ChemSusChem

Chemistry–Sustainability–Energy–Materials

Chemistry Europe

European Chemical Societies Publishing

Accepted Article

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To be cited as: *ChemSusChem* **2023**, e202300192

Link to VoR: https://doi.org/10.1002/cssc.202300192

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10.1002/cssc.202300192

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RESEARCH ARTICLE

A Multitool for Circular Economy – Fast Ring-Opening Polymerization and Chemical Recycling of (Bio)polyesters Using a Single Aliphatic Guanidine Carboxy Zinc Catalyst

Martin Fuchs,[a] Pascal M. Schäfer,[a] Wolf Wagner,[a] Ian Krumm,[a] Marcel Walbeck,[a] Regina Dietrich,[a] Alexander Hoffmann[a]and Sonja Herres-Pawlis*[a]

[a] M. Fuchs, Dr. P. M. Schäfer, W. Wagner, I. Krumm, M. Walbeck, R. Dietrich, Dr. A. Hoffmann & Prof. Dr. S. Herres-Pawlis
Institut für Anorganische Chemie
RWTH Aachen University
Landoltweg 1A, 52072 Aachen (Germany)
E-mail: sonja.herres-pawlis@ac.rwth-aachen.de

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Abstract: A new aliphatic hybridguanidine *N*,*O*-donor ligand (TMGeech) and its zinc chloride complex ([ZnCl2(TMGeech)]) are presented. This complex displays a high catalytic activity for the ring opening polymerization (ROP) of lactide in toluene, exceeding the toxic industry standard tin octanoate by a factor of 10. The high catalytic activity of [$ZnCl_2$(TMGeech)] was further demonstrated using industrially preferred melt conditions, reaching high lactide conversions within seconds. To bridge the gap towards a sustainable circular (bio)economy, the catalytic activity of [$ZnCl_2$(TMGeech)] for the chemical recycling of polylactide (PLA) *via* alcoholysis in THF was investigated. Fast production of different value-added lactates at mild temperatures was demonstrated. Selective PLA degradation from mixtures with polyethylene terephthalate (PET) and a polymer blend, catalyst recycling as well as a detailed kinetic analysis are presented. For the first time, chemical recycling of post-consumer PET producing different value-added materials was demonstrated using a guanidine-based zinc catalyst. Therefore, [$ZnCl_2$(TMGeech)] is a promising, highly active multitool not only to implement a circular (bio)plastics economy, but also to tackle todays ongoing plastics pollution.

Introduction

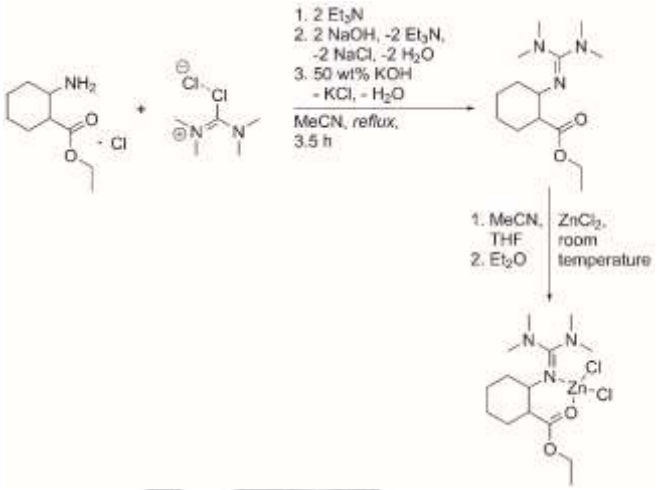
Today´s modern society is heavily dependent on the use of plastic materials. Due to their diverse and tailor-made properties, these materials have become indispensable in almost all areas of our advanced lives within the past century such as transportation, electronics, construction, households or packaging, with the latter making up the largest part.[1] However, many marine and terrestrial ecosystems are facing a massive thread, caused by the still increasing environmental pollution with non-degradable petroleum-based plastics.[1a, 2] On the other hand, high production rates as well as our dependency on plastics in critical life situations, such as the fight against COVID-19 involving massive amounts of face masks and syringes made from plastics, demonstrate that mankind needs these materials to maintain modern life standards.[1b, 3] To face these global challenges, efficient recycling strategies for end of life (eol) plastics are needed, promoting the circularity of these materials.[4] Besides traditional mechanical recycling methods, like melt processing which is today´s standard for thermoplastics such as polyethylene terephthalate (PET), the chemical recycling of plastics is recently gaining more significance.[5] Herein the polymer chain is degraded into smaller molecules, such as the monomer, which allows for the production of new virgin polymer. Compared to mechanical recycling a loss of polymer quality is avoided, which is especially relevant for the recycling of mixed plastic feeds.[6] Polyester materials are promising candidates for chemical recycling methods, such as hydrolysis, alcoholysis or aminolysis, due to their easily activated ester bond in the polymer backbone.[7] Nevertheless, as demonstrated by Bardow et al. various recycling methods must be combined in efficient strategies, powered by renewable energies to achieve carbon neutral plastics.[8] Besides efficient recycling an enforced substitution of today's petroleum-based plastics with adequate bioplastics should be encouraged.[9] These plastics are either derived from bio-based sources, biodegradable or combine both of these attributes.[10] In combination with efficient recycling strategies, their biodegradability acts as an insurance for small amounts of plastics accidentally entering the environment, as suggested by Palkovits et al..[11] A promising candidate, representing the latter class of bioplastics and already found on today's plastic market is polylactide (PLA), a polyester based on lactic acid, easily accessible *via* metal-catalysed ring-opening polymerization (ROP) of lactide, the cyclic dimer of the acid.[10] Lactic acid is derived from bio-based sources such as corn or other sugar containing plants *via* fermentation. The current production of the monomer lactide is a two-step process involving oligomerization of the acid with a subsequent depolymerization.[12] Due to its physical properties PLA is mostly used as packaging material, but also for single use cutlery, beverage cups, agricultural foils or for medical applications.[13] With a production of around 0.46 mio. tons in 2021, PLA shares the highest production capacity within the current bioplastics. Increased production and use of PLA are indicated in recent studies, further showing its potential for the future.[14] In addition, recycling of the polyester using chemical recycling strategies can provide a new monomer resource. This prevents a competition against food production and can reduce the overall production cost.[15] As recent studies by several groups show, the chemical recycling of PLA is a promising approach, especially for the selective recycling of mixed plastics feed.[16] However, the use of metal-based catalysts is still an emerging field of interest in academia.[15a] Although promising in terms of resource, biodegradability and recyclability, the current production of PLA is not fully sustainable, as the toxic catalyst tin octanoate ($Sn(Oct)_2$) is standardly used in industry. This is a potential thread to the environment, since traces of the catalyst remain in the polymer after production, which can accumulate during degradation.[17] Therefore, numerous studies have been

