



Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

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To cite this article: Sujin Shin, Hyungwoo Cho, Hyosun Lee, Saira Nayab & Younghak Kim (2018): Zinc(II) complexes containing N'-aromatic group substituted N,N',N-bis((1H-pyrazol-1yl)methyl)amines: Synthesis, characterization, and polymerizations of methyl methacrylate and raclactide, Journal of Coordination Chemistry, DOI: <u>10.1080/00958972.2018.1437266</u>

To link to this article: <u>https://doi.org/10.1080/00958972.2018.1437266</u>



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Accepted author version posted online: 07 Feb 2018. Published online: 04 Mar 2018.



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Zinc(II) complexes containing N'-aromatic group substituted N,N',N-bis((1H-pyrazol-1-yl)methyl)amines: Synthesis, characterization, and polymerizations of methyl methacrylate and *rac*-lactide

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ABSTRACT

A novel series of Zn(II) complexes $[L_n ZnCl_2]$ $(L_n = L_A - L_F)$ based on N,N',N-bis((1H-pyrazol-1-yl)methyl)amine bidentate ligands, N,Nbis((1H-pyrazol-1-yl)methyl)-3,5-dimethylaniline [L,], N,N-bis((1Hpyrazol-1-yl)methyl)-2,6-dimethylaniline [L_B], N,N-bis((1H-pyrazol-1-yl) methyl)-2,6-diethylaniline [L], N,N-bis((1H-pyrazol-1-yl)methyl)-2,6diisopropylaniline [L_D], N,N-bis((1H-pyrazol-1-yl)methyl)-4-bromoaniline $[L_{r}]$ and N,N-bis((1H-pyrazol-1-yl)methyl)benzhydrylamine $[L_{r}]$, has been synthesized and characterized. X-ray structures of these Zn(II) complexes showed a distorted tetrahedral geometry. No interaction exists between the N_{amine} and the Zn(II) center in the $[L_n ZnCl_2]$ ($L_n = L_A - L_F$) complexes, resulting in formation of an eightmembered chelate ring. [L,ZnCl,] exhibited the highest catalytic activity $(3.95 \times 10^4 \text{ g PMMA/mol} \cdot \text{Zn} \cdot \text{h})$ for the polymerization of methyl methacrylate (MMA) in the presence of modified methylaluminoxane (MMAO) at 60 °C and yielded high molecular weight (M_{\odot}) (11.0 × 10⁵ g/ mol) of poly(methylmethacrylate) (PMMA). All the complexes resulted in syndiotactic enriched PMMA with high T_{a} (125–131 °C). The steric bulk of ligand architecture plays an influential role in controlling the catalytic activity and stereoregularity of the resultant PMMA. Further, alkyl derivatives $[L_n ZnMe_2]$ ($L_n = L_A - L_F$) of synthesized Zn(II) complexes, generated in situ, showed moderate to high activities toward ring opening polymerization (ROP) of rac-lactide (rac-LA) and yielded heterotactic polylactide (PLA) with P, up to 0.95 at -50 °C. The activity and stereoselectivity toward ROP of rac-LA by these dimethyl Zn(II) complexes should be considered as a combined effect of steric hindrance and electronic density around the metal center.

ARTICLE HISTORY

Received 3 October 2017 Accepted 14 January 2018

KEYWORDS

Zinc(II) complexes; N,N',N-bis((1H-pyrazol-1-yl)methyl)amines; syndiotactic-enriched poly(methylmethacrylate); hetero-enriched polylactide; steric maps

CONTACT Hyosun Lee A hyosunlee@knu.ac.kr; Younghak Kim yikim@postech.ac.kr Supplemental data for this article can be accessed at https://doi.org/10.1080/00958972.2018.1437266.



1. Introduction

Considerable efforts have been made toward the synthesis of pyrazolyl-based transition metal complexes due to their efficient synthesis and various modifications on a linker unit of two or three pyrazole moieties [1–8]. The pyrazolyl group has allowed the construction of various bi- or polydentate ligands, thus furnishing metal complexes of variable coordination geometries and nuclearities [9, 10].

In particular, the *N*,*N*-bispyrazolyl-based chelating ligands were first reported by Driessen in 1982 [11]. Since then, owing to their structural stability and catalytic ability, a variety of pyrazolyl complexes have been employed as cancer sensors and as oxidation and hydrolysis agents [1, 5, 6, 12]. For instance, Driessen *et al.* synthesized and characterized bi- and tridentate pyrazole ligands such as 1-[2-ethylamino]ethyl]-3,5-dimethylpyrazoly(deae), bis-[3,5-dimethylpyrazolyl]methyl]ethylamine (bdmae) and bis-[(3,5-diemtylpyrazolyl)ethyl]ethylamine (ddae) [13, 14]. Specifically, *N*-substituted pyrazolyl amines and their derivatives are versatile ligands due to their ability to change the nature, number, and position of substituents of the amine or pyrazole moiety, thus allowing a fine tuning of the reactivity of the metal center to which they are bound. A variety of transition metal complexes, including Rh(I), Ru(II), Pd(II), Pt(II), Zn(II), and Co(II), ligated to *N*-substituted pyrazolyl amines have exhibited diverse potentially useful chemical properties [15–20], including roles as industrial catalysts in olefin oligomerization or polymerization [21, 22], as bioinorganic materials in pharmaceutical preparations [23–26], and as metal ion extractants [27].

As an extension of our continuing interest in the field of stereoselective methyl methacrylate (MMA) and *rac*-lactide (*rac*-LA) polymerization, we have recently investigated Co(II), Zn(II), Pd(II), Cd(II) and Cu(II) complexes with *N*,*N*-bis(1H-pyrazolyl-1-methyl)aniline and *N*-substituted *N*-(pyridin-2-ylmethyl)amine and their derivatives, exhibiting diverse coordination modes with moderate to high activities and stereoselectivities [28–31].

Recently, the coordination chemistry of Zn(II) toward a polymerization of lactide has received increased attention due to concerns regarding its impact on the environment and its toxicological effects on health [32, 33]. Choosing the appropriate ligand architecture is crucial for controlled polymerization and resultant stereo-regularities. The fact that small

variations in ligand architecture may lead to profound changes in catalytic capabilities and stereoselectivities of polymerization encouraged us to synthesize new Zn(II) complexes bearing *N'*-aromatic-group substituted pyrazolyl amine derivatives. We report in this article the synthesis, structures and reactivities of a series of mononuclear Zn(II) complexes toward MMA polymerization as well as their dimethyl derivatives, generated *in situ*, in ring opening polymerization (ROP) of *rac*-LA. Furthermore, the effect of structural modification of ligand architecture on their catalytic activities and stereoregularities will also be discussed.

2. Experimental

2.1. Materials

1H-pyrazole, *para*-formaldehyde, 3,5-dimethylaniline, 2,6-dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline, 4-bromoaniline, benzhydrylamine, magnesium sulfate (MgSO₄), anhydrous [ZnCl₂] and methyl methacrylate (MMA) were purchased from Sigma-Aldrich (St. Louis, MO) and anhydrous solvents, such as C₂H₅OH, DMF, hexane, and CH₂Cl₂ were purchased from Merck (Darmstadt, Germany) and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation (Tokyo, Japan) as 5.9% aluminum (by weight) in a toluene solution and used without further purification. 1H-pyrazolyl-1-methanol, as starting material, was prepared according to the reported method [11]. The synthesis of $L_A - L_E$ was carried out as reported previously [34–38].

2.2. Physical measurements

Elemental analyses (C, H, and N) of the synthesized ligands and their corresponding dichloro Zn(II) complexes were performed on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ¹H-NMR (operating at 500 MHz) and ¹³C-NMR (operating at 125 MHz) spectra were recorded on an Avance Digital 500 NMR spectrometer (Bruker, Billerica, MA); chemical shifts were recorded in ppm units (δ) relative to SiMe₄ as an internal standard. Infrared (IR) spectra were recorded on a Bruker FT/IR-Alpha (neat) and the data were reported in reciprocal centimeters (cm⁻¹). The molecular weights and molecular weight distributions of the obtained poly(meth-ylmethacrylate) (PMMA) were determined using gel permeation chromatography (GPC) (THF, Alliance e2695; Waters Corp., Milford, MA). Glass transition temperature (T_g) was determined using a thermal analyzer (Q2000; TA Instruments, New Castle, DE).

