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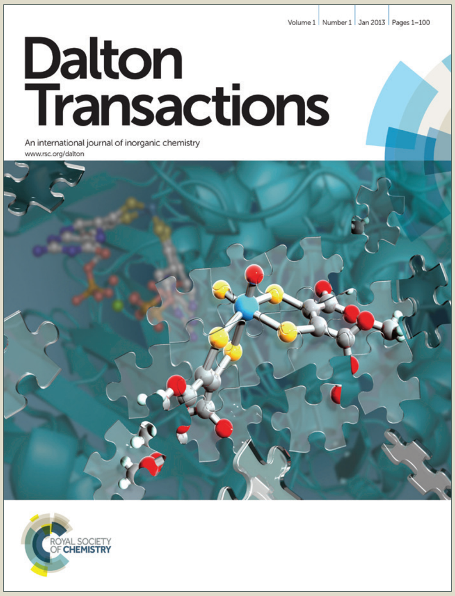

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ARTICLE TYPE

Gallium and indium complexes containing the bis(imino)phenoxide ligand: synthesis, structural characterization and polymerization studies

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A series of gallium and indium complexes containing the bis(imino)phenolate ligand framework were synthesized and completely characterized with different spectroscopic techniques. The molecular structures of a few complexes were determined by single crystal X-ray diffraction studies. These compounds were found to be extremely active towards the bulk ring opening polymerization (ROP) of lactides yielding polymers with high number average molecular weight (M_n) and controlled molecular weight distributions (MWDs). The neutral complexes **1**-**8** produce isotactic enriched poly(lactic acid) (PLA) from *rac*-lactide (*rac*-LA) under melt conditions, whereas the ionic complex **9**, produce atactic PLA. The polymerizations are controlled, as evidenced by the narrow molecular distribution (MWDs) of the isolated polymers in addition to the linear nature of number average molecular weight (M_n) versus conversion plots with variations in monomer to catalyst ratios. The kinetics and mechanistic studies associated with these polymerizations have been performed.

Introduction

Poly(lactic acid) (PLA), has attracted considerable attention as a promising green alternative to petrochemically derived polymers due to its biodegradability, biocompatibility and its synthesis from biorenewable resource.[1] PLA possesses versatile physical properties and has been widely used in spanning packaging, fibers, composites, food commodities, medical devices, tissue engineering and in media for the controlled release of drugs.[2] PLA is mainly produced by the ring opening polymerization (ROP) of lactide, the cyclic diester of lactic acid, because it enables greater control over the molecular weight (M_n) and stereoselectivity than conventional polycondensation of lactic acid.[3] Over the past 10 years, the ring opening polymerization (ROP) of lactide (LA) catalyzed by organocatalysts,[4] as well as discrete metal complexes bearing a variety of ligand architectures,[5] were explored in an attempt to control polymer micro and macrostructures and limit transesterification or other uncontrolled chain transfer processes.[3,6] In this area, well defined and ligand supported complexes of oxophilic and Lewis acidic metals (M = Alkaline metal, Al(III), Sn(II), Zn(II), Mg(II), Ca(II), Ln(III), Ti(IV), Zr(IV)) are efficient ROP catalysts and provide access to chain length control and possibly stereo-control.[7]

ROP catalysts derivative from trivalent Lewis acidic metals such as aluminum,[8] gallium[9] and the rare earth metals[10] have been thoroughly investigated. Recently, compounds of the heavier group13 metal indium[2a,11,] have attracted attention in the context of ROP of cyclic esters. In 2008, Merkhodavandi *et al.* introduced a dinuclear indium compound [{(NNO)InCl}$_2$(μ-OEt)(μ-Cl)] as the first example for an indium catalyst for the living ROP of lactide.[11a] Recently Okuda *et al.* reported that ROP of *rac*- and *meso*-lactide by the indium bis(phenolate) isopropoxy compounds. These are are fast, yet relatively controlled and polymerization proceed through via the coordination insertion mechanism.[12] Tolman *et al.* reported the kinetics and the mechanism of the stereoselective ROP of *rac*-LA initiated by indium catalysts prepared in situ from InCl$_3$, NEt$_3$, and BnOH.[1a,13] Carpentier *et al.* reported (phenoxy-imine)indium compounds for polymerizing lactide through an activated monomer mechanism.[14] The most important results on the ROP of lactide monomers have been reviewed by Dagorne and Carpentier.[7g] Mountford *et al*. introduced sulfonamide, phenolate, and directing ligand-free indium catalyst for the ROP *rac*-LA in toluene solution or in melt to give heterotactic or atactic PLA.[15]

It was quite interesting to discover that Ga complexes have been far less investigated towards the ROP of lactides. Horeglad *et al*. for the first time reported that the simple dialkylgallium alkoxides without any bulky substituents can polymerize *rac*-LA in a living manner, while the coordination of a Lewis base to the gallium center results in an increase of heteroselectivity both in solution and in melt monomer in a controlled manner.[9b] Dagorne *et al*. reported a comparative study of aluminum and gallium complexes for the ROP of lactides. They showed that the Ga catalysts were faster and equally well controlled as the Al counterparts under the same conditions.[16] Recently Williams *et al*. demonstrated that the 8-quinolinolato gallium catalysts, show rates approximately 3 times higher than those of the series of aluminum compounds, while maintaining equivalently high isoselectivity and high degrees of controlled polymerization.[17]

Our continued interest remains in the study of catalytic ROP

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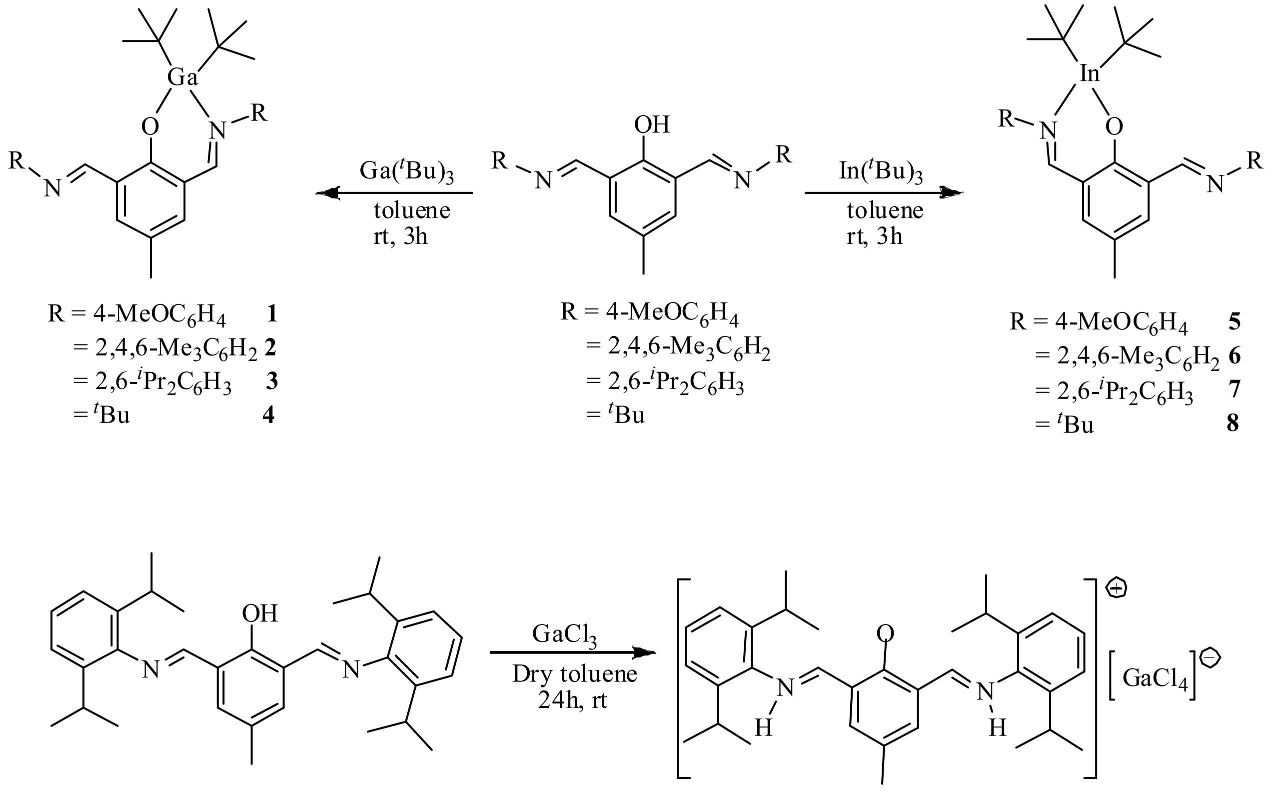
reactions using diverse metal complexes of the imino(phenoxide) scaffold.[18] In this work, we have discussed the synthesis, structural characterization and potential use of Ga and In containing the bis(imino)phenoxide complexes towards the bulk ROP of lactides.

