 5 ml of THF. After six hours of stirring at room temperature another 2 ml of THF and *n*-pentane (2 ml) were added and the resulting mixture was kept at −35 °C. Colorless crystals were obtained after one day.

Route 2. In a 25 ml pre-dried Schlenk flask, potassium salt **4a** (100 mg, 0.156 mmol) was mixed with corresponding metal diiodides (0.156 mmol) in 10 ml of THF solvent at ambient temperature and the reaction mixture was stirred for 12 hours. The white precipitate of KI was filtered and the filtrate was evaporated under reduced pressure. The resulting white compound was further purified by washing with pentane and was recrystallized from the THF-pentane (1:2 ratio) mixture at −35 °C. Yield: 125 mg (90%).

M = Ca (**5b**). Yield: 140 mg (96%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.29-8.18 (m, 8H, Ar*H*), 7.20-7.07 (m, 14H, Ar*H*), 6.66-6.64 (m, 2H, Ar*H*), 3.80-3.70 (m, THF), 1.45 (bs, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 132.5 (P attached ArC), 132.4 (P attached *o*-ArC), 131.8 (P attached *o*-ArC), 128.7 (P attached *p*-ArC), 128.5 (P attached *p*-ArC), 128.2 (P attached *m*-ArC), 125.3 (P attached *m*-ArC), 67.9 (THF), 25.7 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 66.7 ppm. ($C_{44}H_{52}CaN_2O_{3.50}P_2Se_2$) (924.8, **5b.1/2THF**). Calc. C 57.14, H 5.67, N 3.03; found C 56.78 H 5.46, N 2.75.

M = Sr (**6b**). Yield: 145 mg (95%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.24-8.04

(m, 8H, Ar*H*), 7.05-6.96 (m, 14H, Ar*H*), 6.56-6.54 (m, 2H, Ar*H*), 3.55 (bs, THF), 1.40 (bs, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 132.5 (P attached ArC), 132.4 (P attached *o*-ArC), 131.9 (P attached *o*-ArC), 128.3 (P attached *p*-ArC), 128.1 (P attached *p*-ArC), 127.9 (P attached *m*-ArC), 127.8 (P attached *m*-ArC), 68.2 (THF), 25.7 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 66.6 ppm. ($C_{44}H_{52}N_2O_{3.50}P_2Se_2Sr$) (972.3, **6b.1/2THF**). Calc. C 54.35, H 5.39, N 2.88; found C 53.87 H 5.11, N 2.72.

M = Ba (**7b**). Yield: 150 mg (93%). ^{1}H NMR (400 MHz, C_6D_6): δ 8.22-8.17 (m, 8H, Ar*H*), 7.00-6.96 (m, 14H, Ar*H*), 6.45 (m, 2H, Ar*H*), 3.48-3.45 (m, THF), 1.31-1.28 (m, THF) ppm. ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): ^{13}C-{^{1}H} NMR (100 MHz, C_6D_6): δ 132.5 (P attached ArC), 132.4 (P attached *o*-ArC), 131.9 (P attached *o*-ArC), 128.3 (P attached *p*-ArC), 128.1 (P attached *p*-ArC), 127.9 (P attached *m*-ArC), 127.8 (P attached *m*-ArC), 67.9 (THF), 25.7 (THF) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ 66.6 ppm. ($C_{44}H_{52}BaN_2O_{3.50}P_2Se_2$) (1022.1, **7b.1/2THF**) Calc. C 51.70, H 5.13, N 2.74; found C 51.19 H 4.87, N 2.44.

X-ray crystallographic studies of complexes 1-H2, 3a,b, 4b, 5a and **5b, 6a** and **6b** and **7a** and **7b**

X-ray crystallographic analyses. Single crystals of complexes **1-H2**, **3a**, **3b**, **4b**, **5a**, **6a**, and **7a** were obtained from a mixture of THF and *n*-pentane solutions under argon atmosphere at a temperature of –35 °C. However, single crystals of complexes **5b**, **6b**, and **7b** were isolated from hot THF solution. In each case, a crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. All measurements were recorded on an Agilent Supernova X-calibur Eos CCD detector with either graphite-monochromatic Cu-Kα (1.54184 Å for complexes **1-H2**, **3a**, **3b**, **4b**, **5b**, **6b**, and **7b**) or Mo-Kα (0.71073 Å for **5a** and **6a**) radiation. Crystal data and structure refinement parameters are summarized in Table TS1 in ESI. The structures were solved by direct methods (SIR2004)[42] and refined on F^2 using the full-matrix least-squares method, using SHELXL-97.[43] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function *R*1 and *wR*2 were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$ respectively. The ORTEP-3 program was used to draw the molecule. Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1527228-1527236. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

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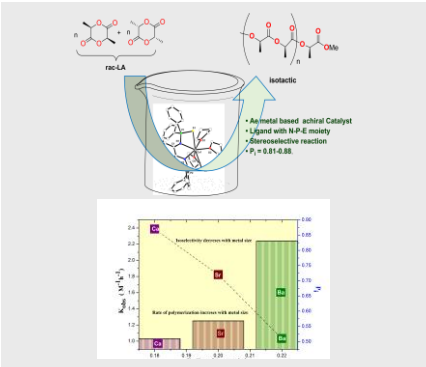
FULL PAPER

Ring-opening polymerization of rac-lactide initiated by novel achiral Ca complexes supported by [{$Ph_2P(E)$-$N\}_2C_6H_4$] moiety is exhibited to yield excellent iso-selectivity, with a P_i value of 0.87 at 298 K with a high degree of polymerization control. Sr and Ba complexes showed moderate to lower selectivity.



Jayeeta Bhattacharjee,[a] A. Harinath,[a] Hari Pada Nayek,[b] Alok Sarkar,[c] and Tarun K. Panda[a]*

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Highly Active and Iso-selective Catalysts for ROP of Cyclic Esters Using Group 2 Metal Initiators