ChemComm
Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Gong and H. Ma, *Chem. Commun.*, 2019, DOI: 10.1039/C9CC04834K.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

ChemComm

View Article Online
DOI: 10.1039/C9CC04834K

COMMUNICATION

High Performance Benzoimidazolyl-Based Aminophenolate Zinc Complexes for Isoselective Polymerization of *rac*-Lactide

*Yanmei Gong and Haiyan Ma**

Received 00th June 2019,
Accepted 00th June 2019

DOI: 10.1039/x0xx00000x

Zinc complexes supported by achiral benzoimidazolyl-based aminophenolate ligands feature high catalytic activities and excellent isoselectivities toward the ring-opening polymerization of *rac*-lactide under mild conditions.

Poly(lactic acid) (PLA) is emerging as one of the most promising bioderived polymers as well as sustainable and eco-efficient alternatives to traditional petrochemical-based polymers. The environmental advantages of PLA, such as renewability, biodegradability and biocompatibility, have contributed to this material a wide range of applications in both commodity and medical fields.[1] The established synthesis of PLA is the ring-opening polymerization (ROP) of lactides (LAs) normally mediated by well-defined metal complexes, which is efficient in obtaining polylactides with high molecular weights, narrow molecular weight distributions and controlled stereo-microstructures.[2] The physicochemical properties and therefore practical applications of PLA strongly depends on the stereochemistry of its microstructure, hence the stereoselective ring-opening polymerization of *rac*-lactide (*rac*-LA) is currently of great interest, particularly those processes that can produce isotactic PLAs from *rac*-lactide.[3] In this subfield, since pioneering studies in 1996 that aluminum Schiff-base complexes exhibited high isoselectivity toward the ROP of *rac*-LA by Spassky's group,[4] the isoselective ROP of *rac*-LA although limited but has been gradually explored by various metal precursors based on rare-earth metals,[5] alkaline-earth metals,[6] zinc,[7] alkaline metals[8] and transition metals[9] besides aluminum.[10] Nevertheless, up to date, initiators which integrate excellent isoselectivity with high activity as well as good control toward the ROP of *rac*-LA are still very rare,[5d,7d,11] and it becomes an abstracting challenge for researches to overcome.

Previously, we reported pyrrolidinyl-based aminophenolate zinc complex **I** possessing multiple stereogenic centers (Chart 1), which was the first zinc complex achieving relatively high activity and isoselectivity for the ROP of *rac*-LA (TOF = 132 h^{-1}, P_m = 0.80, 298 K).[7a] Further mechanism study on isoselectivity however indicated dominant chain-end control. Inspired by the results, we introduced chiral oxazolinyl pendant and constructed a ligand framework with less stereogenic centres. The obtained zinc complex **II** facilitated the isotactic enchainment with high rates and isoselectivities toward the ROP of *rac*-LA (TOF = 792-2014 h^{-1}, P_m = 0.87-0.89, 298 K; TOF = 117 h^{-1}, P_m = 0.92, 253 K),[7d] proving to be the most active and meanwhile highly isoselective catalyst to date together with the yttrium bis(phenolate) ether complex (TOF = 2280 h^{-1}, P_m = 0.84, 298 K; TOF = 120 h^{-1}, P_m = 0.90, 258 K)[5d] and the phosphasalen indium complex (TOF = 480 h^{-1}, P_m = 0.87, 298 K; TOF = 29 h^{-1}, P_m = 0.92, 258 K)[11] reported by Lu's and Williams' groups respectively. When achiral benzoxazolyl pendant was introduced, the resultant aminophenolate zinc complex **III** also exhibited high isoselectivities for the ROP of *rac*-LA but with reduced activities (TOF = 190-450 h^{-1}, P_m = 0.88-0.89, 298 K; TOF = 34 h^{-1}, P_m = 0.92, 253 K).[7e] For both systems **II** and **III**, chain-end control was thoroughly involved, and the chirality of the pendant group does not contribute to the high isoselectivity. In comparison to ligands with chiral fragment(s), achiral ligands can be synthesized from much cheaper chemicals, which is of great benefit to industrial applications; we thus are highly motivated to expand the ligand framework by varying the pendant coordination group with the aim of fur-

Shanghai Key Laboratory of Functional Materials Chemistry and Laboratory of Organometallic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, P. R. China.
E-mail: haiyanma@ecust.edu.cn; Fax: +86 21 64253519; Tel: +86 21 64253519

† Electronic Supplementary Information (ESI) available: Full experimental details, representative NMR spectra and DSC traces of polymers. CCDC 1919496 (**2**), and 1919497 (**6**). For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x.