Results and Discussion

Synthesis and structural characterization of compounds

The bis(imino)phenoxide ligands[19], tri-*tert*-butylgallium and tri-*tert*-butylindium were synthesized according to the literature reported procedures.[20] Reactions of tri-*tert*-butylgallium or tri-*tert*-butylindium with the various bis(imino)phenoxide ligands in 1:1 stoichiometric ratio, in dry toluene at room temperature resulted in the formation of heteroleptic complexes **1−8**. Compound **9** was obtained by the reaction of excess $GaCl_3$ with the corresponding ligands in dry toluene. These reactions are depicted in Scheme 1. These compounds were purified by crystallization from toluene and isolated as yellow to colorless crystalline solids in high yields and purity. These reactions were monitored by recording ^{1}H NMR of aliquots removed from the reaction mixture through the disappearance of the phenolic −OH peak (13.1-13.4 ppm). Complexes **1**–**9** were thoroughly characterized by different spectroscopic techniques like ^{1}H, ^{13}C NMR and electrospray ionization mass spectrometry (ESI-MS) and their purity was assessed through correct elemental analysis. For **2**, **4** and **9** single crystals suitable for X-ray diffraction experiments were obtained from saturated toluene solutions through slow evaporation of the solvent.

The ^{1}H NMR spectra of **1**–**9** reveals all the signals in the correct integration ratio where the resonances assigned to the bis(imino)phenoxide protons were at higher chemical shift as compared to the pro-ligands, due to the Lewis acidity of the Ga and In centers. Analyses of the ^{1}H spectra of compounds **1**–**8** show the presence of two different signals for the imine protons from the CH=N group. This may be rationalized by considering the structure of these molecules wherein out of two imine N centers, one is coordinated with metal through the nitrogen atom and the other remains non coordinated. Analysis of the ^{1}H NMR spectra of compounds **1**–**8,** also show the presence of two different signals for the methyl protons of the two *tert*-butyl groups, which suggest that the two *tert*-butyl groups are inequivalent. The ^{13}C NMR spectrum of **1–8** shows the presence of moieties corresponding to the different carbon environments in these complexes. Analyses of the ^{13}C NMR of these compounds also show the presence of two different signals for the imine moiety, one for the coordinated CH=N and other for the non coordinated moiety. The interesting observation is that the aryl ring attached to the imine moiety of the compounds also shows two sets of signals corresponding to the different carbon environments of the aryl ring.



9

Scheme 1 Synthesis of compounds **1**–**9.**

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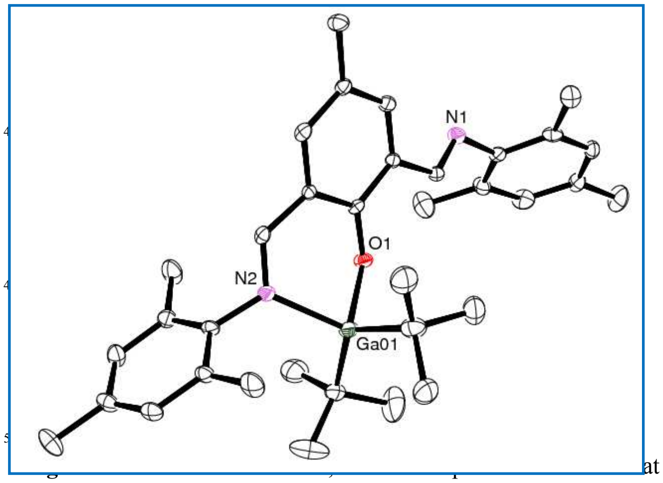
The overall conclusions drawn from ^{13}C NMR spectrum studies are in agreement with the conclusions drawn from the ^{1}H NMR spectrum of **1**–**8**. In the case of **9**, only one signal was observed for the imine proton of the CH=N groups. Analyses of the ^{13}C NMR spectra of compound **9** also shows one signal for the imine moiety, which reveals that the both proton and carbon of the CH=N moiety in the complex are in the same chemical environment. The results of ESI−MS of **1**–**9**, clearly suggest that the compounds are monomeric in nature. The purity of **1**−**9** was unambiguously assured by the proximity of the elemental analyses values to the theoretical figures.

Single crystal X-ray diffraction studies

Single crystals suitable for X-ray crystallographic analysis were grown from a saturated toluene solution of **2** in a glove box at 0 °C over a period of two weeks through slow evaporation of the solvent. Compound **2** crystallizes in the Triclinic *P−1* space group with two molecules in the unit cell. The crystal data is depicted in Table 1. From the analysis of the bond lengths and angles, it is evident that the central gallium center adopts a distorted tetrahedral geometry in the solid state.[21] The molecular structure is depicted in Fig. 1. Compound **4** crystallizes in the Monoclinic $P2_1/c$ space group with eight molecules present in the unit cell. The asymmetric unit of compound **4** contains two symmetry independent molecules. From the analysis of bond lengths and bond angles it is evident that the tetra-coordinated gallium centre adopts a distorted tetrahedral geometry.[21] The molecular structure of **4** is depicted in Fig. 2. The single crystal X-ray analysis for **9** showed that it crystallizes in the Orthorhombic $P2_12_12_1$ space group with four molecules present in the unit cell. The crystal structure is depicted in Fig. 3. X-ray crystallography revealed that the **9** exist as cation–anion ion pairs. This is consistent to the existence of discrete $[GaCl_4]^-$ anion along with corresponding ligand as the counter cation.



at 30 % probability level. Hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (°): Ga01–O1 1.910(3), Ga01–C32 1.986(6), Ga01–C28 2.030(6), Ga01–N2 2.072(4), O1–Ga01–C32 104.70(18), O1–Ga01–C28 104.51(18), C32–Ga01–C28 127.3(2), O1–Ga01–N2 89.52(14), C32–Ga01–N2 109.6 (2), C28–Ga01–N2 113.50 (19).

The $[GaCl_4]^-$ unit adopts a pseudotetrahedral structure as understood from the analysis of the bond lengths and angles. Upon combination with $GaCl_3$, the phenoxide group of the ligand was deprotonated whereas the two −CH=N groups are protonated. The X-ray structure shows that the positive charged bis(imino)phenoxy group incorporates with a pseudo-tetrahedral $[GaCl_4]^-$ group and the observed C=N distances are found to be N1-C8 = 1.290(3) and N2-C21 = 1.301(3) respectively. These are appreciably longer than the normal C=N distance 1.265Å, while the N1-C8-C2 and C8-N1-C9 angles (122.1 (2), 127.3 (2)) are larger than expected angle of 120º. These phenomena are recognized to the electrostatic and/or Van der-Waals forces between the positively charged $[GaCl_4]^-$ and counter ligand cation.[22]

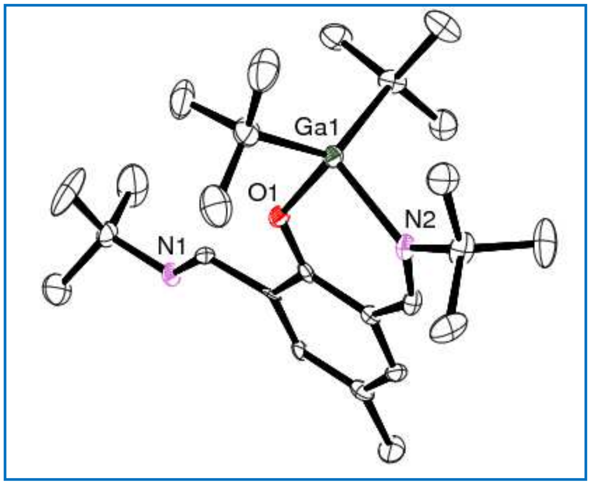


Fig. 2 Molecular structure of **4**; thermal ellipsoids were drawn at 30 % probability level. Hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (°): Ga1–O1 1.899(7), Ga1–C22 1.999(12), Ga1–C18 2.004(10), Ga1–N2 2.064(9), O1–Ga1–C22 100.2(4), O1–Ga1–C18 106.0(4), C22–Ga1–C18 126.2(5), O1–Ga1–N2 92.4(4), C22–Ga1–N2 116.8(4), C18–Ga1–N2 108.2(4).

