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PAPER

Group 4 metal complexes of Trost's semi-crown ligand: Synthesis, structural characterization and studies on the ring-opening polymerization of lactides and ε-caprolactone

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The synthesis of titanium(IV), zirconium(IV) and hafnium(IV) complexes of Trost's semi-crown ligand is described. All complexes were fully characterized by ^{1}H and ^{13}C NMR and mass spectroscopy. The molecular structures of the representative complexes **2**, **3** and **4** were determined by single-crystal X-ray diffraction studies. X-ray diffraction studies reveal that complexes **2**, **3** and **4** crystallized in orthorhombic crystal system. Complexes **2** and **3** have monomeric structure in the solid state with distorted octahedral geometry around the metal center, whereas complex **4** was found to crystallize in a trimeric structure bridging through oxygen atom, where the geometry around the titanium is distorted trigonal bipyramidal. The activities and stereoselectivities of these complexes toward the ring-opening polymerization (ROP) of lactides (*L*-LA and *rac*-LA) and ε-caprolactone (CL) have been investigated. Complexes **1**–**4** were found to be efficient single-component initiators for the ring-opening polymerization of cyclic esters and yielded high molecular weight polymers (M_n) with narrow molecular weight distributions (MWD).The microstructure of the resultant polylactides (PLA) from *rac*-LA was determined. Complexes **2** and **3** have afforded isotactic-enriched PLA (P_m = 0.78–0.71) with narrow MWD (1.07–1.04), on the other hand complexes **1** and **4** produced atactic PLA. Kinetic and post polymerization studies confirm that the polymerization proceeds through the coordination-insertion mechanism.

Introduction

In the recent years, biodegradable polymers have emerged as an excellent alternative to conventional petroleum based materials.[1] Aliphatic polyesters particularly PLA and polycaprolactone (PCL) are the most promising candidates in this class of materials.[2] In the past few decades, PLA has gained increasing interest due to its biodegradability, biocompatibility and the possibility to derive the monomer from natural renewable sources.[3] Well defined PLA with controlled physical and mechanical properties has many potential medical, agricultural, tissue engineering and packaging applications because of their biodegradable and biocompatible nature.[3] Spectacular results are provided by organometallic compound catalyzed ring-opening polymerization of lactide.[4]

A number of initiators with excellent enantioselective control over the chain initiation and propagation steps have been developed in the recent past,[5] and the polymer tacticity provides valuable information about the stereochemical arrangements.[6] Stereoselectivity of an initiator is influenced by factors associated with the type of metal species, chirality of the ligand, and the polymerization medium as well as temperature.[7] The synthesis of the isotactic PLA is trivial from the enantiopure monomer. In fact synthesis of isotactic PLA from *rac*–LA is an area of great interest.[8] Though numerous efforts have been made towards the synthesis of isotactic PLA from *rac*–LA, it is still a challenge for the scientific community.[7a,9] Aluminum,[10] gallium[11], indium[12], magnesium,[11a,13] yttrium,[14] zinc[15] and lanthanide[16] complexes have been used for the isoselective ring-opening polymerization of *rac*–LA. Indubitably, the most important breakthrough was made in 1996, when Spassky *et al.*[17] used enantiopure {(*R*)-SalBinap}Al(OR) (*R*)-**1** for the ring-opening polymerization of *rac*–LA and highly isotactic and crystalline PLA was obtained. Later, Feijen *et al.*[18] and Carpentier *et al.*[19] used aluminum isopropoxide complexes for isoselective ring-opening polymerization of *rac*–LA. Chen *et al.* reported (SB-**2d**)AlO^{i}Pr catalyst which exhibited the highest stereoselectivity and afforded substantially isotactic PLA with a P_m of 0.90.[20] Recently, Stopper *et al.* reported tetradentate diainioniciminethiobis(phenolate)-[{ONSO}Zr(O^{t}Bu)$_2$] complexes.[21] Carpentier *et al.*[22] and Lin *et al*.[23] have used salen complexes for the selective ring-opening polymerization of *rac*–LA. Nevertheless, bulk polymerizations are important for the industrial scale preparation of highly pure PLA and to the best of our knowledge, only a few initiators were able to provide stereoselective ring-opening polymerization of *rac*-LA at high temperature.[18,24] Synthesis of biodegradable polymers using group 4 metal initiators is a popular area of recent hallmark research.[25,26] In our earlier reports, group 4 metal

complexes containing bis(imino-phenoxide), aminophenoxide, salicylaldiminato, salen, salan type and benzotriazol phenoxide ligand backbone independently were found to produce high molecular weight polymer with *rac*–LA under solvent-free conditions.[26u, 27] A recent review describes the importance of group 4 metals in this area of research.[28]

Recent advances in catalyst design inspired us to develop a new catalytic system for the ring-opening polymerization of lactide. We were inclined to investigate the effect of catalyst architecture on the ring-opening polymerization of LA and microstructure of the resultant polymers. Having this in mind we decided to use the well known Trost's semi-crown ligand[29] in combination with group 4 metals. The semi-crown ligand (bearing more hydroxyl groups) has more binding sites towards metals, which can meet both the requirements of higher affinity to metals and produce higher catalytic activity. Trost developed a chiral semi-crown ligand/dinuclear zinc catalyst system, which has been successfully applied in catalytic enantioselective direct aldol reactions,[29,30] nitroaldol (Henry) reactions,[31] Mannich-type reactions[32] and diol desymmetrizations.[33] Wang and Li used chiral gallium complexes of Trost-type semi-crown ligands in aqueous asymmetric Mukaiyama aldol reaction.[34] The applications of Trost's semi-crown ligand towards ring-opening polymerization reactions is not investigated. Herein, we report the synthesis and characterization of Trost's semi-crown ligand supported Ti, Zr and Hf chiral complexes. These complexes are found to be extremely active towards the ring-opening polymerization of lactide and *ε*–caprolactone.

Results and discussion

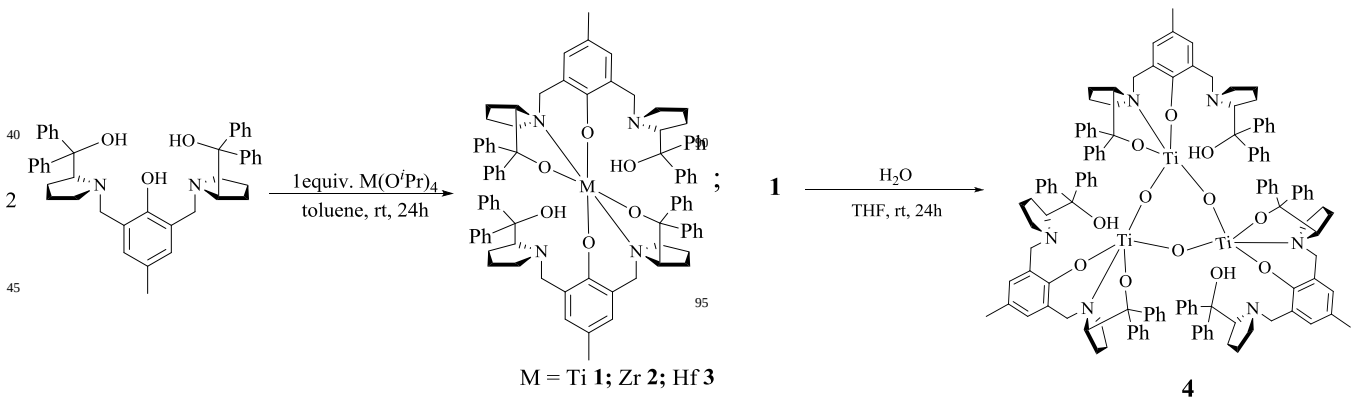
Synthesis and characterization of complexes 1–4

The ligand ((*S*,*S*)-(+)-2,6-Bis[2-(hydroxydiphenylmethyl)-1-pyrrolidinyl-methyl]-4-methylphenol)[29] was reacted with group 4 metal alkoxides in a 2:1 stiochiometric ratio in toluene resulting in the formation of monomeric **1**–**3** respectively.

Furthermore, a stoichiometric reaction of complex **1** with degassed water in dry tetrahydrofuran resulted in the formation of trimeric complex **4** (Scheme 1). The resulting products were purified by crystallization from toluene and isolated in high yield and purity. The aforementioned complexes **1**–**4** have been characterized by ^{1}H, ^{13}C NMR and mass spectroscopy. These complexes were characterized by single crystal X-ray diffraction studies.

Single crystals were grown in a glove box at room temperature from dilute toluene solutions of the respective compounds over a period of ten days. Representative crystal structures for **2**, **3** and **4** are shown in Figs. 1–3 respectively and crystal data is illustrated in Table 1. Complexes **2** and **3** crystallized with orthorhombic $C222_1$ symmetry and contain one disordered toluene molecule per structural unit. Complex **4**, on the other hand, crystallized with $P2_12_12_1$ symmetry and three toluene molecules per structural unit are present. From the molecular structures, it is clear that complexes **2** and **3** are monomeric in the solid state and the corresponding metal atom is present in a distorted octahedral geometry (Figs. 1 and 2) whereas complex **4** was found to crystallize in a trimeric structure, where the geometry around the titanium is distorted trigonal bipyramidal (Fig. 3).

In complex **4** three titanium atoms are trigonally connected with oxygen as a bridging atom and each titanium atom attached to a ligand molecule. The oxo-bridge between the metal centres is from the water molecule and one ligand moiety gets eliminated during the cyclization. In all the structures, we observed that one *N* center and one *O* center from the ligand is coordinated to metal atom along with the phenolic *O* center. Simultaneous coordination of all *N* and *O* centers from a ligand molecule is restricted due to steric crowding around the metal centre. All the bond angles and bond lengths match well with the literature reports.[35] The crystal packing in all the cases is influenced by the inclusion of the toluene molecule which is sandwiched between two structural units and stabilised by weak CH/π interactions



Scheme 1 Synthesis of complexes **1**–**4** containing group 4 metals with Trost's semi-crown ligand

(short contacts ranging 2.78-2.90 Å).[36] In case of **2** and **3**, one toluene molecule is trapped between two monomeric units having 'anti'-conformation. On the contrary, in case of **4**, one of the three toluene molecules actually took part in the columnar packing and the two structural units face the same direction (Fig. 4). The other two toluene molecules are present in the crystal voids with no interactions with the structural units. The molecular Hirshfeld d_{norm} surface gives a better insight into the interactions involved in the crystal packing. The Hirshfeld surface of **2** was generated using Crystal Explorer (version 3.1).[37] The normalised contact distances, d_{norm}, were mapped over a surface property range -0.077-3.526. The negative d_{norm} values are represented by red dots on the mapped surface and indicate to the short contacts having distances less than the sum of the Van der Waals radii. The Hirshfeld surface of **2** clearly shows the presence of weak CH/π interactions in the crystal packing (Fig. 4). The ^{1}H and ^{13}C NMR spectra for all complexes are consistent with the solid state structures.

