

RESEARCH ARTICLE OPEN ACCESS

Open- and Closed-Loop Recycling of Polyesters and Post-Consumer Waste Under Industrially Relevant Conditions Using Bisguanidine Organocatalysts

 Lisa Burkart | Alisa Hahn | Damon Blum | Yasemin Kara | Alexander Hoffmann | Sonja Herres-Pawlis 

Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany

Correspondence: Sonja Herres-Pawlis (sonja.herres-pawlis@ac.rwth-aachen.de)

Received: 12 September 2025 | **Revised:** 21 October 2025 | **Accepted:** 27 October 2025

Keywords: alcoholysis | guanidine | organocatalysis | polyethylene terephthalate | polylactide recycling

ABSTRACT

With the increasing demand for sustainable plastic materials, the implementation of a circular plastics economy starting from designing environmentally friendly polymers and including effective recycling strategies is of the utmost importance. The biobased and biodegradable polyester polylactide (PLA) is a promising candidate for a sustainable, circular plastics economy. Polyesters can be chemically recycled to obtain monomers or value-added chemicals following either a closed- or open-loop recycling approach. However, the requirements for catalysts applicable in post-consumer waste recycling are high: Besides a high activity, robustness and scalability of the catalyst are important factors. We studied highly active, robust bisguanidine organocatalysts for the depolymerization of the polyesters polycaprolactone, polyethylene terephthalate, and PLA. Focusing on PLA, we investigated the structure–reactivity relationship of the length of the aliphatic linker between the guanidine functionalities to identify the most active catalyst: Bis(*N,N,N',N'*-tetramethylguanidino) ethane (TMG₂e) depolymerizes PLA completely *via* alcoholysis within minutes under mild reaction conditions. The bisguanidine shows excellent activity for the alcoholysis of the investigated polymers, the ability to depolymerize binary and ternary plastic mixes, and robustness against additives, plasticizers, and other impurities in different post-consumer waste samples. Thus, TMG₂e has promising properties to be an asset for the implementation of a sustainable, circular plastics economy.

1 | Introduction

The increasing demand for plastics in various application fields is one of the most important challenges of the 21st century [1, 2]. Plastics are everywhere: from everyday household items and food and drink packaging to medical applications and spacecrafts [3, 4]. With increasing demand and increasing production comes an increasing amount of waste that needs to be managed [2, 5]; thus, establishing a sustainable, circular plastics economy is of utmost importance [6–9]. This goal can be achieved by enforcing the policies: reduce, reuse, recycle [2, 4, 10] and switching from petrol-based to biobased polymers [3, 9]. One of the most

promising bioplastics on the market is polylactide (PLA) [11]. PLA is derived from biomass and fully degradable to CO₂ and water under industrial composting conditions [12, 13]. Alongside compostability, other recycling options that offer access to the monomer or new value-added products are an important strategy in a circular economy. Effective recycling reduces the cost of monomer production, saves natural resources, and enables the creation of value from perceived waste material [14–19]. Besides mechanical recycling, which can lead to downcycling [15], chemical recycling is an efficient way to treat plastic-rich waste. In a circular plastics economy, circularity is achieved *via* open- or closed-loop recycling. Open-loop recycling produces

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2026 The Author(s). *ChemSusChem* published by Wiley-VCH GmbH.

new value-added products from end-of-life (EoL) plastics, whereas closed-loop recycling can provide new monomers for polymerization of new polymers [20–23]. For PLA, both ways can be achieved using alcoholysis. The alcoholysis of PLA can be catalyzed by various metal complexes [21, 22, 24–46], organo-catalysts [47, 48], and ionic liquids [17, 49–51] under mild conditions [14–18, 52–55]. Hereby, the ester functionality in the PLA backbone is attacked by the alcohol used. The nucleophilic attack leads to scission of the polymer backbone via a transesterification reaction [25, 35, 36]. Depending on the conditions and the alcohol used, the alkyl lactate is formed either directly by scission of the polymer chain-end (pathway A) or by random scission of the polymer backbone leading to the formation of oligomers (pathway B). The oligomers are then transformed into the alkyl lactate in an equilibrium reaction [20, 25, 28, 35, 36, 41]. Using metal catalysts, pathway A is observed in the absence of solvents and for reactions in solution using a specific nucleophile, that is, benzyl alcohol [33, 36]. Reactions in solution using simpler aliphatic alcohols follow pathway B [30, 33, 34, 36]. The obtained alkyl lactates can be used to regain the monomer lactide (LA) [56], other new monomers [45, 57], or serve as green solvents [42]. Besides working on the integration of biobased polymers such as PLA into a circular plastics economy, the obtained know-how of chemical recycling of polyesters can be applied to conventional, mostly fossil-based polyesters such as polyethylene terephthalate (PET). The mechanical recycling of PET bottles is one of the most prominent recycling approaches nowadays [3, 58, 59]. EoL PET from bottles can be collected in high purity enabling successful mechanical recycling to high-quality PET [60, 61]. But, due to mismanagement of PET waste and its application in multilayer materials, other recycling approaches are necessary to valorize the whole potential of PET waste [58–60, 62]. The separation of waste material is difficult and for some processes, even small impurities can impact the quality of the product [3, 58, 59]. PLA and PET have similar properties, thus aggravating proper separation of mixed waste streams. They have similar densities and cannot be separated optically. For proper separation, near-infrared spectrometers need to be applied but those are expensive, seldomly used in waste management facilities, and have limitations such as dark-colored materials (e.g. black bottles). A solution to this problem could be chemical recycling [60, 63]. The alcoholysis is a promising chemical recycling route enabling proper separation of PET and PLA waste material, especially in a scenario in which further mechanical separation is not possible [63–65]. Besides separation, working with waste materials entails a set of new challenges for chemical recycling: The applied processes and catalysts need to be robust against various impurities, such as organic waste and other polymers as well as plasticizers, pigments, fillers, and different additives [55, 61, 66]. In the last three years, we reported several guanidine metal catalysts active in the alcoholysis of PLA [29–34] and other polyesters such as PET, and polycaprolactone (PCL) [31, 34]. This study focuses on the introduction of bis-guanidine organocatalysts as highly active and robust catalysts for post-consumer waste depolymerization under industrially relevant conditions. We studied the easy-to-synthesize bisguanidines bis(*N,N,N',N'*-tetramethylguanidino)ethane (TMG₂e) [67, 68], bis(*N,N,N',N'*-tetramethylguanidino)propane (TMG₂p or btmgp) [67–68], and bis(*N,N,N',N'*-tetramethylguanidino)pentane (TMG₂pe) [69] concerning their activity for the methanolysis and ethanolysis of PLA (Figure 1).