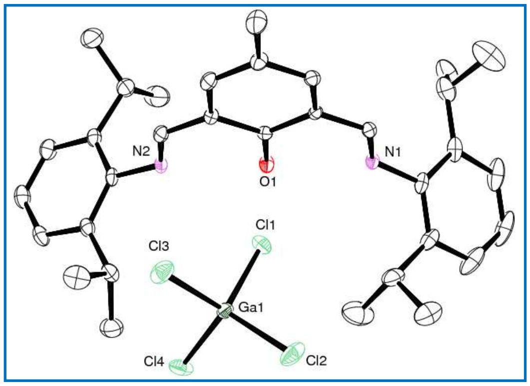


Fig. 3 Molecular structure of **9**; thermal ellipsoids were drawn at 30 % probability level. Hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (°): Ga1–Cl2 2.160(8), Ga1–Cl3 2.165(7), Ga1–Cl4 2.165(7), Ga1–Cl1 2.181(7), Cl2–Ga1–Cl3 109.2(3), Cl2–Ga1–Cl4 111.9(3), Cl3–Ga1–Cl4 109.5(4), Cl2–Ga1–Cl1 110.4(3), Cl3–Ga1–Cl1 108.9(3), Cl4–Ga1–Cl1 106.8(3).

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Table 1 Crystal data and structure refinement details for **2, 4** and **9**

Compounds	**2**	**4**	**9**
Empirical formula	$C_{35}H_{47}GaN_2O$	$C_{25}H_{43}GaN_2O$	$C_{33}H_{43}Cl_4GaN_2O$
Formula weight	581.46	457.33	695.21
T /K	296	173(2)	150
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system,	Triclinic	Monoclinic	Orthorhombic
Space group	*P -1*	$P2_1/c$	$P2_12_12_1$
a /Å	11.1154(12)	26.356(3)	13.082(2)
b /Å	12.4412(12)	10.1106(11)	14.694(2)
c /Å	13.0127(14)	21.7876(18)	18.696(3)
α (°)	72.868(4)	90	90
β (°)	70.445(4)	112.909(4)	90
γ (°)	86.568(4)	90	90
V (Å^3)	1619.0(3)	5348.0(9)	3593.84(9)
Z, Calculated density (mg cm^{-3})	2, 1.193	8, 1.136	4, 1.285
Absorption coefficient (mm^{-1})	0.878	8.349	1.090
Crystal size (mm)	0.10 x 0.05 x 0.04	0.20 x 0.15 x 0.05	0.28 × 0.23 × 0.18
Reflections collected/unique	13687 / 2932	20588 / 13062	25577/ 6196
Independent reflections	3969	5443	7050
Data/restraints/parameters	3969 / 0 / 365	5443 / 168 / 610	7050/ 20/ 387
Goodness-of-fit on F^2	1.053	1.054	0.967
Flack parameter (x)	-	-	0.002(3) for 2534 quotients
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0528$	$R1 = 0.0769$	$R1 = 0.0238$
	$wR2 = 0.1112$	$wR2 = 0.1608$	$wR2 = 0.0518$
R indices (all data)	$R1 = 0.0825$	$R1 = 0.1308$	$R1 = 0.0288$
	$wR2 = 0.1251$	$wR2 = 0.1665$	$wR2 = 0.0524$

$R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$, $wR2 = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Ring opening polymerization studies

Compounds **1−9** were tested as catalyst towards the ROP of *rac*-LA and *L*-LA. All the polymerizations were conducted under solvent free conditions at 140 ºC. The polymerizations were monitored by taking aliquots at regular time intervals, which were analyzed using ^{1}H NMR spectroscopy to determine the lactide conversion, and by GPC (gel permeation chromatography) to determine the number average molecular weight (M_n) and molecular weight distribution (MWDs, M_w/M_n). The polymerization results are summarized in Table 2 Isolated yield of the resulting PLA was found to be more than 90-95%. Analysis of the data depicted in Table 2 shows that compounds **1−9** are good catalysts for the polymerization of lactides. For compounds **1-8,** the results illustrated that there is a close correlation between the observed molecular weight (M_n^{obs}) and the theoretical molecular weight (M_n^{theo}). The Ga compounds show higher reactivity and control in terms of M_n's and MWDs as compared to the In compounds. This is due to the higher Lewis acidity of the Ga center. The ROP are anticipated to proceed via a coordination-insertion mechanism for which the Lewis acidity of metal center is important. The tacticity of the PLA obtained using compounds **1−8** were determined by integration of the methine region of the homonuclear decoupled ^{1}H NMR spectra. The normalized integrals were compared against the values predicted using Bernoullian statistics to give the probability of isotactic linkages, P_m.[23] Analysis of P_m value (Table 2) suggest that the complexes showed moderate isoselectivity towards *rac*-LA polymerization. This is because of two bulky *tert*-butyl groups directly attached to the metal, which sterically crowded the metal centre and controlled the polymerization in a isoselective manner.[24] We have concluded from homonuclear decoupling ^{1}H NMR spectrum that the polymerization of *rac*-LA using **1−8** yields isotactic enriched polymer (Fig. 4). In case of compound **9** the resultant data demonstrated that this compound was found to be less active towards the ROP and took more time for complete ROP. The homonuclear decoupled ^{1}H NMR spectrum shows that

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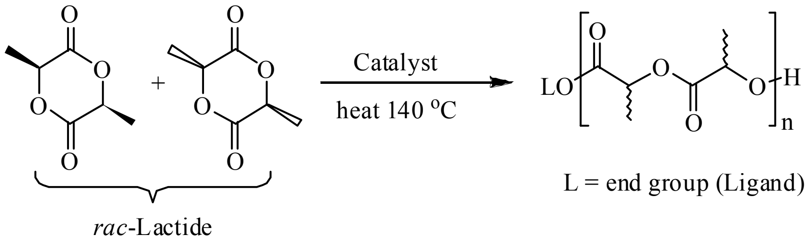

Table 2 Polymerization data for *rac*-LA and *L*-LA is using **1–9** in the ratio 200:1 at 140 °C

Entry	Catalyst	Monomer	Time^{a} (min)	$M_n^{(obs)b}$ (kg mol^{-1})	$M_n^{(theo)c}$ (kg mol^{-1})	M_w/M_n^{d}	P_m^{e}
1	**1**	*rac*-LA	9	29.54	29.19	1.02	0.84
2	**2**	*rac*-LA	14	28.13	29.22	1.04	0.81
3	**3**	*rac*-LA	16	27.26	29.30	1.04	0.80
4	**4**	*rac*-LA	20	25.55	29.10	1.06	0.78
5	**5**	*rac*-LA	16	26.28	29.19	1.08	0.76
6	**6**	*rac*-LA	19	24.31	29.22	1.11	0.74
7	**7**	*rac*-LA	21	24.06	29.30	1.12	0.73
8	**8**	*rac*-LA	25	22.67	29.10	1.15	0.70
9	**9**	*rac*-LA	50	18.38	29.30	1.19	
10	**1**	*L*-LA	9	30.52	29.19	1.01	
11	**2**	*L*-LA	12	28.94	29.22	1.03	
12	**3**	*L*-LA	15	27.86	29.30	1.04	
13	**4**	*L*-LA	18	26.16	29.10	1.05	
14	**5**	*L*-LA	15	27.11	29.19	1.08	
15	**6**	*L*-LA	18	24.79	29.22	1.10	
16	**7**	*L*-LA	19	24.63	29.30	1.11	
17	**8**	*L*-LA	23	22.98	29.10	1.13	
18	**9**	*L*-LA	50	19.07	29.30	1.18	

[a]Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b]Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections; $M_n^{obs} = 0.58\ M_n^{GPC}$ for LA. [c]$M_n^{(theo)}$ at 100% conversion = $[M]_o/[C]_o$ × mol wt (monomer) + $M_{end\ groups}$. [d]Measured by GPC at 27 °C. [e]Calculated from homonuclear decoupled ^{1}H NMR spectrum.