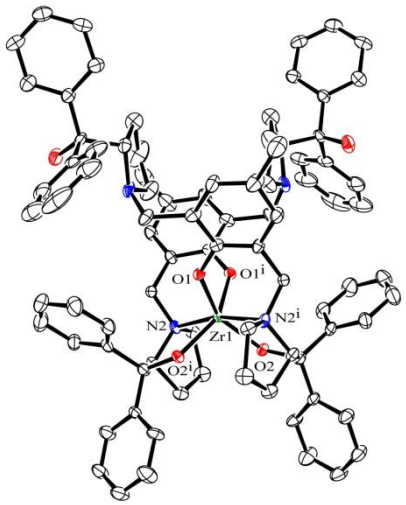


Fig. 1 Molecular structure of **2**; thermal ellipsoids were drawn at 30 % probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zr(1)–O(1) 2.096(4), Zr(1)–O(2) 2.076(4), Zr(1)–O(3) 1.940(4), Zr(1)–O(4), 1.944(4), Zr(1)–N(1) 2.369(5), Zr(1)–N(2) 2.392(5) O(4)–Zr(1)–O(3) 103.61(17), O(4)–Zr(1)–O(2) 90.43(16), O(2)–Zr(1)–O(3) 158.32(16), N(1)–Zr(1)–O(3) 94.78(16), N(1)–Zr(1)–O(4) 85.12(17).

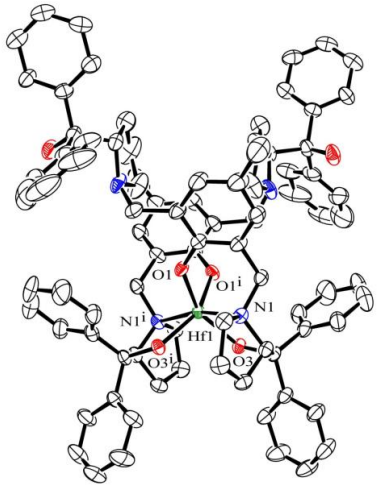


Fig. 2 Molecular structure of **3**; thermal ellipsoids were drawn at 30 % probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°):Hf(1)–O(3)i 1.984(3), Hf(1)–O(3) 1.984(3), Hf(1)–O(1)i 2.022(3), Hf(1)–O(1) 2.022(3), Hf(1)–N(1) 2.353(4), Hf(1)–N(1)i 2.353(4), Hf(1)–N(20) 2.455(3), O O(3)i –Hf(1)–O(3) 102.9(2), O(3)i –Hf(1)–O(1)i 146.80(13), O(3) –Hf(1)–O(1)i 93.86(15), O(3)i –Hf(1)–N(1) 99.20(15), O(3) –Hf(1)–N(1) 73.15(14).

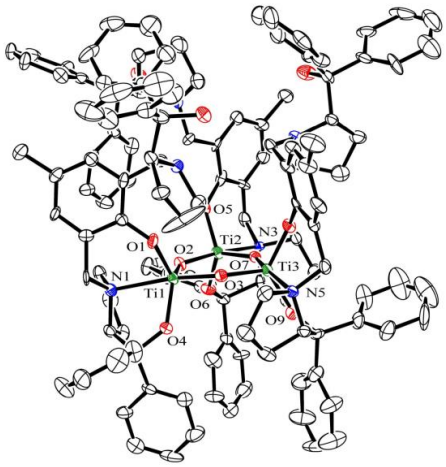


Fig. 3 Molecular structure of **4**; thermal ellipsoids were drawn at 30 % probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°):Ti(3)–O(7) 1.854(9), Ti(3)–O(8) 1.825(11), Ti(2)–O(5) 1.825(12), Ti(2)–O(6), 1.809(10), Ti(1)–N(1) 2.359(11), Ti(2)–N(3) 2.371(12), O(2)-Ti(1)-O(1) 112.3(4), O(2)-Ti(1)-N(1) 88.5(4), O(7)-Ti(2)-O(6) 118.0(4), O(7)-Ti(2)-N(3) 87.6(4), O(8)-Ti(3)-N(5) 83.1(4), O(8)-Ti(3)-O(9), 123.5(5).

Polymerization studies

Complexes **1**–**4** were screened towards the ring-opening polymerization of *rac*–LA, *L*–LA and CL. The polymerizations were performed in solvent free conditions. Results revealed that high molecular weights (M_n) PLAs and PCLs in the range of 24.0–33.0 kg/mol with narrow molecular weight distributions (MWDs) were obtained from the polymerization reactions within

2–9 mins (Table 2). Narrow MWDs are characteristic of well controlled propagation. The high level of control afforded by these initiators was further illustrated by linear correlations between M_n and $[M]_o/[I]_o$ ratio. In addition, microstructure analysis (by homonuclear decoupled ^{1}H NMR spectroscopy) results confirmed that a range of microstructures are accessible using these initiators. The zirconium and hafnium complexes (**2** and **3)** have shown stereocontrol in the ring-opening polymerization of *rac*–LA, producing PLA with isotactic-enriched stereoblock microstructures (P_m up to 0.78) (Table 2, Entries 2 and 3). In case of titanium complexes (**1** and **4**), tacticity changes dramatically to atactic (Table 2, Entries 1 and 4). This lack of stereocontrol by the Ti complexes can be explained by Rzepa *et al.*'s analysis of the origin of stereocontrol from the coordination of the growing polymer chain to the metal center and Okuda *et al.*'s similar observation on the group 4 metals based on Salan complexes. As zirconium and hafnium show higher coordination numbers compared to titanium[38], the growing polymer chain tends to coordinate to the metal center through carbonyl group and thereby allowing either *D*- or *L*-LA to approach towards the metal center for further coordination. The titanium complexes, having less coordination numbers, do not favour this coordination from growing polymer chain and

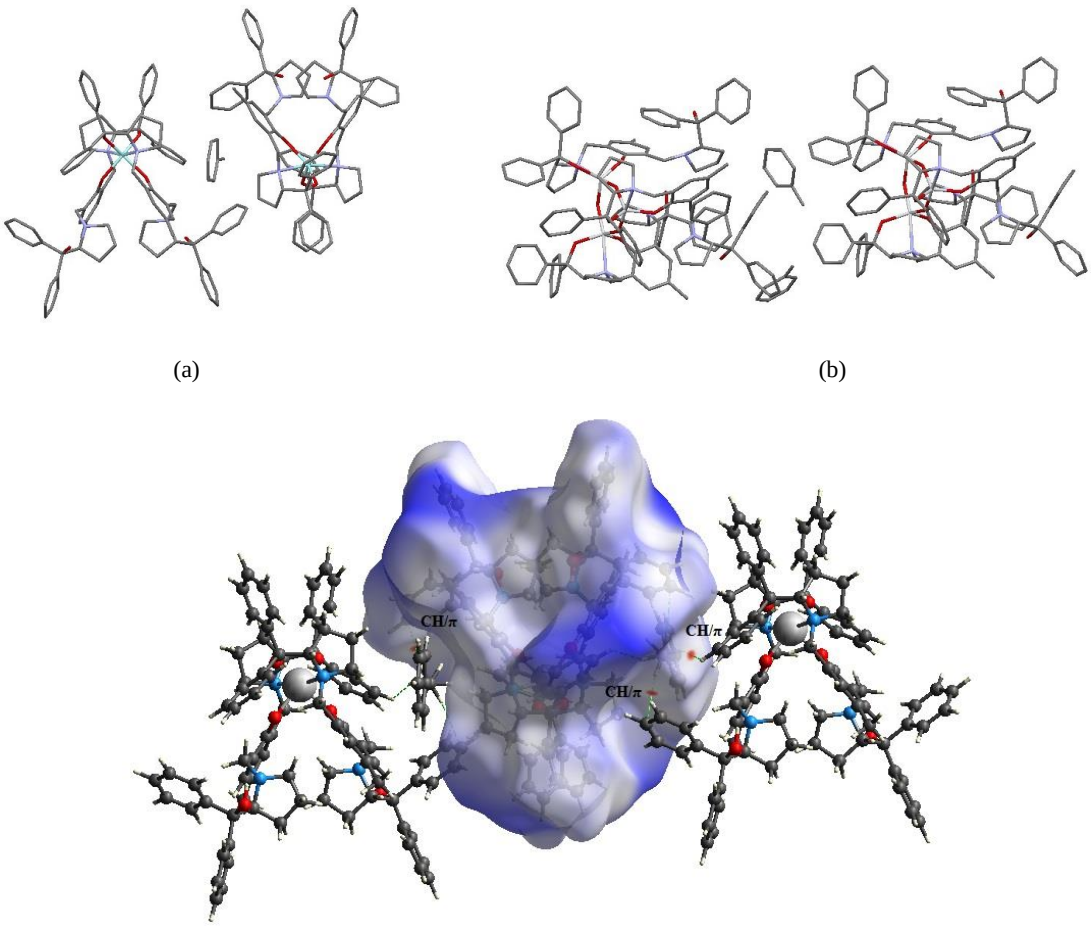


Fig. 4 (a) View of the crystal packing of **2** along *b* axis displaying the toluene molecule sandwiched between two structural units facing opposite direction. (b) View of the crystal packing of **4** along *c* axis displaying the toluene molecule sandwiched between two structural units facing same direction. (c) The Hirshfeld d_{norm} surface of **2** displaying CH/π interactions with adjacent molecules through the negative region (red dots).

eventually the stereocontrol is lost.[28,39] So, the results disclosed that the ligand architecture and the nature of metal centers could be accounted for the stereocontrol in ring-opening polymerization of *rac*-LA. Furthermore, the homonuclear decoupled ^{1}H NMR spectrum of each sample revealed microstructure of the polymer and shows well-resolved peaks in the methine region. The peaks were assigned to the appropriate tetrads in accordance with the shifts reported by Thakur *et al*.[6c] The spectra show two well-resolved peaks, at *ca.* 5.19 and 5.17 ppm representing tetrads stereosequences of *sis* and *sii* respectively. According to pair wise Bernoullian statistics, an unequal probability for *sis* and *sii* stereosequences implies that the polymerization process was not random.[6c]

Table 1 Crystal data for the structures of **2**, **3** and **4**

Complex	**2**	**3**	**4**
Empirical formula	$C_{92}H_{72}N_4O_6Zr$	$C_{106}H_{100}N_4O_6Hf$	$C_{150}H_{156}N_6O_{12}Ti_3$
Formula weight	1420.76	1704.38	2378.50
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$C222_1$	$C222_1$	$P2_12_12_1$
Temp/K	173(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
a (Å)	16.9781(12)	17.1654(6)	19.172(3)
b (Å)	20.6006(10)	20.7645(6)	22.272(3)
c (Å)	24.9765(17)	25.2494(9)	30.035(4)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å^3)	8735.8(10)	8999.7(5)	12825(3)
Z	4	4	4
D_{calc} (g/cm^3)	1.080	1.258	1.232
Reflns collected	13755	27976	33748
No. of indep reflns	6568	17045	17605
GOF	1.112	0.723	1.027
Final *R* indices ($I>2\sigma(I)$)	R_1 = 0.0770,	R_1 = 0.0269,	R_1 = 0.0535,
	wR_2 = 0.2185	wR_2 = 0.0784	wR_2 = 0.1313
R indices (all data)	R_1 = 0.0952,	R_1 = 0.0326,	R_1 = 0.0803,
	wR_2 = 0.2374	wR_2 = 0.0873	wR_2 = 0.1601
CCDC	958283	936922	1414116

$R_1 = \sum|F_0| - |F_c|/\sum|F_0|$, $wR_2 = [\sum (F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