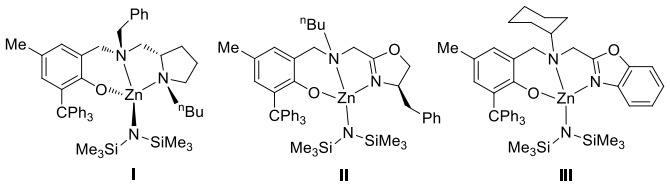
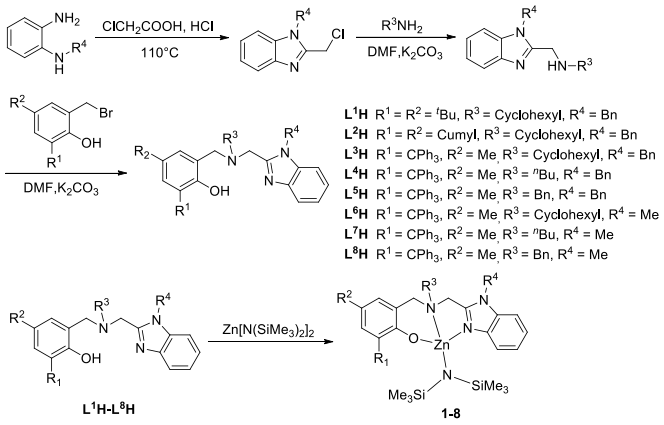


Chart 1. Previously reported aminophenolate zinc complexes



Scheme 1. Synthesis of aminophenol proligands and zinc complexes **1**-**8**

-ther improving the catalytic performance of zinc initiators toward the ROP of *rac*-LA. Herein, we use benzoimidazolyl with adjustable steric and electronic facility to replace benzoxazolyl as the pendant group, and report another series of aminophenolate zinc complexes (Scheme 1) with excellent isoselectivities and high activities toward *rac*-LA polymerization, meanwhile integrating the advantages of cheap raw materials and easy preparation.

Benzoimidazolyl-aminophenol proligands **L$^{1\text{-}8}$H** with various substituents were prepared from substituted 2-chloromethylbenzoimidazoles, primary amines and three substituted 2-bromomethylphenols according to modifications of the published procedures (Scheme 1).[7e,12] The corresponding zinc complexes **1**-**8** were synthesized via the reactions of **L$^{1\text{-}8}$H** with $Zn[N(SiMe_3)_2]_2$ in a 1:1 molar ratio at ambient temperature and were fully characterized by ^{1}H and ^{13}C {^{1}H} NMR spectroscopy as well as elemental analysis methods (see ESI†, Figures S1-S16). Single crystals suitable for X-ray diffraction determination were successfully obtained for complexes **2** and **6**. As depicted in Fig. 1, both complexes possess a monomeric structure in the solid state, where the zinc atom is four-coordinated by three donors of the aminophenolate ligand and one silylamido group, adopting a distorted tetrahedral geometry around the metal center. For complex **2**, the bond distances of Zn−$N_{imidazole}$ and Zn−$N_{skeleton}$ range from 2.0669(17) to 2.2106(16) Å, showing that both the imine N atom of the benzoimidazolyl ring and the skeleton N atom have strong coordination interactions with the metal centre, which is consistent with the structure in solution inferred from the ^{1}H NMR spectroscopic studies. Due to the steric repulsion between the bis(trimethylsilyl)amido group

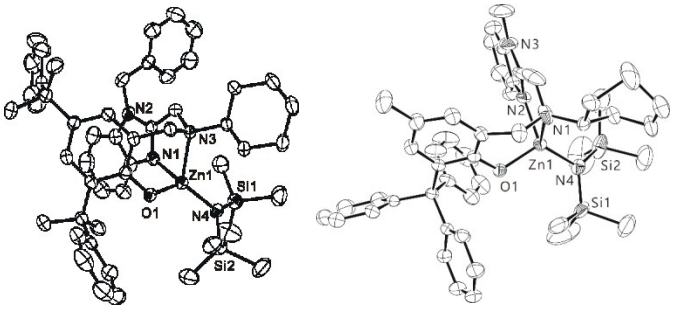


Fig. 1 The solid state structures of complexes **2** (left) and **6** (right). Hydrogen atoms are omitted for clarity.

