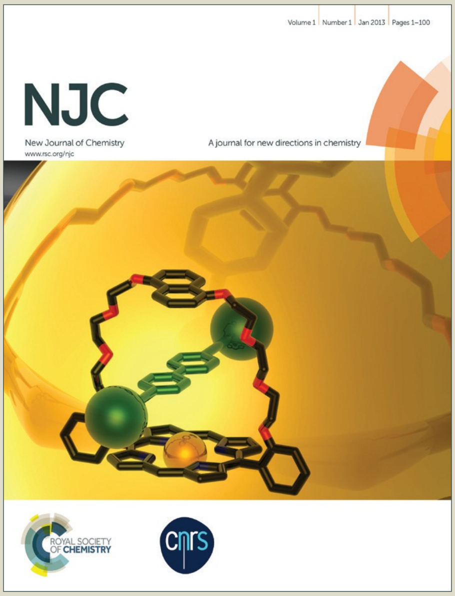
NJC

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Zwitterionic group 4 aminophenolate catalysts for the polymerization of lactides and ethylene

Sagnik K. Roymuhury,[a] Debashis Chakraborty,*[a] and Venkatachalam Ramkumar[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A series of group 4 metal chloride complexes based on aminophenol ligands were synthesized and characterized by conventional spectroscopic techniques, elemental analysis and X-ray crystallography. All the complexes are zwitterionic in nature where the protonated nitrogen atom of the aminophenolate backbone is charge neutralised by a negative charge on the metal center. The molecular structures show that moderate electrostatic hydrogen bonding interactions prevail between the NH^+ donor moieties and acceptor chlorine atoms which stabilise these complexes. These complexes show precise control towards the ring opening polymerization (ROP) of lactides (*rac*-LA, *L*-LA). Heterotactic enriched poly(lactic acid) (PLA) with good number average molecular weight (M_n) and narrow molecular weight distributions (MWDs) were obtained. The MALDI-TOF and ^{1}H NMR spectra of low molecular weight oligomer were analysed to understand polymer microstructure and it revealed that the aminophenolate ligand initiates the ROP. The complexes, activated by methylaluminoxane (MAO), were also found to be moderately active for ethylene polymerization.

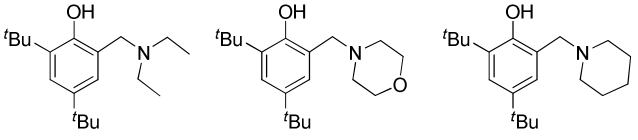
Introduction

Poly(lactic acid) (PLA) has been attracting widespread attention both in research and industry in the past two decades because of its potential as a promising substitute to the polymers derived from rapidly depleting petroleum based raw materials.[1] Having derived from annually renewable resources such as corn starch and sugar beet, PLA undergoes hydrolytic degradation to form lactic acid which can be metabolised *in vivo* and also in the environment.[2] Due to their biodegradability and biocompatibility, PLA finds versatile biomedical as well as pharmaceutical applications as packaging materials, carriers for controlled release of drugs, scaffolds for tissue engineering, medical implants, biomedical sutures etc.[3,4] Controlled ring opening polymerization (ROP) of lactide using a metal complex as catalyst is a convenient method for the synthesis of PLA owing to the advantages of achieving well controlled number average molecular weight (M_n) and narrow molecular weight distributions (MWDs).[5] The degree of stereoregularity in PLA depends on the selectivity of the particular stereoisomer of lactide by the propagating species. As no new stereogenic center is created in ROP, the catalyst system is highly responsible for the tacticity of the PLA derived from *rac*-LA.[6] The key issue in designing the catalyst system has been to obtain PLA with superior thermo-mechanical properties. In this regard, a plethora of catalytic systems of alkaline earth metals[7], group 4 metals[8], aluminium[9], zinc[10], lanthanide metals[11] as well as small organic molecules like ammonium betaines[12] and *N*-heterocyclic carbenes[13] (NHCs) have been synthesized and explored to elucidate the influence of the structure of the catalysts on the activity towards ROP of lactides and microstructures of the produced PLAs. Structurally well defined group 4 metal alkoxide complexes based on several ancillary ligands such as *β*-diketiminate[14], bis (phenolate) (salan, salen, salalen, half-salen/-salan)[15], benzotriazole phenolate[16] etc have been discovered and proved to be playing important role in producing PLA in a controlled and stereoselective manner. Lately, we reported novel group 4 alkoxide complexes based on iminophenoxide and bis(imino)phenoxide ligands as catalysts for the ROP of lactides. Although the polymerization results in toluene were significantly good, we were unable to control M_n under solvent free condition due to slow initiation during polymerization.[8f,8u,8v] To address the issue of control in M_n and MWDs, our prime focus of research has been the development of new catalytic systems and exploration of their activity towards ROP under solvent free condition.

Since the first discovery of homogenous Ziegler-Natta catalysts by group 4 metallocenes, research and development of high-performance catalysts that produce precisely controlled polyolefin in terms of stereochemistry, functionality, composition and molecular weight, has contributed significantly to the advancement of polymer chemistry.[17] An enormous number of single-site group 4 metallocene and half metallocene catalysts have been reported to stabilze homogenous olefin polymerization whereas non metallocene group 4 metal complexes considered so far for olefin polymerization were mainly dihalide or dialkyl complexes.[18] Among them, group 4 chloro complexes based on iminophenoxide ligand commonly called as “FI” catalysts developed by Fujita and Coates are of ongoing interest in research.[19] In our previous work, we reported group 4 iminophenoxide and bis(imino)phenoxide complexes having resemblance to “FI” catalysts for ethylene polymerization but the activities were not as good as the Fujita catalysts.[8f,8u,8v]

Our goal in this work was to synthesize group 4 metal chloride complexes which can show better potential than our previously reported work as catalysts towards ROP of lactides as well as ethylene polymerization. The ROP of lactides using zwitterionic group 4 initiators is an area which has not been studied much. Recently, Mou *et al*. reported both isoselective and heteroselective zwitterionic initiators based on zinc and rare-earth metals respectively for the ROP of *rac*-LA.[20] Herein, we report a series of charge neutral zwitterionic group 4 chloride complexes based on amino(phenolate) ligands and demonstrate the activity towards the ROP of lactides and ethylene polymerization.

Results and Discussion

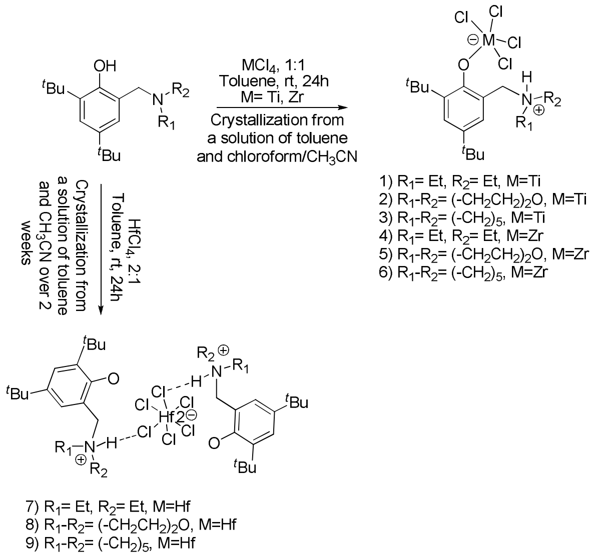


L1 L2 L3

Figure 1. Ligand precursors employed in the study **L1**-**L3**

Synthesis and characterization

The amino phenol ligands in this study, **L1**-**L3** were synthesized according to the literature procedure by simple Mannich reaction (Figure 1).[21] Each of these ligands consists of 2, 4-di-*tert*-butylphenol and they differ only in the structure of the secondary amines employed for the Mannich condensation *i.e.* diethylamine, morpholine and piperidine. The ligands were reacted with Ti, Zr and Hf chlorides in dry toluene at room temperature resulting in the formation of charge neutral zwitterionic complexes **1**-**9** in high yields. The selection of optimum stoichiometric ratios of ligands to metal chlorides for the preparation of metal complexes was a challenge. Wang *et al*. has recently reported the synthesis of zwitterionic (“ferrocene-saladiminato”)$_2$ZrCl$_4$ complexes from reactions between ferrocene-saladiminato ligands and Zr chlorides in 2:1 molar ratios.[17b] We adopted a similar approach and the ligands were reacted with metal chlorides in 2:1 ratio but apart from the reactions with HfCl$_4$, 1 equiv of ligands remained unreacted in case of reactions with TiCl$_4$ and ZrCl$_4$. As a result, we modified the ratio to 1:1 for the later reactions. The resulting brown coloured residue in case of Ti complexes and white coloured residue in case Zr and Hf complexes were purified by crystallization from a 1:1 mixture of toluene and chloroform/acetonitrile. All the complexes were dried in vacuum and fully characterized by ^{1}H, ^{13}C NMR, ESI-MS and elemental analysis. The disappearance of the O-H signals from the ligands **L1**-**L3** (~δ 11.7, 10.7 and 11.5 ppm respectively) in the ^{1}H NMR spectra of the crude products clearly indicated the formation of the metal complexes (Scheme 1).



Scheme 1. Synthesis of group 4 aminophenolate complexes

The ^{1}H NMR shows that the two -CH$_2$NC*H*$_2$ methylene hydrogens in the metal complexes are magnetically distinct and have their own resonances. The generated side product of the reaction *i.e.* HCl as well as the high basic character of the nitrogen atom in aminophenolate complex results in further protonation of the nitrogen atom.[22] A new signal in the region δ 8-9 ppm is attributed to the protonated nitrogen atom. As a result of this protonation, the electron withdrawing effect of the amine fragment increases substantially resulting in the deshielding of the –C*H*$_2$ moieties attached to the nitrogen atom in the ^{1}H NMR spectrum of the metal complexes. The singlet –C*H*$_2$ peaks in the ^{1}H NMR spectra of the ligands appear in the region 3.6-3.8 ppm whereas those peaks get deshielded to the region 4.0-4.5 ppm in the metal complexes. As we move down the group from Ti to Hf, the protonated nitrogen peaks of the metal complexes appear more shielded. This may be due to the fact that metal-oxygen bond distance and hence the distance between amino proton and electron withdrawing chlorine atom increases with the increase in the size of metal atom resulting in the shielding of the amino proton peak. In case of **7**-**9**, the six-coordinated negatively charged Hf center sits entrapped in between two counter positive ions by short-range moderate electrostatic hydrogen bonding interaction.