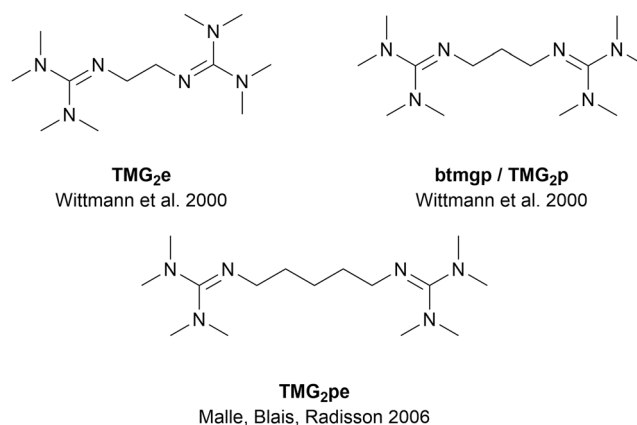


FIGURE 1 | Investigated organocatalysts TMG₂e [67], TMG₂p [67, 68], and TMG₂pe [69].

To investigate the influence of the CH₂-linker between the two guanidine functionalities, we determined the depolymerization rate constant k_{dp} for the methanolysis and ethanolysis for qualitative comparison with each other and other catalysts. Furthermore, the activation energy E_A , the activation entropy $\Delta S^\ddagger$, and the activation enthalpy $\Delta H^\ddagger$ were determined. TMG₂e showed the most promising properties; thus, we investigated the applicability of TMG₂e under industrially relevant conditions, keeping the principles of Green Chemistry in mind [70, 71]. We performed the depolymerizations without solvents using unpurified chemicals [72]. The methanolysis and ethanolysis using TMG₂e were scaled up to 50 g PLA (methanolysis) and 175 g PLA (ethanolysis). The obtained methyl lactate (MeLa) and ethyl lactate (EtLa) can either be used to regain the monomer LA [56] or as green solvents and food additives [73, 74]. TMG₂e was further investigated in the depolymerization of other polyesters showing excellent results for the methanolysis of PCL. Furthermore, we performed the glycolysis and the methanolysis of pristine PET and post-consumer PET waste material as well as the methanolysis of binary and ternary polymer mixes enabling the valorization of waste streams unfit for mechanical recycling.

2 | Results and Discussion

2.1 | Bisguanidines as Organocatalysts for the Alcoholysis of PLA

The recycling of post-consumer waste plastic material under industrially relevant conditions requires catalysts that are highly active, robust, and easy to synthesize. Previously, Conrads et al. reported several easy-to-synthesize Fe hybrid [32, 33] and bisguanidine [32] complexes active in the LA ring-opening polymerization and depolymerization of PLA. The Fe(II) catalysts [FeCl₂(TMG₂e)] and [FeCl₂(TMG₂p)] are synthesized using FeCl₂ and the bisguanidines TMG₂e and TMG₂p [32, 67, 68]. Preliminary tests showed that TMG₂e and TMG₂p depolymerize PLA faster than the corresponding Fe complexes but have a lower selectivity for MeLa (S_{MeLa}) at similar PLA conversions (Table S2). This observation indicates that the metal center, if present, has a significant impact on the alcoholysis of PLA: decreasing the conversion of the internal methine group of

PLA (X_{int}) and increasing the selectivity for the alkyl lactate (S_{RLa}). We propose that the transition state of the metal catalyst is sterically more demanding, aggravating the polymer conversion. However, increasing the selectivity by favoring the more accessible polymer chain-ends or smaller oligomers. Another difference to the Fe complexes is the robustness of the organocatalysts toward impurities like water or air. Furthermore, the bisguanidines can be synthesized in a one-step reaction starting from the diamine and the tetramethylchloroformamidinium chloride Vilsmeier salt (TMG-VS) [32, 33, 67, 68]. With the transfer to industrial application in mind, we synthesized TMG₂e without protective atmosphere using technical-grade solvents to cut the overall costs of the synthesis. TMG₂e was obtained as a colorless solid in a good yield (71%) after sublimation at 135°C. This and the well-established activity of guanidine functionalities for the depolymerization of polyesters make TMG₂e and TMG₂p promising candidates as organocatalysts active in the depolymerization of PLA [20, 47, 54].

To establish a baseline to evaluate the activity of the catalysts, we performed two control experiments without a catalyst: i) one under standard reaction conditions using MeOH (1.0 mL, 7.1 equiv) and PLA (film, 250 mg, 3.47 mmol, 1.00 equiv) at 60°C and at 260 rpm. After 22 h, no depolymerization of PLA could be observed using ¹H NMR spectroscopic analysis (Table 1). ii) The second experiment was performed without tetrahydrofuran (THF) as solvent and with EtOH (1.4 mL, 24 mmol, 6.9 equiv) and PLA (powder, 250 mg, 3.47 mmol, 1.00 equiv) at 100°C and at 260 rpm (Section S6.2). Within 22 h, the polymer swelled, but did not dissolve. We observed traces of oligomeric species in the heterogeneous mixture using ¹H NMR spectroscopic analysis. Thus, we propose that the observed conversion of PLA can be assigned to the catalysts used. First, we investigated if the CH₂-linker between the two guanidine functionalities has a beneficial effect compared to the single guanidine functionality of *N,N,N',N'*-tetramethyl guanidine (TMG). Table 1 shows the obtained results for the methanolysis (1.0 mL, 7.1 equiv MeOH) of PLA (250 mg, 3.47 mmol, 1.00 equiv) using standard conditions: 0.5–1.0 mol% TMG₂e, TMG₂p, and TMG₂pe in THF