2.3. Synthetic procedures

2.3.1. Preparation of ligands and corresponding complexes

2.3.1.1. *N,N-bis((1H-pyrazol-1-yl)methyl)benzhydrylamine* (L_F). A solution of benzhydrylamine (2.00 mL, 11.6 mmol) in CH₂Cl₂ (40.0 mL) was slowly added to a solution of 1H-1-pyrazolyl-1-methanol (2.28 g, 23.2 mmol) in CH₂Cl₂ (40.0 mL). The reaction solution was stirred at ambient temperature for 72 h and dried over MgSO₄. The solvent was removed under reduced pressure and the crude residue was vacuum distilled to give a yellow oil (2.93 g, 73.7%). Analysis calculated for C₂₁H₂₁N₅ (%): C, 73.4; H, 6.16; N, 20.4. Found: C, 73.8; H, 6.26; N, 19.9. ¹H-NMR (DMSO, 500 MHz): δ 7.55 (d, 2H, *J* = 1.5 Hz, -N=CH-CH=CH-N-), 7.51 (d, 2H, *J* = 2.3 Hz, -N=CH-CH=CH=N-), 7.39 (d, 4H, *J* = 7.3 Hz, -N-CH-*m*-(C₆H₅)₂), 7.31 (t, 4H, *J* = 7.6 Hz, -N-CH-o-(C₆H₅)₂), 7.22 (t, 2H, *J* = 7.3 Hz, -N-CH-*p*-(C₆H₅)₂), 6.29 (dd, 2H,

 $J = 2.0 \text{ Hz}, J = 2.0 \text{ Hz}, -N=CH-CH=CH-N-), 5.12 \text{ (s, 1H, -N-CH-(C₆H₅)₂), 4.99 \text{ (s, 4H, -N-CH₂-N-). ¹³C-NMR (DMSO, 125 MHz): <math>\delta$ 141.40 (s, 2C, -N-CH-*ipso*-(C₆H₅)₂), 139.25 (d, 2C, J = 185 Hz, -N=CH-CH=CH-N-), 130.23 (d, 2C, J = 187 Hz, -N=CH-CH=CH-N-), 128.66 (d, 4C, J = 161 Hz, -N-CH- \cdot (C₆H₅)₂), 128.04 (d, 4C, J = 159 Hz, -N-CH- \cdot (C₆H₅)₂), 127.35 (d, 2C, J = 161 Hz, -N-CH- \cdot (C₆H₅)₂), 105.39 (d, 2C, J = 176 Hz, -N=CH-CH=CH-N-), 67.70 (d, 1C, J = 137 Hz, -N-CH-(C₆H₅)₂), 64.11 (t, 2C, J = 151 Hz, -N-CH₂-N-). IR (oily liquid neat; cm⁻¹): 3029 (w), 1598 (w), 1513 (m), 1492 (w), 1451 (m), 1391 (m), 1283 (m), 1188 (s), 1139 (m), 1083 (s), 1044 (s), 963 (m), 741 (s), 701 (s), 612 (m).

2.3.1.2. N,N-bis((1H-pyrazol-1-yl)methyl)-3,5-dimethylanilinezinc(II) chloride([L_AZnCl₂]). A solution of $\boldsymbol{L}_{\mathtt{A}}$ (0.800 g, 2.84 mmol) in anhydrous EtOH (10.0 mL) was slowly added to a solution of [ZnCl,] (0.390 g, 2.84 mmol) in anhydrous EtOH (10.0 mL). Precipitation of white material occurred while stirring at 25 °C for 12 h. The white powder was filtered and washed with cold EtOH (20.0 mL \times 3), followed by washing with hexane (20.0 mL \times 3) to yield a final crystalline product (1.00 g, 84.0%). Analysis calculated for C₁₆H₁₀Cl₂N₅Zn (%): C, 46.0; H, 4.59; N, 16.8. Found: C, 45.8; H, 4.58; N, 16.9. ¹H-NMR (DMSO, 500 MHz): δ 7.81 (d, 2H, *J* = 2.1 Hz, -N=CH-CH=CH-N-), 7.51 (d, 2H, J = 1.2 Hz, -N=CH-CH=CH-N-), 6.77 (s, 2H, o-NC₆H₂(CH₂)₂), 6.44 (s, 1H, p-NC₆H₃(CH₃)₂), 6.25 (dd, 2H, J = 2.0 Hz, J = 2.0 Hz, -N=CH-CH=CH-N-), 5.87 (s, 4H, -N-CH₂-N-), 2.16 (s, 6H, -NC₆H₃(CH₃)₂). ¹³C-NMR (DMSO, 125 MHz): δ 145.49 (s, 1C, *ipso*- $NC_{2}H_{2}(CH_{2})_{2}$, 139.43 (d, 2C, J = 185 Hz, -N=CH-CH=CH-N-), 138.31 (s, 2C, $m-NC_{6}H_{3}(CH_{3})_{2}$), 130.02 (d, 2C, J = 188 Hz, -N=CH-CH=**C**H-N-), 121.46 (d, 1C, J = 157 Hz, p-N**C**₆H₂(CH₂)₂), 112.37 (d, 2C, J = 156 Hz, o-NC₆H₃(CH₃)₂), 105.89 (d, 2C, J = 177 Hz, -N=CH-CH=CH-N-), 66.19 (t, 2C, J = 153 Hz, -N-CH₂-N-), 21.72 (q, 2C, J = 126 Hz, -NC₆H₃(CH₃)₂). IR (solid neat; cm⁻¹): 3114 (w), 2917 (w), 1603 (m), 1517 (w), 1480 (w), 1415 (m), 1325 (m), 1248 (m), 1167 (s), 1073 (s), 958 (w), 823 (s), 764 (s), 687 (m), 613 (m), 585 (w).

2.3.1.3. *N,N-bis((1H-pyrazol-1-yl)methyl)-2,6-dimethylaniline zinc(ll) chloride* ($[L_BZnCl_2]$). Following a procedure similar to that described for $[L_AZnCl_2]$, EtOH solution of L_B (0.800 g, 2.84 mmol) and $[ZnCl_2]$ (0.390 g, 2.84 mmol) was used instead. After workup the white crystalline solid was obtained as a final product (1.05 g, 88.5%). Analysis calculated for $C_{16}H_{19}Cl_2N_5Zn$ (%): C, 46.0; H, 4.59; N, 16.8. Found: C, 45.8; H, 4.61; N, 16.5. ¹H-NMR (DMSO, 500 MHz): δ 7.65 (d, 2H, J = 2.0 Hz, -N=CH-CH=CH-N-), 7.55 (d, 2H, J = 1.4 Hz, -N=CH-CH = CH-N-), 6.97–7.03 (m, 3H, *m,o*-NC₆H₃(CH₃)₂), 6.27 (dd, 2H, J = 2.1 Hz, J = 2.1 Hz, -N=CH-CH=CH-N-), 5.47 (s, 4H, $-N-CH_2-N-$), 1.67 (s, 6H, $-NC_6H_3-(CH_3)_2$). ¹³C-NMR (DMSO, 125 MHz): δ 143.73 (s, 2C, *ipso*-NC₆H₃(CH₃)₂), 139.85 (d, 2C, J = 186 Hz, -N=CH-CH=CH-N-), 137.59 (s, 2C, -N=CH-CH=CH-N-), 130.75 (d, 2C, J = 189 Hz, *m*-NC₆H₃(CH₃)₂), 128.84 (d, 2C, J = 157 Hz, $o-NC_6H_3(CH_3)_2$), 128.84 (d, 2C, J = 157 Hz, $o-NC_6H_3(CH_3)_2$), 126.82 (d, 1C, J = 160 Hz, $p-NC_6H_3(CH_3)_2$), 106.03 (d, 2C, J = 179 Hz, -N=CH-CH=CH-N-), 68.47 (t, 2C, J = 152 Hz, $-N-CH_2-N-$), 17.59 (q, 2C, J = 127 Hz, $-NC_6H_3(CH_3)_2$). IR (solid neat; cm⁻¹): 3136 (w), 2928 (w), 1605 (w), 1515 (w), 1469 (w), 1410 (m), 1301 (m), 1257 (m), 1168 (s), 1067 (s), 976 (w), 949 (w), 917 (w), 779 (s), 742 (s), 639 (m), 610 (s), 587 (m).

2.3.1.4. *N,N-bis((1H-pyrazol-1-yl)methyl)-2,6-diethylaniline zinc(II) chloride* ([$L_c ZnCl_2$]). Following a procedure similar to that described for [$L_a ZnCl_2$], EtOH solution of L_c (0.800 g, 2.59 mmol) and [$ZnCl_2$] (0.350 g, 2.59 mmol) were used instead. After workup the white crystalline solid was obtained as a final product (0.960 g, 83.3%). Analysis calculated for $C_{18}H_{23}Cl_2N_5Zn$

(%): C, 48.5; H, 5.20; N, 15.7. Found: C, 48.0; H, 5.39; N, 15.1. ¹H-NMR (DMSO, 500 MHz): δ 7.66 (d, 2H, J = 2.3 Hz, -N=CH-CH=CH=N-), 7.57 (d, 2H, J = 1.5 Hz, -N=CH-CH=CH-N-), 7.17 (t, 1H, J = 7.6 Hz, $p-NC_6H_3(CH_2CH_3)_2$), 7.06 (d, 2H, J = 7.6 Hz, $m-NC_6H_3(CH_2CH_3)_2$), 6.28 (dd, 2H, J = 2.1 Hz, J = 2.1 Hz, -N=CH-CH=CH-N-), 5.50 (s, 4H, $-N-CH_2-N-$), 1.99 (q, 4H, J = 7.5 Hz, $-NC_6H_3(CH_2CH_3)_2$), 0.91 (t, 6H, J = 7.6 Hz, $-NC_6H_3(CH_2CH_3)_2$). ¹³C-NMR (DMSO, 125 MHz): δ 143.10 (s, 1C, *ipso*-NC₆H₃(CH₂CH₃)₂), 142.67 (s, 2C, $o-NC_6H_3(CH_2CH_3)_2$), 139.58 (d, 2C, J = 186 Hz, -N=CH-CH=CH-N-), 130.32 (d, 2C, J = 187 Hz, -N=CH-CH=CH-N-), 127.19 (d, 2C, J = 160 Hz, $m-NC_6H_3(CH_2CH_3)_2$), 126.26 (d, 1C, J = 157 Hz, $p-NC_6H_3(CH_2CH_3)_2$), 105.89 (d, 2C, J = 177 Hz, -N=CH-CH=CH-N-), 69.18 (t, 2C, J = 152 Hz, $-N-CH_2-N-$), 22.65 (t, 2C, J = 127 Hz, $-NC_6H_3(CH_2CH_3)_2$), 14.77 (q, 2C, J = 126 Hz, $-NC_6H_3(CH_2CH_3)_2$). IR (solid neat; cm⁻¹): 3120 (w), 2970 (w), 2876 (w), 1516 (w), 1460 (w), 1413 (m), 1303 (m), 1257 (m), 1173 (s), 1066 (s), 977 (w), 912 (w), 819 (w), 770 (s), 741 (m), 614 (m), 587 (w).