X-ray diffraction studies

The molecular structures of **1**, **4**, **5** and **7** were determined by single crystal X-ray diffraction studies. Crystals of suitable sizes were grown from a solution of toluene and chloroform/ acetonitrile over a period of 2-3 weeks. The molecular structures of **1**, **4**, **5** and **7** at 30% probability level are illustrated in Figures 2-5 and the crystal data are depicted in Table 1.

Complex **1** crystallized from monoclinic space group *C2*/*c* with 8 molecules in the unit cell and one molecule in the asymmetric unit. Brown-red coloured crystals were obtained from a dilute solution of toluene and chloroform. From the molecular structure of **1**, it is evident that the complex is in zwitterionic form where the nitrogen atom is protonated and the metal center acquires a negative charge because of its five coordinations. The Ti metal center adopts a distorted trigonal bypyramidal geometry coordinating with two Cl atoms and the deprotonated phenolic ligand in the equatorial positions and two chlorine atoms in the axial positions thereby acquiring a negative charge which is counterbalanced by the protonated nitrogen atom. The axial Ti-Cl bond distances (2.313 Å and 2.369 Å) are longer than the equatorial ones (2.237 Å and 2.281 Å). The equatorial O1-Ti1-Cl4, O1-Ti1-Cl3 and Cl3-Ti1-Cl4 bond angles are 114.0°, 116.7° and 129.1° respectively and the axial Cl1-Ti1-Cl2 bond angle is 174.8° which reveals that **1** adopted a distorted trigonal bipyramidal geometry.[23] The distance between Cl2 and N1 is 3.2 Å which shows the presence of moderate electrostatic hydrogen bonding interaction in the complex.[24]

Crystals of Zr complexes **4** and **5** were grown from a solution of toluene and CH_3CN. As a result, one CH_3CN molecule is coordinated to the Zr metal center, resulting in a distorted octahedral geometry around the metal center in each case. Complex **4** crystallized from monoclinic space group *C2*/*c* with one toluene molecule as solvent of crystallization. All four Cl atoms occupy the equatorial positions. The equatorial Cl-Zr-Cl bond angles are 86.7°, 86.8°, 89.9° and 93.3° respectively and the axial O1-Zr1-N1 angle is 176.3° which proves a distorted octahedral geometry.[8f,8o,16e,25] Complex **5** crystallized from monoclinic $P2_1/c$ space group with 4 molecules in a unit cell and one molecule in the asymmetric unit. From the molecular structure, it is clear that complex **5** has similar structural features to that of **4** and the Zr center adopted a distorted octahedral geometry. The Cl4-Zr and Cl2-Zr in complex **4** and **5** are 3.2 Å which confirms the presence of moderate to weak hydrogen bonding interaction. Selected bond lengths and bond angles of **5** are listed in Table S2 (see ESI).

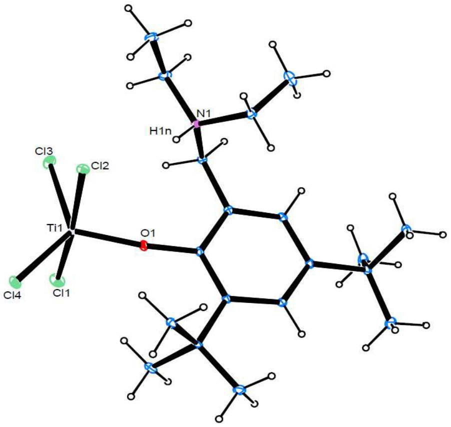


Figure 2. Molecular structure of **1**; thermal ellipsoids were drawn at 30% probability level, Selected bond lengths (in Å) and bond angles (in °) are: O1-Ti1 1.76(2), Cl1-Ti1 2.31(9), Cl2-Ti1 2.37(7), Cl3-Ti1 2.28(7), Cl4-Ti1 2.24(6), O1-Ti1-Cl3 116.7(6), O1-Ti1-Cl4 114.0(6), Cl3-Ti1-Cl4 129.1(3), Cl1-Ti1-Cl2 174.8(3).

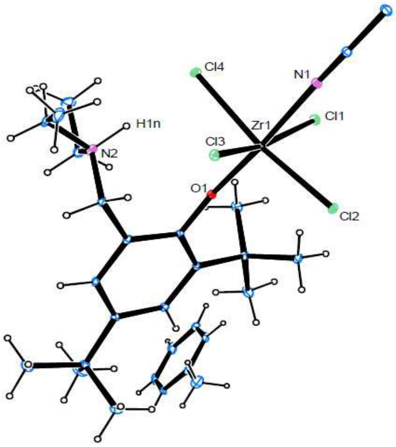


Figure 3. Molecular structure of **4**; thermal ellipsoids were drawn at 30% probability level, Selected bond lengths (in Å) and bond angles (in °) are: O1-Zr1 1.95(2), Cl1-Zr1 2.43(1), Cl2- Zr1 2.45(1), Cl3- Zr1 2.49(1), Cl4- Zr1 2.50(1), N1- Zr1 2.34(3), O1-Zr1-N1 176.3(1), Cl1-Zr1-Cl2 93.3(4), Cl1-Zr1-Cl4 89.9(3), Cl2-Zr1-Cl4 167.3(4)

Complex **7** was crystallized from a solution of toluene and chloroform over a period of 2 weeks. The molecular structure of **7** has monoclinic *C2*/*c* symmetry and the Hf metal center adopted an octahedral geometry coordinating to six Cl atoms. The doubly negatively charged $[HfCl_6]^{2-}$ moiety is neutralised by two positively charged aminophenolate ligands through moderate electrostatic hydrogen bonding interaction. The weak hydrogen bonding interaction was confirmed from the unit cell crystal packing where the distance between the acceptor Cl atom and the H atom of the donor NH^+ moiety is 2.7 Å (Figure 6). The asymmetric unit also confirms a good hydrogen bonding interaction between NH^+ and the oxygen atom of the ligand. The Hf-Cl bond distances are almost identical ranging between 2.44-2.45 Å. The axial bond angle of 180° and equatorial angles ranging between 89°-90° confirms a perfect octahedral geometry around Hf metal center.

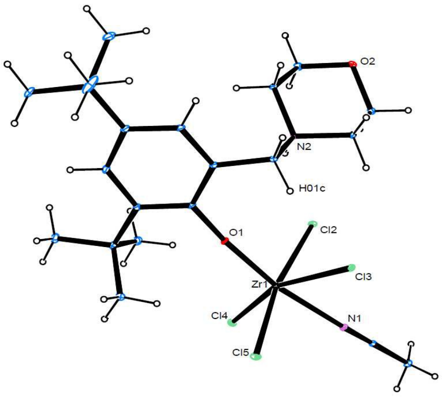


Figure 4. Molecular structure of **5**; thermal ellipsoids were drawn at 30% probability level, Selected bond lengths (in Å) and bond angles (in °) are: O1-Zr1 1.92(2), Cl2-Zr1 2.51(9), Cl3- Zr1 2.52(1), Cl4- Zr1 2.43(1), Cl5- Zr1 2.44(1), N1- Zr1 2.38(3), O1-Zr1-N1 168.9(1), Cl2-Zr1-Cl3 87.1(3), Cl3-Zr1-Cl5 85.9(3) Cl5-Zr1-Cl4 89.6(3)

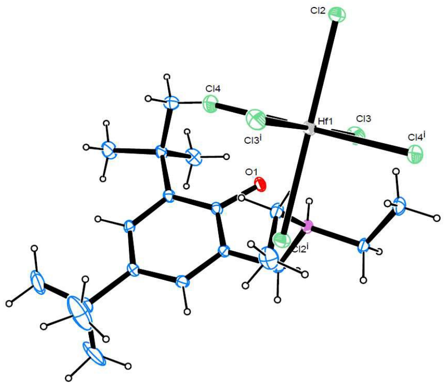


Figure 5. Molecular structure of **7**; thermal ellipsoids were drawn at 30% probability level, Selected bond lengths (in Å) and bond angles (in °) are: Cl2-Hf1 1.92(2), Cl3-Hf1 2.51(9), Cl4-Hf1 2.52(1), Cl2-Hf-Cl2i 180.0(4), Cl2-Hf1-Cl3 90.1(4), Cl2-Hf1-Cl4 89.5(5) Cl3-Hf1-Cl4 90.5(5)

Ring opening polymerization of *rac*-LA and *L*-LA

The activity of the compounds **1-9** towards the ROP of lactides was explored. All the complexes have shown good activity towards the polymerization. These polymerizations were performed at 140 °C under solvent free condition. In this regard, we performed the polymerizations first at 200:1 $[M]_0/[Cat]_0$ ratio using all the complexes. Homonuclear decoupled ^{1}H NMR spectrum reveals heterotactic enrichment in the PLA obtained from *rac*-LA (Figure S28, see ESI). Analysis of the data depicted in Table 2, 3 and 4 shows a precise control in the polymerizations where the observed number average molecular weights (M_n) are in close proximity to the theoretical values and molecular weight distributions (MWDs) are narrow. Variation of M_n and MWDs with $[M]_0/[Cat]_0$ ratio using **1-9** for the polymerizations of *rac*-LA monomer were studied. The linear plots in Figure 7 and Figure S30-S31 (see ESI) show that M_n increases continuously with an increase in the monomer to catalyst ratio whereas the MWDs are almost invariable with increasing ratios for a given monomer, suggesting that the polymerization proceeds in a controlled manner (Table 2, 3 and Table S1, see ESI).