View Article Online
DOI: 10.1039/C9CC04834K

and the aminophenolate ligand, the corresponding angles of O1−Zn1−N4 (122.63(7)°), N4−Zn1−N3 (122.66(7)°), and N4−Zn1−N1 (123.85(7)°) in complex **2** are all deviated significantly from ideal 109.5°. The corresponding structural features of complex **6** are similar, except that shorter Zn−$N_{imidazole}$, Zn−O distances and longer Zn−$N_{skeleton}$, Zn−$N_{silylamido}$ distances are observed for complex **6**, likely arising from the larger size of the *o*-trityl group of the ligand. It should be further noted that, in these two structures, the Zn−$N_{imidazole}$ bond lengths (2.0669(17) Å for **2**; 2.051(3) Å for **6**) are obviously shorter than the corresponding Zn−$N_{pyrrolidinyl}$ or Zn−$N_{oxazolinyl}$ bond lengths in our previously reported zinc complexes (**I** and analogues: Zn−$N_{pyrrolidinyl}$, 2.108-2.137 Å; **II-III** and analogues: Zn−$N_{oxazolinyl}$, 2.074-2.1124 Å),[7a,7e] indicating that the benzoimidazolyl groups exert stronger coordination interaction with the zinc centre than the other two types of heterocyclic structures.

Complexes **1-8** are active catalysts toward the ROP of *rac*-LA to afford isotactic PLAs (P_m = 0.68−0.89) at ambient temperature either alone or in the presence of 2-propanol (Table 1). The polymerization runs normally can reach completion within a few minutes or hours depending on the structures of the complexes, and the substituents on the ligand framework exert remarkable influences on the catalytic performance of the corresponding zinc complexes.

As shown in Table 1, complex **1** with an *o*-*tert*-butyl group on the phenolate ring showed the highest activity among complexes **1**−**3** bearing different *ortho*-substituents. Whereas, the stereoselectivity of complex **1** toward the ROP of *rac*-LA is the lowest (P_m = 0.69). The introduction of an *o*-trityl group in complex **3** resulted in high isoselectivity toward the polymerization of *rac*-LA (P_m = 0.89), which is in a sharp contrast to complexes **1** (^{t}Bu, P_m = 0.69) and **2** (Cumyl, P_m = 0.79). The high level of isoselectivity of complex **3** is corroborated by the dominant proportion of the *mmm* tetrad in the homonuclear decoupled ^{1}H NMR spectrum and the ^{13}C NMR spectrum of the resulting polymer sample (Figures S19-S20, ESI†). Obviously, the isoselectivity of complexes **1**-**3** is determined essentially by the steric bulkiness of the *ortho*-substituent on the phenolate ring; the bulkier the *ortho*-substituent, the higher the isoselectivity of the corresponding zinc complex is.

Keeping the superior *o*-trityl group unchanged, the replacement of the cyclohexyl on the skeleton N atom with an *n*-butyl group led to a considerable increase of the catalytic activity of complex **4**. We tentatively attribute this to the smaller steric hindrance and a more flexible nature of the *n*-butyl group when compared with the rigid cyclohexyl group. However, when a benzyl group was introduced to the skeleton N atom, the activity of the corresponding complex **5** was even higher than that of complex **4**, and complex **5** proved to be the most active catalyst in this series of zinc complexes. Herein the electronic withdrawing effect of the benzyl group seems to exert a more dominant influence on activity. By comparing the isoselectvities of complexes **3**-**5**, it is further noticed that the introduction of the benzyl group brought an unfavorable effect

on the isoselectivity of complex **5** (P_m = 0.85). Meanwhile, complexes **3** and **4** with a distinct alkyl substituent on the skel-

