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[Bis(guanidine)]zinc Complexes and Their Application in Lactide Polymerisation

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The bis(guanidine)-stabilised zinc complexes [N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]dichloridozinc(II), [Zn(DMEG$_2$e)Cl$_2$] (**C1**), diacetato[N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]zinc(II), [Zn(DMEG$_2$e)(CH$_3$COO)$_2$] (**C2**), and bis[N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]zinc(II) bis(trifluoromethanesulfonate), [Zn(DMEG$_2$e)$_2$](CF$_3$SO$_3$)$_2$ (**C3**), have been synthesised and completely characterised by means of X-ray structure analysis, NMR spectroscopy and mass spectrometry. These [bis(guanidine)]zinc complexes were investigated regarding their activity in the bulk polymerisation of D,L-lactide. It could be shown that these compounds are able to act as initiators for lactide polymerisation, and polylactides with molecular weights (M_w) of around 18000–59000 g/mol could be obtained. Variation of the reaction temperature revealed that the molecular weights decrease with increasing temperature. Additionally, the correlation of the intrinsic viscosity with the molecular weight demonstrates that the obtained polymers are linear and structurally homogeneous.

Introduction

The increasing shortage of resources has enforced the search for production techniques for biodegradable polymers made of renewable raw materials. An example is polylactide (PLA), an aliphatic polyester, which can be obtained by the ring-opening polymerisation (ROP) of cyclic esters like lactide. The monomer for PLA production is available from renewable raw materials like corn or sugar beets by a bacterial fermentation process. The polylactide that is obtained by metal-catalysed ROP can be either recycled or composted after use, and therefore it is CO$_2$-emission-neutral. Also, its unique physical properties qualify PLA to be a viable alternative to petrochemical-based plastics. Combined with its biocompatibility and its ability to degrade both in vivo and in vitro, PLA has a great range of potential applications ranging from widespread use, including coatings, fibres, films and packages, to use in specialised medical and pharmaceutical fields.[1]

Until now, the ROP of lactide could not be accomplished economically, and therefore PLA has only been used in biomedical applications.[2] To change the polymer from a speciality material to a large-volume commodity plastic,[3] the development of new polymerisation catalysts is required. Most large-scale processes are based on the use of stannous compounds as initiators.[4] However, for use in food packaging or similar applications, heavy metals are undesirable because of accumulation effects.[5] Particularly suitable for this purpose in order to substitute heavy-metal-based catalyst systems are zinc complexes with N-donor-functionalised ligands because they are mostly colourless, inexpensive and nontoxic.[6]

Examples of (guanidine)zinc complexes have already been reported.[7] It could be shown that some of these possess catalytic activity, which makes guanidines a very promising ligand class leading to catalytically active zinc complexes.[8] Bis(guanidines) offer excellent donor properties that allow the coordination of metal ions and enable the access of substrate molecules to the metal centre at the same time. A great advantage of bis(guanidines) is their modular synthesis protocol, which combines different spacer and guanidine groups and thus admits a flexible ligand design.[9] The variation of the ligands allows an optimal adaptation to actual demands. Moreover, the guanidine ligands are strongly related to the essential and ubiquitous amino acid arginine, which is nontoxic.[10]

Herein we report on the synthesis and characterisation of the first zinc complexes including N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine (DMEG$_2$e, **L1**)[11] as bis(guanidine) ligand, which are actually the first examples of aliphatic bis(guanidine)-stabilised zinc complexes. The complexes [N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]dichloridozinc(II), [Zn(DMEG$_2$e)Cl$_2$] (**C1**), diacetato[N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]zinc(II), [Zn(DMEG$_2$e)(CH$_3$COO)$_2$] (**C2**), and bis[N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-

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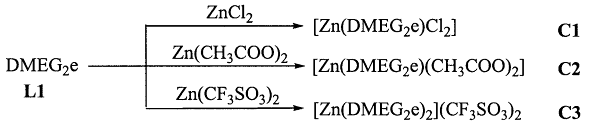
1,2-diamine]zinc(II) bis(trifluoromethanesulfonate), [Zn($DMEG_2e$)$_2$](CF_3SO_3)$_2$ (**C3**), were investigated regarding their activity in the bulk polymerisation of D,L-lactide. Our results prove that the bis(guanidine) complexes possess catalytic activity in the ROP of D,L-lactide. PLAs with molecular weights (M_w) of around 18000–59000 g/mol could be obtained.