forming a homogeneous solution (THF (4 mL)) at 60°C (stirring speed = 260 rpm). TMG was tested using 0.5 and 1.0 mol%. We doubled the catalyst loading of TMG to achieve the same number of guanidine functionalities present in the reaction mixture as for the bisguanidine catalysts. Table 1 shows the reaction time *t*, the S_{RLa} , and the yield of the alkyl lactate (Y_{RLa}) determined for a conversion $X_{\text{int}} \geq 98\%$. TMG₂e, containing two CH₂-units, reached 98% after 10 min, whereas TMG₂p required 15 min and TMG₂pe required 20 min. TMG (1 mol%) shows a lower apparent reaction rate constant k_{app} than the bridged bisguanidine catalysts and reaches $X_{\text{int}} = 98\%$ after 3 h. 0.5 mol% of TMG showed an even lower conversion of PLA as expected. Thus, we propose a structure-reactivity relationship between the length of the linker and the reactivity of the catalysts. Our results indicate a beneficial influence of a linker on the alcoholysis and an increased reactivity for shorter linkers. We propose that both guanidine functionalities are involved in the scission of the polymer backbone (Scheme S1). S_{MeLa} is low until complete conversion is achieved and increases with time as MeLa is formed via an equilibrium reaction between the oligomers and MeOH (Figure S1).

In comparison with other organocatalysts active in the alcoholysis of PLA, all three bisguanidine catalysts show promising results [47, 54]. McKeown et al. introduced the cheap organocatalyst $[\text{NMe}_3]^+[\text{OCO}_2\text{Me}]^-$ able to depolymerize PLA within 1 h using various solvents at 50°C [17]. In THF, $Y_{\text{MeLa}} = 83\%$ could be reached within 1 h using 0.5 mol% of catalyst [17]. In 2011, 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) was introduced as a highly active, versatile catalyst for the alcoholysis of PLA using different alcohols [20]. Complete methanolysis of PLA could be observed within 2 min in methylene chloride at room temperature [20]. TBD has one guanidine functionality but shows a fast conversion of PLA under the reported reaction conditions. Another highly active organocatalyst for the alcoholysis of PLA was introduced by Alberti et al. They reported 4-dimethylaminopyridine (DMAP) active in the microwave-assisted methanolysis of PLA without solvent at 180°C [47]. Due to the varying reaction conditions, a direct comparison between these literature-known catalysts and

TABLE 1 | Overview of obtained X_{int} , S_{MeLa} , Y_{MeLa} , and k_{app} for the methanolysis (7.1 equiv MeOH) of PLA (250 mg, 3.47 mmol, 1.00 equiv) using TMG₂e, TMG₂p, TMG₂pe, TMG, and no catalyst in THF (4 mL) at 60°C and 260 rpm.

Catalyst	# CH ₂ ^a	cat. loading ^b (mol%)	<i>t</i> (min)	X_{int} ^c (%)	S_{MeLa} ^c (%)	Y_{MeLa} ^c (%)	k_{app} (min ⁻¹)
TMG ₂ e	2	0.5	10	98	46	45	0.346 ± 0.002
TMG ₂ e	2	1.0	3	99	51	51	n.d.
			10	100	91	91	
TMG ₂ p	3	0.5	15	99	51	50	0.217 ± 0.003
TMG ₂ p	3	1.0	5	98	59	59	n.d.
			25	100	98	98	
TMG ₂ pe	5	0.5	20	100	61	61	0.274 ± 0.016
TMG	–	0.5	180	66	19	12	0.00629 ± 0.00018
TMG	–	1.0	180	98	40	39	n.d.
- ^d	–	–	1320	0	0	0	n.d.

^aNumber of CH₂ groups of the linker between the guanidine functionalities.

^bCatalyst loading in regards to ester bonds in the PLA used.

^c X_{int} , S_{RLa} , and Y_{RLa} were calculated from ¹H NMR spectroscopic analysis according to literature [28].

^dNo catalyst was used.

the three investigated bisguanidine catalysts is difficult. However, TMG₂e, TMG₂p, and TMG₂pe achieve complete conversion of PLA within short time periods under very mild reaction conditions (Table 1). TMG₂e (1 mol%) depolymerizes PLA within 3 min completely and we achieve high yields of MeLa ($Y_{\text{MeLa}} = 91\%$) within 10 min. TMG₂p (1 mol%) shows similar results after 5 min ($X_{\text{PLA}} = 98\%$) and reaches $Y_{\text{MeLa}} = 98\%$ within 25 min. To gain a better understanding of the activity of the bisguanidines, the influence of the two guanidine functions, and the length of the linker between them, we investigated the methanolysis and ethanolysis of PLA. Therefore, we determined k_{dp} of the first depolymerization step and evaluated the catalysts concerning their E_{A} , $\Delta S^{\ddagger}$, and $\Delta H^{\ddagger}$.

2.2 | Evaluation of k_{dp}

For the determination of k_{dp} , kinetic experiments were performed using different catalyst loadings under standard reaction conditions (250 mg PLA, 7 equiv alcohol, 4 mL THF, 60°C, 260 rpm) for each catalyst and alcohol. The k_{app} values (Figures S5–S9) were determined and plotted against the catalyst loading to obtain k_{dp} .

Figure 2 displays the obtained k_{dp} values for the methanolysis of PLA using TMG₂e (red, $(1.03 \pm 0.011) \text{ mol}\%^{-1} \text{ min}^{-1}$), TMG₂p (black, $(0.717 \pm 0.011) \text{ mol}\%^{-1} \text{ min}^{-1}$), and TMG₂pe (blue, $(0.664 \pm 0.010) \text{ mol}\%^{-1} \text{ min}^{-1}$). The linear regressions for the obtained k_{dp} values cut the y-axis below zero. This behavior can be explained by catalyst deactivation under the given reaction conditions. The obtained k_{dp} values show that with the increasing length of the CH₂-linker, the activity for the methanolysis decreases further undermining the beneficial influence of a short linker. In Figure 3, a similar trend is displayed for the ethanolysis: The obtained k_{dp} for the ethanolysis using TMG₂e (red, $(0.0794 \pm 0.0007) \text{ mol}\%^{-1} \text{ min}^{-1}$) is higher than using TMG₂p (black, $(0.04154 \pm 0.00001) \text{ mol}\%^{-1} \text{ min}^{-1}$). As reported previously,