2.3.1.5. N,N-bis((1H-pyrazol-1-yl)methyl)-2,6-diisopropylanilinezinc(II) chloride([L,ZnCl_]). Following a procedure similar to that described for [L, ZnCl,], EtOH solution of L, (0.800 g, 2.37 mmol) and [ZnCl,] (0.320 g, 2.37 mmol) were used instead. After workup the white crystalline solid was obtained as a final product (1.05 g, 93.4%). Analysis calculated for C₂₀H₂₇Cl₂N₅Zn (%): C, 50.7; H, 5.74; N, 14.8. Found: C, 51.1; H, 6.23; N, 13.9. ¹H-NMR (DMSO, 500 MHz): δ 7.76 (d, *J* = 1.8 Hz, –N=C**H**–CH=CH–N–), 7.54 (d, 2H, *J* = 1.4 Hz, –N=CH–CH=C**H**–N–), 7.20 $(t, 1H, J = 7.6 Hz, p-NC_6H_3(CH(CH_3)_2)_2), 7.08 (d, 2H, J = 7.6 Hz, m-NC_6H_3(CH(CH_3)_2)_2), 6.27$ (dd, 2H, J = 2.0 Hz, J = 2.0 Hz, -N=CH-CH=CH-N-), 5.55 (s, 4H, -N-CH₂-N-), 2.64 (m, 2H, - $NC_{c}H_{3}(CH(CH_{3})_{2})_{2}$, 0.90 (d, 12H, J = 6.7 Hz, $-NC_{c}H_{3}(CH(CH_{3})_{2})_{2}$). ¹³C-NMR (DMSO, 125 MHz): δ 148.24 (s, 1C, *ipso*-NC₆H₃(CH(CH₃)₂)₂), 141.29 (s, 2C, -N=CH-CH=CH-N-), 139.87 (d, 2C, $J = 184 \text{ Hz}, o-NC_{6}H_{3}(CH(CH_{3})_{2})_{2}), 130.91 \text{ (d, 2C, } J = 187 \text{ Hz}, -N=CH-CH=CH-N-), 127.95 \text{ (d, 2C, } J = 187 \text{$ 2C, $J = 183 \text{ Hz}, m-NC_{6}H_{3}(CH(CH_{3})_{2})_{2}$, 124.63 (d, 1C, $J = 157 \text{ Hz}, p-NC_{6}H_{3}(CH(CH_{3})_{2})_{2}$), 105.91 (d, 2C, J = 176 Hz, -N=CH-CH=CH-N-), 70.72 (t, 2C, J = 151 Hz, -N-CH₂-N-), 27.99 (d, 2C, $J = 130 \text{ Hz}, -\text{NC}_{6}\text{H}_{3}(\text{CH}_{3}(\text{CH}_{3})_{2}), 24.79 \text{ (q, 4C, } J = 126 \text{ Hz}, -\text{NC}_{6}\text{H}_{3}(\text{CH}_{3}(\text{CH}_{3})_{2}), \text{.] R (solid neat;}$ cm⁻¹): 3108 (w), 2970 (w), 2870 (w), 1515 (w), 1408 (m), 1300 (m), 1254 (m), 1174 (s), 1072 (s), 978 (m), 812 (m), 779 (s), 609 (s), 539 (m).

2.3.1.6. *N,N-bis((1H-pyrazol-1-yl)methyl)-4-bromoanilinezinc(II) chloride* ($[L_EZnCl_2]$). Following a procedure similar to that described for [L_AZnCl_2], EtOH solution of L_E (0.800 g, 2.41 mmol) and [$ZnCl_2$] (0.390 g, 2.41 mmol) were used instead. After workup the white crystalline solid was obtained as a final product (0.89 g, 79.3%). Analysis calculated for $C_{14}H_{14}BrCl_2N_5Zn$ (%): C, 35.9; H, 3.01; N, 15.0. Found: C, 36.2; H, 3.04; N, 14.8. ¹H-NMR (DMSO, 500 MHz): δ 7.84 (d, 2H, J = 2.1 Hz, -N=CH-CH=CH-N-), 7.52 (d, 2H, J = 1.4 Hz, -N=CH-CH=CH-N-), 7.34 (d, 2H, J = 9.2 Hz, $m-NC_6H_4Br-$), 7.16 (d, 2H, J = 9.2 Hz, $o-NC_6H_4Br-$), 6.27 (dd, 2H, J = 2.0 Hz, J = 2.0

2.3.1.7. N,N-bis((1H-pyrazol-1-yl)methyl)benzhydrylamine zinc(II) chloride ([L_zZnCl_z]). Following a procedure similar to that described for [L, ZnCl,], EtOH solution of L_E (0.800 g, 2.33 mmol) and [ZnCl,] (0.320 g, 2.33 mmol) were used instead. The solution was stirred for 12 h. After workup the white crystalline solid was obtained as a final product (0.860 g, 76.8%). Analysis calculated for C₂₁H₂₁Cl₂N₅Zn (%): C, 52.6; H, 4.41; N, 14.6. Found: C, 52.5; H, 4.41; N, 15.1. ¹H-NMR (DMSO, 500 MHz): δ 7.54 (d, 2H, J = 1.4 Hz, -N=CH–CH=CH–N–), 7.51 (d, 2H, J = 2.1 Hz, -N=CH−CH=C**H**−N−), 7.38 (d, 4H, J = 7.4 Hz, −N−CH-*m*-(C_c**H**_c)₂), 7.31 (t, 4H, J = 7.6 Hz, −N− CH-o-(C₆ H_5)₂), 7.23 (t, 2H, J = 7.2 Hz, -N-CH-p-(C₆ H_5)₂), 6.28 (dd, 2H, J = 2.1 Hz, J = 2.1 Hz, -N=CH-CH=CH-N-), 5.13 (s, 1H, -N-CH-(C₆H₅)₂), 5.01 (s, 4H, -N-CH₂-N-). ¹³C-NMR (DMSO, 125 MHz): δ141.24 (s, 2C, -N-CH-ipso-(**C**₆H₅)₂), 139.38 (d, 2C, J = 187 Hz, -N=**C**H-CH=CH-N-), 130.51 (d, 2C, J = 188 Hz, -N = CH - CH = CH - N -), 128.65 (d, 4C, J = 160 Hz, $-N - CH - m - (C_{e}H_{z})_{2}$), 128.07 (d, 4C, J = 158 Hz, $-N-CH-o-(C_{6}H_{5})_{2}$), 127.36 (d, 2C, J = 161 Hz, $-N-CH-p-(C_{6}H_{5})_{2}$), $105.42 (d, 2C, J = 176 Hz, -N=CH-CH=CH-N-), 67.63 (d, 1C, J = 137 Hz, -N-CH-(C_{c}H_{z})_{2}), 64.48$ (t, 2C, J = 151 Hz, -N-**C**H₂-N-). IR (solid neat; cm⁻¹): 3115 (w), 1514 (w), 1494 (w), 1448 (w), 1404 (m), 1373 (m), 1245 (m), 1168 (m), 1134 (m), 1070 (s), 968 (m), 917 (w), 776 (s), 736 (s), 695 (s), 607 (m), 561 (w).

2.4. Typical procedures for MMA polymerization

The methyl methacrylate (MMA) was extracted with 10% sodium hydroxide, washed with water, dried over MgSO₄, and distilled over CaH₂ under reduced pressure before use. In a Schlenk line, complex (15.0 µmol, 6.30 mg for [L_AZnCl₂]; 6.30 mg for [L_BZnCl₂]; 6.70 mg for [L_CZnCl₂]; 7.10 mg for [L_DZnCl₂]; 7.00 mg for [L_EZnCl₂]; 7.20 mg for [L_FZnCl₂]; 0.70 mg for [L_CZnCl₂]; 7.10 mg for [L_DZnCl₂]; 7.00 mg for [L_EZnCl₂]; 7.20 mg for [L_FZnCl₂]; 0.00 mL) followed by the addition of modified MMAO (5.90 wt% in toluene, 3.80 mL, 7.50 mmol, and [MMAO]₀/[catalyst]₀ = 500) as a co-catalyst. The solution was stirred at 60 °C for 20 min. The MMA (5.00 mL, 47.10 mmol, [MMA]₀/[catalyst]₀ = 3100) was added to the above reaction mixture and stirred at 60 °C for 2 h to obtain a viscous solution. MeOH (2.00 mL) was added to terminate the polymerization. The reaction mixture was poured into a large quantity of MeOH (500 mL), and 35% HCl (5.00 mL) was injected to remove the remaining co-catalyst. The resulting polymer was filtered and washed with MeOH (250 mL × 2) to yield PMMA, which was vacuum-dried at 60 °C. The polymers were isolated as white solids and characterized by GPC in THF using standard polystyrene as the reference.