Results and Discussion

The bis(guanidine) ligand *N*^{1},*N*^{2}-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine ($DMEG_2e$, **L1**) was synthesised by condensation of the Vilsmeier salt *N*,*N*′-dimethyl-*N*,*N*′-ethylenechloroformamidinium chloride with ethylenediamine, as previously reported.[11] In the reaction of **L1** with $ZnCl_2$ in MeCN, colourless crystals of [Zn($DMEG_2e$)Cl_2] (**C1**) could be obtained in 98% yield. The reaction of **L1** with Zn(CH_3COO)$_2$ and Zn(CF_3SO_3)$_2$ in THF leads to the formation of colourless crystals of [Zn($DMEG_2e$)(CH_3COO)$_2$] (**C2**) in 97% yield and [Zn($DMEG_2e$)$_2$](CF_3SO_3)$_2$ (**C3**) in 73% yield, respectively (Scheme 1). The described guanidine-stabilised zinc complexes formed independently of the molar ratio of the starting materials.



Scheme 1. Schematic synthesis of **C1**–**C3**.

The molecular structures of compounds **C1**–**C3** (Figures 1, 2 and 3), determined by X-ray crystallography at 120 K, reveal that each Zn^{II} atom is fourfold coordinated. In **C1** and **C2**, two coordination sites are occupied in a chelating manner by the N-donor atoms of $DMEG_2e$, forming a five-membered heterocycle that adopts a half-chair conformation, whereas in **C3**, four coordination sites are occupied analogously by the N-donor atoms of two $DMEG_2e$ molecules. In **C1** and **C2**, the remaining coordination sites are occupied by chloride ions [Zn–Cl distance: 2.260(1) Å] or acetate ions [average of the Zn–O distances: 1.963(2) Å]. The distances between the zinc ion and the N-donor atoms decrease, going from **C1** [2.038(2) Å] over **C2** [av. 2.025(2) Å] to **C3** [av. 2.012(4) Å], while the length of the C=N bonds of the guanidine residues are identical in all three compounds [av. **C1**: 1.309(3); **C2**: 1.307(2); **C3**: 1.309(5) Å]. The zinc atoms in **C1** and **C2** are coordinated in a distorted tetrahedral manner. The sums of the angles at the Zn atom are 656.18° for **C1** and 659.48° for **C2** and therefore fit well with the value for a perfect tetrahedral geometry (656.82°). However, the bite angle of 86.18(10)° (**C1**) and 86.16(6)° (**C2**) is too small for a perfect tetrahedral geometry, resulting in a distortion. This distortion is reflected in the values of the angles between the $ZnCl_2$ and the ZnN_2 plane (74.5°) and the ZnO_2 and the ZnN_2 plane (76.3°), which is 90° in a tetrahedron. In contrast, the environment of the Zn atom in **C3** lies between tetrahedral and square-planar coordination. The sum of the angles at the Zn atom is 670.41° and lies between the values for a tetrahedron (656.82°) and a square-planar coordination (720°), indicating more tetrahedral character. The bite angles of both $DMEG_2e$ ligands are identical [85.5(1) and 85.2(1)°]. The bite angles defined by the ligands are significantly smaller than the tetrahedron angle (109.47°) and therefore lead to a distortion of the tetrahedral structure in the direction of square-planar coordination. This is also shown in the value of the angle between the ZnN_2 planes (53.9°), which is between the tetrahedral (90°) and the square-planar coordination (0°). Furthermore, the distorted structure favours the minimisation of the interactions between the sterically demanding guanidine residues. The twist within the guanidine heterocycle, which minimises the ecliptic interactions of the ring-bound hydrogen atoms, is limited in the $DMEG_2e$ systems by the rigid ethylene bridge between the two amine functions. The values of

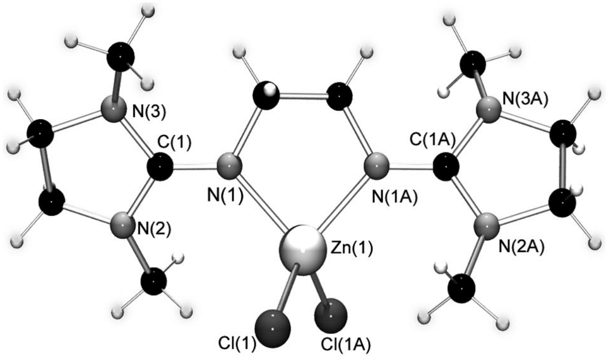


Figure 1. Molecular structure of [Zn($DMEG_2e$)Cl_2] (**C1**) as determined at 120 K. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 2.038(2), Zn(1)–Cl(1) 2.260(1), N(1)–C(1) 1.309(3); N(1)–Zn(1)–N(1A) 86.18(10), N(1)–Zn(1)–Cl(1) 105.05(6), Cl(1)–Zn(1)–Cl(1A) 111.60(4).