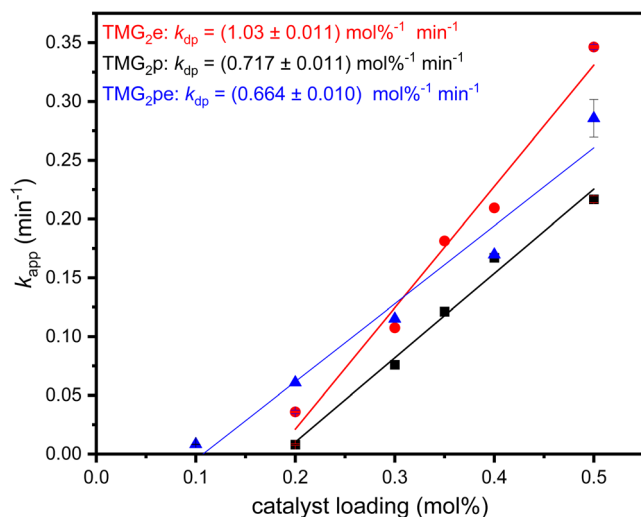


FIGURE 2 | Plot of k_{app} against the catalyst loading in mol% for the methanolysis of PLA (250 mg, 3.47 mmol, 1.00 equiv) using TMG₂e (red dots), TMG₂p (black squares), and TMG₂pe (blue triangles) using MeOH (1.0 mL, 7.1 equiv) in THF (4 mL) at 60°C and 260 rpm. All obtained linear regressions show signs of catalyst deactivation as they are no lines through the origin.

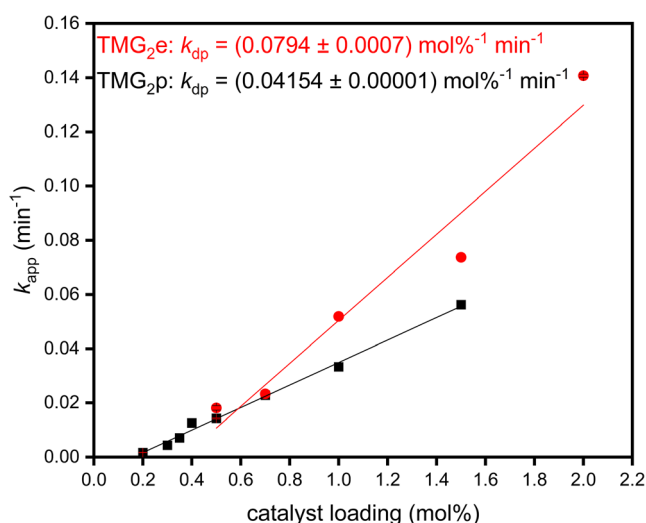


FIGURE 3 | Plot of k_{app} against the catalyst loading in mol% for the ethanolysis of PLA (250 mg, 3.47 mmol, 1.00 equiv) using TMG₂e (red dots) and TMG₂p (black squares) using EtOH (1.4 mL, 6.9 equiv) in THF (4 mL) at 60°C and 260 rpm. All obtained linear regressions show signs of catalyst deactivation as they are no lines through the origin.

we observed a significant influence of the alcohol on the reaction progress [30, 33, 34, 42]: The k_{dp} value for the ethanolysis using TMG₂e and TMG₂p is reduced by one order of magnitude compared to the methanolysis of PLA. This decrease in activity switching from MeOH to EtOH can be observed using various catalysts [20, 31, 33, 34, 42, 75]. Petrus et al. discuss the influence of the number of C atoms of the alcohols used and propose a beneficial impact of shorter alcohols with high nucleophilicity. [75] Further investigations of the alcoholysis using more challenging alcohols could provide more insight into their influence on TMG₂e and TMG₂p.

Compared to literature-known metal catalysts, all three bisguanidine organocatalysts exhibit higher activity for the methanolysis and the ethanolysis of PLA in THF [30, 33, 34]. Very recently, we reported the bisguanidine Zn complex $[\text{Zn}(\text{DMEG}_2\text{ch})_2](\text{OTf})_2 \cdot \text{THF}$ as a promising catalyst for the alcoholysis of PLA with a $k_{\text{dp}} = (0.078 \pm 0.001) \text{ mol}\%^{-1} \text{ min}^{-1}$ for the methanolysis and a $k_{\text{dp}} = (0.028 \pm 0.001) \text{ mol}\%^{-1} \text{ min}^{-1}$ for the ethanolysis [34]. The bisguanidine Zn catalyst shows a higher activity for the methanolysis of PLA than the hybrid guanidine Zn catalyst $[\text{ZnCl}_2(\text{TMGeech})]$ [31] as well as the hybrid guanidine Fe catalyst $[\text{FeCl}_2(\text{TMG5NMe}_2\text{asme})]$ [33]. The determined k_{dp} values for all three bisguanidine organocatalysts are higher than for the bisguanidine Zn catalyst: TMG₂e has a 13-fold higher k_{dp} value for the methanolysis and 25-fold higher k_{dp} value for the ethanolysis [34]. The use of organocatalysts increases the activity whilst reducing the number of steps and the overall costs of the catalyst synthesis facilitating the translation of the processes from laboratory to industry.

2.3 | Evaluation of E_{A} , $\Delta S^{\ddagger}$, and $\Delta H^{\ddagger}$

To gain insight into the temperature dependency of the alcoholysis, experiments under standard reaction conditions (250 mg (3.47 mmol, 1.00 equiv) PLA, 0.5 mol% catalyst, 7 equiv alcohol,

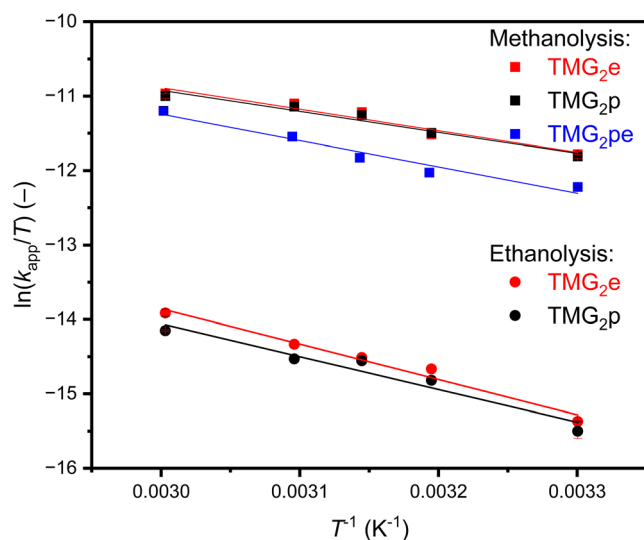


FIGURE 4 | Eyring plots for the methanolysis (7.1 equiv, squares) and ethanolysis (6.9 equiv, dots) of PLA (250 mg, 3.47 mmol, 1.00 equiv) using 0.5 mol% of TMG₂e (red), TMG₂p (black), and TMG₂pe (blue) in THF (4 mL) at 30, 40, 45, 50, and 60°C at 260 rpm.