The polymerizations of *rac*-LA and *L*-LA in the presence of benzyl alcohol (BnOH) were also performed using these complexes. The catalytic activity of the complexes increased in presence of BnOH. In all cases, the observed M_n is in close correlation with the theoretical M_n. Blank polymerization of lactide both in absence of catalyst or in presence of free ligand (**L1-L3**) was performed and polymeric products were not obtained which signifies the role of the Lewis acidic metal centers in the metal complexes towards the ROP of lactides as coordination sites for the lactide monomers. The higher reactivity of Ti complexes compared to Zr and Hf complexes can be explained by the higher Lewis acidity of the Titanium center. The effect of variation of ancillary ligand on the catalytic activities towards the ROP of lactide is marginal. As we move from piperidinophenolate complex to diethylaminophenolate complex of a particular metal, we observe slight increase in activity which may be due to the higher *s* character of the N atom of the diethylamine side arm compared to the morpholine and piperidine side arm. As the *s* character and hence the electronegativity of the N atom increases, the lewis acidity of the metal center increases resulting in higher activity towards the ROP. However, the lewis acidic character of different metal center rather plays a bigger role towards the activity. The plot of M_n *vs*. % conversion for *rac*-LA polymerization using **4** and **7** is shown in Figure 8. The linear relationship of the plot suggests again a good degree of control in these polymerizations. The sigmoidal curves in the plot of % conversion of *rac*-LA using **4** and **7** against time suggest a high rate of polymer formation at the initial stage which approaches towards almost constant value with the progress of time (Figure S29, see ESI). We compared the polymerization results with our previous reports on iminophenoxide complexes and we observed a far better control in M_n and MWDs.[8f,8u-8v]

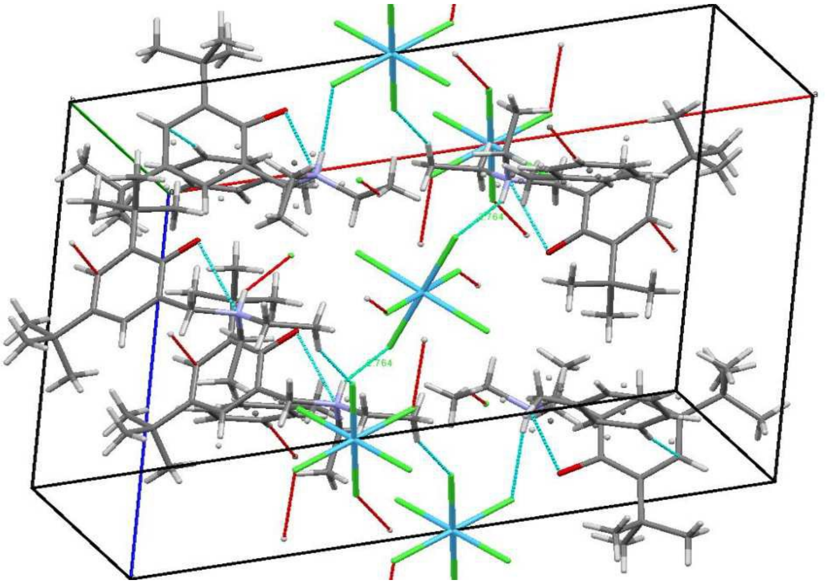


Figure 6. Unit cell crystal-packing of **7** showing NH^+---Cl hydrogen bonding

Table 1. Crystal data for the structures **1**, **4, 5** and **7**

Compounds	**1**	**$4\cdot C_7H_8$**	**5**	**$7\cdot 2C_7H_8$**
Molecular formula	$C_{19}H_{33}Cl_4NOTi$	$C_{28}H_{41}Cl_4N_2OZr$	$C_{21}H_{32}Cl_4N_2O_2Zr$	$C_{52}H_{82}Cl_6HfN_2O_2$
Formula weight	481.16	654.65	577.50	1158.38
T/K	173(2) K	298(2) K	293(2) K	296(2) K
Wavelength (Ǻ)	0.71073	0.71073	0.71073	0.71073
Crystal system, Space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a/Å	11.0722(3)	29.4978(15)	21.5507(13)	20.6487(9)
b/Å	22.8910(7)	11.1493(5)	11.4122(6)	10.3507(4)
c/Å	19.0774(6)	21.1407(9)	10.7699(6)	14.0719(7)
α (°)	90	90	90	90
β (°)	98.0330(10)	112.578(2)	95.411(2)	99.266(2)
γ (°)	90	90	90	90
V/Å^3	4787.8(2)	6419.9(5)	2637.0(3)	2968.3(2)
Z, Calculated density(Mg/ m^3)	8, 1.329	8, 1.355	4, 1.455	2, 1.296
Absorption coefficient (mm^{-1})	0.813	0.698	0.842	2.063
Reflections collected/Independent reflections	15513/5095	18939/5530	17245/5463	22537/5234
Data/restraints/parameters	5095/0/247	5530/6 /371	5463/0/287	5234/1/342
Goodness of fit on F^2	1.052	1.034	1.074	1.227
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0367$, $wR_2 = 0.0923$	$R_1 = 0.0415$, $wR_2 = 0.1146$	$R_1 = 0.0414$, $wR_2 = 0.0956$	$R_1 = 0.0358$, $wR_2 = 0.0887$
R indices (all data)	$R_1 = 0.0482$, $wR_2 = 0.0994$	$R_1 = 0.0517$, $wR_2 = 0.1238$	$R_1 = 0.0535$, $wR_2 = 0.1021$	$R_1 = 0.0503$, $wR_2 = 0.1122$

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

In the next segment, kinetics for the polymerization of *rac*-LA using **1** and **7** in the ratio $[rac\text{-LA}]_0/[\text{Cat}]_0 = 200$ at 140 °C were studied. These catalysts were chosen because the reactivity of **1** is comparatively more than others and high M_n polymers were obtained using **7**. The plot depicted in Figure 9 confirms first-order dependence of the rate of polymerization on the monomer concentration without induction period. The plot of $\ln[rac\text{-LA}]_0/[rac\text{-LA}]_t$ *vs*. time was found to be linear. The values of the apparent rate constant (k_{app}) were calculated from the slope of these lines and were found to be 0.119 min^{-1} and 0.103 min^{-1} for **1** and **7** respectively.

Table 2. Polymerization data for *rac*-LA and *L*-LA catalyzed by complexes **1-9** in 200:1 ratio at 140 °C

Entry	Cat.	LA	time^a (min)	Yield (%)	M_n(GPC)^b (kg/mol)	$M_n^{(\text{theoretical})c}$ (kg/mol)	TOF^d (min^{-1})	M_w/M_n	P_r^e
1	**1**	*rac*-LA	20	99	28.67	29.12	9.90	1.08	0.73
2	**2**	*rac*-LA	20	97	28.04	29.13	9.70	1.10	0.71
3	**3**	*rac*-LA	22	99	30.38	29.13	9.00	1.12	0.72
4	**4**	*rac*-LA	20	98	31.30	29.12	9.80	1.10	0.72
5	**5**	*rac*-LA	24	98	27.88	29.13	8.17	1.11	0.74
6	**6**	*rac*-LA	27	99	31.65	29.13	7.33	1.14	0.70
7	**7**	*rac*-LA	23	98	30.87	29.12	8.52	1.10	0.70
8	**8**	*rac*-LA	25	97	29.18	29.13	7.76	1.12	0.72
9	**9**	*rac*-LA	30	99	30.51	29.13	6.60	1.14	0.71
10	**1**	*L*-LA	16	98	32.05	29.12	12.25	1.17	
11	**2**	*L*-LA	17	98	28.44	29.13	11.53	1.07	
12	**3**	*L*-LA	20	98	30.27	29.13	9.80	1.08	
13	**4**	*L*-LA	16	97	33.25	29.12	12.13	1.07	
14	**5**	*L*-LA	20	99	33.76	29.13	9.90	1.11	
15	**6**	*L*-LA	25	99	29.50	29.13	7.92	1.10	
16	**7**	*L*-LA	20	97	30.68	29.12	9.70	1.09	
17	**8**	*L*-LA	25	98	32.34	29.13	7.84	1.10	
18	**9**	*L*-LA	28	99	30.96	29.13	7.07	1.12	

[a] Time of polymerization was measured by quenching the polymerization reaction when all the monomer were found to be consumed. [b] Measured by GPC at 27 ºC in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. [c] $M_n^{(\text{theoretical})}$ at 100% = $[M]_0/[C]_0$ × molecular weight of monomer + molecular weight of end group. [d] TOFs were calculated as (mol of LA consumed) / (mol of catalyst × time of polymerization). [e] The probability for heterotactic enchainment was calculated from homonuclear decoupled ^{1}H NMR spectrum.

Table 3. Polymerization data for *rac*-LA catalyzed by complexes **1**, **4** and **7** in different $[rac\text{-LA}]_0/[\text{Cat}]_0$ ratio at 140 °C

Entry	Cat.	$[rac\text{-LA}]_0/[\text{Cat}]_0$	time[a] (min)	Yield (%)	M_n(GPC)[b] (kg/mol)	$M_n^{(\text{theoretical})c}$ (kg/mol)	TOF[d] (min^{-1})	M_w/M_n	P_r^e
1	**1**	200/1	20	99	28.67	29.12	9.90	1.08	0.73
2	**1**	400/1	45	98	55.71	57.94	8.71	1.09	
3	**1**	800/1	80	98	112.90	115.60	9.80	1.11	
4	**4**	200/1	20	98	31.30	29.12	9.80	1.10	0.72
5	**4**	400/1	52	99	58.40	57.94	7.62	1.12	
6	**4**	800/1	84	98	109.33	115.60	9.33	1.12	
7	**7**	200/1	23	98	30.87	29.12	8.52	1.10	0.70
8	**7**	400/1	64	98	57.15	57.94	6.13	1.10	
9	**7**	800/1	90	98	113.47	115.60	8.71	1.13	

[a]Time of polymerization was measured by quenching the polymerization reaction when all the monomer were found to be consumed. [b]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. [c]$M_n^{(\text{theoretical})}$ at 100% = $[M]_0/[C]_0$ × molecular weight of monomer + molecular weight of end group. [d]TOFs were calculated as (mol of LA consumed) / (mol of catalyst × time of polymerization). [e]The probability for heterotactic enchainment was calculated from homonuclear decoupled ^{1}H NMR spectrum.