Table 1 ROPs of *rac*-LA initiated by zinc complexes **1**–**8** and **I**-**III**[a]

Cat.	Feed ratio	Time (min)	Conv.[b] (%)	TOF[c] (h^{-1})	M_n[d] ($\times10^4$)	M_w/M_n[d]	P_m[e]
1	200:1:0	40	85	255	13.33	1.42	0.69
	200:1:1	12	80	800	3.59	1.12	0.68
2	200:1:0	50	95	228	16.97	1.54	0.79
	200:1:1	15	96	768	5.49	1.27	0.78
3	200:1:0	56	90	193	4.84	1.32	0.89
	200:1:1	15	80	640	3.24	1.19	0.88
4	200:1:0	28	94	403	11.59	1.63	0.88
	200:1:1	13	94	868	3.25	1.34	0.87
5	200:1:0	19	93	587	5.42	1.56	0.85
	200:1:1	11	91	993	2.72	1.29	0.85
6	200:1:0	102	78	92	29.13	1.38	0.89
	200:1:1	25	90	432	6.35	1.19	0.88
7	200:1:0	25	91	437	16.88	1.22	0.89
	200:1:1	13	91	840	5.58	1.18	0.88
	500:1:0	45	86	573	17.69	1.56	0.87
	500:1:1	30	90	900	6.69	1.25	0.87
	200:1:1	8 h[f]	76	19	3.06	1.19	0.91
	200:1:1	18 h[g]	77	8.5	2.91	1.07	0.93
8	200:1:0	25	87	418	9.40	1.28	0.85
	200:1:1	12	89	890	4.63	1.13	0.84
I[h]	200:1:1	90	99	132	3.00	1.12	0.80
II[i]	500:1:0	36	95	792	9.31	1.39	0.87
	500:1:1	14	94	2014	7.18	1.32	0.86
III[j]	500:1:0	148	94	190	15.6	1.48	0.89
	500:1:1	62	93	450	6.46	1.17	0.88

[a] [*rac*-LA]$_0$ = 1.0 M, Feed ratio = [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$, toluene, 25 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Turnover frequency (TOF) = mol of product (polylactides)/mol of catalyst per hour. [d] Determined by GPC. [e] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy. [f] at –20 ℃. [g] at –40 ℃. [h] See ref. 7a. [i] See ref. 7d. [j] See ref. 7e.

-eton N atom of the ligand displayed more or less the same high level of isoselectivities (P_m = 0.89, 0.88). In general, the steric hindrance of substituents in the ligand framework was reported to play a dominant role in determining the stereoselectivity of organometallic catalysts adopted for ROP of *rac*-LA;[7d,13] whereas some recent studies did show that the electronic effect of substituents would also exert a certain influence on the stereoselectivity.[7a,7e,14] Herein, we suggest that substituents with distinguished electronic effects might influence the stereoselectivity by varying the coordination parameters (bonds and angles) around the metal center, which should be crucial in selective coordination/insertion of monomer.

Being different from above, changing the out-sphere substituent on the benzoimidazolyl moiety from benzyl to methyl had hardly influence on isoselectivities of the corresponding zinc complexes **6**-**8**, but led to slight to moderate decreases of activities. Therefore, the electronic withdrawing nature of substituent on the benzoimidazolyl moiety is also benefit for the activity, which increases the Lewis acidity of the zinc centre to facilitate the monomer coordination. At present, it is not clear why the variation of the benzoimidazolyl substituent from benzyl to methyl does not improve the isoselectivity as one might suspect from the influence of benzyl on the skeleton N atom. We tent to attribute to its location being far away from the coordination centre.