4 mL THF, 260 rpm) were performed at 30, 40, 45, 50, and 60°C. In Figure 4, the obtained Eyring plots for the methanolysis (squares) and the ethanolysis (dots) show a similar linear regression for TMG₂e and TMG₂p, whereas the C₅-linker of TMG₂pe has a significant impact on the results for E_A , $\Delta S^\ddagger$, and $\Delta H^\ddagger$. The obtained Arrhenius plots for the methanolysis and ethanolysis are shown in Figure S10. Here, similar behavior of the obtained plots can be observed. Table 2 lists the calculated values for E_A , $\Delta S^\ddagger$, and $\Delta H^\ddagger$. TMG₂e and TMG₂p have the same values for all investigated parameters regardless of the alcohol. Therefore, the elongation of the linker by one CH₂ unit seems to have no influence on the temperature dependency.

The C₂- and C₃-bridged organocatalysts show lower values for E_A and $\Delta H^\ddagger$ than Fe hybrid guanidine [33] and Zn bisguanidine complexes [34] explaining the faster conversion of PLA under comparable reaction conditions (see also Table 1). The values for E_A and $\Delta H^\ddagger$ for the methanolysis of the C₅-bridged TMG₂pe are similar to the values determined for the Zn catalyst [Zn(DMEG₂ch)₂](OTf)₂ · THF ($E_A = 36 \pm 2$ kJ mol⁻¹; $\Delta H^\ddagger = 33 \pm 2$ kJ mol⁻¹) presented by Becker et al. in 2024. However, TMG₂pe depolymerizes the methanolysis faster than the metal complex. All organocatalysts show a more negative $\Delta S^\ddagger$ than reported metal complexes [33, 34], which suggests an associative reaction mechanism. Comparing the

results of TMG₂p and TMG₂e for the methanolysis with the results for the ethanolysis exhibits a similar trend as reported in literature [34, 42]. The methanolysis has a lower E_A and $\Delta H^\ddagger$, thus facilitating the conversion of PLA.

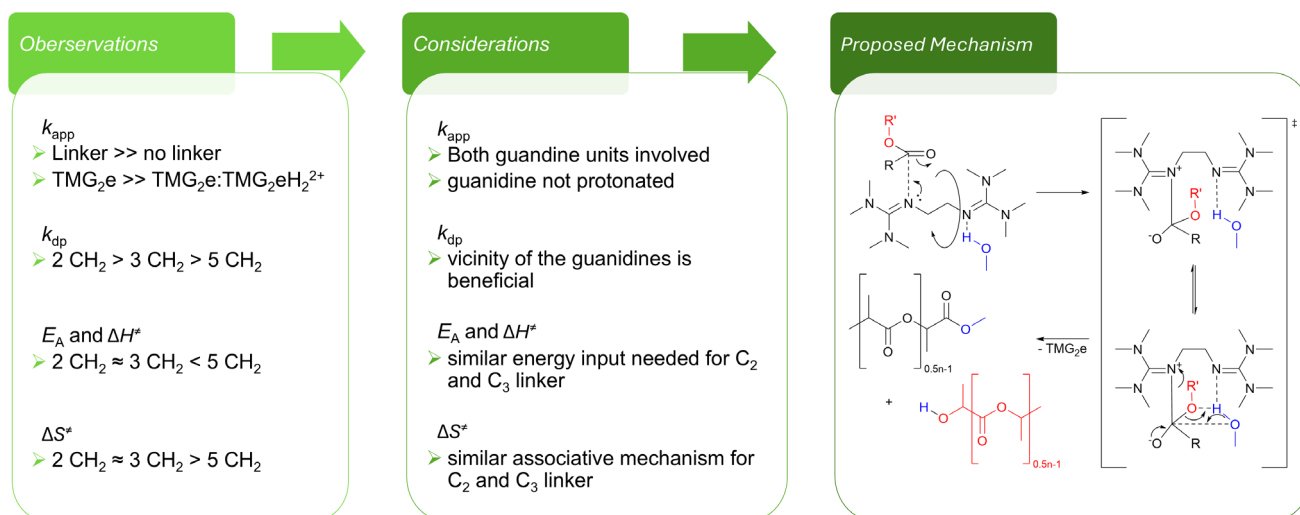
2.4 | Mechanistic Consideration

To gain insight into the mechanism of the alcoholysis using bisguanidine organocatalysts, we drew conclusions from the performed experiments and performed further experiments to exclude other theories. The presented results suggest that the length of the linker between the guanidine functionalities influences the alcoholysis. The elongation of the linker from two to three CH₂ units has no significant impact on the determined E_A , $\Delta H^\ddagger$, and $\Delta S^\ddagger$; whereas, an elongation of the linker to five CH₂ units leads to higher E_A and $\Delta H^\ddagger$, and a less negative $\Delta S^\ddagger$. However, the shorter linker of TMG₂e significantly improves the k_{dp} value compared to TMG₂p and TMG₂pe. Thus, we observe a beneficial effect of the spatial proximity of the guanidine functionalities. A similar trend was recently reported by Kamaraj et al. for the polymerization of LA to PLA using multiple bis- and monoguanidine organocatalysts [76]. The presented kinetic experiments suggest that the methanolysis and ethanolysis using all three bisguanidine organocatalysts follow a pseudo-first-order mechanism; therefore, only one catalyst molecule plays a role in the scission of the polymer backbone. Furthermore, the significant increase in the activity of the bisguanidines compared to TMG (Table 1) suggests that both guanidine functionalities are involved in the backbone scission of PLA. To further investigate the mechanism of the methanolysis using TMG₂e, we synthesized the hydrochloride of TMG₂e (TMG₂eH₂Cl₂) [67]. The methanolysis using the hydrochloride of TMG₂e showed complete inhibition of the catalysis. To further investigate the negative effect of the protonation of the catalyst, an experiment using a 1:1 ratio of TMG₂e (1 mol%) to the hydrochloride was performed (Table S4). The obtained k_{app} (0.0637 min⁻¹) is a magnitude lower than the obtained k_{app} value for 0.5 mol% TMG₂e (Table 1). Nonetheless, the k_{app} obtained for the methanolysis of PLA using the 1:1 catalyst mixture is still high compared to other catalysts under similar conditions and shows the robustness of TMG₂e against additional protons [32–34, 46]. Additionally, MeOH does not protonate the guanidine functionalities. These observations dismiss a transition state in which a protonated guanidine function activates the carbonyl oxygen in the polymer backbone as proposed for TBD [20]. Instead, we propose a dual nucleophilic activation mechanism *via* the imines of the two guanidine