In order to have a clear understanding of the initiation of the ROP, low molecular weight (M_n) oligomer of *rac*-LA was prepared by reacting *rac*-LA with complex **1** in 10:1 ratio at 140 °C under solvent free condition. The residue was dissolved in minimum amount of CH_2Cl_2 and then poured into cold methanol. The oligomer was isolated and subjected to MALDI-TOF and ^{1}H NMR analysis. The ^{1}H NMR spectrum of purified PLA-1 (Figure S32, see ESI) shows that the oligomer is end capped with the aminophenolate ligand and one hydroxyl group. The MALDI-TOF mass spectrum of the oligomer contains all the peaks as Na adducts (Figure 10). The peaks are equally spaced by 72 a.u. and resemble a linear PLA bearing the ligand at the chain end. It is noted that intermolecular transesterification product was observed in the MALDI-TOF mass spectrum. The results depict that the ligand initiates the ROP.

Table 4. Polymerization data of *rac*-LA in presence of BnOH catalyzed by complexes **1**, **4** and **7** in 100:1:5 ratio at 140 °C

Entry	Cat.	LA	$[\text{LA}]_0/[\text{Cat}]_0/[\text{BnOH}]_0$	time[a] (min)	Yield (%)	M_n(GPC)[b] (kg/mol)	$M_n^{(\text{theoretical})c}$ (kg/mol)	TOF[d] (min^{-1})	M_w/M_n	P_r^e
1	**1**	*rac*-LA	100/0/5	-	-	-				
2	**1**	*rac*-LA	100/1/5	7	98	3.17	2.99	2.80	1.10	0.76
3	**2**	*rac*-LA	100/1/5	8	98	2.92	2.99	2.45	1.09	0.74
4	**4**	*rac*-LA	100/1/5	8	99	2.94	2.99	2.48	1.12	0.74
5	**5**	*rac*-LA	100/1/5	9	99	2.89	2.99	2.20	1.12	0.72
6	**7**	*rac*-LA	100/1/5	10	97	3.21	2.99	1.94	1.11	0.75
7	**1**	*L*-LA	100/1/5	6	98	3.05	2.99	3.27	1.09	
8	**2**	*L*-LA	100/1/5	7	99	2.88	2.99	2.83	1.07	
9	**4**	*L*-LA	100/1/5	7	99	3.18	2.99	2.83	1.10	
10	**7**	*L*-LA	100/1/5	8	97	3.12	2.99	2.43	1.12	

[a]Time of polymerization was measured by quenching the polymerization reaction when all the monomer were found to be consumed. [b]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. [c]$M_n^{(\text{theoretical})}$ at 100% = $[M]_0/[C]_0$ × molecular weight of monomer + molecular weight of end group. [d]TOFs were calculated as (mol of LA consumed) / (mol of catalyst × mol of BnOH × time of polymerization). [e]The probability for heterotactic enchainment was calculated from homonuclear decoupled ^{1}H NMR spectrum.

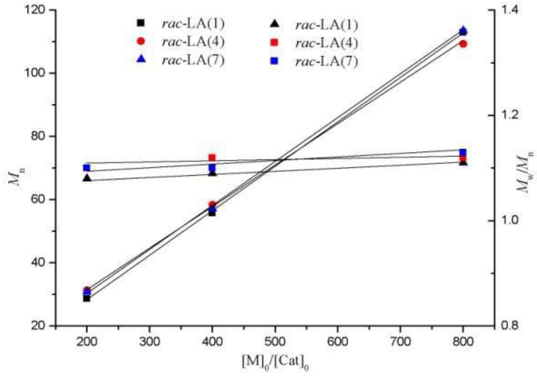


Figure 7. Plot of M_n and MWD *vs*. $[M]_0/[\text{Cat}]_0$ for *rac*-LA polymerization at 140 °C using **1**, **4** and **7**

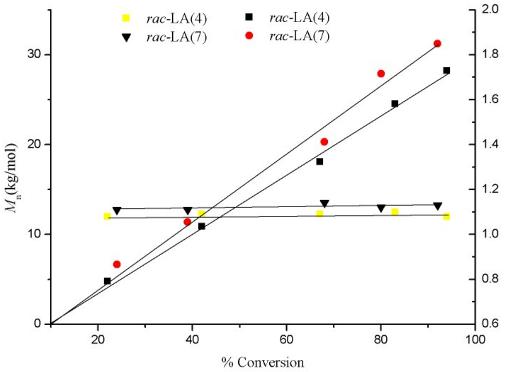


Figure 8. Plot of M_n and M_w/M_n *vs*. % conversion for *L*-LA and *rac*-LA polymerization at 140 °C using **4** and **7**

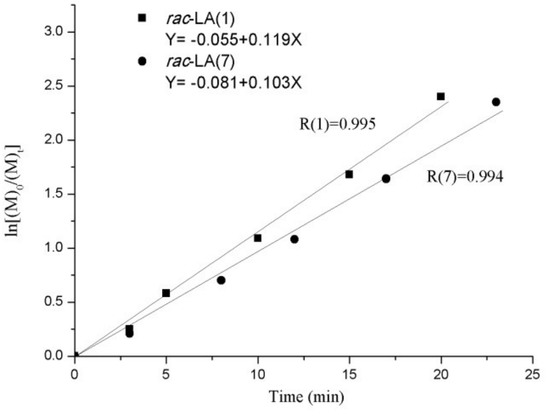
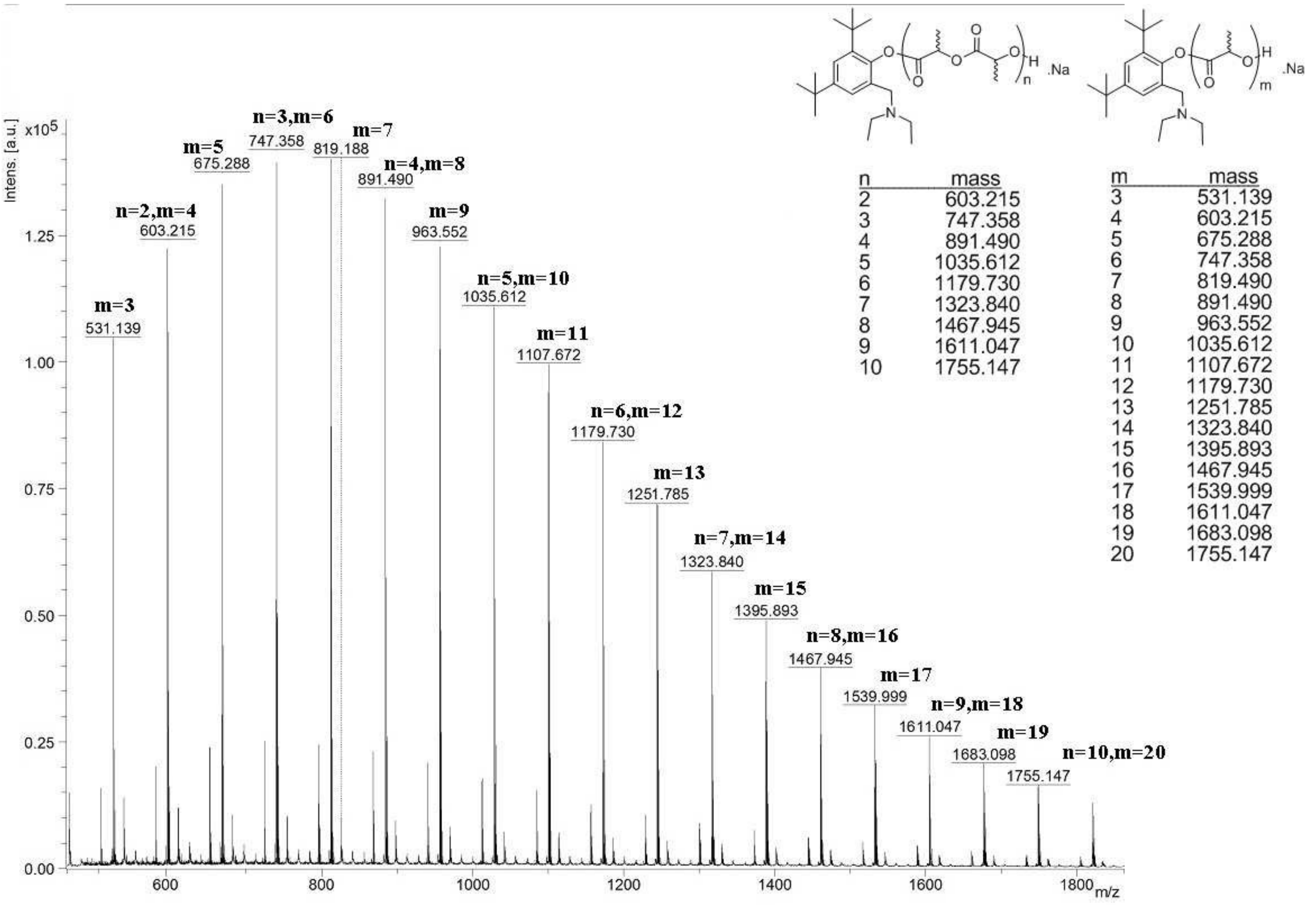


Figure 9. Semi-logarithmic plots of *rac*-LA, conversion in time initiated by **1** and **7**

In order to have a clear understanding of the charge distribution, the geometries of **1**, **4** and **5** were optimized first at B3LYP/LANL2DZ level. The actual and optimized bond lengths and bond angles obtained from X-ray crystallographic studies as well as theoretical calculations of the structures **1, 4** and **5** correlated well and are reported in Table S1. The slight variations in bond parameters are observed because single crystal X-ray structure were recorded in the solid state and DFT calculations belong to gaseous phase. The optimized geometries proved the labile nature of one metal-chlorine axial bond. More electronegative atoms always occupy the position having more *p* character. Hence, the axially placed atoms have higher Mulliken charges. But here we observed significantly higher charge distribution for one axial Cl atom (-0.337, -0.379 and -0.379 for **1**, **4** and **5** respectively) which may be due to the hydrogen bonding interaction with the NH$^+$ moiety (Figures 12 and S34-S35, see ESI).