2.5. Typical procedure for ROP of rac-lactide

In a general polymerization reaction for *rac*-LA with the dimethyl zinc initiators, the catalyst species were generated as follows. 0.50 mmol of zinc complexes and dried THF (7.37 mL) were added to a 100 mL Schlenk flask under argon atmosphere. To this solution was added MeLi (1.00 mmol, 0.63 mL of 1.6 *M* solution in diethyl ether) dropwise at -78 °C to generate *in situ* dimethyl Zn(II) species. After stirring for 2 h at room temperature, the resulting THF solution of dimethyl Zn(II) complexes, i.e. [L_nZnMe₂] (L_n = L_A - L_F) was used as an initiator for ROP of *rac*-LA. The general procedure for the polymerization reaction was as follows. A Schlenk flask (100 mL) was charged with *rac*-LA (0.901 g, 6.25 mmol) under argon atmosphere and 5.0 mL of dried CH₂Cl₂ was added. The polymerization was initiated by slow addition of the catalyst solution (1.0 mL, 0.0625 mmol) via a syringe under argon at -50 °C. The reaction mixture was stirred for the allotted time and the polymerization reactions were

quenched using H₂O (1.0 mL). Then hexane (2.0 mL) was added to precipitate the polymer. The monomer conversion was measured by ¹H-NMR spectroscopy. ¹H-NMR (CDCl₃, 500 MHz) for the obtained polymer: δ = 5.13–5.20 (m, 1H), 1.51–1.63 (m, 3H).

2.6. X-ray crystallographic studies

X-ray quality crystals for crystallographic studies of the synthesized Zn(II) complexes were obtained from layering of ether on methanol solution. A colorless single crystal of each zinc complex was picked up with paraton-*N* oil and mounted on a Bruker SMART CCD diffractometer or PHOTON 100 CMOS equipped with a graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation source under nitrogen cold stream (200 K or 223 K). Data collection and integration were performed with SMART or APEX2 and SAINT-Plus software packages [39]. Multi-scan absorption corrections based on equivalent reflections were applied by SADABS [40]. Structures were solved by direct methods and refined using a full-matrix least-squares on F^2 using SHELXTL or SHELXL-2016 [41]. In [L_cZnCl₂], the C17 and C18 atoms of the [L_c] ligand were refined as disordered over two set of sites (C17a/C17b and C18a/C18b) with refined occupancies.

Crystallographic and structural data are summarized in Table 1. The void volumes of $[L_c ZnCl_2]$ and $[L_p ZnCl_2]$, estimated by PLATON, are 1629 and 1699 Å³, respectively. The solvent molecules, presumably methanol or water, were not identified or refined because of their severe disorder and distribution over multiple sites, so that they could not be reliably modeled with discrete atoms. Thus, the final refinement was performed with modification of the structure factors to allow for the contribution of disordered solvent electron density using the SQUEEZE option of PLATON. The electron densities assigned thus were 299 electrons/unit cell for $[L_c ZnCl_2]$ and 387 electrons/unit cell for $[L_c ZnCl_2]$, respectively.

3. Results and discussion

3.1. Synthesis and chemical properties

Ligands in the current study were obtained by the single step condensation reaction of the substituted aniline and 1H-pyrazolyl-1-methanol in CH_2CI_2 or MeCN. The corresponding $[L_nZnCI_2] (L_n = L_A - L_F)$ complexes were obtained (approximately 76 ~ 94% yields) by straightforward reaction of metal starting material $[ZnCI_2]$ with ligands in a 1:1 ratio in anhydrous EtOH (Scheme 1). All the synthesized complexes were stable and stored without any decomposition. The formation and identity of the synthesized complexes were structurally characterized using ¹H-NMR, ¹³C-NMR, IR, elemental analysis, and X-ray diffraction studies. There is a slight difference of proton and carbon signals in ¹H-NMR and ¹³C-NMR spectrum of the Zn(II) complexes relative to their respective free ligand signals. For example, the resonance for methylene $-N-CH_2-N-$ protons appeared at $\delta 4.99$ (s, 4H) in L_F , however, in $[L_FZnCI_2]$ the signals appeared at $\delta 7.55$ (d, 2H, J = 1.5 Hz, -N=CH-CH=CH-N-) and $\delta 7.51$ (d, 2H, J = 2.3 Hz, -N=CH-CH=CH-N-) in L_F while in the corresponding Zn(II) complex these signals appeared at $\delta 7.54$ and 7.51 ppm, respectively.

Comparison of the IR spectra of the ligands with those of the synthesized dichloro Zn(II) complexes was also performed. New absorption bands at 585, 587, 587, 539, 591, and

Table 1. Crystal data an	d structural refinement i	for $[L_nZnCl_2]$ ($L_n = L_A - I$	L _F).			
	[L _A ZnCl ₂]	[L _B ZnCl ₂]	[L _c ZnCl ₂]	[L _D ZnCl ₂]	[L _E ZnCl ₂]	[L _F ZnCl ₂]
Empirical formula Formula weight	C ₁₆ H ₁₉ Cl ₂ N ₅ Zn, CH ₂ Cl ₂ 502.56	C ₁₆ H ₁₉ Cl ₂ N ₅ Zn 417.63	C ₁₈ H ₂₃ Cl ₂ N ₅ Zn 445.68	C ₂₀ H ₂₇ Cl ₂ N ₅ Zn 473.73	C ₁₄ H ₁₄ BrCl ₂ N ₅ Zn 468.48	C ₂₁ H ₂₁ Cl ₂ N ₅ Zn 479.7
Temperature (K)	200(2)	200(2)	223(2)	223(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Trigonal	Trigonal	Monoclinic	Triclinic
Space group	CC	P2(1)/n	R-3	R-3	P2(1)/n	P-1
Unit cell dimensions						
a (Å)	13.6753(1)	11.0110(5)	30.115(3)	30.533(3)	9.6059(1)	8.0293(1)
<i>b</i> (Å)	19.1860(2)	13.6752(6)	30.115(3)	30.533(3)	13.2958(1)	10.0527(1)
c (Å)	8.6866(8)	12.3892(5)	13.3692(18)	13.9240(2)	14.3896(2)	14.1143(2)
a (°)	90	06	06	06	90	73.480(2)
β (°)	99.875(2)	94.8890(1)	06	06	107.833(2)	89.773(2)
(°) V (°)	90	06	120	120	06	75.360(3)
Volume (ų), Z	2245.4(3), 4	1858.75(1), 4	10,500(3),18	11,242(2),18	1749.5(3), 4	1053.9(2), 2
Density (calculated) (g/	1.487	1.492	1.269	1.26	1.779	1.512
Absorption coefficient (mm ⁻¹)	1.582	1.616	1.292	1.211	3.997	1.436
F(000)	1024	856	4140	4428	928	492
Crystal size (mm ³)	$0.30 \times 0.22 \times 0.15$	$0.25 \times 0.23 \times 0.15$	$0.180 \times 0.120 \times 0.100$	$0.180 \times 0.150 \times 0.080$	$0.41 \times 0.33 \times 0.32$	$0.38 \times 0.29 \times 0.23$
θ range for data collection (°)	1.85 to 28.27	2.22 to 28.30	2.182 to 28.418	2.124 to 28.322	2.13 to 28.32	1.51 to 28.35
Index ranges	$-18 \le h \le 11, -25 \le k \le 2411 \le l \le 11$	$-6 \le h \le 14, -18 \le k \le 18, -16 \le l \le 16$	−39 ≤ h ≤ 40, −40 ≤ k ≤ 40. −17 < l < 17	$-40 \le h \le 40, -40 \le k \le 40, -18 \le l \le 18$	$-12 \le h \le 12, -17 \le k \le 17, -10 \le l \le 19$	$-10 \le h \le 10, -13 \le k \le$ 818 < l < 18
Reflections collected	8277	13,631	132,604	126,424	12,301	7874
Independent reflections	4595 [<i>R</i> (int) = 0.0551]	4620 [R(int) = 0.0489]	5838 [<i>R</i> (int) = 0.1474]	6227 [R(int) = 0.1222]	4260 [R(int) = 0.0183]	5149 [R(int) = 0.0263]
Completeness to $\theta = 28.27^{\circ}$	99.40%	%06.66	100.00%	100.00%	97.70%	97.80%
Absorption correction	None	None	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	None

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Refinement method	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
	on F ²	on F ²	on F ²	on F ²	on F ²	on F ²
Data/restraints/	4595/2/246	4620/0/219	5838/1/245	6227/0/257	4260/0/208	5149/0/263
parameters						
Goodness-of-fit on F ²	1.037	1.085	1.029	1.028	1.193	1.224
Final R indices	$R_1 = 0.0551$,	$R_1 = 0.0440$,	$R_1 = 0.0453$,	$R_1 = 0.0366$	$R_1 = 0.0359$,	$R_1 = 0.0562$
[/ > 2sigma(/)]	$WR_{2} = 0.1045$	$w\dot{R}_{2} = 0.0903$	$wR_{2} = 0.0973$	$wR_{2} = 0.0677$	$w\dot{R}_{2} = 0.0728$	$W\dot{R}_{2} = 0.1063$
R indices (all data)	$R_1 = 0.1097$	$R_{1}^{2} = 0.0969$	$R_1 = 0.0831$,	$R_1 = 0.0676$,	$R_{1}^{2} = 0.0680,$	$R_1 = 0.1073$,
	$W\dot{R}_{3} = 0.1413$	$w\dot{R}_{2} = 0.1390$	$wR_{3} = 0.1121$	$wR_{2} = 0.0771$	$w\dot{R}_{3} = 0.1412$	$W\dot{R}_{2} = 0.1867$
Largest diff. peak and hole (e.Å ^{–3})	0.712 [°] and –0.662	0.912 [°] and1.365	0.761 [°] and –0.384	0.406 [°] and –0.258	1.196 and –1.732	1.617 [°] and –2.819

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561 cm⁻¹ have been observed for newly formed Zn–N bonds in the synthesized complexes $[L_n ZnCl_2]$ ($L_n = L_A - L_F$). Elemental analyses of the synthesized complexes were consistent with the proposed structures in Scheme 1 and confirmed the purity of isolated complexes $[L_n ZnCl_2]$ ($L_n = L_A - L_F$).