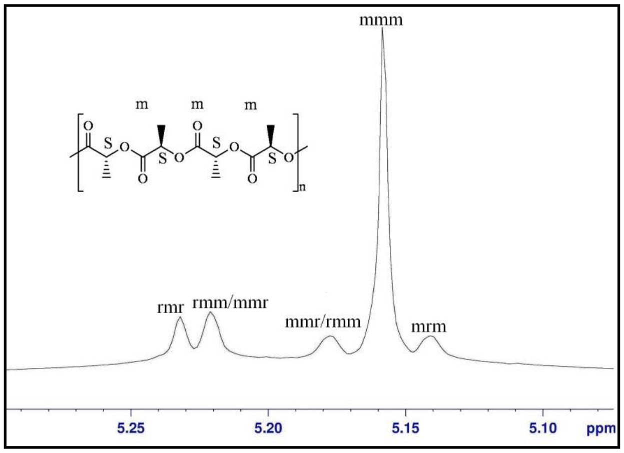

Fig. 4 ^{1}H homonuclear decoupled spectrum of isotactic enriched PLA obtained from a reaction between *rac*-LA and **2** in the ratio 200:1

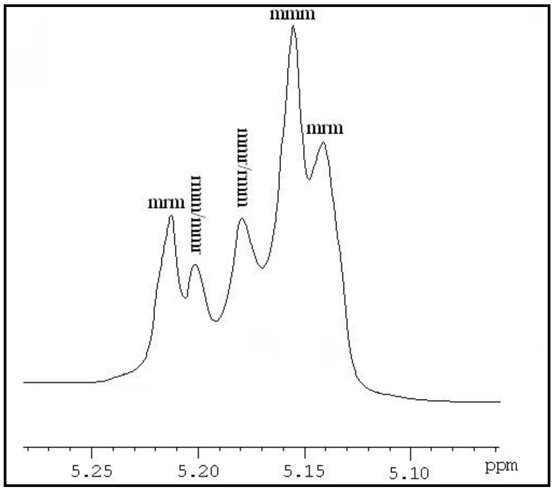

Fig. 5 ^{1}H homonuclear decoupled spectrum of atactic PLA obtained from a reaction between *rac*-LA and **9** in the ratio 200:1.

the polymerization of *rac*-LA using **9** yields atactic PLA (Fig. 5). The variation of M_n and MWDs with increasing $[M]_o/[C]_o$ ratio for *rac*-LA and *L*-LA polymerization using **2** and **7** was studied. The results are depicted in Table 3. A plot of M_n *vs.* $[M]_o/[C]_o$ ratio for **2** and **7** with *rac*-LA revealed that the variation of M_n is

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Table 3 Polymerization data based on changing ratios in case of *rac*-LA and *L*-LA using **2** and **7** at 140 °C

Entry	Catalyst	Monomer	$[M]_o/[C]_o$	Time[a] min	Yield (%)	$M_n^{(obs)b}$ kg mol^{-1}	$M_n^{(theo)c}$ kg mol^{-1}	M_w/M_n
1	**2**	*rac*-LA	100	6	99	13.26	14.81	1.03
2	**2**	*rac*-LA	200	14	98	28.13	29.22	1.04
3	**2**	*rac*-LA	400	33	98	56.82	58.07	1.04
4	**2**	*rac*-LA	800	68	96	112.34	115.69	1.06
5	**2**	*L*-LA	100	5	99	13.72	14.81	1.03
6	**2**	*L*-LA	200	12	98	28.94	29.22	1.03
7	**2**	*L*-LA	400	29	97	58.49	58.07	1.04
8	**2**	*L*-LA	800	64	96	114.63	115.69	1.05
9	**7**	*rac*-LA	100	9	99	12.06	14.81	1.09
10	**7**	*rac*-LA	200	19	98	24.31	29.22	1.11
11	**7**	*rac*-LA	400	45	96	50.19	58.07	1.12
12	**7**	*rac*-LA	800	91	95	101.24	115.69	1.14
13	**7**	*L*-LA	100	8	99	12.73	14.81	1.09
14	**7**	*L*-LA	200	18	98	24.79	29.22	1.10
15	**7**	*L*-LA	400	40	97	52.87	58.07	1.12
16	**7**	*L*-LA	800	84	97	104.06	115.69	1.13

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. [b] Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n; $M_n^{obs} = 0.58\ M_n^{GPC}$ for LA. [c] $M_n^{(theo)}$ at 100% conversion = $[M]_o/[C]_o \times$ mol wt (monomer) + $M_{end\ groups}$.

linear (Fig. 6) with increasing ratios whereas the MWDs remain almost consistent with the increase in $[M]_o/[C]_o$ ratio which demonstrate that these polymerizations are well controlled.

Again, the plot of M_n vs. % conversion for **2** and **7** (Fig. 7) was found linear, suggesting a good degree of control in these polymerizations.

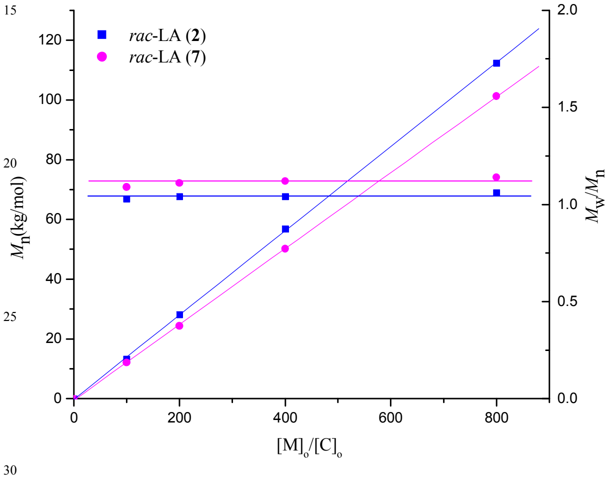

Fig. 6 Plot of M_n and M_w/M_n vs. $[M]_o/[C]_o$ for *rac*-LA polymerization at 140 °C using **2** and **7**.

Fig. 6 and Fig. 7 seem to suggest that the polymerization of *rac*- LA is controlled and propagates in a living manner.

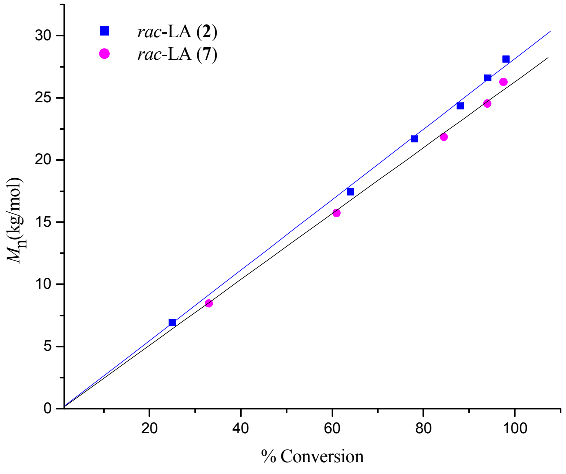

Fig. 7 Plot of M_n vs. conversion for *rac*-LA using **2** and **7**.

Kinetics of polymerization

In the next section of work, the kinetics of *rac*-LA polymerization for **2** and **6** were studied. The kinetic studies for the polymerization of *rac*-LA in ratio $[rac\text{-LA}]_o/[C]_o = 200$ were performed at 140 °C. From the kinetic experiment results

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it is clear that there is a first order dependence of the rate of polymerization upon *rac*-LA concentration without induction period. The plot of ln([*rac*-LA]$_o$/[*rac*-LA]$_t$) vs. time was found to be linear (Fig. 8). The values of the apparent rate constant (k_{app}) for *rac*-LA polymerization catalyzed by **2** and **6** were evaluated from the slope of these straight lines and were found to be 6.03×10^{-2} min^{-1} and 2.08×10^{-2} min^{-1} respectively. From these rate constants, it may be inferred that the polymerization rate is faster for the Ga compounds in comparison with the In compounds. This is justified by the time taken for the polymerization.