n	mass
2	603.215
3	747.358
4	891.490
5	1035.612
6	1179.730
7	1323.840
8	1467.945
9	1611.047
10	1755.147

m	mass
3	531.139
4	603.215
5	675.288
6	747.358
7	819.490
8	891.490
9	963.552
10	1035.612
11	1107.672
12	1179.730
13	1251.785
14	1323.840
15	1395.893
16	1467.945
17	1539.999
18	1611.047
19	1683.098
20	1755.147

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

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

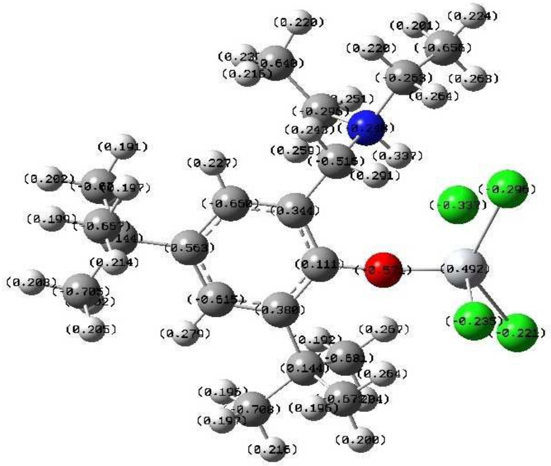


Figure 12. Mulliken net charges for the optimized geometry of **1**

Ethylene polymerization

The catalytic activity of the complexes **1-9** activated by MAO towards the polymerization of ethylene were tested. With MAO as co-catalyst, all the complexes exhibited moderate to good catalytic activity (Table 5). We performed blank polymerization of ethylene in absence of cocatalyst MAO and the catalysts were found to be inactive. In presence of MAO, the catalysts were activated to form the alkyl cationic complexes which propagated the polymeric chains.[26] The presence of bulky *tert*-butyl group at the *ortho* position of the phenoxy oxygen prevents the cocatalyst from coordination to the metal center. As a result of it, the cationic activated complex and anionic cocatalyst remain separated which expose more space for the ethylene monomers to coordinate to the metal center and insert into the carbon-metal bond, thereby resulting in higher activity of the complexes.[26d] As we move from Ti to Hf, the electrophilic character of the metal center decreases and hence the activity towards ethylene polymerization decreases.[26b] The plot of the activity *vs*. [MAO]/[C] ratio is depicted in Figure 13. Different solvents were used to understand the effect on activity and highest activity was observed in toluene (Figure S33, see ESI). Although good polymer yield was found for all the catalysts, the activities were lower than Fujita's catalysts.[19a]

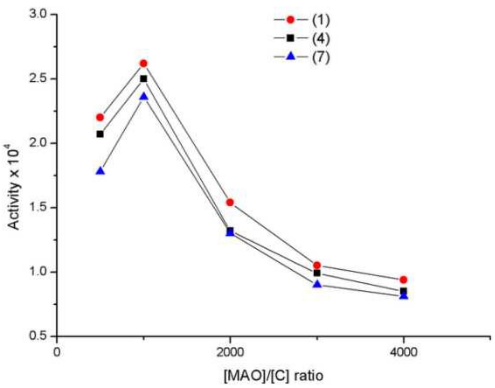


Figure 13. Plot of activity *vs* [MAO]/[C] ratio for **1**, **4** and **7** for ethylene polymerization

Table 5. Data for the Polymerization of ethylene catalyzed by complexes **1−9** with MAO

Entry	Catalyst	Activity[a]	Yield [b] (g)	M_n [c] (Kg/mol)	M_w/M_n
1	**MAO**	-	-	-	
2	**1**	2.62	1.31	48.62	1.87
3	**2**	2.64	1.32	47.19	1.94
4	**3**	2.57	1.28	47.08	1.91
5	**4**	2.50	1.25	45.38	2.04
6	**5**	2.54	1.27	47.34	2.11
7	**6**	2.44	1.22	45.91	2.05
8	**7**	2.36	1.18	45.28	1.94
9	**8**	2.40	1.20	43.73	2.04
10	**9**	2.48	1.24	44.15	2.12

All experiments were done in toluene at MAO:catalyst ratio = 1000, unless otherwise indicated. Ethylene pressure = 8 atm, 80 °C for 30 min, catalyst = 0.104 mmol, solvent = 45 mL. [a]Activity = Activity in (g PE/mol cat ×h) $\times 10^4$. [b]g of PE obtained after 30 min. [c]Determined by GPC in 1,2,4- $C_6Cl_3H_3$ *vs*. narrow polystyrene standards.

Conclusion

In summary, we have synthesized a series of zwitterionic group 4 metal chloride complexes based on aminophenol ligands and characterized those using various spectroscopic techniques. The single crystal X-ray diffraction studies showed that the zwitterionic molecules are stabilised by moderate to weak electrostatic hydrogen bonding interactions. The complexes were proved to be potent catalysts for the ROP of lactides and gave much better results in terms of control of number average molecular weights (M_n) and molecular weight distributions (MWDs) under solvent free condition than our previous report on the iminophenoxide complexes based on group 4 metal alkoxides[8f,8u-v]. Titanium complexes were found to be more active than zirconium and hafnium complexes. The observed number average molecular weights (M_n) are in close proximity to the theoretical values with narrow MWDs. MALDI-TOF and ^{1}H NMR spectra reveals that the poly(lactic acid) is end capped with the ligand. Using methylaluminoxane (MAO) as cocatalyst, the complexes were found to be moderately active for ethylene polymerization.

Experimental

Materials and general details

All reactions and manipulations were carried out under argon atmosphere using either standard schlenk or glove box techniques. The solvents were freshly distilled from suitable drying agent (toluene over sodium/benzophenone and CH_3CN over calcium hydride) and degassed prior to use. *rac*-LA, *L*-LA, $CDCl_3$ for NMR studies were purchased from Aldrich and. *rac*-LA and *L*-LA were purified by sublimation twice whereas $CDCl_3$ were dried over calcium hydride followed by distillation before use. All chemicals needed for the preparation of ligands, $TiCl_4$ in 1.0 M CH_2Cl_2, $ZrCl_4$, $HfCl_4$ were purchased from Aldrich and used as such without any further purification. The ligands **L1**-**L3** were synthesized according to the standard literature procedures[21] and purified by azeotropic distillation prior to use. All ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz Bruker Avance with chemical shifts given in parts per million (ppm). ESI-MS spectra of the compounds were performed using Waters Q-TOF micro mass spectrometer. Elemental analyses were performed using Perkin Elmer Series 11 analyzer. MALDI-TOF of oligomer sample was performed on a Bruker Daltonics instrument using dihydroxybenzoic acid matrix. Molecular weights and the polydispersity indices of the polymer samples obtained by the ring opening polymerization of lactide monomers were determined by using 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 (7.8×300 mm) were connected in series. Measurements were done in THF at 27 °C. In case of ethylene samples, number average molecular weights (M_n) and MWDs were determined by GPC instrument with Waters 510 pump and Waters 2414 differential refractometer as the detector. The column namely WATERS STRYGEL-HR4 of dimensions (4.6×300 mm) was connected during the experiment. Measurements were done in tri-chloro benzene. Number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) (MWDs) of polymers were measured relative to polystyrene standards.

Preparation of 1-9

The general procedure for the preparation of **1-9** is given below.

To a stirred solution of **L1**- **L3** (0.10 mmol) in 10 mL of dry toluene was added a solution of metal chloride (0.10 mmol) in 5 mL of chloroform in 1:1 ratio at -24 °C in an argon filled glove box. The solution was allowed to come to room temperature. The reaction mixture started becoming turbid over a period of 1-2 hours and the colour changed to brown-red in case of Ti complexes and pale white for Zr and Hf complexes. The solution was stirred for an additional 24 hours after which the solvent was removed under reduced pressure to give complexes **1-9**.

Complex 1. The resultant brown-red solid was crystallized from a 1:1 mixture of chloroform and toluene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.17-1.21 (m, 6H, $-CH_2CH_3$), 1.38 (s, 9H, $-C(CH_3)_3$), 1.52 (s, 9H, $-C(CH_3)_3$), 3.14-3.21 (m, 2H, $-C(H)HCH_3$), 3.38-3.45 (m, 2H, $-C(H)HCH_3$), 4.43 (s, 2H, Ar-CH_2), 6.92-6.93 (m, 1H, Ar-*H*), 7.39-7.40 (m, 1H, Ar-*H*), 8.75 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 18.7, 31.8, 34.0, 36.3, 37.2, 47.8, 60.7, 120.9, 124.4, 124.6, 137.7, 156.9. ESI *m/z* calculated for $[M-Cl]^+$. $C_{19}H_{33}Cl_3NOTi$: 445.70, found 444.10. Anal. Calc. for $C_{19}H_{33}Cl_4NOTi$: C, 47.43; H, 6.91; N, 2.91; found C, 47.02; H, 7.01; N, 2.95.

Complex 2. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.28 (s, 9H, $-C(CH_3)_3$), 1.42 (s, 9H, $-C(CH_3)_3$), 3.38 (m, 2H, $-NC(H)HCH_2$), 3.61 (m, 2H, $-NC(H)HCH_2$), 4.44 (s, 2H, Ar-CH_2), 4.54 (m, 4H, $-OCH_2CH_2$), 6.84-6.85 (m, 1H, Ar-*H*), 7.22-7.23 (m, 1H, Ar-*H*), 8.50 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 30.2, 32.1, 35.3, 37.0, 36.8, 56.8, 66.8, 69.2, 122.4, 123.9, 124.2, 138.5, 144.9, 156.6. ESI *m/z* calculated for $[M+H]^+$. $C_{19}H_{32}Cl_4NO_2Ti$: 496.13, found 495.15. Anal. Calc. for $C_{19}H_{31}Cl_4NO_2Ti$: C, 46.09; H, 6.31; N, 2.83; found C, 46.28; H, 6.14; N, 2.79.