presented in literature showcasing non-toxic alternatives for lactide ROP based on various metals such as Al, Fe, Mg, Ge, Sc, group 4 metals.[18] Among the plethora of catalysts, special interest is drawn to the use of Zn, due to its low cost and availability.[16a, 16b, 19] Although different candidates have been presented, exceeding the activity of toxic tin octanoate towards lactide ROP, like the fast di-zinc catalyst by Williams et al., the majority of these examples require specific polymerization conditions such as additional solvents, low temperatures, a strictly inert atmosphere and a heavily purified monomer feed.[19a, 19b, 19d, 19g, 19j-s, 20] Only few examples have been published using temperatures of 150 °C and above, mimicking the industrial lactide polymerization without the use of an additional solvent in the polymer melt.[16a-c, 16e, 16f, 19c, 19e, 19r, 19t, 21] In recent years we have published several Zn-based catalysts in combination with various neutral bis- and hybrid guanidine ligands suitable for lactide ROP under industrially relevant melt conditions.[16b, 19f, 21-22] Resulting from this specific combination of easily accessible Zn salts with neutral guanidine-based ligands, these catalysts have proven to be non-toxic and robust against impurities in the lactide feed, which recently lead to a Zn-bisguanidine catalysts exceeding the catalytic activity of the industrial relevant catalyst.[19e, 23] Among the hybrid-guanidine ligands, aromatic *N*,*O*-donor ligands ("asme"-type) were presented, as robust polymerization catalysts with tunable catalytic activity, depending on the substituents at the aromatic bridging motive.[21b] Herein we present a new type of guanidine based *N*,O-donor ligand featuring cyclohexane as an aliphatic bridging motive. The resulting Zn-chloride catalyst displayed a high activity towards the ROP of lactide under industrially relevant melt conditions, as well as in toluene exceeding toxic tin octanoate by a factor of 10 under these conditions. In this study we will further present an in-depth analysis of this new catalyst towards the chemical recycling of (bio-based) polyesters. A high catalytic activity was found for the alcoholysis of PLA, giving access to different value-added lactates. Therefore, a single catalyst can be used along the whole PLA value chain, making **C1** a promising candidate to implement a circular PLA economy in the future. Moreover, we report on the methanolysis of polycaprolactone (PCL), a PLA-PCL-blend and, for the first time using a *N*,*O*-guanidine Zn catalyst, the alcoholysis of polyethylene terephthalate (PET) which further highlights the industrial relevance of the new catalyst. With the catalytic activity towards polyester alcoholysis being dependent on the polymer structure as well as the reaction temperature, a route to a selective chemical recycling process of mixed plastic feeds without prior sorting is paved using **C1**, underlining its use as a circular economy multitool.

Results and Discussion

Synthesis

The new hybrid guanidine *N*,*O*-donor ligand ethyl *cis*-2-((bis(dimethylamino)methylene)amino)cyclohexane-1-carboxylate (TMGeech, **L1**) was synthesized, slightly adapting the protocol of the previously published aromatic *N*,*O*-guanidine ligands.[21, 24] According to Scheme 1, ethyl *cis*-2-amino-1-cyclohexanecarboxylate hydrochloride was combined with the Vilsmeier salt *N,N,N',N'*-tetramethylchloroformamidinium chloride (TMG-VS), to afford **L1** after two deprotonation steps.



Scheme 1. Synthesis of the ligand **L1** from cis-2-amino-1-cyclohexane-carboxylate hydrochloride with TMG-VS and subsequent reaction with $ZnCl_2$ forming the complex **C1**.

Reacting **L1** with anhydrous $ZnCl_2$ gave access to the corresponding zinc chloride complex [$ZnCl_2$(TMGeech)]·THF (**C1**). Using a mixture of THF and MeCN with subsequent diffusion of Et_2O afforded the complex as crystals suitable for structural analysis. The molecular structure of **C1** was determined using single crystal X-ray diffraction (XRD). The Zn center in **C1** is four-coordinate by the two donors in **L1** and two chloride ions (Figure 1). In the solid state the complex displays a slightly distorted tetrahedral coordination, which is expressed by the parameter τ_4 taking a value of 0.84. In the case of ideal tetrahedral coordination, the parameter would take a value of 1.[25] With a ρ-value of 0.97 the guanidine unit in **C1** is well delocalized, according to literature.[26] Changing the bridging unit to cyclohexane resulted only a slight effect on the characteristic structural parameters, when compared to the previously published "asme"-type Zn-complex [$ZnCl_2$(TMGasme)] (Table 1). Within the scope of the error the most important structural parameters are in the same order of magnitude for **C1** as for the "asme"-catalyst. Both, **L1** and **C1** were further characterized using ^{1}H and ^{13}C NMR spectroscopy as well as IR spectroscopy and mass spectrometry (see supplementary information and repository).

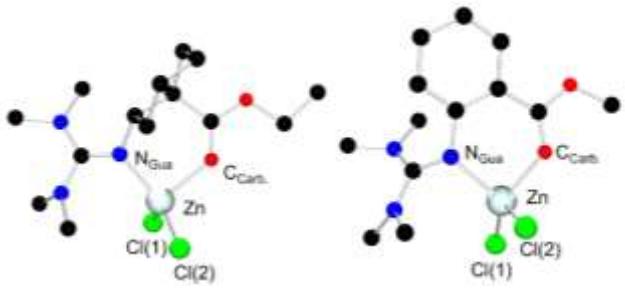


Figure 1. Molecular structures in the solid state of **C1** (left) and [$ZnCl_2$(TMGasme)][21a] (right) (H atoms and solvent molecules omitted for clarity).

Table 1. Important structural parameters of **C1** and the previously published catalyst [$ZnCl_2$(TMGasme)].

Complex	Zn-N_{gua} [Å]	Zn-O [Å]	N_{gua}-Zn-O [°]	ρ[a]
C1	1.974(2)	2.079(2)	91.9(1)	0.97
[$ZnCl_2$(TMGasme)][21a]	1.998(4)	2.038(3)	90.2(1)	1.00

[a] ρ = 2a/(b+c) according to[26]. [b] τ_4 = [360°-(α+β)]/141° according to[25].

Ring-opening polymerization of lactide

The catalytic activity of **C1** was first tested towards the ring-opening polymerization (ROP) of lactide using industrially preferred melt conditions at 150 °C. To ensure a consistent monomer quality recrystallized l-lactide was used. A very high catalytic activity was detected, reaching a conversion of 90 % in 70 s at a [LA]/[**C1**]-ratio of 1000:1 (Table 2). At present, this ranks **C1** as the fastest *N*,*O*-hybrid guanidine Zn catalyst, when compared to other ROP catalysts presented in literature. A Zn-chloride catalyst utilizing the aromatic *N*,*O*-guanidine ligand TMG5NMe$_2$asme was applied in the ROP of technical grade l-lactide at 150 °C, using the same [M]/[I]-ratio of 1000:1. Herein a conversion of 49 % was reached in 90 min, which made this catalyst the fastest of the "asme"-catalysts.[21b] The iron analogon was the first catalyst using guanidine ligands to exceed the activity of the toxic industry standard Sn(Oct)$_2$, but **C1** displays a 30 % higher lactide conversion as the Fe-based catalyst, using the same reaction conditions. Compared to Sn(Oct)$_2$, the polymerization time of **C1** is around 20-times shorter (Table 2).[18d] This shows the high potential of **C1** to replace the toxic Sn(Oct)$_2$ in industrial lactide ROP. Reducing the catalyst loading to a [LA]/[**C1**]-ratio of 2000:1 resulted in a lactide conversion of 74 % within 2 minutes. It should be noted that the viscosity of the polymerization mixture drastically increases during the reaction, which prevents a full lactide conversion. Doubling the monomer loading resulted in a larger deviation of the theoretical and experimental molar masses of the produced polymer, reaching an experimental molar mass of 108000 gmol^{-1} with a very low dispersity of only 1.2. With a theoretical molar mass of 213000 gmol^{-1} chain initiation by residual water, present in the monomer is indicated. For a highly active bis-guanidine Zn catalyst previously presented by our group lactide conversion of 84 % was reached in 700 s using technical grade *rac*-LA but otherwise same reaction conditions ([M]/[I] = 2000:1, T = 150 °C). Jones et al. presented the ROP of l-lactide with different Zn Schiff base catalysts, using industrially preferred melt conditions. At temperatures between 130 °C to 180 °C these Zn catalysts produce PLA in the presence of an additional co-initiator within 1 to 60 minutes, depending on the initial [M]/[ROH]/[I]-ratios. This further makes **C1** a highly attractive candidate for industrial lactide polymerization, when compared to these state-of-the-art ROP catalysts.[16f, 18i, 19e] However, the high activity of the catalyst limits the reliability of a kinetic evaluation for the lactide ROP in the monomer melt. Even if the fastest scanning rate of our *in-situ* Raman spectrometer was used to monitor the polymerization, the recorded data would not be sufficient for a meaningful determination of the observable rate constant k_{obs}, by plotting ln(LA_0/LA_t) against time according to pseudo first order kinetics (see ESI, Figure S11). A further kinetic evaluation for the lactide ROP in bulk was therefore not performed. Nevertheless, in order to obtain a rate constant for a better comparison of the catalysts activity with literature, the reaction was slowed down by performing the polymerization at 100 °C in toluene. Using a [LA]/[**C1**]-ratio of 100:1 almost full monomer conversion was achieved in under 50 minutes, affording a PLA with a molar mass of 31.000 g mol^{-1} and a dispersity of 1.7 (ESI, Table S3). Similar to the results of the melt polymerization, the experimental molar masses deviate from the theoretical ones indicating chain initiation by residual water present in the monomer. The increased dispersity further hints on the presence of transesterification side reactions (ESI, Table S3). Adding BnOH as a co-initiator gave a better control over the molar mass of the obtained PLA. For a [LA]/[BnOH]/[**C1**]-ratio of 100:1:1 a molar mass of 8340 gmol^{-1} was obtained. Compared to previous experiment ([LA]/[**C1**] = 100:1), adding BnOH further improved the dispersity of the produced PLA to 1.2 (ESI, Table S3) According to pseudo first order kinetics, the observable rate constant was determined for different [LA]/[**C1**]-ratios from the slope of a plot of ln(LA_0/LA_t) against time (ESI Figure S12). The resulting k_{obs} values were plotted against catalyst concentration to obtain the polymerization rate constant k_p from the slope of the resulting plot (Figure 2).