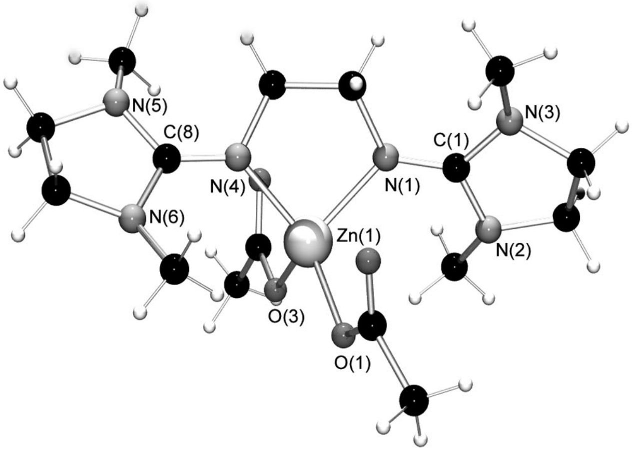


Figure 2. Molecular structure of [Zn($DMEG_2e$)(CH_3COO)$_2$] (**C2**) as determined at 120 K. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 2.011(2), Zn(1)–N(4) 2.038(2), Zn(1)–O(1) 1.969(2), Zn(1)–O(3) 1.956(2), N(1)–C(1) 1.308(2), N(4)–C(8) 1.305(2); N(1)–Zn(1)–N(4) 86.16(6), N(1)–Zn(1)–O(1) 110.98(7), N(1)–Zn(1)–O(3) 129.98(6), N(4)–Zn(1)–O(1) 123.57(7), N(4)–Zn(1)–O(3) 109.89(6), O(1)–Zn(1)–O(3) 98.90(6).

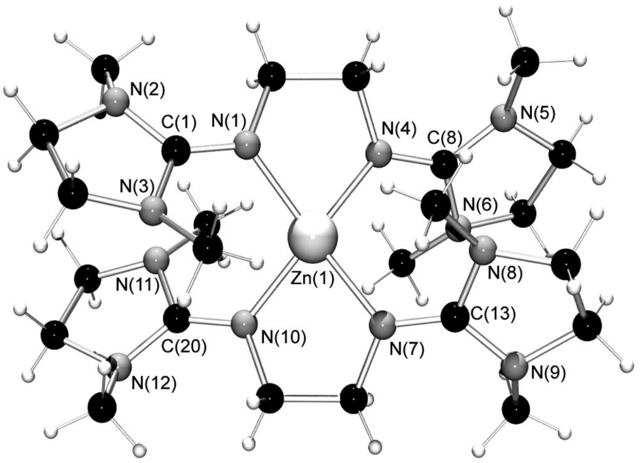


Figure 3. Molecular structure of $[Zn(DMEG_2e)_2]^{2+}$ in crystals of $[Zn(DMEG_2e)_2](CF_3SO_3)_2$ (**C3**) as determined at 120 K. Selected bond lengths [Å] and angles [°]: Zn(1)–N(1) 2.028(3), Zn(1)–N(7) 2.021(3), Zn(1)–N(10) 2.004(3), Zn(1)–N(4) 1.996(3), N(1)–C(1) 1.303(5), N(4)–C(8) 1.307(5), N(7)–C(13) 1.315(5), N(10)–C(20) 1.311(5); N(4)–Zn(1)–N(10) 145.3(1), N(4)–Zn(1)–N(7) 106.0(1), N(10)–Zn(1)–N(7) 85.5(1), N(4)–Zn(1)–N(1) 85.2(1), N(10)–Zn(1)–N(1) 105.3(1), N(7)–Zn(1)–N(1) 143.1(1).

the angles between the $C_{gua}N_3$ and the NC_3 plane are thus slightly smaller (**C1**: 15.5°; **C2**: 14.9°; **C3**: 15.6°) than those reported for a similar DMEG-containing system (17.4°).[9a]

The comparison of $[Zn(DMEG_2e)_2](CF_3SO_3)_2$ (**C3**) with its copper and iron analogues $[Cu(DMEG_2e)_2][Cu_2I_4]$[11] (**C4**) and $[Fe(DMEG_2e)_2][Fe_2(CO)_8]$[11] (**C5**) shows a great similarity of all three complex cations. The metal atoms in the $[M(DMEG_2e)_2]^{2+}$ unit are present in the oxidation state +2 and are coordinated by four ethylene-bridged imine nitrogen atoms of the bis(guanidine) ligands in a strongly distorted tetrahedron. The five-membered chelate heterocycles adopt a half-chair conformation. The angles between the MN_2 planes (**C3**: 53.9°; **C4**: 44.5°; **C5**: 48.7°) show that the coordination mode remains in the intermediate position between the tetrahedral (90°) and the square-planar coordination (0°). The averaged bite angles of the complexes do not differ considerably [**C3**: 85.4(1)°; **C4**: 84.4(1)°; **C5**: 83.5(1)°] and also the averaged distances of the C=N bonds [**C3**: 1.309(5) Å; **C4**: 1.302(4) Å; **C5**: 1.307(3) Å] are identical. The values of the metal–nitrogen bonds [**C3**: 2.012(3) Å; **C4**: 1.970(2) Å; **C5**: 2.044(2) Å] are, despite the different metal ions and their varying ion radii, in a similar range.