From the perspective of structure-property relationships, complexes **3**, **4**, **6** and **7** with a trityl group on the *ortho*-phenoxide unit and a cyclohexyl or an *n*-butyl group on the central skeleton N atom showed the highest isoselectivities (P_m = 0.88-0.89, see ESI†, Figures S19, S21-S23) among these complexes, which parallel those observed for complexes **II** and **III** (Chart 1, Table 1). Although the activity of the best performed complex **7** (TOF = 573 h^{-1}) is somewhat lower than that of complex **II** with a chiral oxazolinyl pendant (TOF = 792 h^{-1}), it is significantly improved when compared to that of complex **III** with an achiral benzoxazolyl pendant (TOF = 190 h^{-1}). We believe the introduction of benzoimidazolyl in the ligand framework afford a good opportunity to improve the catalytic activities of this series of zinc complexes meanwhile maintaining the high isoselectivities by simply varying the *N*-substituent on the benzoimidazolyl unit.

As reported in the literatures, the addition of 2-propanol has a beneficial effect on the catalytic activities of all these zinc complexes, meanwhile providing PLAs in a more controlled manner as indicated by the matched molecular weights with the calculated ones as well as narrower molecular weight distributions (PDI = 1.11-1.34).[15] The same level of isoselectivity was maintained in all cases as witnessed by comparing the runs carried with or without alcohol. Moreover, when THF was used as the polymerization solvent, the above mentioned structure-property relationships of these zinc complexes were also found and so did the effect of ^{i}PrOH on activity and stereoselectivity (see ESI†, Table S2).

By carrying the polymerization run at −20 °C in toluene, the P_m value of the representative complex **7** was improved to 0.91; further decreasing the reaction temperature to −40 °C, an even higher isoselectivity of P_m = 0.93 could be achieved (see ESI†, Figures S24, S25). DSC measurement of this sample indicates a significantly higher T_m of 186 °C than that of the homochiral PLLA (T_m = 170 °C), which agrees well with the highly isotactic chain microstructure and indicates the formation of stereocomplexed structure (see ESI†, Figure S28).[7e]

Complex **4** with high activity and high isoselectivity among these complexes further promoted us to study its catalytic performance under melt conditions. As illustrated in Table 2, at 110 °C, in the presence of exogenous alcohol, complex **4** could tolerate catalyst loadings as low as 0.0002 mol (*vs*. monomer). With [*rac*-LA]$_0$/[**4**]$_0$/[^{i}PrOH]$_0$ molar ratios of 1000:1:5, 2000:1:10, 5000:1:50, high monomer conversions were obtained within 20, 20 and 23 min. respectively, and good isoselectivities were still maintained (P_m = 0.76-0.78).

To acquire some information about the isoselective polymerization mechanism of *rac*-LA enabled by these zinc complexes, we monitored at first the NMR tube reactions of the representative complex **3** with ca. 1 equiv. of 2-propanol and sequentially with 5 equiv. of *rac*-LA (see ESI†, Figure S29).

Table 2 ROPs of *rac*-LA initiated by zinc complex **4**[a]

Feed ratio	Time (min)	Conv.[b] (%)	TOF[c] (h^{-1})	M_n[d] ($\times10^4$)	M_w/M_n[d]	P_m[e]
1000:1:5	20	97	2910	7.90	1.70	0.78
2000:1:10	20	98	5880	8.29	1.61	0.76
5000:1:50	23	90	11739	4.08	1.30	0.78

[a][*rac*-LA]$_0$ = 1.0 M, Feed ratio = [*rac*-LA]$_0$:[Zn]$_0$:[^{i}PrOH]$_0$, 110 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Turnover frequency (TOF) = mol of product (polylactides)/mol of catalyst per hour. [d] Determined by GPC. [e] P_m is the probability of forming a new *m*-dyad, determined by homonuclear decoupled ^{1}H NMR spectroscopy.

The treatment of 2-propanol resulted in the substitution of the $N(SiMe_3)_2$ group boned to the zinc atom, yielding the isopropoxide derivative "**L**^{3}ZnO^{i}Pr". The 5-fold sequential addition of *rac*-LA to this system led to a fast oligomerization and the signals assignable to the active oligomer {**L**^{3}Zn[(OCH(CH$_3$)CO)$_n$O^{i}Pr]} could be identified roughly. The end-capping groups of a typical oligomer were recognized by ^{1}H NMR and MALDI-TOF mass spectroscopy to be hydroxy and isopropoxyl ester as expected (see ESI†, Figures S30-S31). All these features are in line with a coordination-insertion polymerization process.