Table 2. Polymerisation results of **C1** and further comparable catalysts.

[LA]/[I]	Catalyst	eq. BnOH	t[b]	C [%][c]	$M_{n,theo.}$ [gmol^{-1}][d]	$M_{n,exp.}$ [gmol^{-1}][e]	$Đ$[f]
1000:1	**C1**	0	70 s	90	130000	85000	1.4
1000:1[g]	[$ZnCl_2$(TMG5NMe$_2$asme)][21b]	0	90 min	49	83500	45000	1.2
1000:1	[$FeCl_2$(TMG5NMe$_2$asme)][18d]	0	84 s	67	96500	89600	1.6
1000:1	Sn(Oct)$_2$[18d]	0	25 min	69	99400	168000	1.9
2000:1	**C1**	0	120 s	74	213000	108000	1.2
2000:1[g]	[Zn(*R*,*R*)-DMEG$_2$(1,2)ch}$_2$](OTf)$_2$ ·THF[19e]	0	700s	82	23600	90800	1.6
10000:1	**C1**	100	5 h	51	n.d.	n.d	n.d.

[a] solvent free polymerization of recrystallized l-lactide at 150 °C in a steel reactor with overhead stirring (260 rpm). [b]: reaction time adapted to the viscosity of the polymerization mixture. [c]: determined *via* ^{1}H NMR spectroscopy. [d]: *via* M(LA) x c ([LA]/[**C1**]). [e]: *via* GPC (in THF). [f]: M_w/M_n [g]: technical grade *rac* lactide.

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This resulted in a k_p value of (1.78 ± 0.15) x 10^{-1} $Lmol^{-1}s^{-1}$, which is compared to the bis-guanidine zinc catalyst reported by us earlier, in the same order of magnitude ((4.11 ± 0.4) x 10^{-1} $Lmol^{-1}s^{-1}$). In both cases the catalytic activity of the Zn-based catalysts is over 10 times higher than the activity of toxic $Sn(Oct)_2$ under the same conditions.[19e] This further supports the previous findings, ranking **C1** as a highly active lactide ROP catalyst.

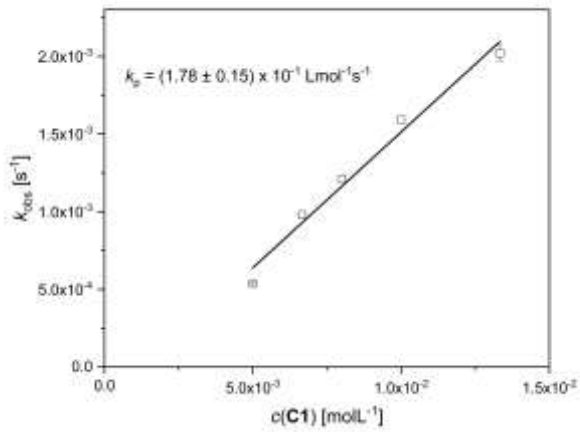
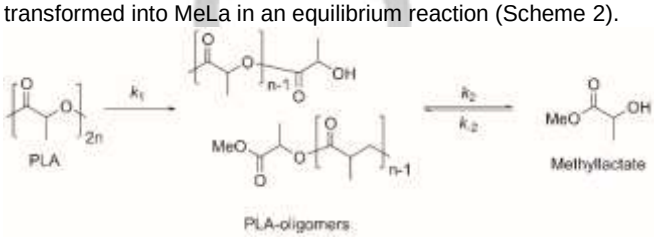


Figure 2. Plot of k_{obs} against catalyst concentration for the ROP of recrystallized l-lactide at 100 °C in toluene.

Due to the high catalytic activity of **C1** in the previous experiments, "immortal"-like ROP conditions, using BnOH as an additional co-initiator, were applied to test the limits of the catalyst. The used reaction conditions more closely mimic the ROP in industry.[27] Here the catalyst loading is decreased to a minimal amount, whilst a co-Initiator is used to control the chain length. As a proof of principle ROP was performed for an [LA]/[**C1**]/[BnOH]-ratio of 10000:1:100 at 150 °C in the polymer melt. With a reasonable LA conversion of 51 % after 5 h, the catalyst proofs to tolerate high amounts of additional alcohol. Nevertheless, the observed reaction profile of the $\ln(LA_0/LA_t)$ vs. time plot, shows a decrease of catalytic activity after around 30 minutes of reaction time (ESI, Figure S14). This matches the findings for the previously published "asme"-type catalysts, when characterized *via* model-based analysis. Herein, the occurring decrease in catalytic activity was found to be caused by chain initiation by the ligand. Over the course of the polymerization time, this leads to an overall decreased catalytic activity.[28] However, the reached lactide conversion further indicates the applicability of the catalyst under industrial conditions.

Chemical recycling of renewable polyesters

To implement a circular (bio)plastics economy and preserve the value of these materials, efficient recycling strategies at the end of life are of utmost importance for the use of (bio)plastics. As described by Bardow et al., a combination of traditional mechanical recycling and chemical recycling methods must be implemented in order to achieve a net-zero plastics production.[8] Since the polyester PLA is a well suited candidate for chemical recycling, a catalyst combining both production and recycling of PLA materials would be a great benefit in a circular economy setting. **C1** was therefore tested towards its catalytic activity in the alcoholysis of polylactide (foil, M_n = 49700 $gmol^{-1}$), producing different value-added alkyl lactates. To set a benchmark for this study, methanolysis was performed at 60 °C in THF using a catalyst loading of 1 mol%, regarding the maximum polymer ester bonds, with an excess amount of MeOH (7.1 eq) and a stirrer speed of 260 rpm, which is the standard procedure of our group.[16d, 29] The formation of the desired product methyl lactate (MeLa) was confirmed via ^{1}H NMR spectroscopy (ESI, Figure S15). Characteristic signals at 4.30 ppm, attributed to the respective PLA oligomers were found, indicating that the reaction follows a two-step consecutive mechanistic pathway as described in literature. [16f] The mechanism is described by Jones et al. is depicted in the Supporting Information Scheme S1.[16f] Herein, PLA is first converted to oligomers which are subsequently transformed into MeLa in an equilibrium reaction (Scheme 2).