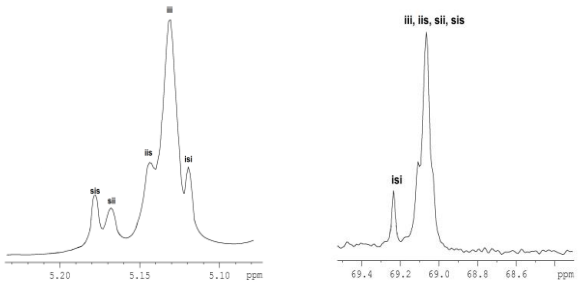
Table 2 Polymerization data for *rac*–LA, *L*–LA and CL with **1**−**4** in the ratio $[M]_o/[I]_o$ = 200 at 140 °C for LA and 80 °C for CL

Entry	Initiator	Monomer	Time[a] (min)	Yield (%)	M_n[b] (kg/mol)	$M_{n[the]}$[c] (kg/mol)	MWD	P_m[d]
1	1	*rac*-LA	4	98	28.16	29.46	1.12	atactic
2	2	*rac*-LA	6	97	28.90	29.46	1.06	0.78
3	3	*rac*-LA	7	98	29.17	29.46	1.07	0.71
4	4	*rac*-LA	3	99	28.74	29.46	1.10	atactic
5	1	*L*-LA	5	98	28.92	29.46	1.10	
6	2	*L*-LA	7	98	29.23	29.46	1.06	
7	3	*L*-LA	8	97	30.15	29.46	1.05	
8	4	*L*-LA	4	97	30.98	29.46	1.08	
9	1	CL	2	98	24.66	23.46	1.08	
10	2	CL	2	98	24.70	23.46	1.05	
11	3	CL	2	97	26.18	23.46	1.07	
12	4	CL	2	98	23.95	23.46	1.09	

[a]Time of polymerization measured by quenching the polymerization reaction at 100 % conversion. [b]Measured by gel permeation chromatography at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections. [c]M_n (theoretical) at 100% conversion = $[M]_o/[I]_o$ × mol wt (monomer) + $M_{end\ groups}$. [d]P_m is the probability of isotactic enchainment determined by ^{1}H NMR spectroscopy.[13b]

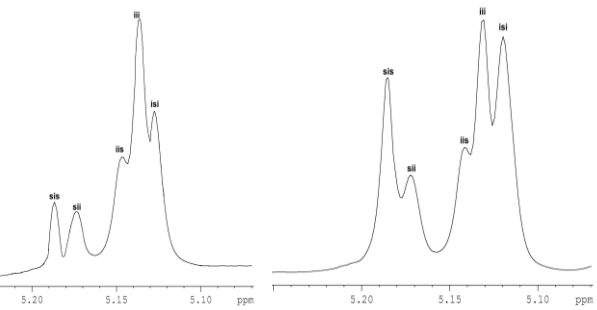
Further, methine carbon peaks are also an evidence for an isotactic-enriched PLA (Fig. 5b).[6c] Complex **4** produced atactic PLA (Fig. 6b). Moreover, the homonuclear decoupled ^{1}H NMR spectrum of PLA obtained from the polymerization of *L*–LA initiated by **2** showed the retention of stereochemistry (P_m = 0.96) (ESI, Fig. 14).

To confirm that the polymerizations proceed in a controlled fashion, polymerizations were performed in 100, 200, 400 and 800 monomer to initiator concentration ratio for *rac*–LA, *L*–LA and CL using **2** as an initiator which has produced polymers with high M_n with narrow MWDs (Table 3). The polymerization results showed that the M_n of the resultant PLA and PCL linearly increased with the increasing initial ratio of $[M]_o/[I]_o$ (Fig. 7). The small change in MWDs supports the controlled nature of these polymerizations.



a **b**

Fig. 5 a) Methine region of homonuclear decoupled ^{1}H NMR spectrum of PLA obtained from *rac*-LA polymerization initiated by **2**. b) Methine carbon resonances in the ^{13}C NMR spectrum for PLA initiated by **2**.



a **b**

Fig. 6 a) Homonuclear decoupled ^{1}H NMR spectrum of PLA obtained from *rac*-LA polymerization initiated by **3**. b) Homonuclear decoupled ^{1}H NMR spectrum of PLA obtained from *rac*-LA polymerization initiated by **4** ($CDCl_3$, 500 MHz).

To gain insight into the stereoselectivity of the polymerization solvent polymerization reactions were carried out maintaining monomer to initiator ratio 200:1 at 110 °C using toluene as a solvent. It was found that the stereoselectivity of the polymers were slightly improved and polymerizations proceed in a controlled manner, whereas the polymerization rates were 3 to 4 times slower as compared to that of the solvent-free polymerizations (Table 4).

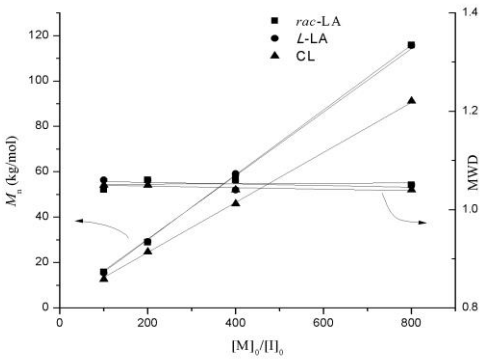


Fig. 7 Plot of M_n and MWDs *vs.* $[M]_o/[I]_o$ ratio for *rac*-LA, *L*-LA and CL polymerization at 140 °C and 80 °C using **2**.

To determine the rate of the reaction, kinetic analyses for ring-opening polymerization of *rac*–LA and *L*–LA initiated by **2** were performed at 140 °C. A plot of conversion of *rac*–LA and *L*–LA *vs*. time resulted in a sigmoidal curve (ESI, Fig. 13), which reveals that the polymer formation rate was high initially and after a point conversion was almost constant. From the kinetic data, it is clear that there is a first-order dependence of the rate of polymerization on *rac*–LA and *L*–LA concentration without any induction period. The plot of $[M]_o/[M]_t$ *vs*. time is linear (Fig. 8). The values of the apparent rate constant (k_{app}) for *rac*–LA and *L*–LA polymerizations initiated by **2** were evaluated from the slope of these lines and were found to be 7.21×10^{-3} sec^{-1} and 5.83×10^{-3} sec^{-1} respectively and the apparent rate constant (k_{app}) for *rac*–LA and *L*–LA solvent polymerizations initiated by **2** were found to be 0.102 sec^{-1} and 0.114 sec^{-1} respectively (Fig. 9). In addition, a plot of M_n *vs* % conversion of monomer depicts M_n of the polymer increases with the increase in monomer conversion, which supports the controlled chain propagation (Fig. 10).

Table 3 Polymerization studies on the variations of $[M]_o/[I]_o$ ratio using **2** at 140 °C for LA and 80 °C for CL

Entry	Monomer	$[M]_o/[I]_o$	Time[a] (min)	M_n[b] (kg/mol)	$M_{n[the]}$[c] (kg/mol)	MWD
1	*rac*-LA	100:1	3	15.76	15.05	1.04
2	*rac*-LA	200:1	6	28.90	29.46	1.06
3	*rac*-LA	400:1	8	57.14	58.28	1.06
4	*rac*-LA	800:1	17	115.77	115.94	1.05
5	*L*-LA	100:1	3	15.41	15.05	1.06

6	*L*-LA	200:1	7	29.23	29.46	1.06
7	*L*-LA	400:1	9	59.11	58.28	1.04
8	*L*-LA	800:1	20	115.70	115.94	1.05
9	CL	100:1	2	12.63	12.05	1.05
10	CL	200:1	2	24.70	23.46	1.05
11	CL	400:1	5	45.89	46.29	1.04
12	CL	800:1	8	91.12	91.94	1.04

[a] Time of polymerization measured by quenching the polymerization reaction at 100 % conversion. [b] Measured by gel permeation chromatography at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections. [c] M_n (theoretical) at 100% conversion = $[M]_o/[I]_o$ × mol wt (monomer) + $M_{end\ groups}$.

Table 4 Polymerization data for *rac*–LA, *L*–LA and CL with **1**−**4** in the ratio $[M]_o/[I]_o$ = 200 at 110 °C in toluene

Entry	Initiator	Monomer	Time [a] (min)	Yield (%)	M_n [b](kg/mol)	$M_{n[the]}$ [c] (kg/mol)	MWD	P_m [d]
1	1	*rac*-LA	13	91	28.23	29.46	1.08	atactic
2	2	*rac*-LA	17	92	29.13	29.46	1.03	0.80
3	3	*rac*-LA	25	91	28.10	29.46	1.07	0.74
4	4	*rac*-LA	14	91	28.47	29.46	1.09	atactic
5	1	*L*-LA	19	88	27.59	29.46	1.08	
6	2	*L*-LA	22	90	29.51	29.46	1.05	
7	3	*L*-LA	33	91	30.01	29.46	1.04	
8	4	*L*-LA	14	93	31.20	29.46	1.07	
9	1	CL	7	90	25.25	23.46	1.08	
10	2	CL	8	92	25.04	23.46	1.03	
11	3	CL	10	90	27.18	23.46	1.07	
12	4	CL	7	92	25.05	23.46	1.08	

[a]Time of polymerization measured by quenching the polymerization reaction at 100 % conversion. [b] Measured by gel permeation chromatography at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections. [c] M_n (theoretical) at 100% conversion = $[M]_o/[I]_o$ × mol wt (monomer) + $M_{end\ groups}$. [d]P_m is the probability of isotactic enchainment determined by ^{1}H NMR spectroscopy.[13b]

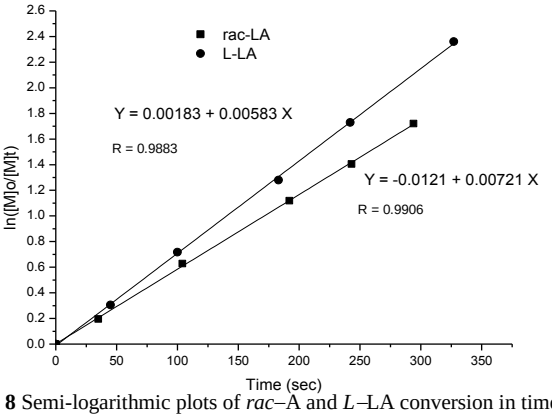


Fig. 8 Semi-logarithmic plots of *rac*–A and *L*–LA conversion in time initiated by **2**: $[M]_o/[I]_o$ = 200 at 140 ℃.

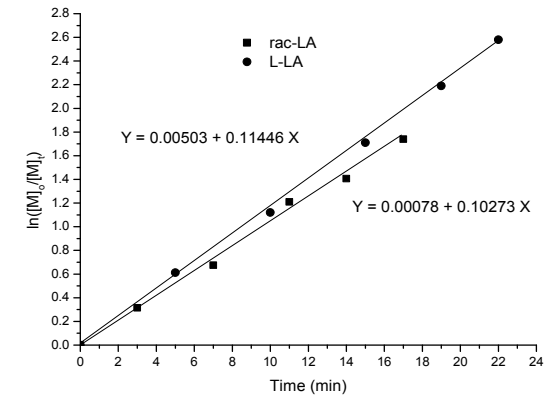


Fig. 9 Semi-logarithmic plots of *rac*–A and *L*–LA conversion in time initiated by **2**: $[M]_o/[I]_o$ = 200 at 110 ℃ in toluene.