As mentioned before, guanidines are a very promising ligand class leading to catalytically active zinc complexes. Therefore, the obtained complexes **C1**–**C3** were investigated regarding their activity in the bulk polymerisation of D,L-lactide. For this purpose D,L-lactide and the initiator (*I*/*M* ratio 1:500 or 1:1000) were tempered at 135 °C, 150 °C and 165 °C. After a reaction time of 24 or 48 h, the polymer melt was dissolved in dichloromethane, and then the polylactide was precipitated in cold methanol. We could prove that all three bis(guanidine) complexes possess catalytic activity in the ROP of D,L-lactide. A great advantage of the described zinc compounds is their stability towards air and moisture because they can be handled exposed to air without loss of activity. Complexes **C1** and **C3** are stable on air for months, while **C2** is hygroscopic but stable on air for hours. In order to specify the catalytic activity of the complexes, the monomer conversion was defined, and the molecular weights of the obtained polylactide were determined by gel permeation chromatography (see Table 1).

In general, the monomer conversion as well as the weight-averaged molar mass values (M_w) of the corresponding polymer are higher for **C1** than for **C2** and **C3**. At the standard temperature for lactide polymerisations, which is 150 °C,[5] **C3** shows the best results for M_w (32000–38000 g/mol) and the best yields. The acetate complex **C2** exhibits a weaker performance. This indicates the effect of the anionic component of the zinc salt on the catalytic activity of the corresponding zinc complex. Interestingly, an increase of the reaction time from 24 to 48 h does not improve the conversion, nor does it increase the molecular weight of the obtained polymer. On the contrary, a decrease of conversion and molecular weight

Table 1. Polymerisation of D,L-lactide initiated by **C1**–**C3**.

Initiator	Temp. [°C]	Time [h]	Mon./Init.	Yield [%]	M_w [g/mol]	*U*
None	165	24	–	0	–	–
C1	135	24	500	82	58800	1.74
C1	150	24	500	79	38000	1.72
C1	150	24	1000	70	32900	1.55
C1	150	48	500	67	32900	1.56
C1	165	24	500	61	33800	1.62
C2	135	24	500	63	34700	1.63
C2	150	24	500	69	24300	1.63
C2	150	24	1000	86	27600	1.77
C2	150	48	500	66	17900	1.60
C2	165	24	500	46	21500	1.54
C3	135	24	500	82	37200	1.74
C3	150	24	500	83	38200	1.61
C3	150	24	1000	93	34100	1.88
C3	150	48	500	83	31600	1.68
C3	165	24	500	51	23200	1.58

can be observed. Similar observations were reported by Chisholm et al. and Schwach et al.,[12] who considered side reactions like the interchain or intrachain transesterification as well as the chain-transfer reaction to be responsible for this effect. In this context, it is expected that a decrease of reaction temperature would lead to minor side reaction effects.[12] Our results (see Figure 4) support this hypothesis. At 135 °C, **C1** and **C2** lead to considerably larger polymers than at higher temperatures, with M_w values up to 59000 g/mol. Thus, molecular weights achieved by the present procedure decreased with increasing temperature. Only in the case of **C3** is this temperature effect not pronounced, because a maximum for the degree of polymerisation is reached at 150 °C.

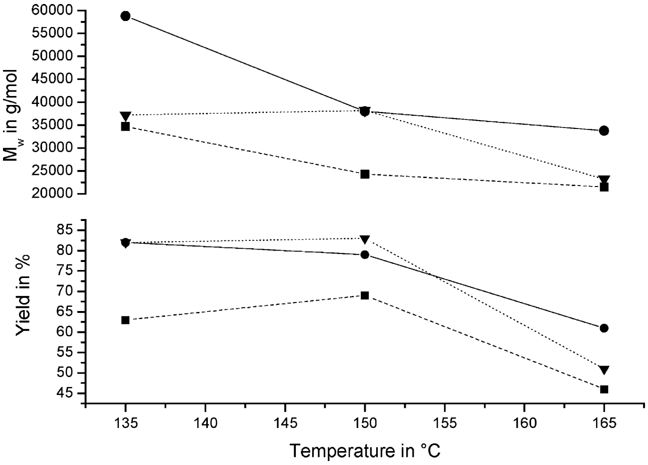


Figure 4. Dependence of weight-averaged molar mass (M_w) and yield vs. reaction temperature for the three initiator systems **C1**–**C3** (straight line: **C1**; dashed line: **C2**; dotted line: **C3**).

In order to study the structural characteristics of the synthesised polymers, the intrinsic viscosities were correlated with the molecular weight *M* of the polymers. As outlined in Figure 5, all polymer samples exhibited a unique trend. For polymers large enough, this correlation is described by the Mark–Houwink equation (see Figure 5):[13] $[\eta] = K{\cdot}M^{\alpha}$.