3.2. Description of X-ray structures

Single crystals for X-ray diffraction studies of $[L_n ZnCl_2]$ ($L_n = L_A - L_F$) were obtained by layering hexane on the CH₂Cl₂ solution of the synthesized complexes. Selected bond angles (°) and lengths (Å) for $[L_n ZnCl_2]$ ($L_n = L_A - L_F$) are compiled in Table 2. The crystal structures of $[L_n ZnCl_2]$ ($L_n = L_A - L_F$) at 30% probability with the atomic labeling are shown in Figures 1–6. Among the synthesized complexes, $[L_A ZnCl_2]$, $[L_B ZnCl_2]$, and $[L_E ZnCl_2]$ crystallized in monoclinic system, while $[L_C ZnCl_2]$ (Figures 3a and 3b) and $[L_D ZnCl_2]$ crystallized in the trigonal system, and $[L_E ZnCl_2]$ crystallized in the triclinic system.

It is evident from the molecular structures of the synthesized Zn(II) complexes that the central zinc ion of each complex adopts distorted tetrahedral geometry by coordinating with two pyrazole nitrogen atoms in a chelating manner and two chloro ligands. The average Zn–N_{pyrazole} bond lengths lie in the range of 2.014(5)–2.058(4) Å for the synthesized Zn(II) complexes and do not vary much from similar reported complexes [42–46]. Similarly, an average Zn–Cl (2.226 Å) bond distance is in good agreement with the analogous distance



Figure 1. ORTEP drawing of $[L_AZnCl_2]$ with thermal ellipsoids at 30% probability. Note: All hydrogens are omitted for clarity.



Figure 2. ORTEP drawing of $[L_BZnCl_2]$ with thermal ellipsoids at 30% probability. Note: All hydrogens are omitted for clarity.



Scheme 1. Synthetic route of ligands and their corresponding Zn(II) complexes $[L_nZnCl_2]$ $(L_n = L_A - L_F)$.

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Table 2. Selecte	d bond lei	ngths (Å) and ang	lles (°) of [l	$-n^{2}$ (L $_{n} = L_{A}$	– L _F).						
[L _A ZnCl ₂]		[L _B ZnCl ₂	2]	[L _C Z	2nCl ₂]	[L _D Z	[nCl ₂]	[L _E ZnCl ₂]		[L _F ZnCl	2]
Bond lengths (Å)											
Zn(1)–N(1)	2.029(6)	Zn(1)–N(1)	2.049(3)	Zn(1)–N(5)	2.027(2)	Zn(1)–N(5)	2.033(2)	Zn(1)–N(1)	2.034(5)	Zn(1)–N(1)	2.025(5)
Zn(1)–N(4)	2.015(6)	Zn(1)–N(4)	2.058(4)	Zn(1)–N(1)	2.042(2)	Zn(1)–N(1)	2.034(2)	Zn(1)–N(4)	2.014(5)	Zn(1)–N(4)	2.045(5)
Zn(1)–Cl(1)	2.246(2)	Zn(1)-Cl(1)	2.215(1)	Zn(1)-Cl(2)	2.221(8)	Zn(1)–Cl(1)	2.217 (6)	Zn(1)-Cl(1)	2.236(2)	Zn(1)-Cl(1)	2.224(2)
Zn(1)–Cl(2)	2.219(2)	Zn(1)-Cl(2)	2.224(1)	Zn(1)-Cl(1)	2.232(8)	Zn(1)–Cl(2)	2.230(6)	Zn(1)-Cl(2)	2.205(2)	Zn(1)-Cl(2)	2.237(2)
N(1)-C(1)	1.321(9)	N(1)-C(1)	1.324(5)	N(1)-C(1)	1.330(4)	N(1)-C(1)	1.335(3)	N(1)-C(1)	1.328(8)	N(1)-C(1)	1.328(8)
N(1)–N(2)	1.358(7)	N(1)–N(2)	1.360(5)	N(1)–N(2)	1.356(3)	N(1)–N(2)	1.358(2)	N(1)-N(2)	1.360(7)	N(1)–N(2)	1.355(6)
N(2)–C(3)	1.350(8)	N(2)-C(3)	1.341(5)	N(2)-C(3)	1.333(4)	N(2)-C(3)	1.340(3)	N(2)–C(3)	1.355(8)	N(2)-C(3)	1.336(8)
N(2)–C(4)	1.460(9)	N(2)–C(4)	1.466(5)	N(2)–C(4)	1.468(3)	N(2)-C(4)	1.469(2)	N(2)–C(4)	1.479(8)	N(2)-C(4)	1.472(7)
N(5)–C(9)	1.417(8)	N(5)-C(9)	1.443(5)	N(3)–C(9)	1.437(4)	N(3)–C(9)	1.446(2)	N(5)–C(9)	1.409(8)	N(5)–C(9)	1.468(7)
Bond angles (°)											
N(4)-Zn(1)-N(1)	104.9(2)	N(1)-Zn(1)-N(4)	101.9(1)	N(5)–Zn(1)–N(1)	113.5(1)	N(5)-Zn(1)-N(1)	112.8(7)	N(4)–Zn(1)–N(1)	99.5(2)	N(4)-Zn(1)-N(1)	105.3(2)
N(4)-Zn(1)-Cl(1)	111.2(2)	N(1)-Zn(1)-Cl(1)	104.9(1)	N(5)-Zn(1)-Cl(2)	104.7(8)	N(5)-Zn(1)-Cl(1)	106.2(5)	N(4)-Zn(1)-Cl(1)	112.7(2)	N(4)-Zn(1)-Cl(1)	114.2(2)
N(1)-Zn(1)-Cl(1)	108.3(2)	N(4)-Zn(1)-Cl(1)	105.8(1)	N(1)-Zn(1)-Cl(2)	104.8(7)	N(1)-Zn(1)-Cl(1)	104.0(5)	N(1)-Zn(1)-Cl(1)	112.2(2)	N(1)-Zn(1)-Cl(1)	111.4(2)
N(4)-Zn(1)-Cl(2)	105.1(2)	N(1)-Zn(1)-Cl(2)	112.7(1)	N(5)-Zn(1)-Cl(1)	107.1(8)	N(5)-Zn(1)-Cl(2)	106.2(5)	N(4)-Zn(1)-Cl(2)	110.4(2)	N(4)-Zn(1)-Cl(2)	101.9(1)
N(1)-Zn(1)-Cl(2)	109.2(2)	N(4)-Zn(1)-Cl(2)	110.8(1)	N(1)-Zn(1)-Cl(1)	107.1(7)	N(1)-Zn(1)-Cl(2)	108.7(5)	N(1)-Zn(1)-Cl(2)	107.7(2)	N(1)-Zn(1)-Cl(2)	105.4(1)
Cl(1)-Zn(1)-Cl(2)	117.4(9)	Cl(1)-Zn(1)-Cl(2)	119.1(5)	Cl(2)–Zn(1)–Cl(1)	120.0(3)	Cl(1)-Zn(1)-Cl(2)	119.2(2)	Cl(1)-Zn(1)-Cl(2)	113.4(7)	Cl(1)-Zn(1)-Cl(2)	117.5(7)
C(1)-N(1)-N(2)	105.7(6)	C(1)-N(1)-N(2)	107.0(3)	C(1)-N(1)-N(2)	105.7(2)	C(1)-N(1)-N(2)	105.3(2)	C(1)-N(1)-N(2)	106.2(5)	C(1)-N(1)-N(2)	106.1(5)
C(1)–N(1)–Zn(1)	127.8(5)	C(1)-N(1)-Zn(1)	126.3(3)	C(1)–N(1)–Zn(1)	125.6(2)	C(1)–N(1)–Zn(1)	126.7(2)	C(1)–N(1)–Zn(1)	124.5(5)	C(1)-N(1)-Zn(1)	125.7(4)
N(2)–N(1)–Zn(1)	125.9(4)	N(2)-N(1)-Zn(1)	126.6(3)	N(2)-N(1)-Zn(1)	128.6 (2)	N(2)-N(1)-Zn(1)	128.1(1)	N(2)–N(1)–Zn(1)	128.4(4)	N(2)-N(1)-Zn(1)	127.3(3)
C(3)–N(2)–N(1)	109.6(6)	C(3)–N(2)–N(1)	109.3(4)	C(3)-N(2)-N(1)	110.5(2)	C(3)-N(2)-N(1)	110.6(2)	C(3)–N(2)–N(1)	110.4(6)	C(3)–N(2)–N(1)	110.3(5)