Scheme 2. Two-step consecutive methanolysis of polylactide (PLA). Step 1: PLA degradation *via* transesterification to oligomers and Step 2: equilibrium reaction of oligomers to methyllactate.[16f] Scheme adapted from.[30]

After 6 h of reaction time full PLA degradation was achieved, receiving a MeLa yield and selectivity of 88 % (Table 3). These were calculated, using Equations S1 to S4 according to literature.[16f, 31] To further quantify the degradation of PLA, a kinetic evaluation of the polymer degradation to oligomers and MeLa was performed. Using the obtained data, the observable reaction rate constant k_{obs} was determined *via* the slope of a semilogarithmic plot of $\ln(PLA_0/PLA_t)$ *vs*. time (Figure 3). Herein, a k_{obs} of 2.75 x 10^{-4} s^{-1} was determined for **C1**.

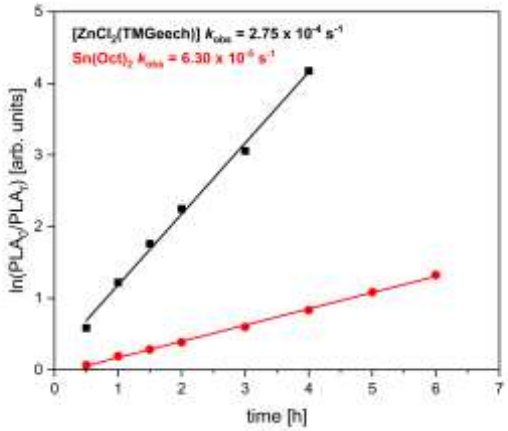


Figure 3. Plot of $\ln(PLA_0/PLA_t)$ against time for the PLA degradation at 60 °C in THF using a catalyst loading of 1.0 mol% and a MeOH loading of 7.1 eq. regarding regarding the PLA ester bonds with **C1** (black) and $Sn(Oct)_2$ (red).

For $Sn(Oct)_2$, the toxic catalyst used in industrial PLA production, a k_{obs} of 6.30 x 10^{-5} s^{-1} was determined using the same depolymerization conditions. This ranks the catalytic activity of tin octanoate towards PLA methanolysis almost 5 times slower, compared to **C1**, further stressing the industrial importance of the catalyst as an multitool for a circular (bio)economy. This is further supported, when **C1** is compared to Zn-based catalysts used for PLA methanolysis, described in recent literature. Jones et al.

Table 3. Results of polyester alcoholysis[a]

#	Time [h]	polyester	alcohol	polyester conversion [%]	product selectivity [%]	product yield [%]	k_{obs} x 10^{-4} [s^{-1}]
1	6	PLA	MeOH	100	88	88	2.75
2[b]	6	PLA	MeOH	73	66	48	0.63
3	6	PLA	*n*-BuOH	82	34	28	0.79
4	6	PLA	*i*-BuOH	72	23	16	0.57
5	6	PLA	*t*-BuOH	0	0	0	n.d.
6[c]	5	PLA	MeOH	100 (82)	89 (37)	89 (30)	n.d.
7	4.5	PLA:PET (0.25:0.75)	MeOH	99	68	68	n.d.
8	4.5	PLA:PET (0.5:0.5)	MeOH	100	70	70	n.d.
9	4.5	PLA:PET (0.75:0.25)	MeOH	100	64	64	n.d.
10[d]	6	PLA-PCL-blend	MeOH	100	88	88	3.40
11[e],	1	PCL	MeOH	79	100	79	n.d.
12[e],	0.17	PLA	MeOH	100	98	98	n.d.
13[e]	6	PET	MeOH	-	-	65	n.d.
14[e]	6	PET	BnOH	-	-	42	n.d.
15[f]	6	PET	Ethylene glycol	-	-	58	n.d.

[a] As standard depolymerization conditions a **C1** loading of 1.0 mol% and alcohol loading of 7.1 eq., regarding the respective ester bonds was used at a temperature of 60 °C in THF. [b] 1.0 mol% $Sn(Oct)_2$. [c] results after catalyst recycling in brackets. [d] 5.63 wt% catalyst loading, regarding the overall polymer weight. [e] solvent free at 150 °C. [f] solvent free at 180 °C.

reported a series of simple Zn Schiff base complexes utilizing different thioether motives, reaching almost full PLA conversion within 8 h at 80 °C in THF using a catalyst loading of 8 wt% (1.3 – 2.1 mol%).[16e] Another Zn-catalyst presented by Jones et al. fully degraded PLA within 3 to 8 h at 80 °C in THF, depending on the catalyst loading (4 to 8 wt%, regarding the polymer weight), whilst for a Zn-catalyst reported by Mazzeo et al. full PLA degradation was reached within 1 h at room temperature, using a catalyst loading of 0.6 mol%.[16c, 16g] It should be noted that there is no established benchmark protocol for testing the activity of new catalysts towards PLA alcoholysis, which is why various reaction conditions (catalyst/alcohol loading, temperature etc.) are presented in literature. For a further kinetic analysis of the performance of **C1** the reaction rate constant of the polymer decomposition was determined, using catalyst loadings between 0.25 – 5.0 mol% at a fixed MeOH loading (ESI, Figure S16). Therefore, this reaction rate constant is labelled $k_{1.1}$. In the further course of the discussion, a second reaction rate constant ($k_{1.2}$) will be determined, using various MeOH loadings at a fixed **C1** loading. From these constants the reaction rate constant of the polymer decomposition k_{dp} will then be derived (see next section, in depth kinetic analysis). The resulting k_{obs} values were plotted against the catalyst concentration affording the reaction rate constant $k_{1.1}$ for a fixed MeOH loading from the slope of the resulting plot (Figure 4). The determined $k_{1.1}$ value of 3.14 ± 0.07 x 10^{-2} $Lmol^{-1}s^{-1}$ further demonstrates the high catalytic activity of **C1** towards the methanolysis of PLA, when compared to the previously published "asme"-type catalysts using the exact same depolymerization conditions. As for the lactide ROP a drastic increase in activity is achieved using an aliphatic bridging motive. With a rate constant of 0.94 x 10^{-2} $Lmol^{-1}s^{-1}$ ("asme"-catalyst) **C1** is almost 4 times more active, when compared to the fastest "asme" catalyst.[16d]

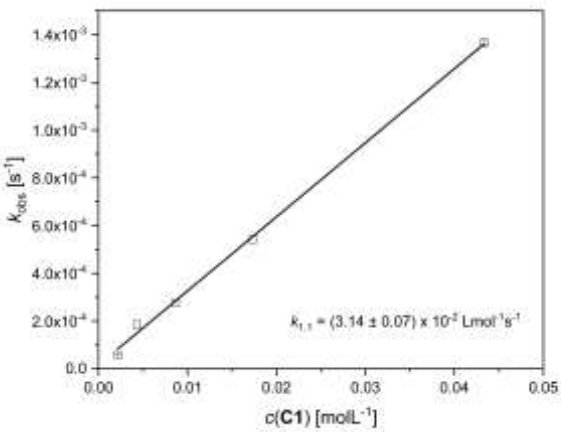


Figure 4. Plot of k_{obs} against the catalyst loading for the depolymerization of PLA at 60 °C in THF using **C1** and a fixed MeOH loading of 7.1 eq. regarding the PLA ester bonds.