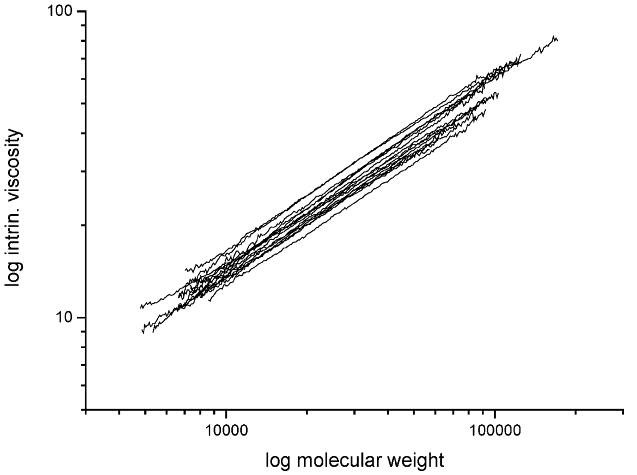


Figure 5. Mark–Houwink plot of all obtained PLAs. The calculated mean value for *α* is 0.59 and for *K* is 0.068 at 35 °C in THF.

The linear behaviour and unique trend of all examined polymers indicates that the obtained PLA samples are structurally homogeneous and linear. Hence, the structure of the polymer reported herein is independent of the initiator used and the averaged values for the Mark–Houwink constants at 35 °C in THF were calculated to be $\alpha = 0.59$ and $K = 0.068$. Further values for different temperatures and solvents were reported by Rafler et al.[14] and Schindler and Harper.[15]

In order to classify the polymerisation activity of the (guanidine)zinc systems, a comparison of catalyst systems reported in the literature is summarised in Table 2. This comparison reveals that our systems do not achieve the highest molecular mass values, but compared to Entries 1 and 2 the chosen *M*/*I* ratios are more favourable. Furthermore, the reaction times for polymerisations initiated by **C1**–**C3** are acceptable for the industrial standard. Compared to the highly active systems (Entries 4, 5, 8), **C1**–**C3** yielded similar or even higher molecular masses. The catalyst in Entry 7 is fast at ambient temperature and yields PLAs with high molecular masses, but the zinc alkoxide complexes are only stable under

Table 2. Selective summary of the reactivity of catalyst systems used for the ROP of lactide.

Entry	Polymer	Catalyst (cocatalyst)	Solvent(s)	*T* [°C]	Time	Mon./Init.	Molecular weight [g/mol]	Catalyst stability	Ref.
1	L-PLA	stannous octoate (alcohols)	none	200	60–75 min	33	468000 (M_w)[a]	stable	Seppälä et al.[16]
2	PLA-PCL-PLA	zinc powder (ethylene glycol)	none	140	8 h (for PLA)	20	61000 (M_n)[a]	stable	Li et al.[17]
3	D,L-PLA	zinc lactate	none	140	96 h	5000	155000 (M_n)[a]	stable	Schwach et al.[18]
4	D,L-PLA	(β-diiminato)zinc complexes	THF CH_2Cl_2	20	10 min 3 min	100	18100 (M_n)[a] 16800 (M_n)[a]	n/a	Chisholm et al.[19]
5	D,L-PLA	(carbene)zinc complexes	CH_2Cl_2 none	25 140	16 min 5 min	200 200	30000 (M_n)[a] 20000 (M_n)[a]	n/a	Tolman et al.[20]
6	D,L-PLA L-PLA	zinc alkoxides	toluene CH_2Cl_2	60 25	4.5 h 24 h	150 50	34100 (M_n)[a] 9900 (M_n)[a]	n/a	Lin et al.[21]
7	D,L-PLA	zinc alkoxides	CH_2Cl_2	25	18 min	1500	130000 (M_n)	only stable under glovebox conditions	Tolman et al.[22]
8	L-PLA	zinc alkoxides	toluene	25	13 min	400	25500 (M_n)[a]	n/a	Lin et al.[23]

[a] Expressed in polystyrene standards.

exclusion of moisture and air. Hence, the (guanidine)zinc complexes combine several factors that are necessary requirements for an efficient catalyst. These systems can be handled in air and give polymers with molecular masses that allow the application in industrial production processes. To increase the activity of the (guanidine)zinc catalysts, the reaction conditions have to be further optimised. The structural influences of the guanidine ligand on the activity of the zinc complexes in lactide polymerisation are being studied at the moment.