	-	-				
Complexes	Geometry	τ_4^{a}	ТНС _{DA} /100 ^b	FCGP/100 ^c	References	
Tetrahedral (T_{a})	Tetrahedral	-	-	0	[51]	
(N,N-bis((1H-pyrazol-1-yl)methyl)aniline)ZnCl,] = [L'ZnCl ,]	Tetrahedral	0.926	0.729	0.11	[42]	
[L _x ZnCl _y]	Tetrahedral	0.932	0.777	0.134	This work	
(L, ZnCl, Ĵ	Tetrahedral	0.909	0.667	0.181	This work	
(L,ZnCl,Ĵ	Tetrahedral	0.897	0.68	0.0614	This work	
[L,ZnCl,]	Tetrahedral	0.908	0.712	0.063	This work	
lL,ZnCl,Ĵ	Tetrahedral	0.95	0.75	0.166	This work	
[L, ZnCl,]	Tetrahedral	0.91	0.661	0.129	This work	
[(N,N-bis((1H-pyrazol-1-yl)methyl)-p-methoxyaniline)ZnCl2] = [L _c ZnCl,J]	Tetrahedral	0.93	0.776	0.094	[42]	
(N,N-bis((1H-pyrazol-1-yl)methyl)-p-fluoroaniline)ZnCl2] = [L_ZnCl,]	Tetrahedral	0.933	0.73	0.163	[42]	
(N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)aniline)ZnCl2] = [L,ZnCl,J	Tetrahedral	0.945	0.806	0.167	[42]	
(N,N-bis((1H-pyrazol-1-yl)methyl)-3-methoxypropan-1-amine)ZnCl2	Tetrahedral	0.934	0.698	0.225	[20]	
(N,N-bis((1H-pyrazol-1-yl)methyl)cyclopentanamine)ZnCl2]	Tetrahedral	0.924	0.726	0.187	[61]	
(N,N-bis((1H-pyrazol-1-yl)methyl)cyclohexanamine)ZnCl2]	Tetrahedral	0.92	0.733	0.149	[29]	
Square planar ($D_{a, b}$)	Square Planar	0	-1.43	-0.4	[51]	
Trigonal pyramidal (C_{3v})	Trigonal pyramidal	0.85	0	1	[52–54]	
Saa rafaranca [51]						

Table 3. Four-coordinate geometry indices for [L, ZnCl,] (L, $= L_A - L_F$) and representative examples from the literature.

^aSee reference [51]. ^b See references [52–54]. ^c See reference [55]. S. SHIN ET AL.



Figure 3a. ORTEP drawing of [L_cZnCl₂] with thermal ellipsoids at 30% probability. Note: All hydrogens are omitted for clarity.

found in similar complexes [47–49]. Lack of interaction between N_{amine} and the Zn(II) center in these four-coordinate complexes resulted in an eight-membered chelate ring which is consistent with our previously reported complexes [29]. The crystallographic data revealed that much smaller $N_{pyrazole}$ -Zn- $N_{pyrazole}$ angles have been observed compared to $CI_{terminal}$ -Zn–Cl_{terminal} bite angles around the central zinc ion in $[L_n ZnCl_2]$ ($L_n = L_A - L_F$) (Table 2). This is a common structural feature for [LZnX,] type of complexes, where L acts as a bidentate chelating ligand attached to the zinc center and X is a halide, with the ligands forming a distorted tetrahedral geometry around the zinc center. It has been observed that the N_{pyrazole}-Zn-N_{pyrazole} angles lie in an accepted range i.e. 101.9(1)-113.5(1)° [29, 35, 50]. It is evident that N_{pyrazole}-Zn-N_{pyrazole} angles are slightly affected by the substituents attached to aniline moiety. For instance, the presence of bulky substituents at ortho position leads to wider N_{pyraole}-Zn-N_{pyrazole} angles (Table 2). However, the Cl(1)-Zn-Cl(2) angles are not much affected by the substituents of the phenyl moiety. Similarly, the bond angles N_{pvrazole}-Zn(1)-Cl(1) and $N_{pyrazole} - Zn(1) - Cl(2)$ lie in the [104.0(5)°-112.2(2)°] and [104.8(7)-112.7(1)] range for [L_nZnCl₂] $(L_n = L_A - L_F)$, respectively. These values are similar to those reported previously for similar complexes [29, 50]. τ_4 values [51] provide useful information regarding geometry of four-coordinate complexes, i.e. for perfect tetrahedron, τ_{4} is 1.00 and 0 for perfect square planar, D_{4h} [52]. In addition, THCDA/100 index provides useful analysis of tetrahedral complexes; a value 1.00 of THC_{DA}/100 index represents perfect tetrahedral geometry, whereas a 0 value

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Figure 3b. ORTEP drawing of $[L_c ZnCl_2]$ with thermal ellipsoids at 30% probability. Note: All hydrogens are omitted for clarity. The C17 and C18 atoms were refined as disordered over two set of sites (C17a/C17b and C18a/C18b) with refined occupancies.

Complexes	Tilt angles (°)	References
$[(N,N-bis((1H-pyrazol-1-yl)methyl)aniline)ZnCl_{3}] = [L'ZnCl_{3}]$	52.7	[42]
[L _a ZnCl ₂]	49	This work
[L _B ZnCl ₂]	1.99	This work
[L _c ZnCl ₂]	0.41	This work
[L _D ZnCl ₂]	2.14	This work
[L _F ZnCl ₂]	50.8	This work
[L _r ZnCl ₂]	-	This work
$[(\dot{N}, N-bis((1H-pyrazol-1-yl))methyl)-p-methoxyaniline)ZnCl_{3}] = [L_{3}ZnCl_{3}]$	8.25	[42]
$[(N,N-bis((1H-pyrazol-1-yl)methyl)-p-fluoroaniline)ZnCl_{2}] = [L_{H}ZnCl_{2}]$	40.7	[42]
$[(N,N-bis((3,5-dimethylpyrazol-1-yl)methyl)aniline)ZnCl_{2}] = [L_{1}ZnCl_{2}]$	9.3	[42]

Table 4. Tilt angles of $[L_n ZnCl_2]$ ($L_n = L'$ and $L_A - L_1$).

of THC_{DA}/100 refers to perfect trigonal pyramidal geometry (C_{3v}) [53, 54]. Similarly, for useful structural information the FCGP/100 index (Table 3) can be applied to the tetrahedral geometry of main group complexes, *i.e.* 1.00 value defines perfect trigonal pyramidal (C_{3v}) and 0 value reflects perfect tetrahedral geometry [55]. Table 3 shows four-coordinate geometry indexes for the Zn(II) complexes with N'-aromatic-group substituted N,N',N-bis((1H-pyrazol-1-yl)methyl)amine derivatives. τ_4 values for all the [L_nZnCl_2] ($L_n = L_A - L_F$) complexes falls

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Figure 4. ORTEP drawing of [L_DZnCl₂] with thermal ellipsoids at 30% probability. Note: All hydrogens are omitted for clarity.

into the range of 0.897–0.950 and indicated the distortion from ideal tetrahedral geometry. All these values are comparable to those observed in reported complexes with similar ligand architecture (Table 3) [42, 50].

The tilt angles (Table 4) between the N'-aromatic rings on the amine moiety and the plane of the N,N-bispyrazole ring were calculated to find the effect of N'-substitution toward tetrahedrality of synthesized complexes. It has been observed that the complexes with alkyl substituents at an ortho position of the aromatic ring of amine moieties have smaller tilt angles $[L_n ZnCl_2]$ ($L_n = L_{R'}L_c$ and L_D tilt angles; 2°, 0°, and 2°, respectively) compared to complexes without alkyl moieties at ortho position of aromatic ring of amine moiety [L, ZnCl,] $(L_n = L_A \text{ and } L_E \text{ tilt angles}; 51^\circ \text{ and } 53^\circ, \text{ respectively})$. This is consistent with previously reported complexes' tilt angles (Table 4); more steric bulk in the vicinity of the metal center results in smaller tilt angles [42]. Further, the tilt angle between the N'-aromatic ring on the amine moiety and the plane of the N,N-bispyrazole ring was not significantly related to the τ_{4} values of complexes.

3.3. Methyl methacrylate (MMA) polymerization

As part of our ongoing investigations toward the stereoselective application of bis-pyrazolylbased initiators in MMA polymerization, the catalytic capabilities of N'-substituted

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Figure 5. ORTEP drawing of [L_EZnCl₂] with thermal ellipsoids at 30% probability. Note: All hydrogens and water molecule are omitted for clarity.

N,*N*',*N*-bis((1H-pyrazol-1-yl)methyl)amine-based Zn(II) complexes were assessed toward MMA polymerization in the presence of modified MMAO at 60 °C. All the complexes [$L_n ZnCl_2$] ($L_n = L_A - L_F$) polymerized MMA effectively yielding PMMA with T_g ranging from 125 to 131 °C. The polymers were isolated as white polymeric material and characterized by GPC in THF using standard polystyrene as a reference. The results of polymerization are summarized in Table 5.

The blank polymerization of methyl methacrylate (MMA) was performed using starting materials, *i.e.* [**ZnCl**₂]/MMAO or solely MMAO under the same experimental conditions in order to realize the ligand effect on the metal center. It is clear from polymerization data that the [**ZnCl**₂]/MMAO system exhibited comparable activity with [**L**_D**ZnCl**₂] (Table 5, entry 7) and resulted in PMMA with low molecular weights. However, the rest of the Zn(II) initiators showed better activities as well as superior stereoselectivities and yielded PMMA with higher molecular weights compared to starting materials. Similarly, no polymerization activity was observed with dichloro Zn(II) complexes in the absence of MMAO.

In the case of using $[L_n ZnCl_2]$ ($L_n = L_A - L_F$) for MMA polymerization, $[L_F ZnCl_2]$ exhibited the highest activity (3.95 × 10⁴ g/mol·Zn·h) and yielded PMMA with high molecular weights

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Figure 6. ORTEP drawing of [L_cZnCl₂] with thermal ellipsoids at 30% probability. Note: All hydrogens and water molecule are omitted for clarity.