Subsequently, preliminary kinetic studies for the ROP of *D*-LA, *L*-LA and *rac*-LA were conducted by using complex **8** as the initiator. It is found that complex **8** exerts no difference on the polymerization rates of *D*-LA and *L*-LA (*D*-LA, k_{app}= (1.54 ± 0.09)×10^{-1} min^{-1}; *L*-LA, k_{app} = (1.55 ± 0.02)×10^{-1} min^{-1}, in toluene at 25 ℃), which however are obviously larger than that of *rac*-LA (k_{app}= (0.95 ± 0.04)×10^{-1} min^{-1}) (see ESI†, Figure S32). In lacking of a polymer exchange process as observed for analogue zinc systems,[7e] these kinetic results indicate the operation of a chain-end control mechanism.

The stereoerrors in the microstructure of typical polymer samples were analysed via homonuclear-decoupled ^{1}H NMR spectroscopy (see ESI†, Figures S19, S21-S26). It shows that the intensity ratio of *rmm* : *mmr* : *mrm* tetrad signals is about 1:1:1, suggesting the formation of isotactic stereoblocks along the polymer chain. The relatively small *rmr* stereoerror sequence may be ascribed to consecutive chain end control errors.[5b,16] These features further imply that a chain-end control mechanism is involved in producing isotactic stereoblock PLAs by these zinc complexes.

In summary, we have prepared a series of benzoimidazolyl-based aminophenolate zinc complexes exhibiting excellent isoselectivities (P_m = ca. 0.89) and high activities toward the ROP of *rac*-LA at ambient temperature. The replacement of previous benzoxazolyl pendant with benzoimidazolyl in the ligand framework provides a good opportunity of improving the activities of the corresponding zinc complexes meanwhile maintaining the high isoselectivities. The advantages of cheap raw materials and easy preparation further afford potential industrial applications.

Financial supports from the National Natural Science Foundation of China (NNSFC, Grant 21474028 and 21871082) are gratefully acknowledged.