Influence of the alcohol and in-depth kinetic analysis

So far, an excess amount of alcohol was used for all depolymerization experiments. According to the rate law of the reaction (Equation 1) $-d[PLA]/dt = -k_{obs}[PLA]^c$(1) with k_{obs} according to Equation 2 $k_{obs} = k_{dp}[\mathbf{C1}]^a[MeOH]^b = k_{1.1}[\mathbf{C1}]^a = k_{1.2}[MeOH]^b$ (2), higher alcohol loadings accelerate the transesterification of PLA during alcoholysis as reported by Sobota et al.[32] To gain a deeper understanding, PLA methanolysis was tested using different MeOH loadings with a fixed **C1** loading of 1 mol% at 60 °C in THF (ESI, Figure S17). Using a plot of the obtained k_{obs} values against time, the reaction rate constant $k_{1.2}$ was derived from the slope to (4.30 ± 0.07) x 10^{-5} $Lmol^{-1}s^{-1}$ (Figure 5). In both cases, when the MeOH concentration is varied and when the catalyst concentration is varied, a linear curve is obtained (compare Figure 4 (**C1**) and Figure 5 (MeOH)), which indicates first order dependence of the reaction on the PLA concentration, which sets $c = 1$.

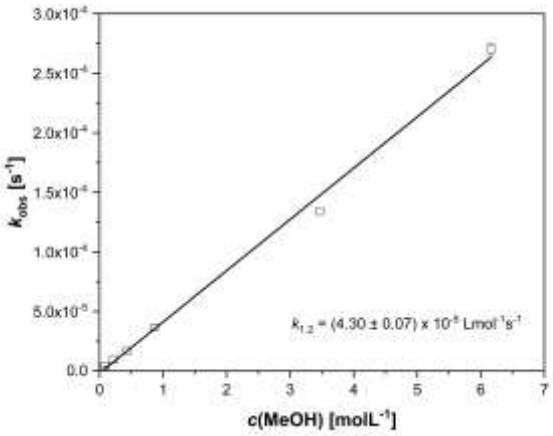


Figure 5. Plot of k_{obs} values against the MeOH loading for the depolymerization of PLA at 60 °C in THF using **C1** at a fixed loading of 1.0 mol% regarding the PLA ester bonds.

From the plot of ln(k_{obs}) vs ln([**C1**]) as well as the corresponding plot of ln(k_{obs}) vs ln([MeOH]) the respective reaction orders *a* and *b* were derived to 1 (ESI Figure S22 and Figure S23). The PLA degradation therefore also shows a first order dependence in catalyst concentration as well as in the MeOH concentration. Using the obtained values for $k_{1.1}$ and $k_{1.2}$, a k_{dp} of $5.00 \pm 0.03 \times 10^{-3}$ $L^2mol^{-2}s^{-1}$ was calculated for the PLA degradation (ESI, Equation S5). Since the use of discrete metal complexes as catalysts for PLA alcoholysis is a relatively new field in academic research, a common method for in-depth kinetic analysis of such catalysts has not yet been described in literature. However, there is a study by Wood et al. on the PLA methanolysis kinetics using $Zn(OAc)_2$ in THF. Here a model-based analysis is presented, which also includes the equilibrium reaction between PLA oligomers and MeLa and can be used to calculate the thermodynamic parameters of the overall reaction from PLA to MeLa. However, this kinetic analysis was evaluated using a fixed excess loading of MeOH (7.1 eq). Further a temperature of 130 °C was used, which makes it difficult to compare the study by Wood et al. to the findings presented for **C1** considering the reaction rate constant $k_{1.2}$. Nonetheless, the general trends for the PLA depolymerization to oligomers are in line with the findings of Wood et al. .[30] Therefore, to the best of our knowledge this is the first study to present an in-depth kinetic analysis for the PLA methanolysis at mild reaction conditions in THF taking into account both, catalyst and alcohol loading.

Applicability of the catalyst in an industrial context & solvent free PLA degradation

Due to the high catalytic activity of **C1** in the methanolysis of PLA, the suitability of the catalyst in scenarios relevant to an actual industrial application was further investigated. First the alcohol scope was broadened to synthesize a variety of value-added lactates. Therefore, PLA alcoholysis was tested for *n*-BuOH, *i*-BuOH and *t*-BuOH at 60 °C in THF using a catalyst loading of 1 mol%. Formation of the desired lactates was confirmed via ^{1}H NMR spectroscopy[33] (ESI, Figure S18, Figure S19 and Figure S20). As to be expected, no reaction occurred using *t*-BuOH, which is due to the inactivity of tertiary alcohols in transesterification reactions. In addition, the activity of **C1** is further dependent on the steric demand of the used alcohol, resulting in a decreased k_{obs} with increasing bulkiness of the alcohols compared to MeOH (Table 3). The synthesized lactates can directly be used as starting materials in different transformations or as green solvents.[34] Giving industry access to these value-added materials from end of life PLA further highlights the benefits of alcoholysis as a recycling tool and the industrial relevance of **C1**.

Furthermore, recycling of the catalyst after the methanolysis was studied using the aforementioned reaction conditions. After 5 h depolymerization time the liquid components were removed *in vacuo*. To the residue fresh solvent, alcohol and PLA were added. Compared to the first run, the activity of the catalyst was slightly decreased resulting in a polymer conversion of 82% after 5 h, (Table 3 & ESI, Figure S24). To further stress the usage of **C1** in industry, PLA methanolysis was tested in the presence of different polyesters, mimicking mixed plastic waste streams. This serves to address catalyst stability towards such impurities in the PLA feed as well as a selective degradation of PLA into MeLa. Considering an industrial application both have a high impact on the overall process, as sorting of the PLA feed to exclude other plastics prior to recycling could potentially be neglected which can cut the overall costs. Further, a selective formation of MeLa ensures a consistently high quality of the recycled PLA, when compared to traditional mechanical polyester recycling methods. Herein, contamination of the polymer feed causes a loss in quality of the recycled polyester.[35] First, polyethylene terephthalate (PET) was chosen as the contaminating agent, since it is a widely used petroleum-based polyester. PLA is found to be one of the major impurities in PET waste streams.[36] Vice versa PET will be found in real life post-consumer PLA waste.[37] Mixtures of PLA and PET with varied polyester content were exposed to the methanolysis, using the aforementioned reaction conditions. To ensure comparability of the results the same catalyst loading of 1.0 mol% regarding the overall amount of ester bonds was used. The PLA conversion as well as MeLa yield and selectivity were determined. Compared to the results of pure PLA methanolysis no loss of catalytic activity towards the formation of MeLa was observed (Table 3). In all cases no reaction with PET was observed (ESI, Figure S25, Figure S26, Figure S27), highlighting the methanolysis as selective towards PLA degradation. Furthermore, the selective PLA recycling from a polylactide-polycaprolactone blend was studied. Therefore, k_{obs} was determined for the methanolysis at 60 °C in THF, using a catalyst loading of 5.63 wt% regarding the overall polymer weight, which is the same as for the experiments using pure PLA. Compared to these experiments k_{obs} is slightly increased to 3.40×10^{-4} s^{-1} (Table 3 &ESI Figure S29), which is due to the increased ratio of catalyst to PLA ester bonds. Selective PLA methanolysis was confirmed via NMR spectroscopy, with no signals attributed to methyl 6-hydroxyhexanoate, which would derive from PCL methanolysis, observable in the recorded spectrum (ESI, Figure S28).[38] This effect is caused by the much lower reactivity of PCL in the methanolysis, as it was recently reported by our group for the use of aromatic *N*,*O*-guanidine Zn-chloride catalysts.[16d] After 6 h of reaction time a full PLA degradation was observed with a MeLa yield and selectivity of 88 %. However, to test the limits of our catalyst methanolysis of pure polycaprolactone (PCL, 45.000 $gmol^{-1}$) was studied. Due to the findings regarding PCL methanolysis using the less active aromatic "asme"-catalysts, we adopted the depolymerization procedure and studied the reaction at elevated temperatures without the use of an additional solvent.[16d] Within just 1 h of

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depolymerization time a PCL conversion of 79 % was reached using a catalyst loading of 1.0 mol% at 150°C, giving access to methyl 6-hydroxyhexanoate (ESI, Figure S32). Enthaler et al. recently demonstrated the depolymerization of PCL using Zn acetate as a catalyst at 160 °C in the microwave. Herein, a conversion of 74 % was reached after 30 mins, ranking the catalytic activity of **C1** in the same order of magnitude, which further shows the industrial relevance of the catalyst.[38]