Complex 3. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.35 (s, 9H, $-C(CH_3)_3$), 1.51 (s, 9H, $-C(CH_3)_3$), 1.56 (m, 2H, $-CH_2CH_2CH_2$), 1.64-1.70 (m, 4H, $-CH_2CH_2CH_2$), 3.38 (m, 4H, $-NCH_2CH_2$), 4.40 (s, 2H, Ar-CH_2), 6.90-6.91 (m, 1H, Ar-*H*), 7.21-7.22 (m, 1H, Ar-*H*), 8.34 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 25.1, 26.6, 30.3, 33.7, 36.7, 36.8, 56.9, 67.1, 123.4, 125.9, 126.9, 138.5, 144.6, 156.8. ESI *m/z* calculated for $[M]^+$. $C_{20}H_{33}Cl_4NOTi$: 493.16, found 493.90. Anal. Calc. for $C_{20}H_{33}Cl_4NOTi$: C, 48.71; H, 6.74; N, 2.84; found C, 48.58; H, 6.77; N, 2.91.

Complex 4. The resultant pale white solid was crystallized from a 1:1 mixture of CH_3CN and toluene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.09-1.12 (m, 6H, $-CH_2CH_3$), 1.37 (s, 9H, $-C(CH_3)_3$), 1.49 (s, 9H, $-C(CH_3)_3$), 3.15-3.20 (m, 2H, $-C(H)HCH_3$), 3.36-3.42 (m, 2H, $-C(H)HCH_3$), 4.42 (s, 2H, Ar-CH_2), 6.82-6.83 (m, 1H, Ar-*H*), 7.25-7.26 (m, 1H, Ar-*H*), 8.27 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 17.7, 29.5, 31.7, 34.1, 34.8, 47.5, 59.2, 121.6, 122.3, 123.2, 135.2, 139.9, 155.1. ESI *m/z* calculated for $[M+CH_3CN]^+$. $C_{21}H_{36}Cl_4N_2OZr$: 564.51, found 563.9. Anal. Calc. for $C_{19}H_{33}Cl_4NOZr$: C, 43.51; H, 6.34; N, 2.67; found C, 43.58; H, 6.77; N, 2.72.

Complex 5. The resultant pale white solid was crystallized from a 1:1 mixture of acetonitrile and toluene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.26 (s, 9H, $-C(CH_3)_3$), 1.40 (s, 9H, $-C(CH_3)_3$), 3.32 (m, 2H, $-NC(H)HCH_2$), 3.49 (m, 2H, $-NC(H)HCH_2$), 4.28 (s, 2H, Ar-CH_2), 4.41 (m, 4H, $-OCH_2CH_2$), 6.84-6.85 (m, 1H, Ar-*H*), 7.23-7.24 (m, 1H, Ar-*H*), 8.28 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 29.9, 32.1, 34.9, 35.3, 53.2, 63.1, 67.3, 120.5, 123.6, 124.1, 136.1, 141.2, 154.4. ESI *m/z* calculated for $[M+CH_3CN]^+$. $C_{21}H_{35}Cl_4N_2O_2Zr$: 578.49, found 577.13. Anal. Calc. for $C_{19}H_{31}Cl_4NO_2Zr$: C, 42.38; H, 5.80; N, 2.60; found C, 42.94; H, 5.26; N, 2.90.

Complex 6. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.29 (s, 9H, $-C(CH_3)_3$), 1.43 (s, 9H, $-C(CH_3)_3$), 1.53 (m, 2H, $-CH_2CH_2CH_2$), 1.60-1.66 (m, 4H, $-CH_2CH_2CH_2$), 3.25 (m, 4H, $-NCH_2CH_2$), 4.37 (s, 2H, Ar-CH_2), 6.81-6.82 (m, 1H, Ar-*H*), 7.20-7.21 (m, 1H, Ar-*H*), 8.31 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ

= 27.1, 29.8, 32.6, 34.7, 37.1, 38.8, 56.7, 66.9, 121.0, 122.6, 123.3, 135.4, 140.2, 154.5. ESI *m/z* calculated for $[M+CH_3CN]^+$. $C_{22}H_{36}Cl_4N_2OZr$ 576.52, found 576.14. Anal. Calc. for $C_{20}H_{33}Cl_4NOZr$: C, 44.77; H, 6.20; N, 2.61; found C, 44.82; H, 6.14; N, 2.67.

Complex 7. The resultant pale white solid was crystallized from a 1:1 mixture of chloroform and toluene. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.27 (m, 6H, -CH_2CH_3), 1.39 (s, 9H, -C(CH_3)$_3$), 1.59 (s, 9H, -C(CH_3)$_3$), 3.11 (m, 2H, -C(*H*)HCH_3), 3.40 (m, 2H, -C(H)*H*CH_3), 4.41 (s, 2H, Ar-CH_2), 7.00 (m, 1H, Ar-*H*), 7.38 (m, 1H, Ar-*H*), 8.16 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 17.3, 26.9, 30.6, 32.9, 34.6, 46.1, 55.4, 126.3, 126.7, 127.1, 133.2, 138.3, 152.9. ESI *m/z* calculated for $[M–HfCl_6]^+$. $C_{19}H_{33}NO$: 291.26, found 291.34. Anal. Calc. for $C_{38}H_{66}Cl_6HfN_2O_2$: C, 46.85; H, 6.83; N, 2.88; found C, 47.51; H, 6.97; N, 3.04.

Complex 8. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.25 (s, 9H, -C(CH_3)$_3$), 1.41 (s, 9H, -C(CH_3)$_3$), 3.26 (m, 2H, -NC(*H*)HCH_2), 3.46 (m, 2H, -NC(H)*H*CH_2), 4.28 (s, 2H, Ar-CH_2), 4.41 (m, 4H, -OCH_2CH_2), 6.80-6.81 (m, 1H, Ar-*H*), 7.20-7.21 (m, 1H, Ar-*H*), 8.026 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 29.6, 31.7, 33.5, 34.9, 52.8, 62.6, 66.8, 120.1, 123.2, 123.6, 135.6, 140.8, 153.9. ESI *m/z* calculated for $[M–HfCl_6]^+$. $C_{19}H_{31}NO_2$: 305.23; found 306.91. Anal. Calc. for $C_{38}H_{62}Cl_6HfN_2O_4$: C, 45.54; H, 6.24; N, 2.80; found C, 46.21; H, 6.85; N, 2.72.

Complex 9. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.28 (s, 9H, -C(CH_3)$_3$), 1.48 (s, 9H, -C(CH_3)$_3$), 1.59 (m, 2H, -$CH_2CH_2CH_2$), 1.60-1.65 (m, 4H, -$CH_2CH_2CH_2$), 3.23 (m, 4H, -NCH_2CH_2), 4.31 (s, 2H, Ar-CH_2), 6.64-6.65 (m, 1H, Ar-*H*), 6.97-6.98 (m, 1H, Ar-*H*), 8.28 (s, 1H, N*H*-CH_2). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 26.0, 27.0, 30.4, 31.6, 34.7, 35.4, 54.9, 65.1, 121.9, 124.1, 125.5, 135.5, 140.6, 154.5. ESI *m/z* calculated for $[M–HfCl_6]^+$. $C_{20}H_{33}NO$: 303.26; found 303.92. Anal. Calc. for $C_{40}H_{66}Cl_6HfN_2O_2$: C, 48.13; H, 6.66; N, 2.81; found C, 47.66; H, 6.29; N, 2.68.

X-ray crystallography

Single crystals of the metal complexes were obtained for X-ray structural determination by crystallization from a 1:1 mixture of toluene and acetonitrile. In each case, suitable crystal of proper size was selected from mother liquor and mounted on Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with 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 were 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 to Lorentz and polarization corrections using SAINT-NT. The data set was subjected to multi-scan absorption. All structures were solved using SIR-92 and refined using SHELXL-97.[27] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. These data were deposited with CCDC with the following CCDC numbers: 1050370 (**1**), 1050371 (**4**), 1050372(**5**) and 1050373 (**7**).

General procedure for the polymerization of *rac*-LA and *L*-LA

The polymerizations were performed under solvent free condition by heating the monomer and the catalyst in a closed glass vessel to 140 °C for a period of time by which the melt had become viscous. Here, 0.25 g of *rac*-LA or *L*-LA and 8.67 μmol of the desired catalyst were introduced in 200:1 ratio into a dry reaction vessel equipped with a magnetic stirrer bar. After the reaction time, the reaction mixture was dissolved in dichloromethane and then poured into cold methanol. The polymers thus precipitated were dried to a constant weight. The conversion yield of *rac*-LA and *L*-LA were analyzed by ^{1}H NMR spectroscopic studies. Number average molecular weight (M_n) and M_w/M_n (MWDs) were determined by GPC measurements.

General procedure for ethylene polymerization

A 100 mL container made of stainless steel was charged under argon atmosphere with 45 mL of freshly distilled toluene and 0.104 mmol of **1-9** along with the required amount of MAO to activate the catalyst. The polymerizations were performed in high pressure autoclave reactor with mechanical stirring. Subsequently the autoclave was heated up to 80 °C and the ethylene gas was bubbled for 30 min through the reactor inlet. The polymerization was quenched with acidic methanol. The resultant polymer was filtered and dried until constant weight was achieved.

General procedure for kinetic studies of lactides

For the kinetic studies, the polymerizations of *rac*-LA using **1** and **7** were carried out in 200:1 ratio at 140 °C. 0.035 mmol of **1** or **7** was added to 1 g of monomer in a sealed tube under argon atmosphere. The contents were stirred and immersed in a bath at 140 °C. 0.2 mL aliquots were taken out at appropriate interval of time from the reaction mixture and analyzed by ^{1}H NMR. The $[rac\text{-LA}]_0/[\,rac\text{-LA}]_t$ ratio was calculated by integration of the peak corresponding to the methine proton for the monomer and polymer. Apparent rate constant (k_{app}) were obtained from the slopes of the best-fit lines.

Computational details

The molecular geometry optimizations were performed by using GAUSSIAN 09 (Rev C.01) package of quantum chemical programs. The calculations employed B3LYP method, a version of the DFT method which uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) and LANL2DZ basis set.[28]

Acknowledgements

The authors are grateful to the Department of Science and Technology, New Delhi for funding this work. SKR thanks the University Grants Commission, New Delhi for a research fellowship.