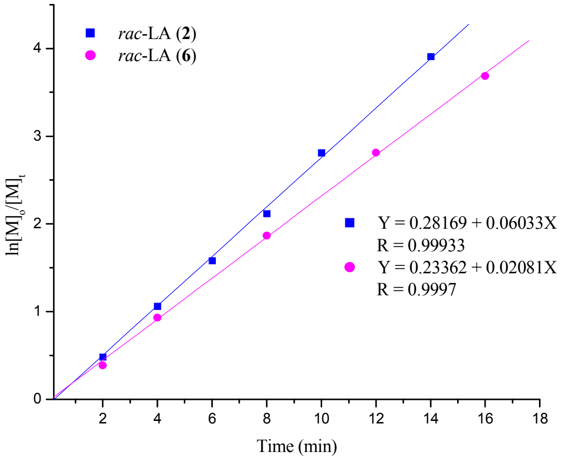

Fig. 8 Semi-logarithmic plots of *rac*-LA conversion in time initiated by **2** and **6**: [*rac*-LA]$_o$/[C]$_o$= 200 at 140 °C.

Rationalization of polymerization pathway

In order to have a complete insight into the polymerization mechanism, we synthesized low molecular weight oligomers of *rac*-LA. Compound **2** was reacted with *rac*-LA in 1:15 stoichiometric ratio at 140 ºC. The residue was dissolved in minimum amount of CH_2Cl_2 and precipitated by pouring into cold methanol. The oligomer was isolated and was subjected to ^{1}H NMR and MALDI-TOF studies. The results (Fig. 9 and Fig. 10) indicate that the polymerization proceeds with the coordination-insertion mechanism and the ligand is incorporated as one of the end terminal groups. The results have depicted that M–O linkage initiates the polymerization and not the M–N linkage. The OH peak from the ligand fragment contributing towards the end terminal group of the oligomer would have been clearly visible in the ^{1}H NMR spectrum. From the MALDI-TOF spectrum (Fig. 10) it is clearly observed that intramolecular transesterification is negligible during the polymerization reaction since the cyclic product is not observed.[18a] Analysis of the oligomer by ^{1}H NMR demonstrates a characteristic methine peak at 5.16–5.23 ppm and a doublet peak at 1.57–1.59 ppm along with a quartet peak at the chemical shift of the (HOC*H*Me) end group at 4.36–4.38 ppm and a doublet peak at the chemical shift of the (HOCH*Me*) end group at 1.47–1.48 ppm (Fig. 9). This shows that the obtained oligomer is linear PLA. The linear structure is also confirmed by MALDI-TOF spectrometry of the oligomer (Fig. 10) exhibiting the mass difference 144n or 72m corresponding to oligomers of the formula $[COCH(Me)O]_nH{\cdot}Na^+$. This observation proves that the ligand participates in the ring opening step of the polymerization reaction. We also synthesized the low molecular weight oligomers of *L*-LA using **9** in 10:1 stoichiometric ratios at 140 °C. The low molecular weight oligomers were thoroughly characterized using MALDI-TOF and ^{1}H NMR spectroscopy. These results are depicted in ESI (Figs. S27 and S28 respectively). Analysis of the results indicates that the ligand is incorporated as one of the end terminal groups and initiating the polymerization chain.

CONCLUSION

In conclusion, we report here a series of gallium and indium complexes containing the bis(imino)phenoxide ligand backbone. All the complexes were completely characterized by different spectroscopic methods. These compounds are found to be extremely active towards the ROP of LA under solvent free condition at 140 ºC. The gallium catalysts were found to yield better polymerization results in comparison to the indium analogues. We have achieved good control over M_n and MWDs and there was a very close correlation between observed molecular weight (M_n^{obs}) and theoretical molecular weight (M_n^{theo}). Kinetics data analysis suggests that, the polymerizations of LA by these complexes are first order in monomer concentration. Analysis of low molecular weight oligomers reveal that the ligand is incorporated as one of the end terminal groups in the polymer chain and is initiating the polymerization.

Experimental

General experimental details

All the reactions were done under a dry argon atmosphere using standard Schlenk techniques or using glove box techniques with rigorous exclusion of moisture and air. Toluene was dried by heating under reflux for 6 h over sodium and benzophenone and distilled fresh prior to use. $CDCl_3$ used for NMR spectral measurements was dried over calcium hydride for 48 h, distilled and stored in a glove box. ^{1}H and ^{13}C NMR spectra during the synthesis were recorded with a Bruker Avance 400 instrument. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to residual solvent resonances and are reported as parts per million relative to SiMe4. ESI-MS spectra of the samples were recorded using Waters Q-Tof micro mass spectrometer. Elemental analyses were performed with a Perkin Elmer Series 11 analyzer. MALDI-TOF measurements were done on a Bruker Daltonics or Bruker Ultraflextreme instrument in dihydroxy benzoic acid matrix. ^{t}BuLi (1.6 M in hexane), $GaCl_3$ and calcium hydride were purchased from Sigma-Aldrich and used without further purification. *rac*-LA and *L*-LA were purchased from Sigma-Aldrich and sublimed twice under argon atmosphere and stored in glove box. The tri-*tert*-butyl gallium and ligands, were prepared according to literature reported procedures.[20]

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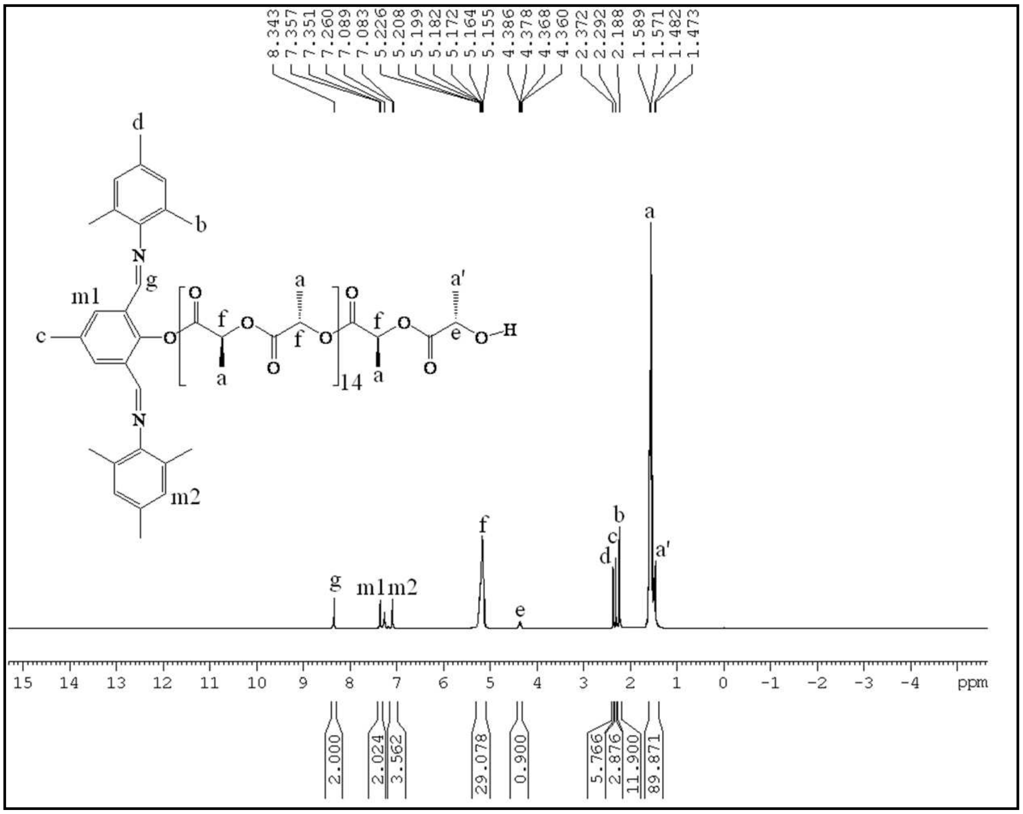

Fig. 9 ^{1}H NMR spectrum of the crude product obtained from a reaction between *rac*-LA and **2** in the ratio 15:1.