Polymerization mechanism

To elucidate the ring-opening polymerization mechanism, a *rac*–LA low molecular weight oligomer was synthesized by stirring *rac*–LA with **2** in 10:1 molar ratio under solvent free conditions at 140 °C. The resulting low molecular weight oligomer was characterized using MALDI-TOF and ^{1}H NMR

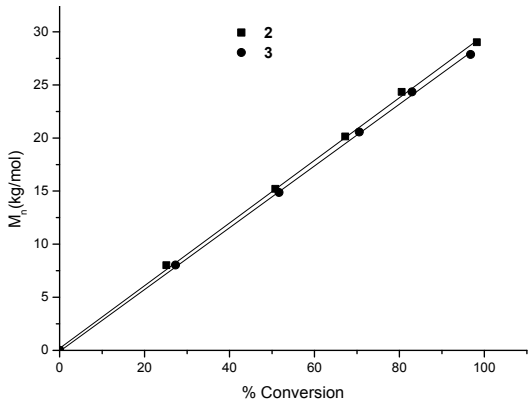


Fig. 10 Plot of M_n vs % conversion of *rac*-LA using **2** and **3.**

spectroscopy. The ^{1}H NMR spectrum of the oligomer showed the presence of ligand moiety as one of the end group (Fig. 11). In addition, MALDI-TOF spectrum also supports the same conclusion, and all the high intensity peaks are assigned as acetonitrile adduct resulting from the oligomers (Fig. 12). Moreover, the low intensity peaks present in the spectrum are identified as peaks corresponding to the cyclic PLA. From the

intensity of the cyclic PLA peaks, it is evident that the fraction of cyclic PLA is minor and the methyl and methine peaks of cyclic PLA merge with the respective peaks of linear PLA in ^{1}H NMR spectrum of the oligomer. The MALDI-TOF and ^{1}H NMR spectra analysis implies that the polymerization proceeds via the coordination insertion mechanism where the monomer coordinates to the metal centre followed by the acyl oxygen bond cleavage of the monomer, as a result of which polymerization will be initiated and chain propagation proceeds (Scheme 2).

Density functional theory (DFT) calculations

In order to gain some insight into the structure and reactivity of complexes **2**, **3** and **4** towards ring-opening polymerization, theoretical calculations were carried out at the DFT level using the hybrid functional B3LYP with Gaussian 09[40] suite of programs with LANL2DZ basis set. The calculations are well in agreements with the experimental results. MPA (Mulliken population Analysis) method was applied to all the complexes using LANL2DZ as basis set. For all compounds **1**–**4** HOMO and LUMO energy gaps are calculated at the B3LYP/LANL2DZ level (Fig. 13). The energy gap between HOMO and LUMO is related to the reactivity/stability of a species according to Pearson's concept of chemical hardness (η).[41] Pearson utilized Koopman's depiction of frontier orbital energies ($-\varepsilon_{HOMO}$ and $-\varepsilon_{LUMO}$) as ionisation potential (*I*) and electron affinity (*A*) respectively to define chemical hardness as $\eta = \frac{1}{2}(I-A)$. The increasing order of η or the energy gap between HOMO and LUMO indicates a decreasing trend in reactivity, with harder species having lesser polarizability and more stability. Hence, the catalytic activity decreases with the increase in the energy gap between HOMO and LUMO. We employed this concept in explaining the catalytic activities of **1**, **2**, **3** and **4**. The low energy difference between HOMO and LUMO of **4** results in higher activity towards the ring-opening polymerization.

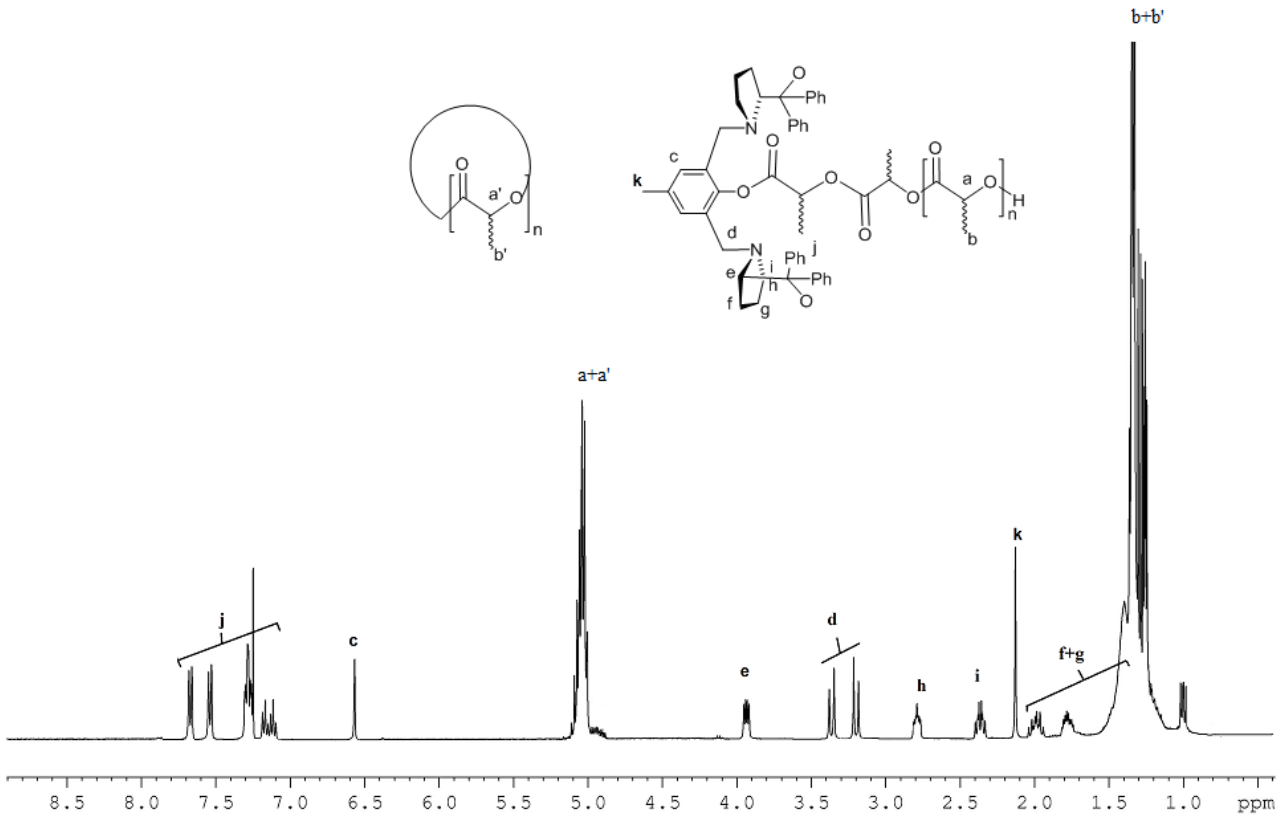


Fig. 11 ^{1}H NMR spectrum of the product obtained from a reaction between *rac*-LA and **2** in 10:1 ratio at 140 °C.

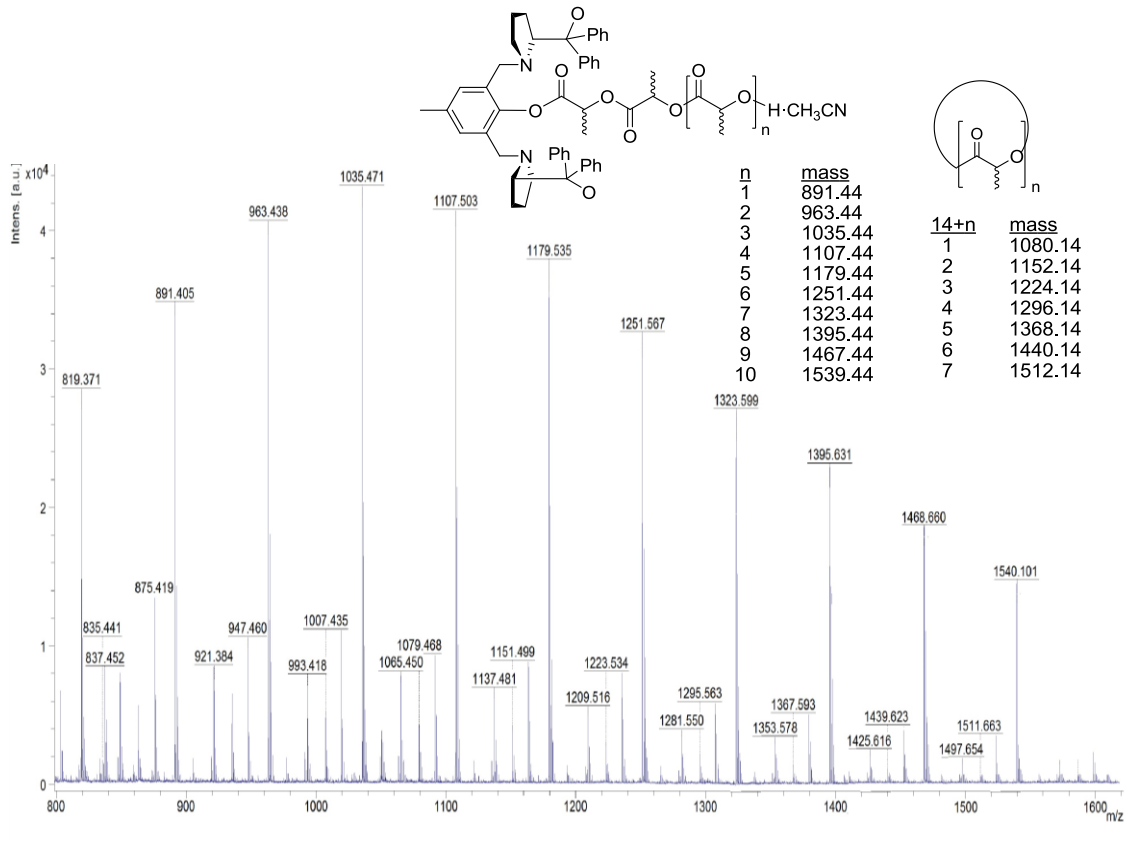
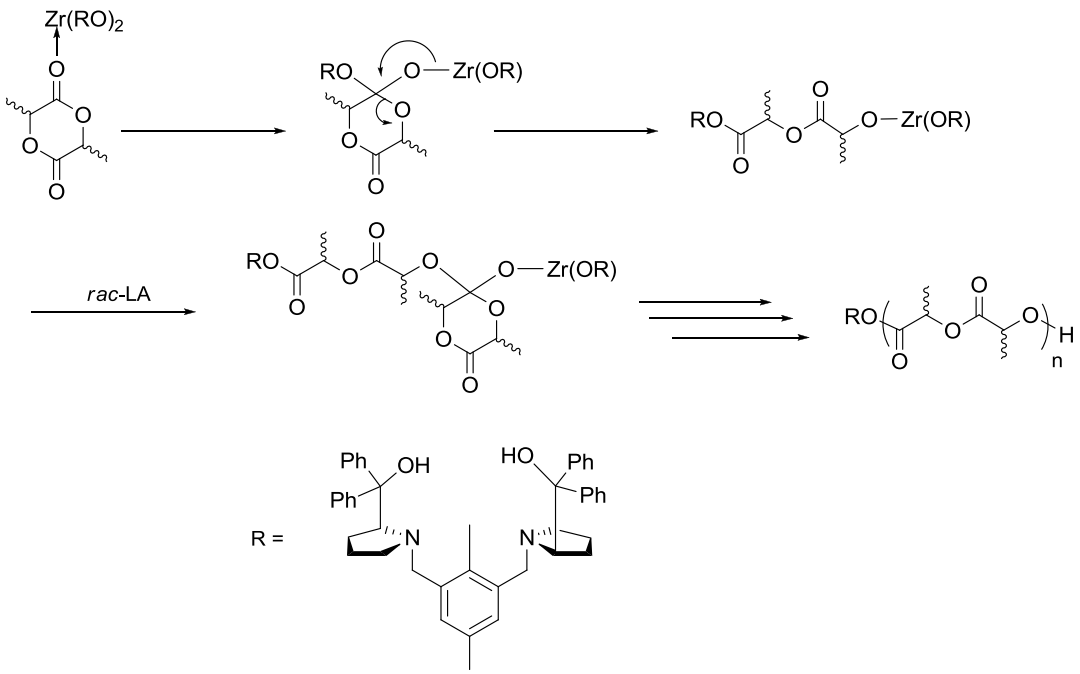


Fig. 12 MALDI-TOF spectrum of the product obtained from a reaction between *rac*-LA and **2** in 10:1 ratio at 140 °C.