Notes and references

[a] *Department of Chemistry, Indian Institute of Technology Patna, Patna-800 013, Bihar, India. Fax: +91 612 2277383; Tel: +91 612 2552171; E-mail: dc@iitp.ac.in, debashis.iitp@gmail.com*
[b] *Department of Chemistry, Indian Institute of Technology Madras, Chennai- 600 036, Tamil Nadu, India.*

† Electronic Supplementary Information (ESI) available: Crystallographic data for the structural analysis of complexes **1**, **4**, **5** and **7** have been deposited at the Cambridge Crystallographic Data Center (CCDC). CCDC 1050370-1050373. See DOI: 10.1039/b000000x/

1) (*a*) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147-6176; (*b*) F. D. Monica, E. Luciano, G. Roviello, A. Grassi, S. Milione and C.Capacchione, *Macromolecules*, 2014, **47,** 2830-2841; (*c*) F. E. Kohn, J. G. V. Ommen and J. Feijen, *Eur. Polym. J.*, 1983, **19**, 1081-1088.
2) *(a)* 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; *(b)* R. H. Platel, L.M. Hodgson and C.K. Williams, *Polymer Reviews*, 2008, **48,** 11-63; *(c)* R. Langer, *Acc. Chem. Res.*, 2000, **33,** 94-101; *(d)* A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Jr. Fredrick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489.
3) Z. Zhong, P. J. Dijkstra and J. Feijen, *Angew. Chem. Int. Ed.*, 2002, **41**, 4510-4513.
4) *(a)* R. G. Sinclair, *Pure Appl. Chem.*, 1996, **A33**, 585-597; *(b)* Y. Sun, L. Wang, D. Yu, N. Tang and J. Wu, *Journal of Molecular Catalysis A: Chemical*, 2014, **393**, 175-181; *(c)* C. T. Altaf, H. Wang, M. Keram, Y. Yang and H. Ma, *Polyhedron*, 2014, **81**, 11-20; *(d)* J. C. Middleton and A. J. Tipton, *Biomaterials*, 2000, **21**, 2335-2346; *(e)* Y. Ikada and H. Tsuji, *Macromol. Rapid Commun.*, 2000, **21**, 117-132; *(f)* W. Amass, A. Amass and B. Tighe, *Polym. Int.*, 1998, **47**, 89-144; *(g)* E. Chiellini and R.Solaro, *Adv. Mater.*, 1996, **8**, 305-313.
5) *(a)* A. Amgoune, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Chem. Eur. J.*, 2006, **12,** 169-179. *(b)* C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, 4832–4846. *(c)* R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11–63. *(d)* N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer and J. L. Hedrick, *Chem. Rev.*, 2007, **107**, 5813–5840. *(e)* J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602–626.
6) A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007-9023.
7) *(a)* J. P. Davin, J. C. Buffet, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2012, **41**, 12612-12618; *(b)* H.-Y. Tang, H.-Y. Chen, J.-H. Huang and C.-C. Lin, *Macromolecules*, 2007, **40**, 8855-8860; *(c)* C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, **25**, 4832-4846; *(d)* L. Wang and H. Ma, *Macromolecules*, 2010, **43**, 6535-6537; *(e)* M. H. Chisholm, J. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2002, **41**, 2785-2794; *(f)* H. R. Kricheldorf, M. Berl and N. Scharnagl, *Macromolecules*, 1988, **21**, 286-293.
8) *(a)* D. Chakraborty, D. Mandal, V. Ramkumar, V. Subramanian and J. V. Sundar, *Polymer*, 2015, **56**, 157-170; *(b)* Z. R. Turner, J.-C. Buffet and D. O'Hare, *Organometallics*, 2014, **33**, 3891-3903; *(c)* A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, *Inorg. Chem.*, 2014, **53**, 9140-9150; *(d)* T. R. Forder, M. F. Mahon, M. G. Davidson, T. Woodman and M. D. Jones, *Dalton Trans.*, 2014, **43**, 12095-12099; *(e)* H.-W. Ou, H.-Y. Chen, H.-C. Tseng, M.-W. Hsiao, Y.-L. Chang, N.-Y. Jheng, Y.-C. Lai, T.-Y. Shih and Y.-T. Lin, Chen, H.-Y. *J. Mol. Catal. A: Chem.*, 2014, **394**, 97-104; *(f)* T. K. Saha, B. Rajashekhar and D. Chakraborty, *RSC Adv.*, 2012, **2**, 307-318; *(g)* 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; *(h)* F. D. Monica, E. Luciano, G. Roviello, A. Grassi, S. Milione and C. Capacchione, *Macromolecules*, 2014, **47**, 2830-2841; *(i)* A. J. Chmura, D. M. Cousins, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2008, **11**, 1437-1443; *(j)* E. L. Whitelaw, M. D. Jones, M. F. Mahon and G. Kociok-Köhn, *Dalton Trans.*, 2009, **41**, 9020-9025; *(k)* S. L. Hancock, M. F. Mahon and M. D. Jones, *Dalton Trans.*, 2011, **40**, 2033-2037; *(l)* M. D. Jones, S. L. Hancock, P. McKeown, P. M. Schäfer, A. Buchard, L. H. Thomas, M. F. Mahon and J. P. Lowe, *Chem. Commun.* 2014, **50**, 15967-15970; *(m)* E. L. Whitelaw, M. D. Jones and M. F. Mahon, *Inorg. Chem.*, 2010, **49**, 7176-7181; *(n)* M. D. Jones, M. G. Davidson and G. Kociok-Köhn, *Polyhedron*, 2010, **29**, 697-700; *(o)* R. R. Gowda, D. Chakraborty and V. Ramkumar, *Polymer*, 2010, **51**, 4750-4759; *(p)* J.-C. Buffet, A. N. Martin, M. Kol and J. Okuda, *Polym. chem.*, 2011, **2**, 2378-2384; *(q)* J.-C. Buffet and J. Okuda, *Chem. Commun.* 2011, **47**, 4796-4798; *(r)* Y. Takashima, Y. Nakayama, K. Watanabe, T. Itono, N. Ueyama, A. Nakamura, H. Yasuda, A. Harada and J. Okuda, *Macromolecules*, 2002, **35**, 7538-7544. *(s)* B. Gao, Q. Duan, Y. Li, D. Li, L. Zhang, Y. Cui, N. Hu and X. Pang, RSC Adv., 2015, 5, 13437-13442; *(t)* H.-W. Ou, M. Y. Chiang, J. K. Vandavasi, W.-Y. Lu, Y.-J. Chen, H.-C. Tseng, Y.-C. Lai and H.-Y. Chen, RSC Adv., 2015, 5, 477-484. (u) T. K. Saha, M. Mandal, D. Chakraborty and V. Ramkumar, *New J. Chem.*, 2013, **37**, 949-960; *(v)* T. K. Saha, B. Rajashekhar, R. R. Gowda, V. Ramkumar and D. Chakraborty, *Dalton Trans.*, 2010, **39**, 5091-5093.
9) *(a)* Z. Zhong, P. J. Dijkstra and J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291-11298; *(b)* D. Chakraborty and E. Y. X. Chen, *Organometallics*, 2002, **21**, 1438-1442; *(c)* M.-L. Hsueh, B.-H. Huang and C.-C. Lin, *Macromolecules*, 2002, **35**, 5763-5768; *(d)* D. J. Darensbourg and O. Karroonnirun, *Organometallics*, 2010, **29**, 5627-5634; *(e)* C.-Y. Li, D.-C. Liu and B.-T. Ko, *Dalton Trans.*, 2013, **42**, 11488-11496; *(f)* X.-F. Yu and Z.-X. Wang, *Dalton Trans.*, 2013, **42**, 3860-3868; *(g)* K. Majerska and A. Duda, *J. Am. Chem. Soc.*, 2004, **126**, 1026-1027; *(h)* Y.-C. Liu, B.-T. Ko and C.-C. Lin, *Macromolecules*, 2001, **34**, 6196-6201; *(i)* N. Nomura, R. Ishii, M. Akakura and K. Aoi, *J. Am. Chem. Soc.*, 2002, **124**, 5938-5939; *(j)* Z.-Y. Chai, C. Zhang and Z.-X. Wang, *Organometallics*, 2008, **27**, 1626-1633; *(k)* C. P. Radano, G. L. Baker and M. R. Smith, *J. Am.Chem. Soc.*, 2000, **122**, 1552-1553; *(l)* T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 1316-1326; *(m)* 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.
10) *(a)* G. Schwach, J. Coudane, R. Engel and M. Vert, *Polym. Int.*, 1998, **46**, 177-182; *(b)* W.-C. Hung, Y. Huang and C.-C. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6466-6476; *(c)* C.M. Silvernail, L. J. Yao, L. M. R. Hill, M. A. Hillmyer and W. B. Tolman, *Inorg. Chem.*, 2007, **46**, 6565-6574; *(d)* C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2003, **125**, 11350-11359; *(e)* D. J. Darensbourg and O. Karroonnirun, *Inorg. Chem.*, 2010, **49**, 2360-2371; *(f)* B.-H. Huang, C.-N. Lin, M.-L. Hsueh, T. Athar and C.-C. Lin, *Polymer*, 2006, **47**, 6622-6629; *(g)* S. Abbina and G. Du, *ACS Macro Lett.*, 2014, **3**, 689-692; *(h)* M. H. Chisholm, J. C. Gallucci and H. Zhen, *Inorg. Chem.*, 2001, **40**, 5051-5054; *(i)* M. Bero, J. Kasperczyk and G. Adamus, *Makromol. Chem.*, 1993, **194**, 907-912; *(j)* H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Macromolecules*, 2006, **39**, 3745-3752; *(k)* Y.-L. Hsieh, Y.-C. Lin, G.-H. Lee and C.-H. Peng, *Polymer*, 2015, **56**, 237-244; *(l)* K. S. Kwon, S. Nayab and J. H. Jeong, *Polyhedron*, 2015, **85**, 615-620.
11) *(a)* B. M. Chamberlain, Y. Sun, J. R. Hagadorn, E. W. Hemmesch, V. G. Jr. Young, M. Pink, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 1999, **32**, 2400-2402; (b) W. Li, Z. Zhang, Y. Yao, Y. Zhang and Q. Shen, *Organometallics*, 2012, **31**, 3499-3511; *(c)* M. Sinenkov, E. Kirillov, T. Roisnel, G. Fukin, A. Trifonov and J. F. Carpentier, *Organometallics*, 2011, **30**, 5509-5523; *(d)* H. Y. Ma and J. Okuda, *Macromolecules*, 2005, **38**, 2665-2673; *(e)* Z. J. Zhang, X. P. Xu, W. Y. Li, Y. M. Yao, Y. Zhang, Q. Shen and Y. J. Luo, *Inorg. Chem.*, 2009, **48**, 5715-5724; *(f)* Y. Luo, W. Li, D. Lin, Y. Yao, Y. Zhang and Q. Shen, *Organometallics*, 2010, **29**, 3507-3514; *(g)* I. Peckermann, A. Kapelski, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2009, **48**, 5526-5534; *(h)* J.-C. Buffet and J. Okuda, *Dalton Trans.*, 2011, **40**, 7748-7754; *(i)* B. M. Chamberlain, B. A. Jazdzewski, M. Pink, M. A. Hillmyer and W. B. Tolman, Macromolecules, 2000, 33, 3970-3977; *(j)* K. B. Aubrecht, K. Chang, M. A. Hillmyer and W. B. J. Tolman, Polym. Sci., Part A: Polym.Chem., 2001, 39, 284-293; *(k)*