TABLE 2 | Overview of obtained E_A , $\Delta S^\ddagger$, and $\Delta H^\ddagger$ for the methanolysis (7.1 equiv MeOH) and ethanolysis (6.9 equiv EtOH) of PLA (250 mg, 3.47 mmol, 1.00 equiv) using 0.5 mol% catalysts in THF (4 mL) at 30, 40, 45, 50, and 60°C and 260 rpm.

Catalyst	#CH ₂ ^a	ROH	E_A (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)
TMG ₂ e	2	MeOH	26.7 ± 0.4	24.1 ± 0.4	-216 ± 1
TMG ₂ p	3	MeOH	26 ± 1	23 ± 1	-218 ± 5
TMG ₂ pe	5	MeOH	32 ± 2	30 ± 2	-202 ± 6
TMG ₂ e	2	EtOH	42 ± 1	40 ± 1	-194 ± 4
TMG ₂ p	3	EtOH	39 ± 3	37 ± 3	-205 ± 9

^aNumber of CH₂ groups of the linker between the guanidine functionalities.



SCHEME 1 | Proposed dual nucleophilic activation mechanisms for the methanolysis of PLA using TMG₂e. The chain scission leads to the formation of two oligomers with different chain ends.

functionalities as displayed in Scheme 1 [20, 77–80]: One guanidine functionality could activate the electrophilic carbonyl C atom of the polymer backbone, the other could activate MeOH *via* an H-bond.

We suggest that the higher activity for the ethylene-bridged TMG₂e routes in the spatial proximity of the guanidine functionalities and the fewer possibilities to arrange the reactive partners, thus facilitating the chain scission by aligning the polymer backbone with the alcohol more efficiently. The proposed mechanism is plausible for TMG₂p. For TMG₂pe, the mechanism might be aggravated due to the C_5 -linker explaining the higher E_A and $\Delta H^\ddagger$. The longer chain could lead to a less simultaneous reaction process (less negative $\Delta S^\ddagger$), in which the alcohol functionality of the polymer (OR') functions as a leaving group prior to the attack of MeOH. This could lead to a reversible protonation of the catalyst by the proton of MeOH or longer coordination of the ester chain end to the catalyst. Protic impurities such as water could hinder the reaction by protonating the OR'-functionality of the polymer themselves, which might lead to protonation of the catalyst during the transition state with the proton from MeOH, and hence, reducing the catalytic activity.

2.5 | Industrial Relevance

Real-life applications entail new challenges such as the separation of plastic mixes and handling materials with varying compositions. Catalysts used for industrial applications need to be robust toward impurities such as water and air as well as toward other plastics and additives. Further, the catalysts need to be able to handle feedstocks with varying quality and composition. This is even more important considering mixed plastic waste streams. The reaction conditions should be as mild as possible while still achieving an effective catalysis and reducing costs and environmental impact. With these challenges in mind, TMG₂e was investigated under industrially relevant conditions: We performed experiments in contact with air and used chemicals as bought. The ethanolysis and methanolysis were performed without solvent to reduce the amount of chemicals

used. Further, we investigated the challenges of depolymerizing binary and ternary plastic mixes of PLA, PCL, and PET, and performed multiple depolymerization reactions using post-consumer waste materials provided by Vestforbrænding (Denmark) and AIMPLAS (Spain).

2.6 | Large-Scale Methanolysis and Ethanolysis

The large-scale methanolysis (5–50 g of PLA) and ethanolysis (5–175 g of PLA) were performed at 60, 100, and 150°C. Preliminary small-scale methanolysis (7.1 equiv) of PLA (250 mg, 3.47 mmol, 1.00 equiv) using 1 mol% of TMG₂e under solvent-free conditions at 150°C achieved complete selective depolymerization of PLA to MeLa ($Y_{MeLa} = 98\%$) within 5 min. Thus, to reduce the used chemicals, and to facilitate the purification process of the obtained alkyl lactates, we performed the reactions without THF. At temperatures below 150°C, the methanolysis and ethanolysis are heterogeneous reactions; neither EtOH nor MeOH acts as solvent for PLA [73]. Thus, we were not able to monitor the reactions as closely using ¹H NMR spectroscopic analysis as the reactions using THF as solvent. In Table S6, an overview of the obtained X_{int} , S_{RLA} , and Y_{RLA} for the depolymerizations is given after a homogenous reaction mixture was observed. Moreover, we reduced the amount of alcohol used from 7 equiv down to 3.7 equiv (120 mL EtOH). Here, the limiting factor is the stirring behavior if less alcohol is used. To further reduce the overall input of reagents, we collected the alcohol removed during the isolation process of EtLa and reused it successfully in another ethanolysis (Table 3). The methanolysis was scaled up to 50 g PLA and the ethanolysis was scaled up even further to 175 g PLA due to ethanol being the less toxic, biobased alcohol.

First, we tested a smaller approach using 5 g of PLA reaching complete selective methanolysis after 15 min. For the isolation of MeLa, the reaction approach was scaled up to 50 g. The reaction was conducted at 60°C to reduce energy consumption. After 1.25 h, ¹H NMR spectroscopic analysis showed complete conversion of PLA to MeLa. The product could be isolated in a moderate yield of 54% using rotary evaporation. The relatively low isolated

TABLE 3 | Large-scale methanolysis and ethanolysis of PLA using 1 mol% TMG₂e without THF as solvent.