Scheme 2 Proposed mechanistic pathway for the ring-opening polymerization.

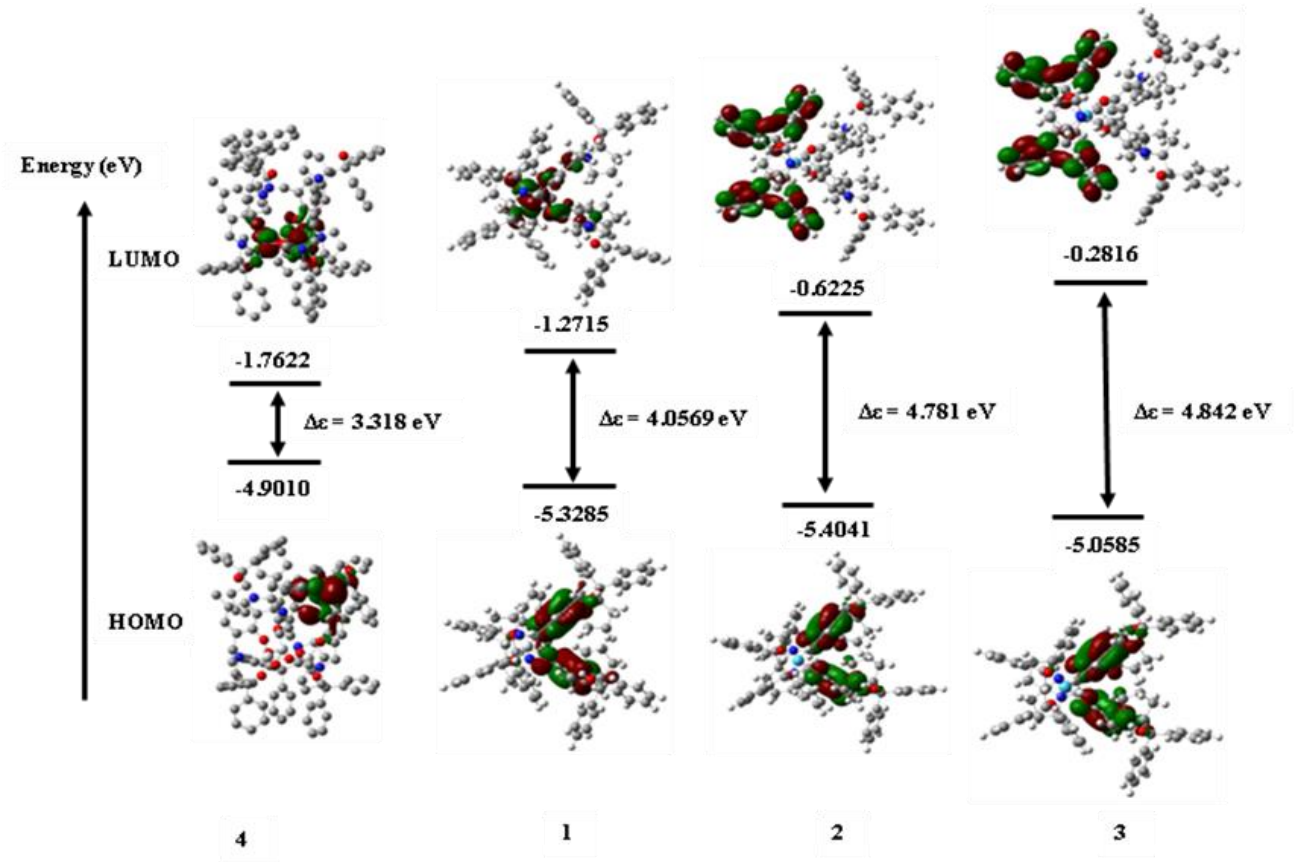


Fig. 13 Frontier molecular orbital diagrams of complexes **4**, **1**, **2** and **3** associated with HOMO-LUMO energy gap of 3.318 eV, 4.0569 eV, 4.781 eV and 4.842 eV respectively.

Conclusions

In summary, group 4 chiral complexes of (*S*, *S*)-(+)-2,6-Bis[2-(hydroxydiphenylmethyl)-1-pyrrolidinyl-methyl]-4-methylphenol were synthesized and structurally characterized by ^{1}H, ^{13}C NMR and mass spectroscopy. The molecular structures of complex **2**, **3** and **4** were confirmed by single crystal X-ray diffraction. Complexes **1**–**3** are proved to be active single site catalysts for controlled ring-opening polymerization of *rac*–LA, *L*–LA and CL. Microstructural analyses of the polymers reveal that complexes **2** and **3** induce stereoselectivity and have the abilities to control the tacticity of the growing polymer chains whereas complexes **1** and **4** lack stereocontrol towards the polymerization. Notably, their catalytic behaviour in the ring-opening polymerization of *rac*–LA polymerization varies remarkably. Complex **2** has shown the highest activity and stereoselectivity among all complexes. Furthermore, kinetic analysis suggests that polymerizations of *rac*–LA and *L*–LA follow first order kinetics. ^{1}H NMR, MALDI-TOF analysis of oligomer reveals that the polymerization proceeds though coordination-insertion mechanism. DFT calculations are well in agreement with the experimental studies.

Experimental section

General Experimental Details

All reactions were performed under a dry argon atmosphere employing standard Schlenk techniques or in a glove box where the oxygen and moisture levels were maintained below 1 ppm. The reactions for the synthesis of complexes **1**−**4** were done in toluene and THF which were rigorously dried over sodium benzophenone ketyl and distilled fresh prior to use. $CDCl_3$ used for NMR studies was dried by stirring over CaH_2, distilled and stored in the glove box. Bruker Avance 400/500 NMR instrument were employed to record ^{1}H and ^{13}C NMR with the chemical shifts referenced to residual solvent resonances and are reported as parts per million relative to $SiMe_4$. ESI-MS spectra were recorded using a Waters Q-Tof micro mass spectrometer and MALDI-TOF spectra were spectra were procured using a Bruker Daltonics instrument in dihydroxy benzoic acid matrix. The starting materials and metal alkoxides were purchased from Aldrich and used without further purification. *L*–LA and *rac*–LA monomers used for this study were purchased from Aldrich, purified by sublimation twice and stored in the glove box. CL was dried over CaH_2 and distilled prior to use. Solvents used for this study were purchased from Ranchem India. Number average molecular weights (M_n) and the molecular weight distributions (MWD) of the polymers were determined by a GPC instrument with Waters 510 pump and Waters 410 Differential

Refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 mm×300 mm) were connected in series. Measurements were done in THF at 27 °C. M_n and MWD of the polymers were measured relative to polystyrene standards. M_n were corrected according to Mark-Houwink corrections.[42] Kinetics of the polymerization reactions was determined for the small scale reactions. Based on the polymerization time for the maximum conversion of the monomer five different time laps of regular intervals were assumed. We have carried out five different polymerization reactions in a sealed tube on small scale (0.5 g of monomer) maintaining monomer to catalyst ratio 200:1 at 140 °C and allowed to stir for the stipulated time as assumed earlier. After that each polymerization reaction was quenched separately by dissolving the reaction mixture in little amount of dichloromethane and poured into cold methanol to afford a precipitate. The precipitate was filtered off and dried completely under the high vacuum. Later, a part of the precipitate was subjected to NMR analysis and the other part to HPLC analysis. From both the techniques conversion of the monomer was estimated and the results were found to be in good agreement. The ligand was synthesized using reported literature methods.[29]

Synthesis and characterization

Complex 1 To a stirred solution of 2,6-Bis[2-(hydroxyldiphenylmethyl)-1-pyrrolidinyl-methyl]-4-methylphenol (0.224 g, 0.350 mmol) in 10 mL of toluene was added a solution of $Ti(O^iPr)_4$ (0.05 g, 0.175 mmol) in 5 mL toluene at room temperature. The colour of the resulting solution immediately turned yellow, the reaction mixture allowed to stir for additional 24 h and the solvent was removed under vacuum. The resulting yellow solid was crystallized from toluene.

Physical State: Yellow solid; Yield = 0.151 g (86 %); Mp: 148 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, 4H, *Ar*, *J* = 7.2), 7.56 (d, 4H, *Ar*, *J* = 8), 7.53 (d, 4H, *Ar'*, *J* = 8), 7.50 (d, 4H, *Ar'*, *J* = 7.2), 7.48-7.02 (m, 24H, *Ar*), 6.68 (s, 2H, *Ar*), 6.58 (s, 2H, *Ar'*), 4.39 (m, 2H, N-C*H*pro), 4.00 (m, 2H, N-C*H'*pro), 3.93 (d, 2H, -CH_2-Ar, *J* = 14.8), 3.76-3.73, (m, 2H, N-CH_2-pro), 3.13 (d, 2H, CH_2-Ar', J = 14.8), 3.06 (d, 2H, CH_2-Ar, *J* = 14.4), 2.86-2.85 (m, 2H, CH_2-pro,), 2.66 (d, 2H, d, 2H, CH_2-Ar', *J* = 14.4), 2.18 (s, 6H, -CH_3), 1.97-1.82 (m, 8H, CH_2-pro), 1.81-1.50 (m, 4H, CH_2'-pro), 1.50-1.45 (m, 4H, CH_2'-pro) 1.02-0.95 (m, 2H, CH_2'-pro), 0.80-0.67 (m, 2H, CH_2'-pro); ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ = 157.24 (-*C*-O), 148.96 ((*Ar*-*C*), 148.75 (*Ar*-*C*), 148.24 (*Ar'*-C-O), 147.00 (*Ar'*-C-O), 128.98 (*Ar*-C), 128.52 (*Ar*-CH_3), 128.17 (*Ar'*-C), 127.86 (*Ar*-C), 127.74 (*Ar'*-C), 126.60 (*Ar*-C), 125.95 (*Ar'*-C), 125.78 (*Ar*-C), 125.60 (*Ar'*-C), 125.54 (*Ar*-C), 125.38 (*Ar'*-C), 125.24 (*Ar*-C), 125.04 (*Ar'*-C), 124.71 (*Ar*-CH_2), 123.18 (*Ar'*-CH_2), 86.33 (-*C*O(C)(Ph)$_2$), 79.10 (*C*-pro), 67.07 (N-CH_2-Ar), 60.77 (N'-CH_2-Ar), 55.27 (N-*C*-pro), 49.25 (N-*C'*-pro), 29.90 (*C*-pro and *C'*-pro), 23.70 (CH_3-Ar), 20.65 (*C*-pro), 20.52 (*C'*-pro); ESI m/z calculated for $[M+CH_3CN]^+$: $C_{86}H_{87}KN_4O_6Ti$ 1358.58, found: 1358.6328; Anal. Calc for $C_{86}H_{88}N_4O_6Ti$: C, 78.16; H, 6.71; N, 4.24, Found: C 78.09, H 6.31, N 4.06.