Conclusions

In this contribution we reported on the synthesis and complete characterisation of the first examples of aliphatic bis(guanidine)-stabilised zinc complexes that were proven to be active initiators in the ring-opening polymerisation of D,L-lactide. PLAs with molecular weights (M_w) of around 18000–59000 g/mol could be obtained. In complexes with the same ligand the activity of the initiator depends on the anionic component of the zinc salt. We found that complexes with zinc bis(triflate) and zinc dichloride seem to be the most auspicious candidates for application in the ROP of lactide. By changing the reaction temperature it could be shown that lower temperatures allow side reactions to be avoided during the polymerisation and thus give higher molecular masses. Moreover, the Mark–Houwink correlation demonstrates that the obtained polymers are linear and homogeneous. Compared to other systems the (guanidine)zinc complexes possess an advantageous combination of properties: they are non-toxic, comparably stable and give PLAs with good M_w values at industrial conditions. This makes the (guanidine)zinc systems a promising class of catalysts for the ring-opening polymerisation of D,L-lactide. The reaction control and the clarification of the reaction mechanism as well as the synthesis of more active (guanidine)zinc complexes for the ROP of lactide are topics of current research.

Experimental Section

Materials and Methods: All manipulations were performed under nitrogen (99.996%) dried with P_4O_{10} granulate using Schlenk techniques. Solvents were purified according to literature procedures and also kept under nitrogen. Zinc dichloride (99.99%, Acros), zinc diacetate (99.99%, Acros), zinc bis(trifluoromethanesulfonate) (98%, Aldrich) and D,L-lactide (3,6-dimethyl-1,4-dioxane-2,5-dione, Aldrich) were used as purchased. The N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine (**L1**) was prepared according to a literature procedure.[11]

Physical Measurements: NMR: Bruker Avance 500. The NMR signals were calibrated to the residual signals of the deuterated solvents ($CDCl_3$: δ_H = 7.26 ppm; CH_3CN: δ_H = 1.94 ppm). IR: Nicolet P510. MS (EI, 70 eV): Finnigan MAT 40. Elemental analyses: Perkin–Elmer analyser Model 2400.

Crystal Structure Analyses: Crystal data for compounds **C1**, **C2** and **C3** are presented in Table 3. X-ray diffraction data were collected with a Bruker-AXS SMART APEX CCD, using Mo-K_α radiation (λ = 0.71073 Å) and a graphite monochromator. SAINT and SADABS were used for data reduction and absorption correction.[24] The structures were solved by direct and conventional Fourier methods, and all non-hydrogen atoms were refined anisotropically with full-matrix least squares based on F^2 (SHELXTL[24]). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}$(C methyl). All methyl groups were allowed to rotate but not to tip. CCDC-652328 (for **C1**), -652329 (for **C2**) and -652330 (for **C3**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Gel Permeation Chromatography: The GPC measurements were accomplished with a Waters GPC 2000 instrument equipped with a precolumn (10 µm) and a combination of three PSS-SDV columns (10^6 Å, 10^5 Å, 10^3 Å). The detection system included an integrated refractive index (RI) detector and an integrated viscosity detector H502B (Visotek). All measurements were performed at 35 °C with THF as eluent. The flow rate was 1 mL/min. Sample concentrations amounted to 2–3 g/L. Molecular weight analysis was based on a universal calibration, carried out with polystyrene standards (Polymer Standard Service) in THF at 35 °C. Use of the universal calibration gave way to absolute values for the molecular weight, which are discussed as weight-averaged molar mass values M_w and the polydispersity index U as a measure of the width of the respective molecular weight distribution $U = M_w/M_n$ with M_n the corresponding number averaged molar mass. Results are summarised in Table 1. Concomitantly, the intrinsic viscosities of the polymer samples were determined as a function of the molecular mass and correlated in the Mark–Houwink plot (Figure 5).