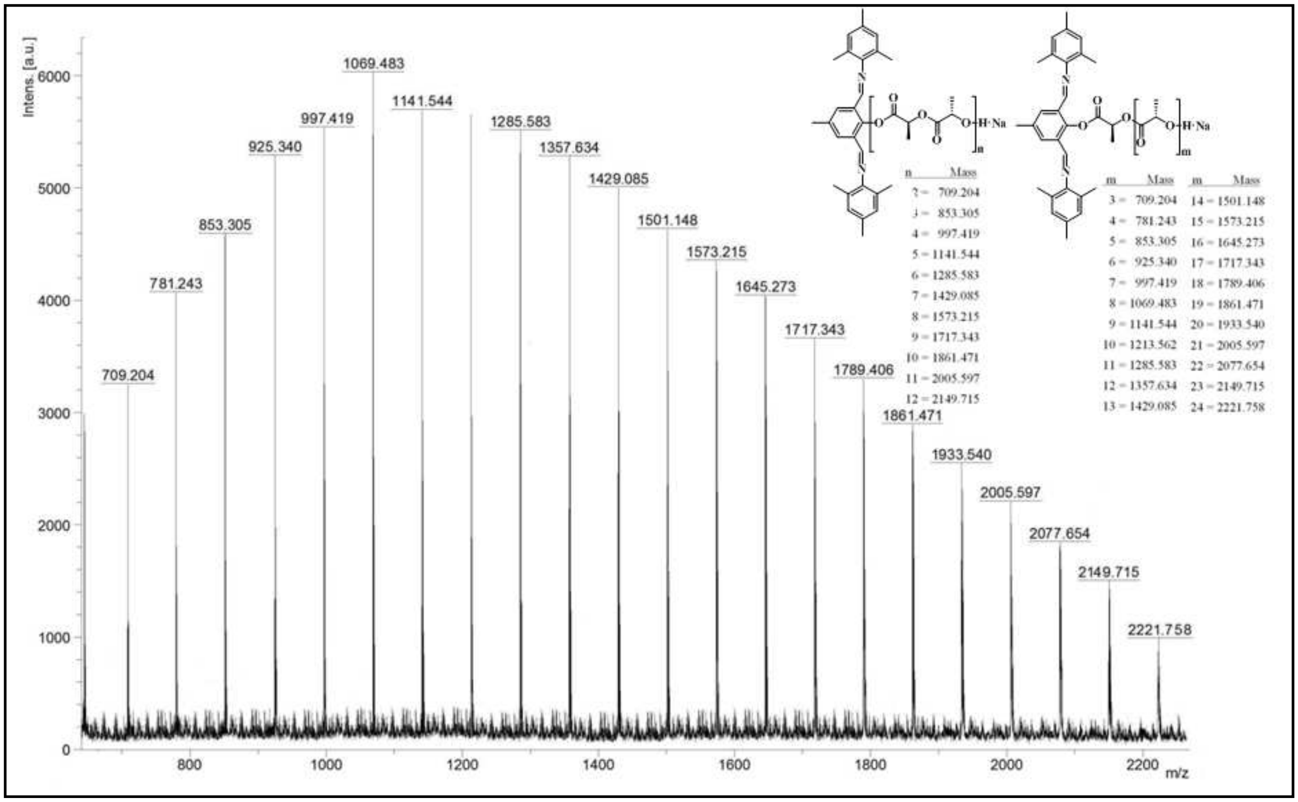

Fig. 10 MALDI-TOF spectrum of the crude product obtained from a reaction between *rac*-LA and **2** in the ratio 15:1.

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Synthesis and characterization of compounds

A general procedure describing the synthesis of **1**–**8** is outlined: In argon filled glove box, to a stirred solution of metal alkyl (0.26 mmol) in 5 mL toluene at 0 °C was added a solution of corresponding ligand (0.26 mmol) in 5 mL toluene. The reaction mixture was allowed to warm up to room temperature and stirred additionally for 3 h (**1-8**). The solvent was removed under reduced pressure and the residue obtained was crystallized from concentrated toluene solution at 0 °C.

Compound 1. Yellow solid; Yield = 0.14 g (91 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (s, $C(CH_3)_3$, 9H), 1.02 (s, $C(CH_3)_3$, 9H), 2.29 (s, Ar-CH_3, 3H), 3.84 (s, Ar–OCH_3, 6H), 6.93–6.98 (m, Ar–*H*, 8H), 7.43 (s, Ar–*H*, 1H), 7.72 (s, Ar–*H*, 1H), 8.23 (s, C*H*=N, 1H), 9.23 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.17 ($C(CH_3)_3$), 23.99 (Ar-CH_3), 30.35 ($C(CH_3)_3$), 55.69 (Ar–OCH_3), 114.52 (Ar–*C*), 115.14 (*Ar*–CH_3), 120.00 (Ar–*C*), 122.45 (Ar–*C*), 122.92 (Ar–*C*), 125.10 (Ar–*C*), 127.93 (Ar–*C*), 135.68 (Ar–*C*), 139.02 (Ar–*C*), 141.36 (Ar–*C*), 155.59 (*Ar*–O), 159.39 (*Ar*–OCH_3), 166.44 (*C*H=N), 167.10 (*C*H=N). ESI m/z calculated for [M]+. $C_{31}H_{39}GaN_2O_3$: 556.231 found 556.239. Anal. Calcd for $C_{31}H_{39}GaN_2O_3$: C, 66.80; H, 7.05; N, 5.03;. Found: C 66.90, H 7.14, N 4.92.

Compound 2. Golden yellow solid; Yield 0.14 g, (94 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (s, $C(CH_3)_3$, 9H), 0.89 (s, $C(CH_3)_3$, 9H), 2.16 (s, Ar-CH_3, 12H), 2.24 (s, Ar-CH_3, 3H), 2.32 (s, Ar-CH_3, 6H), 6.89 (s, Ar–*H*, 2H), 6.93 (s, Ar–*H*, 2H), 7.52 (s, Ar–*H*, 1H), 7.96 (s, Ar–*H*, 1H), 8.21 (s, C*H*=N, 1H), 8.80 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.51 ($C(CH_3)_3$), 19.43 (Ar–CH_3), 24.01 (Ar–CH_3), 24.07 (Ar–CH_3), 30.51 ($C(CH_3)_3$), 125.45 (Ar–*C*), 127.38 (Ar–*C*), 127.48 (Ar–*C*), 128.77 (Ar–*C*), 129.88 (Ar–*C*), 132.21 (Ar–*C*), 134.66 (Ar–*C*), 137.29 (Ar–*C*), 146.47 (Ar–*C*), 147.70 (Ar–*C*), 159.58 (*Ar*–O), 169.77 (*C*H=N), 170.47 (*C*H=N). ESI m/z calculated for $[M]^+$. $C_{35}H_{47}GaN_2O$: 580.294 found 580.038. Anal. Calcd for $C_{35}H_{47}GaN_2O$: C 73.26, H 7.82, N 4.44. Found: C 73.31, H 7.71, N 4.39.

Compound 3. Ligth yellow solid; Yield = 0.15 g (90 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.81 (s, $C(CH_3)_3$, 9H), 0.83 (s, $C(CH_3)_3$, 9H), 1.13 (d, $CH(CH_3)_2$, 12H, J_{HH} = 6.8 Hz), 1.20 (d, $CH(CH_3)_2$, 12H, J_{HH} = 6.8 Hz), 2.27 (s, Ar-CH_3, 3H), 2.94–3.00 (m, $CH(CH_3)_2$, 4H), 7.09–7.16 (m, Ar–*H*, 6H), 7.78 (s, Ar–*H*, 1H), 7.91 (s, Ar–*H*, 1H), 8.16 (s, C*H*=N, 1H), 8.72 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.36 ($C(CH_3)_3$), 22.60 ($CH(CH_3)_2$), 22.69 ($CH(CH_3)_2$), 23.78 ($CH(CH_3)_2$), 23.90 ($CH(CH_3)_2$), 25.17 (Ar–CH_3), 28.09 ($CH(CH_3)_2$), 28.68 ($CH(CH_3)_2$), 30.60 ($C(CH_3)_3$), 121.27 (Ar–*C*), 123.11 (Ar–*C*), 123.95 (Ar–*C*), 124.42 (Ar–*C*), 125.74 (Ar–*C*), 128.04 (Ar–*C*), 128.39 (Ar–*C*), 135.81 (Ar–*C*), 138.27 (Ar–*C*), 142.27 (*Ar*–C), 145.95 (*Ar*–C), 159.37 (Ar–O), 167.06 (*C*H=N), 172.01 (*C*H=N). ESI m/z calculated for $[M]^+$. $C_{41}H_{59}GaN_2O$: 664.338 found 664.466. Anal. Calcd for $C_{41}H_{59}GaN_2O$: C, 73.98; H, 8.93; N, 4.21 Found: C, 73.88; H, 8.86; N, 4.27.