Complex 2 To a stirred solution of 2,6-Bis[2-(hydroxydiphenylmethyl)-1-pyrrolidinyl-methyl]-4-methylphenol (0.164 g, 0.256 mmol) in 10 mL of toluene was added a solution of $Zr(O^iPr)_4.{}^iPrOH$ (0.05 g, 0.128 mmol) in 5 mL toluene at room temperature and allowed to stir for additional 24 h and the solvent was removed under vacuum. The resulting white solid was crystallized from toluene to yield colourless crystals.

Physical State: White solid; Yield = 0.151 g (86 %); Mp: 158 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, 4H, *Ar*, *J* = 7.2), 7.55 (d, 4H, *Ar*, *J* = 8), 7.49 (d, 4H, *Ar'*, *J* = 8), 7.41 (d, 4H, *Ar'*, *J* = 7.2), 7.40-7.03 (m, 24H, *Ar*), 6.68 (s, 2H, *Ar*), 6.58 (s, 2H, *Ar'*), 4.38 (m, 2H, N-C*H*pro), 3.99 (m, 2H, N-C*H'*pro), 3.93 (d, 2H, -CH_2-Ar, *J* = 14.8), 3.76-3.73, (m, 2H, N-CH_2-pro), 3.13 (d, 2H, CH_2-Ar', J = 14.8), 3.03 (d, 2H, CH_2-Ar, *J* = 14.4), 2.86 (m, 2H, CH_2-pro), 2.67 (d, 2H, d, 2H, CH_2-Ar', *J* = 14.4), 2.17 (s, 6H, -CH_3), 1.92-1.83 (m, 8H, CH_2-pro), 1.81-1.49 (m, 4H, CH_2-pro), 1.50-1.45 (m, 4H, CH_2 and CH_2'-pro), 1.02-0.96 (m, 2H, CH_2'-pro), 0.81-0.68 (m, 2H, CH_2'-pro); ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ = 157.34 (-*C*-O), 149.49 ((*Ar*-*C*), 148.82 (*Ar*-*C*), 148.26 (*Ar'*-C-O), 147.00 (*Ar'*-C-O), 128.91 (*Ar*-C), 128.50 (*Ar*-CH_3), 128.16 (*Ar'*-C), 127.98(*Ar*-C), 127.85 (*Ar'*-C), 127.73 (*Ar*-C), 127.69 (*Ar'*-C), 126.31 (*Ar*-C), 125.93 (*Ar'*-C), 125.75 (*Ar*-C), 125.67(*Ar'*-C), 125.60 (*Ar*-C), 125.54 (*Ar'*-C), 125.08 (*Ar*-CH_2), 124.88 (*Ar'*-CH_2), 85.70 (-*C*O(C)(Ph)$_2$), 79.29 (*C*-pro), 67.08 (N-*C*H_2-Ar), 60.77 (N'-*C*H_2-Ar), 55.50 (N-*C*-pro), 49.14 (N-*C'*-pro), 29.89 (*C*-pro and *C'*-pro), 23.70 (CH_3-Ar), 20.65 (*C*-pro), 20.37 (*C'*-pro); ESI m/z calculated for $[M+H]^+$: $C_{86}H_{88}N_4O_6Zr$ 1363.58, found: 1363.3435. Anal. Calc for $C_{86}H_{88}N_4O_6Zr$:C, 75.68; H, 6.50; N, 4.10; Found , C, 75.32; H, 6.27; N, 3.80.

Complex 3 To a stirred solution of 2,6-Bis[2-(hydroxydiphenylmethyl)-1-pyrrolidinyl-methyl]-4-methylphenol (0.135 g, 0.212 mmol) in 10 mL of toluene was added a solution of $Hf(O^tBu)_4$ (0.05 g, 0.106 mmol) in 5 mL toluene at room temperature and allowed to stir for additional 24 h and the solvent was removed under vacuum. The resulting off white solid was crystallized from toluene to yield colourless crystals.

Physical State: Off white solid; Yield = 0.129 g (84 %); Mp: 162 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, 4H, *Ar*, *J* = 7.6), 7.56 (d, 4H, *Ar*, *J* = 7.6), 7.47 (d, 4H, *Ar'*, *J* = 8), 7.30 (d, 4H, *Ar'*, *J* = 8), 7.20-7.03 (m, 24H, *Ar*), 6.72 (s, 2H, *Ar*), 6.58 (s, 2H, *Ar'*), 4.47 (m, 2H, N-C*H*pro), 3.98 (d, 2H, -CH_2-Ar, *J* = 13.2), 3.95-3.91 (d, 2H, -CH_2-Ar, *J* = 12.2), 4.00 (d, 2H, -CH_2-Ar, *J* = 12.2), 3.95-3.91 (m, 2H, N-C*H*pro), 3.10 (d, 2H, CH_2-Ar, *J* = 14.8), 3.04 (d, 2H, CH_2-Ar', *J* = 14.8), 2.94-2.93 (m, 2H, N-CH'_2-pro), 2.67 (d, 2H, -CH_2-Ar', *J* = 12.2), 2.19(s, 6H, -CH_3), 1.97-1.90 (m, 8H, CH_2-pro), 1.80-1.81 (m, 4H, CH_2 and CH'_2-pro), 1.51-1.45 (m, 4H, CH'_2-pro), 1.01-0.96 (m, 2H, CH_2'-pro), 0.82-0.69 (m, 2H, CH_2'-pro); ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ = 157.34 (-*C*-O), 149.49 (*Ar*-*C*), 148.82 (*Ar*-*C*), 148.26 (*Ar'*-C-O), 147.00 (*Ar'*-C-O), 128.91 (*Ar*-C), 128.50 (*Ar*-CH_3), 128.16 (*Ar'*-C), 127.98 (*Ar*-C), 127.85 (*Ar'*-C), 127.73 (*Ar*-C), 127.69 (*Ar'*-C), 126.31 (*Ar*-C), 125.93 (*Ar'*-C), 125.75 (*Ar*-C), 125.67 (*Ar'*-C), 125.60 (*Ar*-C), 125.54 (*Ar'*-C), 125.08 (*Ar*-CH_2), 124.78 (*Ar'*-CH_2), 85.70 (-*C*OH(C_{pro})(Ph)$_2$), 79.29 (*C*-pro), 67.08 (N-*C*H_2-Ar), 60.77 (N'-*C*H_2-Ar), 55.50 (N-*C*-pro), 49.14 (N-*C'*-pro), 29.89 (*C*-pro and *C'*-pro), 23.70 (*C*H_3-Ar), 20.65 (*C*-pro), 20.49 (*C'*-pro); ESI m/z calculated for $[M+H]^+$ $C_{86}H_{88}HfN_4O_6$: 1453.62 found: 1453.7637. Anal. Calc for $C_{86}H_{88}N_4O_6Hf$: C, 71.13; H, 6.11; N, 3.86; Found: C, 70.94; H, 5.91; N, 3.92;

Complex 4 To a stirred solution of complex **1** (0.200 g, 0.01 mmol) in 5 ml of dry THF, degassed water (0.003 g, 0.01 mmol) was added at room temperature and the reaction mixture was allowed to stir for 24 h. The solvent was removed under vacuum and the resulting yellow solid was crystallized from toluene to yield yellow coloured crystals.

Physical State: Yellow solid; Yield = 0.221 g (72 %); Mp: 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.65 (d, 8H, *Ar*, *J* = 7.6), 7.46 (d, 8H, *Ar*, *J* = 7.6), 7.31 (d, 8H, *Ar'*, *J* = 7.6), 7.19-7.08 (m, 24H, *Ar*), 6.77 (s, 3H, *Ar*), 6.66 (s, 3H, *Ar'*), 4.25 (dd, 3H, N-C*H*, *J* = 8.5, 4.4), 3.65 (dd, 3H, N-C*H'*, *J* = 8.5, 4.4), 3.64 (d, 3H, -CH_2-Ar, *J* = 12.5), 3.47-3.40 (m, 6H, N-CH_2pro), 3.07 (d, 3H, CH'_2-Ar, *J* = 15.2), 2.91-2.88 (m, 3H, N-CH'_2pro), 2.74 (d, 3H, CH_2-Ar, *J* = 12.4), 2.68-2.55 (m, 12H, CH_2-pro and CH'_2-pro), 2.35 (s, 9H, -CH_3), 2.35-2.17 (m, 6H, CH_2-pro), 1.27-1.16 (m, 12H, CH_2-pro and CH'_2-pro); ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ = 158.06 (-*C*-O), 148.86 ((*Ar*-C-OH), 148.50 (*Ar*-C-OH), 147.77 (*Ar'*-C-OH), 147.03 (*Ar'*-C-OH), 128.98 (*Ar*-C), 128.31 (*Ar*-CH_3), 128.17 (*Ar'*-C), 127.80 (*Ar*-C), 127.69 (*Ar'*-C), 127.59 (*Ar*-C), 127.43 (*Ar'*-C), 126.36 (*Ar*-C), 125.73 (*Ar'*-C), 125.66 (*Ar*-C), 125.57 (*Ar'*-C), 125.45 (*Ar*-C), 125.24 (*Ar'*-C), 125.12 (*Ar*-C), 124.71 (*Ar*-CH_2), 124.53 (*Ar'*-CH_2) 89.89 (-*C*OH(Cpro)(Ph)$_2$), 77.55 (*C*-pro), 68.81 (N-*C*H_2-Ar), 60.92 (N'-*C*H_2-Ar), 57.55 (N-*C*-pro), 57.36 (N-*C'*-pro), 30.41 (*C*-pro), 29.33 (*C'*-pro), 25.24 (CH_3-Ar), 20.90 (*C*-pro), 20.75 (*C'*-pro); ESI m/z (ligand fragment was observed $[M+3Na]^+$:707.859, found :708.236), Anal. Calc for $C_{129}H_{132}N_6O_{12}Ti_3$: C, 73.71; H, 6.33; N, 4.00; Found C, 73.94; H, 6.12; N, 3.60.

Typical procedure for the polymerization of *rac*-LA, *L*-LA and CL

The procedure for the polymerization of respective monomers using complexes **1**–**4** in 200:1 stoichiometric ratio is as follows. For *L*-LA or *rac*-LA polymerization, 8.67 μmol of catalyst and 0.25 g of *L*-LA or *rac*-LA (34.7 mmol) and for CL polymerization, 43.81 μmol of catalyst and 1 g (1 mL, 8.76 mmol) of CL were taken. The contents were taken into a closed glass vessel under an argon atmosphere followed by which it was heated to 80 °C in case of CL polymerization and 140 °C in case of LA. The contents were rapidly stirred. The progress of polymerization was monitored by recording the ^{1}H NMR spectra of the reaction mixture periodically. The polymerization was quenched by gradually cooling the glass vessel to ambient temperature; the contents were dissolved in minimum amount of CH_2Cl_2 and poured into cold methanol in case of *rac*-LA/*L*-LA and cold heptane in case of CL. The formed polymer was collected by filtration. The filtered product was dried in vacuum until a constant weight was achieved.