Preparation of Compounds

[N^1,N^2-Bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]dichloridozinc(II), [Zn(DMEG$_2$e)Cl$_2$] (C1): The ligand N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine (0.278 g, 1.1 mmol) was added to a solution of zinc dichloride (0.136 g, 1 mmol) in abs. MeCN (15 mL) whilst stirring. This suspension was slowly heated under reflux. A colourless precipitate could be observed; yield: 98% (0.38 g). Colourless crystals suitable for X-ray diffraction could be obtained by recrystallisation from hot MeCN (decomposition at 350 °C). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.06 (s, 12 H, CH_3), 3.40 (s, 8 H, CH_2), 3.46 (s, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 37.1 (CH_3), 49.8 (CH_2), 49.9 (CH_2), 164.4 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 2933 [m, ν(C–H)], 2867 [m, ν(C–H)], 1597 [vs, ν(C=N)], 1508 (m), 1446 (m), 1429 (m), 1404 (m), 1348 (m), 1296 (m), 1227 (w), 1097 (w), 1051 (w), 916 (m), 798 (vw), 766 (w), 727 (w), 652 (vw), 615 (w) cm^{-1}. EI-MS: *m/z* (%) = 392 (17) [M^+: $C_{12}H_{24}{}^{37}Cl_2N_6{}^{66}Zn$, $C_{12}H_{24}{}^{35}Cl^{37}ClN_6{}^{68}Zn$], 391 (10) [$C_{12}H_{24}{}^{35}Cl^{37}ClN_6{}^{67}Zn$, $C_{11}{}^{13}CH_{24}{}^{35}Cl^{37}ClN_6{}^{66}Zn$, $C_{11}{}^{13}CH_{24}{}^{35}Cl_2N_6{}^{68}Zn$], 390 (46) [$M^+$: $C_{12}H_{24}{}^{35}Cl^{37}ClN_6{}^{66}Zn$, $C_{12}H_{24}{}^{37}Cl_2N_6{}^{64}Zn$, $C_{12}H_{24}{}^{35}Cl_2N_6{}^{68}Zn$], 389 (15) [$M^+$: $C_{12}H_{24}{}^{35}Cl_2N_6{}^{67}Zn$, $C_{11}{}^{13}CH_{24}{}^{35}Cl_2N_6{}^{66}Zn$, $C_{11}{}^{13}CH_{24}{}^{35}Cl^{37}ClN_6{}^{64}Zn$], 388 (71) [$M^+$: $C_{12}H_{24}{}^{35}Cl_2N_6{}^{66}Zn$, $C_{12}H_{24}{}^{35}Cl^{37}ClN_6{}^{64}Zn$], 387 (10) [$M^+$: $C_{11}{}^{13}CH_{24}{}^{35}Cl_2N_6{}^{64}Zn$], 386 (65) [$M^+$: $C_{12}H_{24}{}^{35}Cl_2N_6{}^{64}Zn$], 353 (14) [$M^+ - {}^{35}Cl$], 351 (15) [$M^+ - {}^{37}Cl$], 251 (12) [$M^+ - ZnCl_2$], 140 (6) [$C_4H_4N{=}CN_2(CH_3)_2C_2H_4{}^+$], 126 (100) [$CH_2N{=}CN_2(CH_3)_2C_2H_4{}^+$], 112 (7) [$N{=}CN_2(CH_3)_2$-$C_2H_4{}^+$], 98 (12) [$C_5H_{10}N_2{}^+$], 85 (4) [$CN_3(CH_3)_2{}^+ + H$], 56 (22) [$NCH_2CH_2N^+$]. $C_{12}H_{24}Cl_2N_6Zn$ (388.07): calcd. C 37.11, H 6.18, N 21.65; found C 37.41, H 6.10, N 21.24.

Diacetato[N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]zinc(II), [Zn(DMEG$_2$e)(CH$_3$COO)$_2$] (C2): The ligand N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine (0.278 g, 1.1 mmol) was added to a suspension of zinc diacetate (0.183 g,

Table 3. Crystal data for the compounds **C1**, **C2** and **C3**.

	C1	**C2**	**C3**
Empirical formula	$C_{12}H_{24}Cl_2N_6Zn$	$C_{16}H_{30}N_6O_4Zn$	$C_{26}H_{48}F_6N_{12}O_6S_2Zn$
Formula mass	388.6	435.8	868.3
Crystal size [mm]	0.23 × 0.20 × 0.18	0.41 × 0.39 × 0.20	0.16 × 0.15 × 0.13
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.5320(8)	7.7644(5)	12.5916(7)
b [Å]	13.2821(8)	9.1357(6)	12.6664(8)
c [Å]	13.2844(9)	15.0902(10)	14.3728(9)
α [°]	90	102.901(1)	96.624(2)
β [°]	101.318(2)	97.610(1)	108.597(2)
γ [°]	90	94.699(1)	116.279(2)
V [Å^3]	1649.2(2)	1027.3(1)	1857.2(2)
Z	4	2	2
$D_{\text{calcd.}}$ [g/cm^3]	1.565	1.409	1.553
μ(Mo-K_α) [mm^{-1}]	1.82	1.23	0.86
Temperature [K]	120(2)	120(2)	120(2)
θ range [°]	2.6–27.9	1.4–27.1	1.6–27.9
h, k, l	–10/12, ±17, ±17	±9, –11/10, ±19	–16/15, –16/14, ±18
Measured reflections	7633	8548	16702
No. of unique data	1978	4465	8805
Parameters	98	244	486
R_1 [$I \geq 2\sigma(I)$]	0.036	0.034	0.071
wR_2 (all data)	0.086	0.094	0.128
Min/max ΔF [e/Å^3]	–0.34/0.59	–0.30/0.37	–0.49/0.59