Encouraged by the high catalytic activity of **C1** towards the solvent free methanolysis of PCL, the same was tested for PLA at 150 °C, since a procedure without the use of an additional solvent is favoured by industry and the principles of green chemistry.[39] Therefore, solvent free PLA methanolysis was tested using otherwise similar reaction conditions as for the PLA recycling experiments in THF. As to be expected, the activity of **C1** at 150 °C drastically increased, reaching full PLA conversion with a MeLa yield of 98 % after just 10 mins. Herein, **C1** outperforms the previously published "asme"-type catalysts, reaching an activity which is comparable to the super-fast Zn-catalyst presented by Mazzeo. However, it should be noted that the alcoholysis with the catalyst by Mazzeo et. al. was performed at room temperature, which demonstrates the high activity of this catalyst.[16d, 16g] A further unexpected benefit of **C1** is the catalyst recycling after solvent free PLA methanolysis. This was much more beneficial, compared to catalyst recycling after PLA methanolysis in solution. As shown in Figure 6, catalyst activity was fully retained for the second depolymerization run after removal of the liquid components *in vacuo*. Even for the third run under these conditions a high activity was detected, reaching a PLA conversion of 99 % and a product yield of 88 %. A still convenient activity was detected after the fourth run (Figure 6), classifying the recycling of **C1** after solvent free PLA methanolysis in the same region as for the microwave assisted process presented by Enthaler et al.[40] Concerning the potential use of **C1** in industry, the recyclability of the catalyst is a major benefit that needs to be emphasized in the development of new catalysts for chemical recycling of bioplastics, as recently stated by Palkovits et al.[11b]

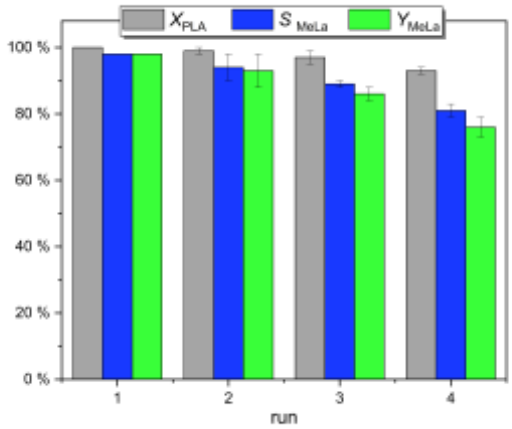

Figure 6. PLA conversion, selectivity towards MeLa formation and MeLa yield for the solvent free PLA methanolysis methanolysis with **C1** (1.0 mol% regarding the polymer ester bonds) at 150 °C with subsequent catalyst recycling.

Chemical Recycling of PET

The high catalytic activity of **C1** in the methanolysis of bio(based) polyesters encouraged us to extend the polymer scope to petroleum-based PET. Chemolytic recycling processes for PET involve hydrolysis, hydrogenolysis, aminolysis, ammonolysis, glycolysis and alcoholysis[41], the last two being the focus in this study. These can result in a variety of different value-added products, suitable for the production of new virgin PET.[7] Alcoholysis of PET oftentimes involves the use of supercritical alcohols at elevated temperatures and pressures.[42] PET alcoholysis at more moderate reaction conditions involves the use of catalysts, with zinc acetate being the most prominent, which is also the case for PET glycolysis.[43] Only a few examples have been presented in literature for the use of discrete metal-based complexes as catalysts for these processes.[44] Recently a zinc-based catalyst was presented by Jones et al. with a high catalytic activity towards PET chemical recycling.[45] Mazzeo et al. presented further examples of highly active zinc-based catalysts with different phenoxy-imine pyridine ligands for the glycolysis of PET to bis(2-hydroxyethyl) terephthalate (BHET).[46] Herein, complete full PET conversion was reached within just 1 h of reaction time at 180 °C, using a catalyst loading of 2.5 mol%. Since no reaction of PET occurred under the benchmark reaction conditions (60 °C, THF), the solvent free alcoholysis of PET was tested as a proof of principle using MeOH, BnOH and ethylene glycol (EG) for 6 h at 150 °C or 180 °C, respectively. For all tested alcohols a good catalytic activity of **C1** towards the formation of the corresponding products could be detected. Analogously to the literature[16f, 47], aqueous workup afforded the products as colourless crystals, giving access to dimethyl terephthalate (DMT) with a yield of 65 % and bis(2-hydroxyethyl) terephthalate (BHET) with a yield of 58 % (Table 3). As to be expected, using the bulkier BnOH resulted in a reduced activity yielding dibenzyl terephthalate (DBT) with 42 % after 6 h of reaction time (Table 3). Especially the recycling of PET to BHET is of great interest, since it can directly be used to produce new virgin-PET.[7] Jones et al. demonstrated the alcoholysis of PET using a Zn Schiff base catalyst. With a DMT yield of 72 % after 1.5 h reaction time, using a catalyst loading of 8 wt% at 150 °C this catalyst converts PET around 4 times faster than **C1**. This is also the case for the production of BHET. Dependent on the quality of the used PET, BHET was produced within 20 min to 1 h with a yield of up to 59 % using the aforementioned catalyst loading at 180 °C.[45] Mazzeo presented different Zn-based catalysts exploiting phenoxy-imine pyridine ligands for the fast chemical recycling of PET to BHET, with full conversion within 1 h at 180 °C using a catalyst loading of 2.5 mol%.[46] Enthaler et al. presented the fast (20 mins) microwave assisted methanolysis of PET, producing DMT with a yield over 90 % depending on the PET quality, using $Zn(OAc)_2$ at 160 °C.[48] However, **C1** is the first guanidine Zn catalyst being active towards the chemical recycling of PET, which enables a selective cascade recycling of biopolyester-(PET)-mixtures, used in packaging industry.[49] This is especially beneficial for industry, since a single catalyst can be applied in a recycling process, without the need for cost intensive separation of the polyester feed, prior to recycling. Such a process was described by Collinson et al. for the use of Zn acetate (0.4 mmol) as a catalyst. Herein PLA was recycled with 65 % MeLa yield from a 1:1 mixture of PLA:PET, whilst recycling of pure PET via glycolysis afforded a product yield of 78 % after each 15 h of reaction time. As demonstrated over the course of this study, the reactivity of **C1** towards polyester alcoholysis is dependent on the polymer structure, solubility and temperature, which enables the described cascade recycling. This further highlights the versatile applicability of **C1** as a multitool in a circular plastics (bio)economy.

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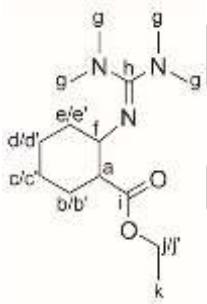
Conclusion

A new aliphatic neutral guanidine-based *N*,*O*-donor ligand (TMGeech, **L1**) and the corresponding Zn chloride complex ([$ZnCl_2$(TMGeech)], **C1**) were successfully synthesized and fully characterized. The complex was tested as a catalyst for the ring-opening polymerization (ROP) of the renewable monomer lactide. Using recrystallized l-lactide and industrially preferred melt conditions at 150 °C the catalyst showed a very high catalytic activity, producing polylactide (PLA) within seconds. Using "immortal"-like reaction conditions with benzyl alcohol as an additional co-initiator, the catalyst proved to tolerate high amounts of additional alcohol, further outlining the industrial relevance of **C1**. Furthermore, ROP of recrystallized l-lactide was demonstrated at 100 °C in toluene, with an activity exceeding the toxic industry catalyst tin octanoate ($Sn(Oct)_2$) by a factor of 10. To bridge the gap towards a circular economy, **C1** was further tested in the chemical recycling of PLA via alcoholysis. Using methanolysis at 60 °C in THF as a benchmark for this study, a high catalytic activity of **C1** towards the formation of methyl lactate (MeLa) was demonstrated, which is again higher than for $Sn(Oct)_2$. An in-depth kinetic analysis of the methanolysis provided the reaction rate constant of the polymer degradation, considering the amount of alcohol used for depolymerization. The catalyst further proved its abilities in different scenarios, relevant for industrial PLA recycling, such as depolymerization to different value-added lactates, recycling of the catalyst, selective depolymerization from mixed plastics feed and polymer blends as well as solvent free depolymerization and the depolymerization of polycaprolactone (PCL), while retaining its high catalytic activity. For the first time, the alcoholysis of polyethylene terephthalate (PET) in the polymer melt was demonstrated for different alcohols using a guanidine zinc catalyst, which in combination with chemical PLA recycling in THF, enables the potential to implement selective cascade recycling processes for biopolyester-PET mixtures. This further demonstrates the qualities of the new catalyst and makes it a multitool to implement a circular (bio)plastics economy by producing and recycling the renewable bioplastic PLA with high activity as well as tackling todays plastic-derived environmental pollution by recycling petroleum-based PET.