X-ray crystallography

Suitable single crystals of complexes **2**, **3** and **4** were obtained by crystallization from a saturated solution of toluene at room temperature for X-ray structural determination. Single crystals were mounted on a Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with a graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation source. A full sphere of data was collected with 100 % completeness for θ up to 25°. ω and φ scans was employed to collect the data. The frame width for ω was set to 0.5 for data collection. The frames were integrated and data were reduced for Lorentz and polarization corrections using SAINT-NT. The multi-scan absorption correction was applied to the data set. All structures were solved using SIR-92 and refined using SHELXL-97. The nonhydrogen atoms were refined with the anisotropic displacement parameter. All the hydrogen atoms could be located on the difference Fourier map. The hydrogen atoms bonded to carbon atoms were fixed at meaningful positions and were allowed to ride with the parent atom during the refinement. The regions of disordered electron density, most probably disordered solvent molecules, occupying voids of 2389 Å^3 for an electron count of 412 in case of **2** and 2524 Å^3 for an electron count of 337 in case of **3**, was treated using the SQUEEZE routine in PLATON.[43] Their formula mass and unit-cell characteristics were not taken into account during refinement. A solvent masking procedure as implemented in *OLEX2* was used to remove the electronic contribution from disordered solvent molecule in case of **3**.[44]

Computational details

All the density functional theory calculations were performed at the B3LYP/LANL2DZ level of theory as implemented in the GAUSSIAN 09 (Rev C.01) package[40b] of quantum chemical programs. The molecular coordinates for the DFT calculations were extracted from single crystal XRD data for **2**, **3** and **4**. MPA (Mulliken Population Analysis) was performed using MPA 3.1 program as implemented in the Gaussian 09W package at the B3LYP/ LANL2DZ level45 in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem.

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Notes and references

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See the Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1. (a) R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841–1846. (b) A. Amgoune, C. M. Thomas, T. Roisnel and J.-F. Carpentier. *Chem. Eur. J.*, 2006 **12**, 169–179.
2. (a) M. Mochizuki and H. Tsuji Properties and applications of aliphatic polyester products. In: Y. Doi, A. Steinbűchel, editors. Polyesters III. Applications and commercial products), Biopolymers. 1st ed. Weinheim (Germany): Wiley-VCH Verlag GmbH; 2002. 1-23. and 129-177. (b) Ph, Degée and Ph. Dubois In recent advances in polylactide chemistry and materials science: Hoboken (NJ): John Wiley & Sons; 2004.

3. (a) E. Chiellini and R. Solaro, *Adv. Mater.*, 1996, **8**, 305–313; (b) A.-C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 14661–486.
4. (a) J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602–626; (b) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176.
5. (a) C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832–4846; (b) K. Numata, R. K. Srivastava, A. Finne-Wistrand, A.-C. Albertsson, Y. Doi and H. Abe, *Biomacromolecules*, 2007, **8**, 3115–3125; (c) H. Ma and J. Okuda, *Macromolecules*, 2005, **38**, 2665–2673; (d) K. Majerska and A. Duda, *J. Am. Chem. Soc*., 2004, **126**, 1026–1027; (e) A. K. Agrawal and R. J. Bhalla, *J. Macromol. Sci., Part C: Polym. Rev*., 2003, **43**, 479–503; (f) B. J. O'Keefe, S. M. Monnier, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2001, **123**, 339–340; (g) J. Kasperczyk and M. Bero, *Polymer*, 2000, **41**, 391–395.
6. (a) J. Belleney, M. Wisniewski and A. Le Borgne, *Eur. Polym. J.* 2004, **40**, 523–530; (b) M. T. Zell, B. E. Padden, A. J. Paterick, K. A. M. Thakur, R. T. Kean, M. A. Hillmyer and E. J. Munson, M*acromolecules*, 2002, **35**, 7700–7707; (c) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad T. A. Lindgren, M. A. Doscotch, J. I. Siepmann and E. J. Munson, *Macromolecules*, 1997, **30**, 2422–2428; (d) J. Coudane, C. Ustariz-Peyret, G. Schwach and M. Vert, *J. Polym. Sci., Part A: Polym. Chem.* 1997, **35**, 1651–1658; (e) Y. Ikada, K. Jamshidi, H. Tsuji, and S.-H. Hyon, *Macromolecules*, 1987, **20**, 904–906.
7. (a) M. J. Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486–494; (b) R. H. Platel, L. M. Hodgson and C. K. Williams *Polym. Rev*., 2008, **48**, 11–63.
8. M. H. Chisholm and Z. Zhou, *J. Mater. Chem.*, 2004, **14**, 3081–3092.
9. (a) S. Inkinen, M. Hakkarainen, A.-C. Albertsson and A. Södergård, *Biomacromolecules*, 2011, **12**, 523–532; (b) C. M. Thomas, *Chem. Soc. Rev*., 2010, **39**, 165–173.
10. (a) H.-L. Chen, S. Dutta, P.-Y. Huang and C.-C. Lin, *Organometallics*, 2012, **31**, 2016–2025; (b) E. L. Whitelaw, G. Loraine, M. F. Mahon and M. D. Jones, *Dalton Trans*., 2011, **40**, 11469–11473; (c) J. Koller and R. G. Bergman, *Organometallics*, 2011, 30, 3217–3224; (d) P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. White and D. J. Williams, *J. Am. Chem. Soc.*, 2004, **126**, 2688–2689; (e) A. Pilone, N. D. Maio, K. Press, V. Venditto, D. Pappalardo, M. Mazzeo, C. Pellecchia, M. Kol and M. Lamberti, *Dalton Trans.*, 2015, **44**, 2157-2165.
11. (a) P. Horeglad, P. Kruk and J. Pécaut, Organometallics, 2010, **29**, 3729-3734; (b) P. Horeglad, G. Szczepaniak, M. Dranka and J. Zachara, Chem. Commun., 2012, **48**, 1171-1173; (c) S. Ghosh, R. R. Gowda, R. Jagan and D. Chakraborty, *Dalton Trans*., DOI: 10.1039/c5dt00811e.
12. (a) A.-F. Douglas, B. O. Patrick and P. Merkhodavandi, *Angew. Chem., Int., Ed*., 2008, **47**, 2290–2293; (b) A. Acosta-Ramírez, A. F. Douglas, I. Yu, B. O. Patrick, P. L. Diaconescu and P. Mehrkhodavandi, *Inorg. Chem.*, 2010, **49**, 5444–5452; (c) D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Chem. Commun*., 2012, **48**, 6806–6808; (d) D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Chem. Commun*., 2013, **49**, 4295–4297; (e) D. C. Aluthge, C. Xu, N. Othman, N. Noroozi, S. G. Hatzikiriakos and P. Mehrkhodavandi, *Macromolecules*, 2013, **46**, 3965–3974; (f) I. Peckermann, A. Kapelski, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2009, **48**, 5526–5534; (g) E. M. Broderick, N. Guo, C. S. Vogel, C. Xu, J. Sutter, J. T. Miller, K. Meyer, P. Mehrkhodavandi and P. L. Diaconescu, *J. Am. Chem. Soc*., 2011, **133**, 9278–9281; (h) K. M. Osten, I. Yu, I. R. Duffy, P. O. Lagaditis, J. C.-C. Yu, C. J. Wallis and P. Mehrkhodavandi, *Dalton Trans.*, 2012, **41**, 8123–8134; (i) L. E. N. Allan, G. G. Briand, A. Decken, J. D. Marks, M. P. Shaver and R. G. Wareham, *J. Organomet. Chem.*, 2013, **736**, 55–62; (j) N. Maudoux, T. Roisnel, V. Dorcet, J.-F. Carpentier and Y. Sarazin, *Chem. Eur. J.*, 2014, **20**, 1–18.
13. (a) C.Y. Sung, C.-Y. Li, J.-K. Su, T.-Y. Chen, C.-H. Lin and B.-T. Ko, *Dalton Trans.* 2012, **41**, 953–961.
14. (a) A. Alaaeddine, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2009, **28**, 1469–1475; (b) W. Miao, S. Li, H. Zhang, D. Cui, Y. Wang and B. Huang, *J. Organomet. Chem.*, 2007, **692**, 4828–4834; (c) Y.-L. Hsieh, Y.-C. Lin, G.-H. Lee and C.-H. Peng, *Polymer*, 2015, **56**, 237-244; (d) K. S. Kwon, S. Nayab and J. H. Jeong, *Polyhedron*, 2015, **85**, 615-620.
15. (a) L. Wang and H. Ma, *Dalton Trans.*, 2010, **39**, 7897–7910; (b) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229–3238.
16. M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889–899.
17. N. Spassky, M. Wisniewski, C. Pluta and A. Le Borgne, *Macromol. Chem. Phys.*, 1996, **197**, 2627–2637.
18. Z. Y. Zhong, P. J. Dijkstra and J. Feijen, *Angew. Chem., Int. Ed.*, 2002, **41**, 4510–4513.
19. M. Bouyahyi, E. Grunova, N. Marquet, E. Kirillov, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2008, **27**, 5815–5825.
20. H. Du, X. Pang, H. Yu, X. Zhuang, X. Chen, D. Cui, X. Wang and X. Jing, *Macromolecules*, 2007, **40**, 1904–1913.
21. A. Stopper, J. Okuda and M. Kol, *Macromolecules*, 2012, **45**, 698–704.
22. M. Bouyahyi, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2012, **31**, 1458–1466.
23. H.-L. Chen, S. Dutta, P.-Y. Huang and C.-C. Lin, *Organometallics*, 2012, **31**, 2016–2025.
24. (a) A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jonesa and M. D. Lunnb, *Chem. Commun*., 2008, 1293–1295; (b) R. Ishii, N. Nomura and T. Kondo, Polym. J. (Tokyo, Jpn), 2004, **36**, 261–264.
25. (a) A. J. Chmura, D. M. Cousins, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans*., 2008, 1437–1443; (b) Y. Ning, Y. Zhang, A. R. Delgado and E. Y.-X. Chen, *Organometallics*, 2008, **27**, 5632–5640; (c) R. F. Munha, L. G. Alves, N. Maulide, M. T. Duarte, I. E. Marko, M. D. Fryzuk and A. M. Martins, *Inorg. Chem. Commun*., 2008, **11**, 1174–1176; (d) K. K. -Dziedzic, J. Ejfler, S. Szafert and P. Sobota, *Dalton Trans*., 2008, 2620–2626; (e) F. Gornshtein, M. Kapon, M. Botoshansky and M. Eisen, *Organometallics*, 2007, **26**, 497–507; (f) R. C. J. Atkinson, K. Gerry, V. C. Gibson, N. J. Long, E. L. Marshall and L. J. West, *Organometallics*, 2007, **26**, 316–320; (g) J. Lee, Y. Kim and Y. Do, *Inorg. Chem*., 2007, **46**, 7701–7703; (h) S. Mun, J. Lee, S. H. Kim, Y. Hong, Y.-H. Ko, Y. K. Shin, J. H. Lim, C. S. Hong, Y. Do and Y. Kim, *J. Organomet. Chem*., 2007, **692**, 3519–3525; (i) C. K. A. Gregson, I. J. Blackmore, V. C. Gibson, N. J. Long, E. L. Marshall and A. J. P. White, *Dalton Trans*., 2006, 3134–3140; (j) D. Patel, S. T. Liddle, S. A. Mungur, M. Rodden, A. Blake and P. L. Arnold, *Chem. Commun*., 2006, 1124–1126; (k) S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt and M. Kol, *Inorg. Chem*., 2006, **45**, 4783–4790; (l) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250–7257;