ROH	<i>m</i> _{PLA} (g)	<i>V</i> _{ROH} (mL)	<i>T</i> (°C)	<i>t</i> (h)	<i>Y</i> _{RLa} ^a (%)	<i>Y</i> _{isolated} (%)
MeOH	5	20	150	0.25	100	–
MeOH	50	200	60	1.25	100	54
EtOH	5	29	60	23	100	76
EtOH ^b	175	750	60–100	2 weeks	–	71
EtOH	30	170 ^c	100	24	89	65
EtOH	40	120	100	6	–	82

^aDetermined with ¹H NMR spectroscopic analysis and calculated according to literature [28].^b0.5 mol% TMG₂e.^cRecycled EtOH from the ethanolysis of 175 g PLA was used.

yield is explained by the evaporation of MeLa during the lab-scale purification process. A technical distillation process could improve the isolation of MeLa and increase the yield significantly. The ethanolysis was performed using 5 g of PLA under mild reaction conditions (60°C). Full conversion to EtLa was observed after 23 h using ¹H NMR spectroscopic analysis. We isolated EtLa in higher yields and purity (99%) compared to MeLa using the same purification procedure. The scale-up to 175 g PLA in a 2 L flask was performed using 0.5 mol% catalyst and a reaction temperature of 60°C. High conversion to EtLa could be detected directly from the reaction mixture using ¹H NMR spectroscopy after 20 h (*Y*_{EtLa} = 72%), but PLA and oligomers were still present after 8 days under these reaction conditions. After 8 days, the reaction was heated to reflux conditions (*T*_{oil bath} = 100°C) to accelerate the conversion of PLA. After an additional 25 h, PLA was depolymerized completely and EtLa was isolated in a good yield. The alcohol removed during the isolation process was reused in the ethanolysis using 30 g of PLA (Table 3). We applied optimized reaction conditions (reflux conditions, 1 mol% TMG₂e) and isolated EtLa (*Y*_{EtLa} = 65%) in high purity (>99%). To further minimize the amount of used chemicals, we reduced the amount EtOH to 3.7 equiv in regards to PLA (40 g). Using 1 mol% of TMG₂e, the heterogeneous reaction mixture was homogenized within 2 h due to complete depolymerization of PLA (*X*_{int} = 100%, *Y*_{EtLa} = 89%). To achieve a higher selectivity, the reaction was treated to reflux conditions for additional 4 h, and we could isolate EtLa in good yields (*Y*_{EtLa} = 82%). These results suggest that the alcoholysis of PLA using TMG₂e under mild reaction conditions is easily scalable and adjustable to specific needs.

2.7 | Depolymerization of PCL and PET

Besides PLA, the activity of TMG₂e toward the depolymerization of fossil-based polyesters in contact with air and under solvent-free conditions was investigated. PET can be depolymerized to dimethyl terephthalate (DMT) using MeOH and bis(2-hydroxyethyl)terephthalate (BHET) using ethylene glycol (EG) [14, 17, 31, 34]. Both depolymerization products can be used to produce PET [28, 81, 82]. PCL was depolymerized to methyl 6-hydroxyhexanoate (MeHe) using MeOH. MeHe serves as a monomer to produce PCL [22, 31, 34]. Table 4 shows the applied reaction conditions and the obtained yields of the corresponding depolymerization product (*Y*_{dp}). PCL was depolymerized at 100°C to MeHe within 60 min (*Y*_{dp} = 97%). TMG₂e shows fast depolymerization of PCL under mild reaction conditions compared to literature-known guanidine Zn catalysts [31, 34]. For example, Cheung et al. reported that Zn(OAc)₂ (2 mol%) depolymerizes PCL at elevated temperatures of 140–170°C achieving a yield of 92% within 60 min [22].

The methanolysis of PET yielded DMT in high isolated yields (*Y*_{DMT} = 90%) compared to Zn catalysts under similar reaction conditions (150°C, 6 h, *Y*_{DMT} = 65%) [17, 34]. The organocatalyst [NMe₃]⁺[OCO₂Me][–] achieved comparable yields of DMT within 16 h at lower temperatures but with a higher catalyst loading [17]. Another commonly used depolymerization method of PET is the glycolysis [17, 54, 82, 83]. Table 4 shows the results of the glycolysis of PET using TMG₂e. We were able to scale up the reaction from 0.67 g scale to 5.0 g scale with high isolated yields (*Y*_{BHET} = 61–76%) under solvent-free conditions [84]. During the glycolysis, the

TABLE 4 | Results for the solvent-free depolymerization of PET (3.5 mmol) and PCL (3.4–3.5 mmol) using 1 mol% TMG₂e with regards to ester bonds using different nucleophiles (Nu: MeOH = 4 mL and EG = 4 mL).

Polymer	<i>m</i> _{polymer} (g)	Nucleophile	<i>T</i> (°C)	<i>t</i> (h)	<i>Y</i> _{dp} (%) ^a
PCL ^b	0.40	MeOH	100	60	97 ± 0 ^c
PET	0.67	MeOH	180	5	90
PET	0.67	EG	180	24	61
PET	3.0	EG	180	30	76
PET [84]	5.0	EG	180	6 days	61

^aIsolated yield.^b2.0 mol% TMG₂e.^cDetermined with ¹H NMR spectroscopic analysis and calculated according to literature [22].