1 mmol) in abs. THF (7 mL) whilst stirring. A white precipitate could be observed. After 20 min of additional stirring, the suspension was slowly heated under reflux to give a clear solution. Colourless crystals suitable for X-ray diffraction were obtained by slowly cooling to room temperature (m.p. 51 °C); yield: 97 % (0.42 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.92 (s, 6 H, CH_3), 2.92 (s, 12 H, CH_3), 3.10 (s, 8 H, CH_2), 3.48 (s, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 23.6 (CH_3), 36.1 (CH_3), 49.6 (CH_2), 49.7 (CH_2), 164.0 (C_{gua}), 177.2 (C_{ac}) ppm. IR (KBr): $\tilde{\nu}$ = 2931 [m, ν(C–H)], 2866 [m, ν(C–H)], 1595 [vs, ν(C=N)], 1508 (m), 1446 (m), 1425 (m), 1404 (m), 1346 (m), 1296 (m), 1227 (w), 1097 (w), 1072 (w), 1049 (w), 1020 (w), 972 (w), 916 (m), 768 (m), 725 (m), 650 (m), 611 (m) cm^{-1}. EI-MS: m/z (%) = 434 (2) [M$^+$], 389 (34) [M$^+$ – $HN(CH_3)_2$], 375 (31) [M$^+$ – CH_3COO], 345 (9) [M$^+$ – CH_3COO – 2 CH_3], 315 (19) [M$^+$ – 2 CH_3COO – H], 299 (5), 251 (19) [M$^+$ – $Zn(CH_3COO)_2$], 236 (11) [M$^+$ – $Zn(CH_3COO)_2$ – CH_3], 220 (7) [M$^+$ – $Zn(CH_3COO)_2$ – 2 CH_3 – H], 153 (5) [M$^+$ – $Zn(CH_3COO)_2$ – $C_5H_{10}N_2$], 140 (28) [$C_4H_4N{=}CN_2(CH_3)_2C_2H_4^+$], 126 (100) [$CH_2N{=}CN_2(CH_3)_2C_2H_4^+$], 112 (11) [$N{=}CN_2(CH_3)_2C_2H_4^+$], 98 (22) [$C_5H_{10}N_2^+$], 85 (24) [$CN_3(CH_3)_2^+$ + H], 56 (48) [$NCH_2CH_2N^+$]. $C_{16}H_{30}N_6O_4Zn$ (434.16): calcd. C 44.22, H 6.91, N 19.35; found C 43.96, H 6.89, N 18.89.

Bis[N^1,N^2-Bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine]-zinc(II) Bis(trifluoromethanesulfonate), [$Zn(DMEG_2e)_2$]($CF_3SO_3)_2$ (C3): The ligand N^1,N^2-bis(1,3-dimethylimidazolidin-2-ylidene)ethane-1,2-diamine (0.278 g, 1.1 mmol) was added to a solution of zinc bis(trifluoromethanesulfonate) (0.182 g, 0.5 mmol) in abs. THF (10 mL) whilst stirring. This suspension was slowly heated under reflux. A colourless precipitate was observed; yield: 73 % (0.32 g). Colourless crystals suitable for X-ray diffraction could be obtained by recrystallisation from hot MeCN (decomposition at 350 °C). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.96 (m, 24 H, CH_3), 3.48 (m, 16 H, CH_2), 3.64 (s, 8 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 35.1 (CH_3), 45.7 (CH_2), 49.2 (CH_2), 122.1 (C), 165.8 (C) ppm. IR (KBr): $\tilde{\nu}$ = 2941 [w, ν(C–$H_{aliph.}$)], 2870 [w, ν(C–$H_{aliph.}$)], 1593 [vs, ν(C=N)], 1506 (m), 1458 (w), 1421 (m), 1342 (m), 1265 (s), 1221 (m), 1163 (m), 1028 (s), 916 (w), 781 (w), 725 (w), 636 (m), 573 (w), 517 (w) cm^{-1}. EI-MS: m/z (%) = 867 (6) [M$^+$], 717 (10) [M$^+$ – CF_3SO_3], 567 (18) [M$^+$ – 2 CF_3SO_3], 251 (100) [M$^+$ – $Zn(CF_3SO_3)_2$], 167 (31) [M$^+$ – $Zn(CF_3SO_3)_2$ – $C_4H_{10}N_2$ + 2 H], 149 (99) [$CF_3SO_3^-$], 126 (54) [$CH_2N{=}CN_2(CH_3)_2C_2H_4^+$], 112 (14) [$N{=}CN_2(CH_3)_2C_2H_4^+$], 100 (21) [$C_5H_{10}N_2^+$ + 2 H], 98 (17) [$C_5H_{10}N_2^+$], 86 (16) [$C_4H_{10}N_2^+$]. $C_{26}H_{48}F_6N_{12}O_6S_2Zn$ (867.25): calcd. C 35.98, H 5.53, N 19.37; found C 35.60, H 5.22, N 19.01.

General Procedure for Lactide Polymerisation: D,L-Lactide (3.603 g, 25 mmol) and the initiator (I/M ratio 1:500 or 1:1000) were weighed into a 50-mL Erlenmeyer flask that was closed with a glass stopper. The reaction vessel was then tempered at 150 °C. After the reaction time, the polymer melt was cooled to room temperature and then dissolved in dichloromethane (25 mL). The polylactide was precipitated in ice-cooled methanol (350 mL) and dried under vacuum.

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