(m) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans*., 2006, 887– 889; (n) K.-C. Hsieh, W.-Y. Lee, L.-F. Hsueh, H. M. Lee and J.-H. Huang, *Eur. J. Inorg. Chem*., 2006, 2306–2312; (o) J. Cayuela, V. Bounor-Legaré, P. Cassagnau and A. Michel, *Macromolecules*, 2006, **39**, 1338–1346; (p) C. J. Chuck, M. G. Davidson, M. D. Jones, G. Kociok- Köhn, M. D. Lunn and S. Wu, *Inorg. Chem*., 2006, **45**, 6595– 6597; (q) Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans*., 2006, 340–350; (r) Y. Kim and J. G. Verkade, *Macromol. Symp*., 2005, 224, 105–118; (s) S. K. Russell, C. L. Gamble, K. J. Gibbins, K. C. S. Juhl, W. S. Mitchell, A. J. Tumas and G. E. Hofmeister, *Macromolecules*, 2005, **38**, 10336–10340; (t) Y. Takashima, Y. Nakayama, T. Hirao, H. Yasuda and A. Harada, *J. Organomet. Chem*., 2004, **689**, 612–619; (u) Y. Kim, G. K. Jnaneshwara and J. G. Verkade, *Inorg. Chem*., 2003, **42**, 1437–1447; (v) Y. Kim and J. G. Verkade, *Macromol. Rapid Commun*., 2002, **23**, 917–921; (w) Y. Kim and J. G. Verkade, *Organometallics*, 2002, **21**, 2395–2399; (x) D. Takeuchi, T. Nakamura and T. Aida, *Macromolecules*, 2000, **33**, 725–729; (y) H. R. Kricheldorf, M. Berl and N. Scharnagl, *Macromolecules*, 1988, **21**, 286–293.

26. (a) M. J. Go, J. M. Lee, K. M. Lee, C. H. Oh, K. H. Park, S. H. Kim, M. Kim, H.–R. Park, M. H. Park, Y. Kim and J. Lee, *Polyhedron*, 2014, **67**, 286–294; (b) C. J. Chuck, M. G. Davidson, G. G. du Sart, P. K. Ivanova-Mitseva, G. I. Kociok-Köhn and L. B. Manton, *Inorg. Chem.*, 2013, **52**, 10804–10811; (c) C.–Y. Li, C.–J. Yu and B.–T. Ko, *Organometallics*, 2013, **32**, 172–180; (d) R. R. Gowda and E. Y.-X. Chen, *Dalton Trans*., 2013, **42**, 9263–9273; (e) R. L. Webster, N. Noroozi, S. G. Hatzikiriakos, J. A. Thomson and L. L. Schafer, *Chem. Commun*., 2013, **49**, 57–59; (f) F. Marchetti, G. Pampaloni, C. Pinzino, F. Renili, T. Repo and S. Vuorinen, *Dalton Trans.*, 2013, **42**, 792–802; (g) I. E. I. Zoghbi, T. J. J. Whitehorne and F. Shaper, *Dalton Trans*., 2013, **42**, 9376–9387; (h) L. G. Alves, F. Hild, R. F. Munhá, L. F. Veiros, S. Dagorne and A. M. Martins, *Dalton Trans.*, 2012, **41**, 14288–14298; (i) C. Romain, B. Heinrich, S. B. Laponnaz and S. Dagorne, *Chem. Commun*., 2012, **48**, 2213–2215; (j) A. Stopper, I. Goldberg and M. Kol, *Inorg. Chem. Commun*., 2011, **14**, 715–718; (k) S. L. Hancock, M. F. Mahon and M. D. Jones, *Dalton Trans*., 2011, **40**, 2033–2037; (l) M. D. Jones, M. G. Davidson and G. Kociok-Kohn, *Polyhedron*, 2010, **29**, 697–700; (m) F. Zhang, H. Song and G. Zi, *J. Organomet. Chem*., 2010, **695**, 1993–1999; (n) E. Sergeeva, J. Kopilov, I. Goldberg and M. Kol, *Inorg. Chem*., 2010, **49**, 3977–3979; (o) A. D. Schwarz, K. R. Herbert, C. Paniagua and P. Mountford, *Organometallics*, 2010, **29**, 4171–4188; (p) M. Hu, M. Wang, H. Zhu, L. Zhang, H. Zhang and L. Sun, *Dalton Trans*., 2010, **39**, 4440–4446; (q) M. G. Davidson, S. D. Bull, T. R. Forder, C. J. Frankis and M. D. Jones, *Polym. Prepr*., 2010, **51**, 390–391; (r) A. Grafov, S. Vuorinen, T. Repo, M. Kemell, M. Nieger and M. Leskela, *Eur. Polym. J*., 2008, **44**, 3797–3805; (s) G. Zi, Q. Wang, L. Xiang and H. Song, *Dalton Trans*., 2008, 5930–5944; (t) P. Dobrzynski, *J. Polym. Sci., Part A: Polym. Chem*., 2004, **42**, 1886–1900; (u) D. Chakraborty, D. Mandal, V. Ramkumar, V. Subramanian and J. V. Sundar, *Polymer*, 2015, **56**, 157-170; (v) Z. R. Turner, J.-C. Buffet and D. O'Hare, *Organometallics*, 2014, **33**, 3891-3903; (w) A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, *Inorg. Chem.*, 2014, **53**, 9140-9150;

27. (a) S. Pappuru, E. R. Chokkapu, D. Chakraborty and V. Ramkumar *Dalton Trans.*, 2013, **42**, 16412–16427; (b) T. K. Saha, M. Mandal and D. Chakraborty, *New J. Chem*., 2013, **37**, 949–960; (c) T. K. Saha, B. Rajashekhar and D. Chakraborty, *RSC Adv.*, 2012, **2**, 307–318; (d) T. K. Saha, V. Ramkumar and D. Chakraborty, *Inorg. Chem*., 2011, **50**, 2720–2722; (e) T. K. Saha, B. Rajashekhar, R. R. Gowda, V. Ramkumar and D. Chakraborty, *Dalton Trans.*, 2010, **39**, 5091–5093; (f) S. K. Roymuhury, D. Chakraborty and V. Ramkumar, *Dalton Trans.*, 2015, **44**, 10352-10367; (g) S. K. Roymuhury, D. Chakraborty and V. Ramkumar, *New J. Chem.*, 2015, **39**, 5218-5230; (h) M. Mandal, D. Chakraborty and V. Ramkumar, *RSC Adv.*, 2015, **5**, 28536-28553.

28. A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne M. Kol and J. Okuda, *Dalton Trans*., 2013, **42**, 9007–9023.
29. B. M. Trost and H. Ito, *J. Am. Chem. Soc.*, 2000, **122**, 12003–12004.
30. (a) B. M. Trost, A. Fettes and B. T. Shireman, *J. Am. Chem. Soc*., 2004, **126**, 2660–2661; (b) B. M. Trost and V. S. C .Yeh, *Org. Lett.*, 2002, **4**, 3513–3516; (c) B. M., Trost, H. Ito and E. R. Silcoff, *J. Am. Chem. Soc.*, 2001, **123**, 3367–3368; (d) B. M., Trost, E. R. Silcoff and H. Ito, *Org. Lett*., 2001, **3**, 2497–2500.
31. (a) B. M. Trost and V. S. C. Yeh, *Angew. Chem. Int. Ed*., 2002, **41**, 861–863; (b) B. M. Trost, V. S. C. Yeh, H. Ito, N. Bremeyer, *Org. Lett.*, 2002, **4**, 2621–2623.
32. B. M. Trost and L. R. Terrell, *J. Am. Chem. Soc*., 2003, **125**, 338–339.
33. B. M. Trost and T. Mino, *J. Am. Chem. Soc.*, 2003, **125**, 2410–2411.
34. H.J. Li, H. Y. Tian, Y. C. Wu, Y. J. Chen, L. Liu, D. Wang and C. J. Li, *Adv. Synth. Catal*., 2005, **347**, 1247–1256.
35. (a) E. T. Kiesewetter, S. Randoll, M. Radlauer and R. M. Waymouth, *J. Am. Chem. Soc.*, 2010, **132**, 5566–5567; (b) C. M. Manna, M. Shavit and E. Y. Tshuva, *J. Organomet. Chem.*, 2008, **693**, 3947–3950; (c) L. S. Natrajan, C. Wilson, J. Okuda and P. L. Arnold, *Eur. J. Inorg. Chem*., 2004, 3724–3732; (d) F. Calderazzo, U. Englert, C. M. -Mossmer, F. Marchetti, G. Pampaloni, D. Petroni, C. Pinzino, C. Strähle and G. Tripepi, *Inorg. Chim. Acta*, 1998, **270**, 177–188; (e) R. C. Fay, *Coord. Chem. Rev*., 1996, **154**, 99–124; (f) H. K. Chun, W. L. Steffen and R. C. Fay, *Inorg. Chem*., 1979, **18**, 2458–2465; (g) J. V. Silverton and J. L. Hoard, *Inorg. Chem*., 1963, **2**, 243–249.
36. M. Nishio, *CrystEngComm*, 2004, **6**, 130-158.
37. (a) S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka and M. A. Spackman, *CrystalExplorer 3.1*, (2012) University of Western Australia (http://hirshfeldsurface.net/CrystalExplorer), Perth; (b) M.A. Spackman, D. Jayatilaka, *CrystEngComm*, 2009, **11** ,19-32.
38. D. C. Bradley, R. C. Mehrotra, I. P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic, San Diego, CA, 2001.
39. E. L. Marshall, V. C. Gibson and H. S. Rzepa, *J. Am. Chem. Soc.*, 2005, **127**, 6048-6051.
40. (a) V. Krishna kumar and V. Balachandran, *Spectochimi Acta.*, A61, 2005, 1811–1819; (b) Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
41. (a) N. de Sousa Sousa, R. B. de Lima, A. L. P. Silva, A. A. Tanaka, A. B. F. da Silva and J. de Jesus Gomes Varela Júnior, *Comput. Theor. Chem.*, 2015, **1054**, 93-99; (b) T. M. Pappenfus, B. J. Hermanson, T. J. Helland, G. G. W. Lee, S. M. Drew, K. R. Mann, K. A. McGee and S. C. Rasmussen, *Org. Lett*., 2008, **10**, 1553-1556; (c) R. G. Pearson, *Inorg. Chem.*, 1988, **27**, 734-740; (d) R. G. Parr and R. G. Pearson, *J. Am. Chem. Soc*., 1983, **105**, 7512-7516.
42. I. Barakat, P. Dubois, R. Jérôme and P. Teyssié, *J .Polym. Sci. A Polym. Chem.*, 1993, **31**, 5051–514.
43. A. L. Spek, *Acta. Cryst., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148-155.

44. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst*., 2009, **42**, 339–341.