Compound 4. Yellow solid; Yield = 0.11 g (94 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, $C(CH_3)_3$, 9H), 1.14 (s, $C(CH_3)_3$, 9H), 1.27 (s, N-$C(CH_3)_3$, 9H), 1.42 (s, N-$C(CH_3)_3$, 9H), 2.23 (s, Ar-CH_3, 3H), 6.94 (s, Ar–*H*, 1H), 7.89 (s, Ar–*H*, 1H), 8.19 (s, C*H*=N, 1H), 8.99 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.13 ($C(CH_3)_3$,), 24.04 (Ar–CH_3), 30.01 ($C(CH_3)_3$), 31.22 ($C(CH_3)_3$), 33.78 ($C(CH_3)_3$), 57.36 ($C(CH_3)_3$), 58.92 ($C(CH_3)_3$), 119.07 (Ar–*C*), 124.33 (Ar–*C*), 134.28 (Ar–*C*), 137.48 (Ar–*C*), 153.42 (*Ar*–O), 167.64 (*C*H=N), 168.63 (*C*H=N). ESI m/z calculated for $[M]^+$. $C_{25}H_{43}GaN_2O$: 456.263 found 456.421 Anal. Calc. for $C_{25}H_{43}GaN_2O$: C, 65.65; H, 9.48; N, 6.13. Found: C, 65.61; H, 9.37; N, 6.16.

Compound 5. Yellow solid; Yield = 0.15 g (91 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (s, $C(CH_3)_3$, 9H), δ = 1.09 (s, $C(CH_3)_3$, 9H), 2.25 (s, Ar-CH_3, 3H), 3.79 (s, Ar–OCH_3, 6H), 6.83–6.94 (m, Ar–*H*, 8H), 7.39 (s, Ar–*H*, 1H), 7.63 (s, Ar–*H*, 1H), 8.09 (s, C*H*=N, 1H), 8.83 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =18.85 ($C(CH_3)_3$), 23.49 (Ar-CH_3), 30.03 ($C(CH_3)_3$), 55.21 (Ar–OCH_3), 114.02 (Ar–*C*), 115.05 (*Ar*–CH_3), 119.44 (Ar–*C*), 122.17 (Ar–*C*), 122.79 (Ar–*C*), 124.29 (Ar–*C*), 127.36 (Ar–*C*), 134.49 (Ar–*C*), 138.94 (Ar–*C*), 140.15 (Ar– *C*), 154.32 (*Ar*–O), 158.79 (*Ar*–OCH_3), 166.21 (*C*H=N), 167.08 (*C*H=N). ESI m/z calculated for [M]+. $C_{31}H_{39}InN_2O_3$: 602.200 found 602.249. Anal. Calcd for $C_{31}H_{39}InN_2O_3$: C, 61.80; H, 6.52; N, 4.65;. Found: C 61.92, H 6.59, N 4.78.

Compound 6. Golden yellow solid; Yield 0.16 g, (92 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.82 (s, $C(CH_3)_3$, 9H), 0.85 (s, $C(CH_3)_3$, 9H), 2.03 (s, Ar-CH_3, 12H), 2.19 (s, Ar-CH_3, 3H), 2.30 (s, Ar-CH_3, 6H), 6.83 (s, Ar–*H*, 2H), 6.89 (s, Ar–*H*, 2H), 7.41 (s, Ar–*H*, 1H), 7.79 (s, Ar–*H*, 1H), 8.16 (s, C*H*=N, 1H), 8.72 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.27 ($C(CH_3)_3$), 19.14 (Ar–CH_3), 23.87 (Ar–CH_3), 24.46 (Ar–CH_3), 30.33 ($C(CH_3)_3$), 124.24 (Ar–*C*), 125.71 (Ar–*C*), 126.27 (Ar–*C*), 128.09 (Ar–*C*), 128.65 (Ar–*C*), 129.07 (Ar–*C*), 131.61 (Ar–*C*), 133.55 (Ar–*C*), 136.87 (Ar–*C*), 145.44 (Ar–*C*), 146.59 (Ar–*C*), 157.82 (*Ar*–O), 167.64 (*C*H=N), 168.29 (*C*H=N). ESI m/z calculated for $[M]^+$. $C_{35}H_{47}GaN_2O$: 626.273 found 626.352. Anal. Calcd for $C_{35}H_{47}InN_2O$: C, 67.09; H, 7.56; N, 4.47;. Found: C 67.04, H 7.66, N 4.38.

Compound 7. Pale yellow solid; Yield = 0.17 g (90 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.75 (s, $C(CH_3)_3$, 9H), 0.71 (s, $C(CH_3)_3$, 9H), 1.11 (d, $CH(CH_3)_2$, 12H, J_{HH} = 6.8 Hz), 1.19 (d, $CH(CH_3)_2$, 12H, J_{HH} = 11.6 Hz), 2.25 (s, Ar-CH_3, 3H), 2.83–2.92 (m, $CH(CH_3)_2$, 4H), 6.93–7.13 (m, Ar–*H*, 6H), 7.69 (s, Ar–*H*, 1H), 7.80 (s, Ar–*H*, 1H), 8.03 (s, C*H*=N, 1H), 8.53 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.38 ($C(CH_3)_3$), 22.04 ($CH(CH_3)_2$), 23.02 ($CH(CH_3)_2$), 24.72 (Ar-CH_3), 28.46 ($CH(CH_3)_2$), 29.36 ($CH(CH_3)_2$), 30.15 ($C(CH_3)_3$), 119.47 (Ar–*C*), 122.39 (Ar–*C*), 123.04 (Ar–*C*), 123.70 (Ar–*C*), 124.82 (Ar–*C*), 127.27 (Ar–*C*), 127.93 (Ar–*C*), 133.75 (Ar–*C*), 137.08 (Ar–*C*), 141.29 (Ar–*C*), 143.86 (Ar–*C*), 157.36 (*Ar*–O), 166.84 (*C*H=N), 170.18 (*C*H=N). ESI m/z calculated for $[M]^+$. $C_{41}H_{59}InN_2O$: 710.367 found 710.397. Anal. Calcd for $C_{41}H_{59}InN_2O$: C, 69.29; H, 8.37; N, 3.94; Found: C, 69.16; H, 8.45; N, 3.99.

Compound 8. Yellow solid; Yield = 0.12 g (95 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, $C(CH_3)_3$, 9H), 1.10 (s, $C(CH_3)_3$, 9H), 1.24 (s, N-$C(CH_3)_3$, 9H), 1.38 (s, N-$C(CH_3)_3$, 9H), 2.19 (s, Ar-CH_3, 3H), 6.87 (s, Ar–*H*, 1H), 7.36 (s, Ar–*H*, 1H), 8.01 (s, C*H*=N, 1H), 8.72 (s, C*H*=N, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.57 ($C(CH_3)_3$,), 23.83 (Ar–CH_3), 29.63 ($C(CH_3)_3$), 30.65 ($C(CH_3)_3$), 33.23 ($C(CH_3)_3$), 55.94 ($C(CH_3)_3$), 57.52 ($C(CH_3)_3$), 118.20 (Ar–*C*), 123.60 (Ar–*C*), 133.85 (Ar–*C*), 135.21 (Ar–*C*),

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151.83 (*Ar*–O), 166.35 (*C*H=N), 167.29 (*C*H=N). ESI m/z calculated for $[M]^+$. $C_{25}H_{43}InN_2O$: 502.241 found 502.384 Anal. Calc. for $C_{25}H_{43}InN_2O$: C, 59.76; H, 8.63; N, 5.58;. Found: C, 59.64; H, 8.74; N, 5.54.