 $(110 \times 10^5 \text{ g/mol})$ compared to the rest of its analogs under the same experimental conditions. It has been observed that substituents at the ortho position of the phenyl group of the amine moiety exhibited significant influence on the activities of these Zn(II) complexes, whereas the stereoselectivities were not much affected. [L_cZnCl₂] and [L_pZnCl₂], with an ethyl (-CH₂CH₃) and isopropyl (-CH(CH₃)₂) groups attached at the ortho position of the phenyl group of the amine moiety, respectively, exhibited the lowest activities among the synthesized Zn(II) complexes. However, when the substituents -CH₂CH₃ and -CH(CH₃), at the ortho position were changed to -H and -CH₃, an increase in activities was observed *i.e.* for [L_AZnCl₂] and [L_ZnCl_], respectively. A trivial tendency between the steric bulk and activities was found in complexes bearing alkyl groups, the ortho position of the phenyl group of the amine moiety, in the order of $-CH(CH_3)_2 < -CH_2CH_3 < -CH_3 < H$ (Table 5). It is also evident from our previous report that the bulky substituents attached to amine or pyrazole moiety negatively affect MMA activation; probably the steric bulk around the metal center depresses the monomer approach to the metal sites [35]. Clearly, in the current study the lower activity of the complexes with bulkier ortho amine substituents toward MMA polymerization might be due to the steric clashes of attached ligand and incoming monomer to a metal center.

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 $(L_n ZnCl_2] (L_n = L' and L_A - L_F)$ $(L_n ZnCl_2] (L_n = L' and L_A - L_F)$

Tab	le 5.	. MMA po	lymerization	by [L _n ZnCl	,] (L	_ = L	' and I	$L_A - L_F$) comp	lexes in t	he presence	of MMAO.
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		Yield⁵	Activity ^c	T_{g}^{d}	Tactio	city (%)		<i>M</i> w ^e	_
			$\times 10^{4}$						
Entry	Catalyst ^a	(%)	(g/molcat·h)	(°C)	mm	mr	rr	× 10⁵ (g/mol)	PDI ^f
1	[ZnCl ₂] ^g	11.1	1.73	129	9.20	24.2	66.6	1.33	1.58
2	MMAO ^h	8.97	1.40	120	37.2	10.9	51.9	6.78	2.09
3	[L'ZnCl ₂] ⁱ	13.0	2.03	130	9.24	27.0	65.8	8.00	1.75
4	[L _A ZnCl,]	15.9	2.48	128	10.8	22.2	69.4	10.3	2.33
5	[L _B ZnCl ₂]	14.7	2.29	130	11.5	23.1	65.4	10.6	2.48
6	[L _c ZnCl ₂]	14.0	2.18	130	10.3	20.5	69.2	10.5	2.38
7	[L _D ZnCl,]	12.4	1.94	128	8.82	17.6	66.7	10.2	2.48
8	[L _c ZnCl ₂]	23.1	3.60	125	11.1	22.2	73.5	11.2	2.47
9	[L̄ZnCl͡,]	25.3	3.95	125	12.5	20.8	66.7	11.0	2.41
10	[L _c ZnCl ₂] ^j	0.81	2.70	132	7.31	22.8	70.0	8.91	1.89
11	[LuZnCl_] ^j	0.34	1.13	122	10.3	24.1	65.6	9.20	1.73
12	[L ['] ZnCl ₂] ^j	1.45	4.83	145	8.51	23.3	68.1	9.39	1.77

^a[M(II) catalyst]₀ = 15 μmol, [MMA]₀/[MMAO]₀/[M(II) catalyst]₀ = 3100:500:1, Temp = 60 °C, time = 2 h.

^bYield defined (a mass of dried polymer recovered)/(a mass of monomer used).

^cActivity is (g PMMA)/(molcat·h).

 ${}^{d}T_{a}$ is glass transition temperature determined using a thermal analyzer.

^eDetermined using gel permeation chromatography (GPC) eluted with THF at room temperature by filtration with polystyrene calibration.

 ${}^{f}M_{n}$ refers to the number average of molecular weights of PMMA.

^gIt is a blank polymerization in which anhydrous [ZnCl₂] were also activated by MMAO.

^hIt is a blank polymerization which was done solely by MMAO.

It is polymerization with $[L'ZnCl_2]$; L' = N, N-bis((1H-pyrazol-1-yl)methyl)aniline activated by MMAO [42].

^jData of MMA polymerization obtained from reference [42].

In order to evaluate the steric hindrance exerted by ligand architecture toward the metal center, a quantitative calculation through comparison of a topographic map of Zn(II) complexes using the "SambVca" [56, 57] program has been carried out. Ball and stick models, space-filling models, and topographic steric maps of $[L_n ZnCl_2]$ $(L_n = L_A - L_F)$ for presenting steric bulk of ligands are shown in Figure 7. The steric hindrance of [L_ZnCl_] bearing at the amine moiety is smaller compared to $[L_n CoCl_2]$ $(L_n = L_A - L_D)$ complexes, judging from the buried volume % of ligands in Figure 7. Similarly, the complex [L_FZnCl₂] with an electron-withdrawing bromo group at the ortho position of the amine moiety exhibited lesser steric bulk (buried volume 41.9%). It is evident from the steric map that the bulkier the substituents at ortho position of phenyl group of amine moiety the less the space provided for monomer approach to the metal center (as evident from their steric maps that only monomer approach may occur only from the bottom, as shown from Figure 7, and hence they showed lower activities. For comparison, the steric maps and models of Zn(II) complexes $[L_n ZnCl_2]$ ($L_n = L_G - L_H$) [42] are presented in Figure 7. Note that the presence of 3,5-dimethyl substituents at the pyrazole rings in [L_GZnCl₂] (with 46.4% buried volume) provides greater steric hindrance than that of the corresponding $[L_n ZnCl_2]$ $(L_n = L_H and L_I)$ which has a



 $[L'ZnCl_2] V_{Bur} = 41.9 \%$



 $[L_AZnCl_2] V_{Bur} = 42.2 \%$



Figure 7a. Ball and stick model, space-filling model, and topographic steric map of $[L_n ZnCl_2]$ ($L_n = L'$ and $L_A - L_1$) for presenting steric bulk ligands.



 $[L_DZnCl_2] V_{Bur} = 44.3 \%$



 $[L_FZnCl_2] V_{Bur} = 41.5 \%$







 $[L_E Zn Cl_2] V_{Bur} = 41.9 \%$



 $[L_G Zn Cl_2] V_{Bur} = 42.9 \%$





Figure 7c.

1-H-pyrazole moiety. Moreover, $[L_{g}ZnCl_{2}]$, with more sterically hindered 3,5-dimethyl substituents at the pyrazolyl residue, gave higher activity (4.68 × 10⁴ g PMMA/mol.Zn.h) (Table 5) for MMA polymerization. This might be due to more open reaction space for entering monomer MMA to the metal center at the top and bottom in the steric map than the less sterically hindered complexes $[L_{n}ZnCl_{2}]$ ($L_{n} = L_{A} - L_{F}$, L_{H} and L_{I}) having 1-H-pyrazole. Thus, it may be a reasonable interpretation that steric hindrance at the proper proximity around the metal center may lead to better activity toward MMA polymerization.

Compared with our previously reported Zn(II) complex bearing N'-cyclohexyl substituted N,N-bispyrazolyl [35], the current catalytic system exhibited higher activities $(3.95 \times 10^4 \text{ g} \text{PMMA/mol·Zn·h})$ and yielding PMMA with improved molecular weights *i.e.* $(11.0 \times 10^5 \text{ g/mol})$ and slightly broader PDIs. The PDI range was slightly narrowed when the molecular weight of PMMA was increased. These results are explained by the narrower PDI range of the higher molecular weight polymer [58, 59]. Similarly, in comparison with our reported Zn(II) complexes bearing N,N-bis((1H-pyrazol-1-yl)methyl)-3-methoxypropan-1-amine and 3-methoxy-N,N-bis((3,5-dimethyl-1H-pyrazol-1-yl)methyl)propan-1-amine [50], the catalytic behavior of the current system yielded PMMA with comparable syndiotacticity (rr = 66.7) and high molecular weights and T_{q} at 60 °C (Table 5).

Syndiotactic-enriched PMMA has been observed in all the synthesized complexes, as analyzed by ¹H-NMR spectroscopy [60, 61]. The syndiotactic enchainment ranged from 0.65 to 0.74 for the current systems and was found to be higher compared to the starting materials. These mediocre stereoselectivities of Zn(II) complexes are slightly higher when

compared with reported complexes [35, 42]. Thus, the resultant syndiotacticity of PMMA was not high enough to confer a mechanism of coordination polymerization for the catalytic species in the current report. It is presumed that the presence of the benzhydrylamine group in [L_FZnCl_2] generates a coordination sphere around the metal center to effectively accommodate any steric clashes between incoming monomer, propagating polymer chain and ligand architecture during MMA polymerization. Thus, it can be concluded that the MMA polymerization activity of Zn(II) complexes of the current study should be considered as a function of steric bulk around the metal center. Further modification in ligand architecture to improve the catalytic performance and the resultant stereo-control of the MMA polymerization is presently going on in our laboratory.