Experimental Section

Further experimental details regarding the polymerization and depolymerization procedures, as well as the specific methods used to characterize the synthesized compounds are listed in the supporting information.

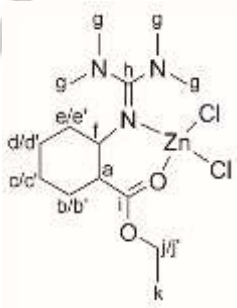
Ligand synthesis and characterization



TMGeech (L1): To an ice-cold and stirred solution of ethyl cis-2-amino-1-cyclohexanecarboxylate hydrochloride (3.00 g, 14.40 mmol, 1.0 eq.) and Et_3N (4.20 ml, 30.30 mmol, 2.1 eq) in MeCN (67.5 ml) a solution of N,N,N',N'-tetramethylchloroformamidinium chloride (2.71 g, 15.84 mmol, 1.1 eq) in MeCN (67.5 ml) was added dropwise. The reaction mixture was heated to 110 °C and was refluxed for 3 h. At room temperature NaOH solution (1.20 g, 30.00 mmol, 2.1 eq) in water (12.0 ml) was added and stirred for 90 s. MeCN and Et3N were removed in vacuo, KOH (50 wt%, 9.0 ml) was added to the reaction mixture and the aqueous phase was extracted with MeCN (3 x 30 ml). The combined organic layers were dried with MgSO4 and filtered over Celite®. The solvent was removed in vacuo affording L1 as a colourless oil (3.00 g, 11.10 mmol, 77 %). ^{1}H-NMR (400 MHz, CDCl3): δ = 4.08 (dq, $^3J_{H,H}$ = 10.9 Hz, $^3J_{H,H}$ = 7.2 Hz, 1H, j), 4.00-3.92 (m, 1H, j') 3.90 (q, $^3J_{H,H}$ = 3.6 Hz, $^3J_{H,H}$ = 3.2 Hz, 1H, f), 2.70 (s, 6H, g), 2.65 (s 6H, g), 2.40 (dt, $^3J_{H,H}$ = 10.7 Hz, $^3J_{H,H}$ = 3.6 Hz, 1H, a), 2.10 (dtd, $^3J_{H,H}$ = 13.0 Hz, $^3J_{H,H}$ = 11.1 Hz, $^3J_{H,H}$ = 3.6 Hz, 1H, b), 1.86-1.69 (m, 3H, c, d, e), 1.66-1.51 (m, 2H, b', e'), 1.43-1.32 (m, 1H, d') 1.31-1.23 (m, 1H, c'), 1.20 (t, $^3J_{H,H}$ = 7.1 Hz, 3H, k) ppm; ^{13}C -NMR (101 MHz, CDCl3) δ = 175.2 (i), 158.9 (h), 59.8 (j/j'), 54.6 (f), 49.4 (a), 40.1 (g), 38.7 (g), 33.0 (e/e'), 25.2 (c/c'), 23.5 (b/b'), 21.8 (d/d'), 14.4 (k) ppm; MS (EI): m/z (%): 269.2 (57) [$C_{14}H_{27}N_3O_2$]$^+$, 240.2 (2) [$C_{12}H_{22}N_3O_2$]$^+$, 225.2 (31) [$C_{12}H_{21}N_2O_2$]+, 196.2 (59) [$C_{11}H_{22}N_3$]$^+$, 181.2 (30) 168.1 (10), 154.0 (74) [$C_8H_{16}N_3$]$^+$, 142.0 (43) [$C_7H_{16}N_3$]$^+$, 126.0 (62) [$C_6H_{12}N_3$]$^+$, 115.1 (49) [$C_5H_{13}N_3$]$^+$, 109.0 (33), 100.0 (53) [$C_4H_{10}N_3$]$^+$, 85.0 (85) [$C_3H_7N_3$]$^+$, 81.1 (64), 72.2 (42), 71.1 (100) [$C_3H_7N_2$]$^+$; IR (ATR, ṽ) = 2987 (vw), 2981 (w), 2928 (m), 2893 (w), 2860 (w), 2851 (w), 2797 (vw), 1734 (s), 1731 (s), 1612 (vs), 1577 (w), 1560 (vw), 1495 (w), 1477 (w), 1465 (w), 1457 (w), 1446 (w), 1425 (w), 1364 (vs), 1309 (w), 1288 (w), 1247 (m), 1233 (w), 1209 (w), 1165 (s), 1131 (s), 1117 (m), 1098 (w), 1079 (w), 1067 (w), 1056 (w), 1041 (s), 1033 (s), 1011 (w), 971 (w), 944 (vw), 926 (w), 912 (w), 893 (vw), 863 (vw), 836 (vw), 810 (vw), 771 (w), 751 (vw), 736 (vw), 604 (vw), 570 (w), 533 (vw), 527 (vw), 480 (vw) cm–1.

Original analysis data of the target compound are available via Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ARVDXDODRG-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ

Complex synthesis and characterization



[$ZnCl_2$(TMGeech)]·THF (C1): Anhydrous $ZnCl_2$ (136 mg, 1.0 mmol, 1.0 eq.) and **L1** (269 mg, 1.0 mmol, 1.0 eq.) were each dissolved in a mixture of MeCN (0.2 ml) and THF (0.8 ml) using slight external heating. The hot solution of **L1** was added dropwise to the dissolved salt solution. Portions of Et_2O (1.0 ml) were added dropwise until the precipitation of the amorphous product was complete. The product was filtered and washed with THF and Et_2O, affording the title compound as colourless crystals suitable for XRD after 24 h (317.0 mg, 0.78 mmol, 78 %). ^{1}H-NMR (400 MHz, CDCl3): δ = 4.47-4.27 (m, 2H, j/j'), 3.38 (dt, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 3.7 Hz, 1H, a), 3.06-2.98 (m, 1H, f) 2.96 (s, 6H, g), 2.82 (s, 6H, g), 2.49-2.38 (m, 1H, b), 1.82 (dtd, $^3J_{H,H}$ = 13.7 Hz, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 3.8 Hz, 1H, e), 1.73-1.61 (m, 1H, d), 1.51 (m 3H, b', c, e'), 1.38-1.14 (m 2H, c', d'), 1.30 (t, $^3J_{H,H}$ = 7.2 Hz, 3H, k) ppm; ^{13}C -NMR (101 MHz, CDCl3) δ = 180.9 (i), 165.5 (h) 64.2 (j/j'), 57.7 (f), 46.3 (a), 40.4 (g), 33.0 (e/e'), 27.7 (b/b'), 23.9 (d/d'), 23.0 (c/c'), 13.9 (k) ppm; HRMS (ESI+, MeCN) m/z (%): calc: 368.1078, found: not found [$C_{14}H_{27}N_3O_2ZnCl$]$^+$; EA: calc (%) for $C_{14}H_{27}N_3O_2ZnCl_2$; C 41.45, H 6.71,

N 10.36; found (%) C 41.46, H 6.85, N 10.19; IR (ATR, $\tilde{\nu}$) = 2932 (m), 2866 (w), 1722 (s), 1670 (m), 1612 (vs), 1568 (vs), 1558 (vs), 1553 (vs), 1464 (m), 1456 (m), 1450 (m), 1425 (w), 1402 (vs), 1377 (w), 1312 (m), 1250 (vs), 1236 (s), 1227 (s), 1194 (s), 1163 (vs), 1150 (m), 1138 (w), 1128 (m), 1111 (w), 1092 (w), 1065 (w), 1030 (vs), 1013 (m), 978 (w), 947 (w), 926 (w), 918 (w), 897 (w), 891 (w), 864 (w), 854 (w), 804 (w), 777 (w), 662 (w), 631 (w), 580 (vw), 551 (w), 528 (vw), 516 (vw), 501 (w), 482 (w), 457 (vw), 444 (w), 414 (vw) cm^{-1}.