The compound **9** was obtained by the reaction of $GaCl_3$ (0.62 mmol) with the corresponding ligand (0.296 mmol) in 5 mL dry toluene at room temperature. The mixture was allowed to stir for 24 hr. The solvent was removed under reduced pressure and the residue obtained was crystallized from concentrated toluene solution at 0 °C. Single crystal X-ray diffraction studies suggest that the two protons are attached at the imino-nitrogen atoms. It is quite clear that one proton is from the phenol proligand and the second proton may be coming from water. This is because the $GaCl_3$ is hygroscopic, it adsorbs moisture and it behaves as analogues to ferric chloride. These reactions were performed using $GaCl_3$ purchased from Aldrich without further purification..[22]

Compound 9. Deep yellow solid; Yield = 0.15 g (92 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (d, CH(C*H*$_3$)$_2$, 24H, J_{HH} = 6.8 Hz), 2.44 (s, Ar-C*H*$_3$, 3H), 3.04–.09 (m, C*H*(CH$_3$)$_2$, 4H), 7.32 (d, Ar–*H*, 4H, J_{HH} = 8 Hz), 7.48 (d, Ar–*H*, 2H, J_{HH} = 3.6 Hz), 7.94 (s, Ar–*H*, 2H), 8.44 (s, C*H*=N, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.03 (CH(*C*H$_3$)$_2$), 23.86 (*C*H$_3$), 28.97 (*C*H(CH$_3$)$_2$), 123.07 (Ar–*C*), 124.77 (Ar–*C*), 127.11 (Ar–*C*), 130.72 (Ar–*C*), 133.28 (Ar–*C*), 135.87 (Ar–*C*), 143.19 (Ar–*C*), 148.44 (*Ar*–O), 168.42 (*C*H=N), 170.18 (*C*H=N). Anal. Calcd for $C_{33}H_{41}Cl_4GaN_2O$: C, 57.18; H, 5.96; Cl, 20.46; N, 4.04. Found: C, 57.26; H, 5.84; Cl, 20.40; N, 4.13.

Crystallographic data

Among the compounds synthesized in this study, suitable crystals for X-ray diffraction studies were obtained from **2, 4** and **9**. Single crystals were grown in a glove box at 0°C from concentrated toluene solution of the compounds trough slow evaporation of solvent over a period of two weeks. X-ray data was collected with a Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation source. The data was collected with 100% completeness for θ up to 25° for compound **9**, whereas for compound **2** and **4**, the data were collected to a completeness of 96.7% and 96.6% for a θ maximum of 22.38° and 20.89° due to poor quality of crystals. However, the structures were solved without ambiguity except for the twin refinement of compound **4**. The frame width for ω for was fixed to 0.5° for data collection. The frames were subjected to integration and data were reduced for Lorentz and polarization corrections using SAINT-NT.[25] The multi-scan absorption correction was applied to the data set. All structures were solved using SIR-92 [26] and the refinement was done using SHELXL-13.[27] Compound **4** was initially refined to a high *R*-index of 0.0934(2) and the difference Fourier map showed relatively large peaks [$\Delta\rho_{max} = 1.36e\text{Å}^{-3}$]. A preliminary check for twinning with Twin RotMat [28] showed that the crystal had a two-fold non-merrohedral twin about a-axis with a twin matrix of [1 0 0.942/0 -1 0/0 0 -1]. The twin law operated from the Fo-Fc table was used to generate a HKLF5 format file suitable for twin refinement, which gives a twin fraction of 0.166(3) and 0.834(3). The crystal structure was refined to an improved R-index of 0.0769(2) with an essentially flattered difference Fourier map [$\Delta\rho_{max} = 0.58e\text{Å}^{-3}$]. In addition to twinning, two of the *tert*- butyl moieties of the molecule A are disordered over two positions refined to major and minor site occupancies of 0.67(1) and 0.33(1) respectively. The C-C bond distances of the disordered components were restrained to a distance of 1.53(2)Å. The atomic displacement parameter of the adjacent carbon atoms of the disordered moiety were made similar using suitable similarity restraints with an effective standard uncertainty of 0.02Å^2, followed by the Anisotropic Displacement Parameters were approximated to behave isotropically with an effective standard uncertainty of 0.02 Å^2 and refined. Anisotropic Displacement Parameters for C11, C12 and C13 atoms of **9** were approximated to behave isotropically with an effective standard uncertainty of 0.02 Å^2 due to its large value of U_{ij} components. All the hydrogen atoms associated with the carbon atoms of compounds **2**, **4** and **9** were identified from the difference Fourier map and were allowed to ride on the parent atom to a distance of 0.93(for aromatic C-H) with $U_{iso}(H) = 1.2U_{eq}(C)$ and 0.98(for CH$_3$) with $U_{iso}(H) = 1.5U_{eq}(C)$ respectively. Whereas in compound 9, the protonated nitrogen hydrogen atoms were located from the difference Fourier map and restrained to a distance of 0.90(1) Å. These data were deposited with CCDC with the following numbers: CCDC 1048007(**2**), CCDC 1048008(**4**) and CCDC 1048009(**9**). The crystal data is given in Table 1.

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

The procedure for the bulk polymerizations in 200:1 ratio between respective monomers and **1−9** are outlined below: For *rac*-LA or *L*-LA polymerization, 173.4 µmol of **1−9** and 5 g *rac*-LA or *L*-LA were introduced into a dry reaction vessel equipped with a magnetic bar under an argon atmosphere. The contents were rapidly stirred at 140 °C. It was observed that the monomer melted completely followed by rise in the viscosity of the polymerization and finally the stirring ceased. The progress of polymerization was monitored by recording the ^{1}H NMR spectra of the reaction mixture periodically. The contents were dissolved into minimum quantity of CH_2Cl_2 and poured into cold methanol. The polymer precipitated immediately and was isolated by filtration. The filtered product was dried in vacuum until constant weight was observed.

Characterization of polymers

Data concerning molecular weights (M_n) and the MWDs (M_w/M_n) of the polymer samples obtained by the ROP of lactide were determined by using a GPC instrument with a Waters 510 pump and a 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. Number average molecular weights (M_n) and MWDs (M_w/M_n) of polymers were measured relative to polystyrene standards.

General procedure for the polymerization kinetics

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Bulk polymerization of *rac*-LA and *L*-LA were carried out at 140 °C under an argon atmosphere in a polymerization Schlenk with173.4 µmol of **1**−**9** and 5 g *rac*-LA or *L*-LA. At different appropriate intervals of time, 0.2 mL aliquots were removed from the reaction mixture. The contents were dried under vacuum and were analyzed by ^{1}H NMR for the determination of conversion. The $\ln\{[M]_o/[M]_t\}$ ratio was calculated by integration of the peak corresponding to the methine proton for the polymer and unreacted monomer. Apparent rate constants were obtained from the slopes of the best fit lines. The contents of the quenched aliquots obtained at various time intervals were analyzed by GPC for the determination of M_n and MWDs.

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Electronic supplementary information (ESI) available: NMR spectrum and Mass spectrum of the reported compounds. CCDC 1048007(**2**), CCDC 1048008(**4**) and CCDC 1048009(**9**) For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/…………

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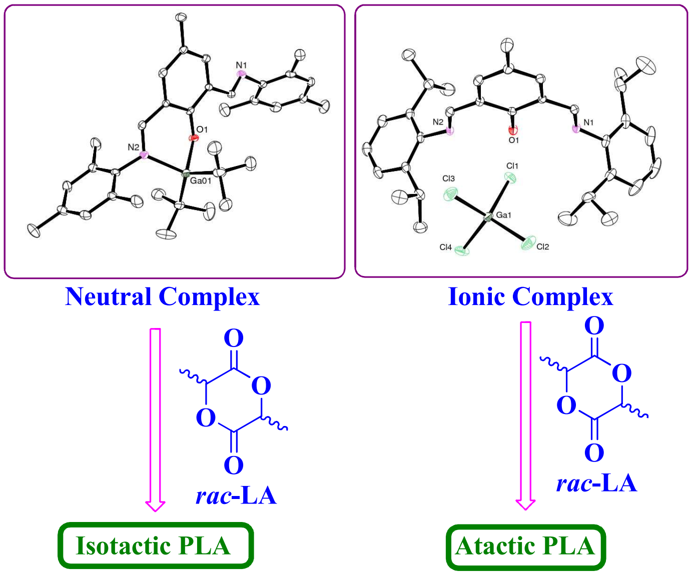

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