3.4. rac-LA polymerization

The synthesis of high molecular weight PLA generally relies on the controlled ROP of LA using well-defined metal complexes. Dimethyl derivatives of the dichloro zinc complexes were assessed for activity in the ROP of rac-LA in CH₂Cl₂. The dimethyl derivatives were generated in situ by treating the dichloro zinc complexes with two equiv. of MeLi in THF. The polymerization was conducted at -50 °C and dimethyl Zn(II) complexes were found to be highly efficient initiators of ROP of rac-LA. Completion of the reaction was confirmed by the absence of monomer signals in the ¹H-NMR spectra. The experimental M_n values (corrected using the Mark– Houwink factor of 0.58) [62–64] and narrower polydispersity indicate that the polymerization was well controlled and occurred through a living polymerization mechanism with a single reaction site provided by these dimethyl zinc complexes. The results of rac-LA polymerization are presented in Table 6. The importance of Mark-Houwink is given as follows; the molecular weights (Mw) and number-average molecular weights (Mn) of the obtained PLA samples were analyzed using GPC, in THF (1 mL/min rate at 25 °C) and were calibrated against polystyrene standards. The calculated Mn values were also obtained using ([molecular weight of rac-LA] × $[rac-LA]/[initiator]) \times (conversion)$ formula. Generally, the values were in reasonable agreement; however, there were always some discrepancies. In order to compensate such discrepancies attention must be paid to the values obtained by GPC, as the Mark-Houwink parameters, k and a are not known for PLA. Thus using the same instrument to estimate the molecular weight of PLA, it has been possible to apply a correction factor (0.58 Mn by GPC) [65].

¹H-NMR spectra showed peaks for the methane protons of $-CH(CH_3)(OH)$ at d 2.90 ppm and the signals for $-C(=O)CH_3$ at the other terminus overlapped with those of PLA backbones. Considering the experimental findings for the ROP of *rac*-LA, under the conditions mentioned, we proposed the mechanism as outlined in Scheme 2. A coordination insertion mechanism [66–68] for the ROP of LA may be predicted, where the pre-coordination of the LA monomer to the Cu(II) center yields a monomeric 5-coordinated intermediate. The *Me* group then acts as a nucleophile and cleavage of acyl-oxygen bond opens the LA ring. The successive addition of LA produced heterotactic PLA.

It is evident from polymerization data that variation in the steric bulk of alkyl groups at the *ortho* position of the aniline moiety has a significant effect on the activity of these Zn(II) complexes. The tendency between steric bulk and catalytic activity toward *rac*-LA for complexes bearing alkyl groups, at the *ortho* position, occurs in the order $-CH(CH_3)_2 > -CH_2CH_3 > -CH_3 > H$ (Table 6). However, the introduction of a bromo group at the *ortho* position of the amine moiety in [L_EZnCl₂] significantly decreased the activity, 84% conversion in 12 h (Table 6, entry 7), which might be due to a decrease in electronic density around the metal center.

 $[L_D^T ZnCl_{,}^2]$

[L_EZnCl₂]

[L_zZnCl_z]

6

7

8

Table 6. Polymerization of *rac*-lactide with *in situ* generated $[L_n ZnMe_2]$ $(L_n = L' \text{ and } L_A - L_F)$ from the reaction of $(L_n = L' \text{ and } L_A - L_F)$ $[L_n ZnMe_2]$ and MeLi.



^aConditions: [Initiator] = 0.0625 mmol, [*rac*-LA]/[Initiator] = 100, 5.0 mL of solvent (CH₂Cl₂), polymerization time = 12 h, temp = -50 °C.

13.25

7.99

6.44

1.26

1.08

1.20

0.91

0.91

0.88

13.98

12.11

12.40

^bMonomer conversion (%) determined by ¹H-NMR spectroscopy.

97

84

86

^cCalculated from ([molecular weight of *rac*-LA] × [mol concentration of used *rac*-LA]/[mol concentration of initiator]) × (conversion).

^dExperimental values (corrected using the Mark-Houwink factor of 0.58) [62–64].

^eDetermined by gel permeation chromatography (GPC) in THF, relative to polystyrene standard.

^fProbability of heterotactic enchainment (P_1) were calculated on the basis of homonuclear decoupled ¹H-NMR spectra according to literature [78–80].

^gIt is polymerization carried out with [L'ZnMe₂] in which L' = N,N-bis((1H-pyrazol-1-yl)methyl)aniline [42].



Scheme 2. Proposed mechanism for ROP of *rac*-LA catalyzed by *N*,*N'*,*N*-bis((1H-pyrazol-1-yl)methyl)amine-based Zn(II) complexes.

These results are in contrast to previously reported systems where sterically hindered groups tended to block the coordination/insertion of incoming monomer and hence were adverse to the catalytic activity [69]. Surprisingly, [L'ZnCl₂], the least sterically demanding, showed 100% conversion and moderate heterotacticity despite having no substituents on the aniline moiety compared to the rest of the complexes of the current study. In addition, [L_FZnCl₂], with –CHPh₂ groups, also showed lower activity and heterotacticity compared to [L_nZnCl₂] (L_n = L_B – L_D). The lower activity of complex [L_FZnCl₂] might be ascribed to the difference of electronic effects between alkylamine [L_nZnCl₂] (L_n = L_A – L_D) and benzhydrylamine groups. In contrast, [L_AZnCl₂] with –*Me* groups at the *meta* position of the amine moiety also showed lower activity, such as 78% conversion with 0.91 heterotactic enchainment. Thus, the activity of these dimethyl Zn(II) complexes can be considered as a composite result of steric and electronic effects.

Compared with our previously reported dimethyl Zn(II) complexes these initiators exhibited significantly lower activities [70–72]. They exhibited higher activities than zinc guanidinate complexes and ketoiminate complexes [73–75]. However, compared to the highly effective zinc initiators, based on phenolate diamines/diimines [76, 77], the catalytic efficacy of Zn(II) complexes in the current study are lower, but produce PLA with better stereoselectivity (Table 6).

The stereo-selectivity of PLA is greatly influenced by the structure of the ancillary ligands attached to the center metal ion during the polymerization process. Microstructural analysis



Figure 8. Homonuclear decoupled ¹H-NMR spectrum of polylactide produced by dimethyl derivative of $[L_B ZnCl_2]$ (for the preparation conditions, see entry 4 in Table 6); $P_r = 2 I_1 [I_1 + I_2] = 2 (7.04 + 1.42)/[(7.04 + 1.42) + (0.96 + 1.48 + 7.00)] \approx 0.95$.



Figure 9. Homonuclear decoupled ¹H-NMR spectrum of polylactide produced by dimethyl derivative of [L_cZnCl₂] (for the preparation conditions, see entry 5 in Table 6); $P_r = 2 I_1/[I_1 + I_2] = 2 (7.24 + 1.41) / 1000$ $[(7.4\24 + 1.41) + (1.17 + 1.48 + 7.76)] \approx 0.91.$

of the obtained PLA was performed by inspecting the methane proton region of homodecoupled ¹H-NMR spectra and P_r values were calculated with the equation $P_r = 211/(11 + 12)$ where I1 = (sis + sii) and I2 = (iis + iii + isi) [78–80]. It is evident from polymerization data that all the complexes exhibited a strong preference for heterotactic enchainment. [L_RZnMe,] produced PLA with a highest degree of heterotacticity with $P_r = 0.95$ compared to the rest of its analogs under the same experimental conditions (Figure 8; Table 6, entry 3). This high degree of heterotacticity obtained with [L_BZnMe₂] is comparable with those obtained with a hetero-bimetallic complex [((R)-{ONNO}),Y·Li] bearing a fluorinated dialkyloxo ligand in ROP of rac-LA [81].

The current system is superior in terms of heterotacticity compared to our previous reported dimethyl complexes [70–72]. It has been observed that enhancing the steric hindrance on amine moiety resulted in decreased heterotacticity for complexes [L, ZnMe,] and $[L_p ZnMe_2]$ ($P_r = 0.91$, Figure 9; Table 6, entries 5 and 6) compared to complex $[L_B ZnMe_2]$ (P, = 0.95, Figure 8; Table 6, entry 4) with less steric bulk around the metal center. Thus, these results indicated that the larger steric hindrance might probably impede the regularity of monomer insertion [63]. The stereoselectivity toward ROP of rac-LA could be realized by variation of the substituents attached to amine moiety. Proper complexity of substituents in the ligand might provide an electronic environment for better accommodation of any

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potential steric clashes between the propagating polymer chain, ligand architecture and the alternative insertion of incoming monomers. These results imply that polymerization proceeded by chain end mechanism. More investigations are underway to fully elaborate structure-activity relationship to produce PLA with better control and stereoregularities.

4. Conclusion

We investigated the synthesis and X-ray crystallographic structures of $[L_n ZnCl_2]$ ($L_n = L_A - L_p$), which were prepared by reaction of the corresponding metal starting materials with *N*,*N'*,*N*bis((1H-pyrazol-1-yl)methyl)amine ligands. The molecular structures of monomeric, four-coordinate Zn(II) complexes were distorted tetrahedral obtained via coordination of N_{pyrazole} atoms to the metal center. [$L_F ZnCl_2$] exhited highest catalytic activity and yielded high molecular weight PMMA with syndiotactic enchainemnt *ca*. 67%. The MMA polymerization activity of the complexes in the current study should be considered in reference to the steric bulk provided by the ligand architecture around the metal center. Dimethyl Zn(II) complexes [$L_n ZnMe_2$] ($L_n = L_A - L_F$), generated *in situ*, polymerized *rac*-LA in a controlled fashion and yielded highly heterotactic PLA. The activities and stereoregularities toward PLA can be considered as a composite result of steric and electronic effects.

Supplementary materials

CCDC 1548747-1548748, 1548750-1548751, and 1549025-1549026 contain the supplementary crystallographic data for complexes [L_AZnCl₂], [L_BZnCl₂], [L_CZnCl₂], [L_CZnCl₂], [L_EZnCl₂], and [L_FZnCl₂], respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This research was supported by the National Research Foundation of Korea (NRF), funded by the Ministry of the Education, Science, and Technology (MEST) [grant number 2017R1A2B4002100]. X-ray crystallography with PLS-II 2D-SMC beamline was supported by MSIP and POSTECH.

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