H. Y. Ma, T. P. Spaniol and J. Okuda, Inorg. Chem., 2008, 47, 3328-3339.

12) *(a)* B. Guillerm, V. Lemaur, J. Cornil, R. Lazzaroni, P. Dubois and O. Coulembier, *Chem. Commun.*, 2014, **50**, 10098-10101.

13) *(a)* R. Stephen, R. B. Sunoj and P. Ghosh, *Dalton Trans.*, 2011, **40**, 10156-10161; *(b)* M. Zhang, X. Ni and Z. Shen, *Organometallics*, 2014, **33**, 6861-6867; *(c)* E. Brulé, V. Guérineau, P. Vermaut, F. Prima, J. Balogh, L. Maron, A. M. Z. Slawin, S. P. Nolan and C. P. Thomas, *Polym. Chem.*, 2013, **4**, 2414-2423; *(d)* E. Kim, J. Jhang and J. S. Chung, *Macromol. Res.*, 2014, **22**, 864-869; *(e)* J. Raynaud, C. Absalon, Y. Gnanou and D. Taton, *J. Am. Chem. Soc.*, 2009, **131**, 3201-3209; *(f)* H. A. Brown, S. Xiong, G. A. Medvedev, Y. A. Chang, M. M. Abu-Omar, J. M. Caruthers and R. M. Waymouth, *Macromolecules*, 2014, **47**, 2955-2963; *(g)* A. K. Acharya, Y. A. Chang, G. O. Jones, J. E. Rice, J. L. Hedrick, H. W. Horn and R. M. Waymouth, *J. Phys. Chem. B*, 2014, **118**, 6553-6560; *(h)* M. Fèvre, J. Vignolle and D. Taton, *Polym. Chem.*, 2013, **4**, 1995-2003.

14) *(a)* I. El-Zoghbi, T. J. J. Whitehorne and F. Schaper, *Dalton Trans.*, 2013, **42**, 9376-9387; *(b)* A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White, D. J. Williams, Chem. Commun. 2001, 283 –284; *(c)* A. P. Dove, V. C. Gibson, E. L. Marshall, H. S. Rzepa, A. J. P. White, D. J. Williams, J. Am. Chem. Soc. 2006, 128, 9834 –9843.

15) *(a)* 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; *(b)* S. H. Kim, J. Lee, D. J. Kim, J. H. Moon, S. Yoon, H. J. Oh, Y. Do, Y. S. Ko, J.-H. Yim and Y. Kim, *J. Organomet. Chem.*, 2009, **694**, 3409-3417; *(c)* M. D. Jones, M. G. Davidson and G. Kociok-Köhn, *Polyhedron*, 2010, **29**, 697-700; *(d)* S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt and M. Kol, *Inorg. Chem.*, 2006, **45**, 4783-4790; *(e)* S. L. Hancock, M. F. Mahon, G. Kociok-Köhn and M. D. Jones, *Eur. J. Inorg. Chem.*, 2011, 4596-4602; *(f)* T. K. Saha, D. Chakraborty and V. Ramkumar, *Inorg. Chem.*, 2011, **50**, 2720-2722; *(g)* R. C. J. Atkinson, K. Gerry, V. C. Gibson, N. J. Long, E. L. Marshall and L. J. West, *Organometallics*, 2007, **26**, 316-320; *(h)* J. Lee, Y. Kim and Y. Do, *Inorg. Chem.*, 2007, **46**, 7701-7703.

16) *(a)* C.-K. Su, H.-J. Chuang, C.-Y. Li, C.-Y. Yu, B.-T. Ko, J.-D. Chen and M.-J. Chen, *Organometallics*, 2014, **33**, 7091-7100; *(b)* H.-J. Chuang and B.-T. Ko, *Dalton Trans.*, 2015, **44**, 598-607; *(c)* H.-J. Chuang, B.-H. Wu, C.-Y. Li and B.-T. Ko, *Eur. J. Inorg. Chem.*, 2014, **2014**, 1239-1248; *(d)* 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; *(e)* S. Pappuru, E. R. Chokkapu, D. Chakraborty and V. Ramkumar, *Dalton Trans.*, 2013, **42**, 10304-10314.

17) *(a)* H. Sinn, W. Kaminsky, H.-J. Vollmer and R. Woldt, *Angew. Chem.,Int. Ed. Engl.*, 1980, **19**, 390-392; *(b)* X. Wang, R. Fröhlich, C. G. Daniliuc, B. Rieger and A. Jonovic, *Organometallics*, 2012, **31**, 6741-6752; *(c)* L. Postigo, A. B. Vásquez, J. Sánchez-Nieves, P. Royo and E. Herdtweck, *Organometallics*, 2008, **27**, 5588-5597; *(d)* P. J. Shapiro, F. Jiang, X. Jin, B. Twamley, J. T. Patton and A. L. Rheingold, *Eur. J. Inorg. Chem.*, 2004, 3370-3378; *(e)* J. J. Eisch and P. O. Otieno, *Eur. J. Org. Chem.*, 2004, 3269-3276; *(f)* Y. H. Kim, T. H. Kim, N. Y. Kim, E. S. Cho, B. Y. Lee, D. M. Shin and Y. K. Chung, *Organometallics*, 2003, **22**, 1503-1511; *(g)* C. C. Lu and J. C. Peters, *J. Am. Chem. Soc.*, 2002, **124**, 5272-5273.

18) *(a)* S. V. Kulangara, A. Jabri, Y. Yang, I. Korobkov, S. Gambarotta and R. Duchateau, *Organometallics*, 2012, **31**, 6085-6094.

19) (a) K. Kawai and T. Fujita, *Top. Organomet. Chem.*, 2009, **26**, 3–46; (b) H. Makio, N. Kashiwa and T. Fujita, *Adv. Synth. Catal.*, 2002, **344**, 477–493; (c) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327–3336; (d) S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847–6856; (e) M. Fujita and G. W. Coates, *Macromolecules*, 2002, **35**, 9640–9647.

20) *(a)* Z. Mou, B. Liu, M. Wang, H. Xie, P. Li, L. Li, S. Li and D. Cui, *Chem. Commun.*, 2014, **50**, 11411-11414; *(b)* Z. Mou, B. Liu, X. Liu, H. Xie, W. Rong, L. Li, S. Li and D. Cui, *Macromolecules*, 2014, **47**, 2233-2241.

21) M. M. Hännien, R. Sillanpää, H. Kivelä and A. Lehtonen, *Dalton Trans.*, 2011, **40**, 2868-2874.

22) T. K. Saha, M. Mandal, M. Thunga, D. Chakraborty and V. Ramkumar, *Dalton Trans.*, 2013, **42**, 10304-10314.

23) *(a)* A. J. Nielson, C. Shen and J. M. Waters, *Acta Cryst.*, 2013, **E69**, m673-m674; *(b)* X.-E. Duan, S.-F. Yuan, H.-B. Tong, S.-D. Bai, X.-H. Wei and D.-S. Liu, *Dalton Trans.*, 2012, **41**, 9460-9467; *(c)* A. Kayal, A. F. Ducruet and S. C. Lee, *Inorg. Chem.*, 2000, **39**, 3696-3704; *(d)* D. M. Goedde and G. S. Girolami, *Inorg. Chem.*, 2006, **45**, 1380-1388; *(e)* R. Fandos, B. Gallego, M. I. López-Solera, A. Otero, A. Rodríguez, M. J. Ruiz, P. Terreros and T. V. Mourik, *Organometallics*, 2009, **28**, 1329-1335.

24) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, 1997.

25) *(a)* T. K. Saha, D. Chakraborty and V. Ramkumar, *Inorg. Chem.*, 2011, **50**, 2720-2722; *(b)* Y. Kim, G. K. Jnaneshwara and J. G. Verkade, *Inorg. Chem.*, 2003, **42**, 1437-1447; *(c)* S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt and M. Kol, *Inorg. Chem.*, 2006, **45**, 4783-4790; *(d)* M. Grellier, L. Vendier, B. Chaudret, A. Albinati, S. Rizzato, S. Mason and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2005, **127**, 17592-17593.

26) *(a)* S. Damavandi, N. Samadieh, S. Ahmadjo, Z. Etemadinia and G. H. Zohuri, *Eur. Polym. J.*, 2015, **64**, 118-125; *(b)* M. Mitani, J.-I. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S.-I. Kojoh, T. Matsugi, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327-3336; *(c)* X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015-10031; *(d)* S. Matsui, M. Mitani, J. Saito, Y. Toshi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847-6856.

27) G. M. Sheldrick, **SHELXL97**. *Program for crystal structure refinement*, Göttingen, Germany.

28) *(a)* I. B. Obot and N. O. Obi-Egbedi, *Corros. Sci.* 2010, **52**, 657-660; *(b)* C. G. Zhan, J. A. Nicholes and D. A. Dixon, *J. Phys. Chem. A*, 2003, **107**, 4184-4195.