Original analysis data of the target compound are available via Chemotion repository: https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-BOGQKRYWPH-UHFFFADPSC-NUHFF-LUHFF-NUHFF-ZZZ

Solvent free ring-opening polymerization of lactide

In a N_2 filled glovebox recrystallized l-lactide (8.0 g, 55.5 mmol) and **C1** were each weighed according to the respective [LA]/[**C1**]-ratio and mixed using an agate mortar. For the ROP under "immortal"-like conditions BnOH was added according to the respective [LA]/[Co-I]/[**C1**]-ratio. The mixture was transferred to the polymerization reactor, equipped with an overhead stirrer and Raman probe, which was preheated to 150 °C and flushed with Ar three times prior to the reaction. As soon as the reactor was closed the in-situ Raman measurement was started, which marks the start of the kinetic analysis. The reaction time was adapted to the viscosity of the resulting polymerization mixture as well as the catalysts activity regarding the respective [LA]/[**C1**]-ratio. An aliquot of the crude polymerization mixture was taken to determine the lactide conversion via ^{1}H NMR spectroscopy ($CDCl_3$), after the respective reaction time. The crude polymer was dissolved in DCM (2 – 4 ml) and precipitated from EtOH at room temperature. After drying in high vacuum, the polymer molar mass was further analysed by GPC.

Ring-opening polymerization of lactide in solution

In a N_2 filled glovebox recrystallized l-lactide and **C1** were each weighed according to the respective [LA]/[BnOH]/[**C1**]-ratio and mixed using an agate mortar (for exact weight portions of the experiments see Table S2). If a Co-Initiator was used, half of the reaction mixture was transferred to a screw cap vial, BnOH, according to the respective [La]/[BnOH]/[**C1**] was added, the remaining solid components were added and the screw cap vial was removed from the glovebox. Anhydrous toluene (8.0 ml) was added to the polymerization reactor, equipped with an overhead stirrer and Raman probe, which was preheated to 100 °C and flushed with Ar three times prior to the reaction. A background spectrum was recorded and the reaction mixture was added to the reactor. After closing of the reactor, the in-situ Raman measurement was started, which marks the start of the kinetic analysis. The desired reaction time was adapted to the respective [LA]/[BnOH]/[**C1**]-ratio in order to obtain a data set, sufficient for further kinetic analysis. An aliquot of the crude polymerization mixture was taken from the reactor. After solvent removal in vacuo the conversion was determined via ^{1}H NMR spectroscopy ($CDCl_3$). The polymer was then precipitated from EtOH at room temperature. After drying in high vacuum, the polymer molar mass was further analysed by GPC.

Standard procedure for PLA methanolysis in solution

In the following the procedure for PLA methanolysis is exemplary described. For the use of different alcohols, polyester mixtures, blends and PCL and further deviation from the standard procedure, detailed procedures are described in the supporting information.

In a N_2 filled glovebox **C1** (0.25 - 5.0 mol%, regarding to PLA ester bonds) was charged to a Schlenk tube and dissolved in THF (4.0 ml). PLA (250 mg, 3.47 mmol, 1.0 eq., foil cut in pieces max. size 5 x 5 mm) was added using N_2 counterflow and dissolved using slight external heating. The Schlenk tube was transferred to an oil bath, preheated to 60 °C. MeOH (0.1 – 7.1 eq) was added using N_2 counterflow, which marks the start of the reaction. Aliquots of the reaction mixture were taken in intervals appropriate to the respective reaction conditions. ^{1}H NMR spectroscopy ($CDCl_3$) was used to determine the polymer conversion and further evaluate the kinetics, according to literature.[16f]

Solvent free polyester alcoholysis

In the following the procedure for solvent free PLA methanolysis is exemplary described. For the use of PET and PCL, detailed procedures are listed in the supporting information.

In a N_2 filled glovebox, **C1** (1.0 mol%, regarding the PLA ester bonds) was charged to a Schlenk tube. PLA (1.0 eq., foil cut in pieces max. size 5 x 5 mm) and MeOH (7.1 eq.) were added using N_2 counterflow. The exact weighed portions for all experiments are listed in Table S3. The Schlenk tube was immediately placed in an oil bath, preheated to 150 °C, which marks the start of the reaction. After the desired reaction time, the reaction was stopped by cooling the Schlenk tube in a water bath. An aliquot of the reaction mixture was taken and analysed via ^{1}H NMR spectroscopy to determine the polymer conversion as well as the product selectivity and yield according to literature.[16f]

Acknowledgements

The authors would like to thank the European Commision under H2020 Grant Agreement no. 953073 (Acronym: UPLIFT) for funding this project as well as Total Corbion PLA for the donation of the lactide and BioMi Croatia for the PLA foils, used for this study. PMS wants to thank the Hans Seidel Stiftung for funding. We further thank Dr. M. Paul and H. Hüppe for the XRD measurements, Dr. G. Fink for NMR measurements and Dr. W. Bettray for MS measurements. We thank NDFI4Chem for support and funding of the repositories Chemotion Repository and RADAR4Chem. Open Access funding enabled and organized by project DEAL.

Conflict of Interest

The authors declare no conflict of interests.

Data Availability Statement

All NMR spectroscopic data, GPC data and Raman spectroscopic data for the ring opening polymerisation of lactide of a non-toxic Zn catalyst were deposited. Furthermore, the NMR spectroscopic data for the depolymerisation of various polymers with the Zn complex were deposited. These data were deposited as original data in the repository RADAR4Chem by FIZ Karlsruhe - Leibniz-Institut für Informationsinfrastruktur and are published under an Open Access model (CC BY-NC-SA 4.0 Attribution-NonCommercial-ShareAlike; DOI:10.22000/923 and 10.22000/952).

Keywords: Polylactide • Ring-opening Polymerization • Chemical Recycling • Alcoholysis • Polyethylene Terephthalate

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10.1002/cssc.202300192

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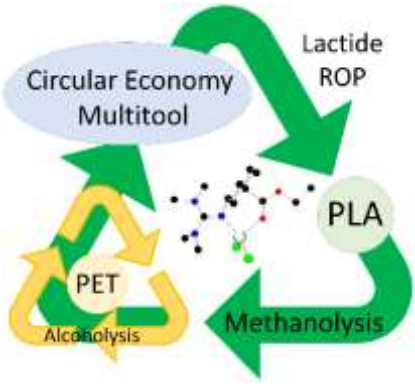

A new aliphatic *N*,*O*-guanidine ligand and its ZnCl2 complex are presented. The complex showed a high catalytic activity towards both, ring opening polymerization of lactide in the monomer melt and the methanolysis of polylactide as well as other (bio)polyesters. It is therefore a highly attractive multitool for industry to implement a circular (bio)polyester economy.

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