Notes and references

View Article Online
DOI: 10.1039/C9CC04834K

1 (a) E. Chiellini and R. Solaro, *Adv. Mater.*, 1996, **8**, 305; (b) C.-S. Ha and J. A. Gardella, *Chem. Rev.*, 2005, **105**, 4205; (c) M. J. Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486.
2 (a) J. M. Becker, R. J. Pounder and A. P. Dove, *Macromol. Rapid Commun*., 2010, **31**, 1923; (b) S. Slomkowski, S. Penczek and A. Duda, *Polym. Adv. Technol*., 2014, **25**, 436.
3 (a) J. Slager and A. J. Domb, *Adv. Drug Delivery. Rev.*, 2003, **55**, 549; (b) K. Fukushima and Y. Kimura, *Polym. Int.*, 2006, **55**, 626; (c) C. M. Thomas, *Chem. Soc. Rev*., 2010, **39**, 165.
4 N. Spassky, M. Wisniewski, C. Pluta and A. Le Borgne, *Macromol. Chem. Phys.*, 1996, **197**, 2627.
5 (a) P. L. Arnold, J. C. Buffet, R. P. Blaudeck, S. Sujecki, A. J. Blake and C. Wilson, *Angew. Chem., Int. Ed*., 2008, **47**, 6033; (b) C. Bakewell, T. P. Cao, N. Long, X. F. Le Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc*., 2012, **134**, 20577; (c) C. Bakewell, A. J. White, N. J. Long and C. K. Williams, *Angew. Chem. Int. Ed.,* 2014, **53**, 9226; (d) T. Xu, G. Yang, C. Liu and X. Lu, *Macromolecules*, 2017, **50**, 515.
6 (a) J. Hu, C. Kan, H. Wang and H. Ma, *Macromolecules*, 2018, **51**, 5304; (b) J. Bhattacharjee, A. Harinath, H. P. Nayek, A. Sarkar and T. K. Panda, *Chem. Eur. J.*, 2017, **23**, 9319; (c) A. Harinath, J. Bhattacharjee, A. Sarkar, H. P. Nayek and T. K. Panda, *Inorg. Chem.*, 2018, **57**, 2503.
7 (a) H. Wang and H. Ma, *Chem. Commun*., 2013, **49**, 8686; (b) H. Wang, Y. Yang and H. Ma, *Macromolecules*, 2014, **47**, 7750; (c) S. Abbina and G. Du, *ACS Macro Lett.*, 2014, **3**, 689; (d) C. Kan, J. Hu, Y. Huang, H. Wang and H. Ma, *Macromolecules*, 2017, **50**, 7911; (e) J. Hu, C. Kan and H. Ma, *Inorg. Chem*., 2018, **57**, 11240.
8 (a) J. Zhang, J. Xiong, Y. Sun, N. Tang and J. Wu, *Macromolecules*, 2014, **47**, 7789; (b) Z. Dai, Y. Sun, J. Xiong, X. Pan and J. Wu, *ACS Macro Lett.*, 2015, **4**, 556; (c) C. Chen, Y. Cui, X. Mao, X. Pan and J. Wu, *Macromolecules*, 2016, **50**, 83; (d) Y. Sun, J. Xiong, Z. Dai, X. Pan, N. Tang and J. Wu, *Inorg. Chem.*, 2016, **55**, 136; (e) C. Chen, J. Jiang, X. Mao, Y. Cong, Y. Cui, X. Pan and J. Wu, *Inorg. Chem.*, 2018, **57**, 3158.
9 (a) E. L. Whitelaw, M. D. Jones and M. F. Mahon, *Inorg. Chem.*, 2010, **49**, 7176; (b) E. L. Whitelaw, M. G. Davidson and M. D. Jones, *Chem. Commun*., 2011, **47**, 10004; (c) M. D. Jones, S. L. Hancock, P. McKeown, P. M. Schafer, A. Buchard, L. H. Thomas, M. F. Mahon and J. P. Lowe, *Chem. Commun.,* 2014, **50**, 15967; (d) M. D. Jones, L. Brady, P. McKeown, A. Buchard, P. M. Schafer, L. H. Thomas, M. F. Mahon, T. J. Woodman and J. P. Lowe, *Chem. Sci.*, 2015, **6**, 5034.; (e) A. Stopper, T. Rosen, V. Venditto, I. Goldberg and M. Kol, *Chem. Eur. J*., 2017, **23**, 11540.
10 (a) N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chem. Eur. J.,* 2007, **13**, 4433; (b) H. L. Chen, S. Dutta, P. Y. Huang and C. C. Lin, *Organometallics*, 2012, **31**, 2016; (c) X. Pang, R. Duan, X. Li, C. Hu, X. Wang and X. Chen, *Macromolecules*, 2018, **51**, 906.
11 D. Myers, A. J. P. White, C. M. Forsyth, M. Bown and C. K. Williams, *Angew. Chem., Int. Ed.*, 2017, **56**, 5277.
12 S. S. Rao, C. V. R. Reddy and P. K. Dubey, *Asian J. Chem*., 2015, **27**, 98.
13 N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chem. Eur. J.*, 2007, **13**, 4433.
14 M. Hu, F. Han, W. Zhang, W. Ma, Q. Deng, W. Song, H. Yan and G. Dong, *Catal. Sci. Technol*., 2017, **7**, 1394.
15 C. R. Arnaud Thevenon, Michael S. Bennington, Andrew J. P. White, Hannah J. Davidson, Sally Brooker, and Charlotte K. Williams, *Angew. Chem. Int. Ed*., 2016, **128**, 1.
16 K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann and E. J. Munson, *Macromolecules*, 1997, **30**, 2422.

High Performance Benzoimidazolyl-Based Aminophenolate Zinc Complexes for Isoselective Polymerization of *rac*-Lactide

Yanmei Gong[a] and Haiyan Ma*[,a]

Shanghai Key Laboratory of Functional Materials Chemistry and Laboratory of Organometallic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China

DOI: 10.1039/C9CC04834K

A series of zinc complexes supported by achiral benzoimidazolyl-based aminophenolate ligands were employed as highly active initiators for the ring-opening polymerization of *rac*-lactide to afford highly isotactic polymers under mild conditions.