reaction mixture turned dark brown, which led to brown coloration of the obtained BHET, which was achieved as a brown solid. The methanolysis of PET under similar conditions shows no discoloration. This indicates that under these conditions, the catalyst is stable. A control reaction using only EG and TMG₂e led to no signs of the formation of polyethylene glycol and the reaction mixture remained colorless. To further investigate the color change, we performed three control experiments using the BHET obtained from the 5 g scale-up experiment. First, BHET and THF were heated to 180°C and stirred for 5 h at 260 rpm. The reaction mixture turned from light brown to dark brown and ¹H NMR spectroscopic analysis showed decomposition of BHET. In a second and third experiment, BHET and TMG₂e were dispersed in THF or EG, heated to 180°C, and stirred for 5 h at 260 rpm. The mixture in THF turned from light brown to dark brown within 1 h and showed more decomposition of BHET than the experiment using EG: Using EG, the reaction mixture turned dark brown within 3 h. Contrary to the other reactions in THF, here, BHET can still be identified as the main species. These results suggest that under the given reaction conditions, BHET is prone to decompose. Thus, milder reaction temperatures could lead to fewer side reactions and improve the color of the product. In this study, we were able to improve the discoloration by washing the product with deionized water. The obtained light gray BHET from the 5 g scale-up experiment using pristine PET, listed in Table 4, and the 7 g scale-up experiment using PET trays, listed in Table 5, were applied successfully in the production of PET. In a previously published study, BHET was polymerized to PET using microwave-assisted solid-state polymerization [84]. The polycondensation of BHET was performed in three heating cycles with Sb₂O₃ and Ti(OBu)₄ ([catalyst]:[BHET] = 0.0001) as catalysts. The performed experiments produced a low molecular weight PET with increased discoloration due to the coloration of the BHET produced in this study [84]. To further improve the molecular weight, a prolonged reaction time is necessary. Nonetheless, these results suggest the BHET obtained *via* glycolysis of PET can be used as monomer for PET production. To reinforce this claim, in-depth polymerization studies with BHET are necessary.

2.8 | Recycling Mixed Plastics

The separation of plastic mixes, especially waste material, is one of the major challenges for a circular plastics economy. Sequential recycling is a promising approach to achieve high-quality products from mixed plastics [3, 5, 46, 63, 85, 86]. A recent study using an imino-pyrrole Zn complex for the sequential recycling of binary mixtures of PLA, PET, and bisphenol A polycarbonate showed promising results for efficient polymer separation [46]. Being able to selectively depolymerize one polymer depending on the temperature enables enhanced treatment of plastic waste streams in a cascade recycling approach [63]. Removing PLA from a PET waste stream could lead to improved mechanical recycling of PET [19, 63, 65, 87]. We investigated the cascade recycling of mixed plastics by creating different polymer mixes with equimolar amounts of each polymer (Figure S17): PLA and PET; PLA and PCL; PCL and PET; and PLA, PET, and PCL.

The sequential degradation with and without removal of the volatile components was evaluated at different temperatures ($T_{\text{PLA}} = 60^\circ\text{C}$, $T_{\text{PCL}} = 100^\circ\text{C}$, $T_{\text{PET}} = 180^\circ\text{C}$) as well as a simultaneous approach at 180°C. Further, we investigated the influence of the physical form of PLA using PLA as powder ($\varnothing = 0.75$ mm) or film (0.5×0.5 cm). PCL was used as pellets ($\varnothing = 3$ mm) and PET as powder ($\varnothing = 0.75$ mm). In Table 6 and Table S7, an overview of the results of the experiments performed is provided. In contrast to PLA and PCL, PET is not dissolved during the reaction but rather depolymerized to soluble oligomers and DMT. Thus, DMT was isolated to determine the Y_{dp} . For the other two polymers, ¹H NMR spectroscopic analysis was deployed to determine the corresponding Y_{dp} because the small scale aggravates the isolation process. The isolation of MeLa from MeOH was performed successfully for the large-scale experiments described in Table 3 and for MeHe a successful isolation process was reported by Cheung et al. [22]. The performed experiments in Table 6 show that TMG₂e can easily depolymerize PLA and PET in the presence of other polymers at different

TABLE 5 | Results for the methanolysis and glycolysis using TMG₂e of post-consumer waste samples at 180°C.

Waste sample	<i>m</i> (g)	<i>n</i> _{PET} (mmol)	<i>c</i> _{cat} ^a (mol%)	Nucleophile	<i>t</i> (h)	<i>Y</i> ^b (%)
Mixed plastic waste Spain ^c	1.0	0	– ^d	EG	72	0
Mixed plastic waste (VFB)	2.25	3.5	2.0	MeOH	5	54
Mixed plastic waste (VFB) ^c	1.0	1.5	2.6	EG	72	9
PET bottles ^c	1.0	5.2	0.8	EG	72	11
PET bottles	0.67	3.5	2.0	EG	24	26
PET trays	0.67	3.0	2.3	MeOH	5	52
PET trays ^c	1.0	4.5	0.9	EG	72	22
PET trays	0.67	3.0	2.3	EG	24	39
PET trays	3.0	16	2.3	EG	51	55
PET trays [84]	7.0	32	1.1	EG	74	49

^aRegarding the PET repeating units.

^bIsolated yield.

^cThe reaction was stirred at 140°C for 18 h prior. After no depolymerization was observed, the temperature was increased to 180°C.

^d1 wt% regarding the waste sample of catalyst was added.

TABLE 6 | Results for the methanolysis (4 mL MeOH) of plastic mixes using 2 mol% TMG₂e regarding PLA or PCL ester bonds, respectively 1 mol% TMG₂e regarding PET ester bonds.

Polymers ^a	T (°C)	t ^b (h)	Y _{MeLa} ^c (%)	Y _{MeHe} ^d (%)	Y _{DMT} ^e (%)
PLA, PCL	60	1	100	24	–
	100	1	100	74	–
	100	20	100	79	–
PLA, PET	60	1	100	–	–
	180	5	100	–	73
PCL, PET	100	1	–	86	–
	180	5	–	95	80
PLA, PCL, PET	180	4.5	100	18	n.d. ^f
PLA, PCL, PET ^g	95	1	100	–	–
	100	2	–	12	–
	180	22.5	–	41	n.d. ^f
PLA, PCL, PET ^g (Figure 5)	60	1	100	–	–
	100	1	–	100	–
	180	5	–	100	60

^aPLA (250 mg, 3.5 mmol), PCL (3.4–3.5 mmol), and PET (3.5 mmol) were applied according to the stated content of the polymer mix.^bTime at given temperature.^cDetermined with ¹H NMR spectroscopic analysis and calculated according to literature [28].^dDetermined with ¹H NMR spectroscopic analysis and calculated according to literature [22].^eDMT was isolated from a clear, homogeneous reaction mixture indicating complete depolymerization of PET to side products or DMT.^fDMT could not be isolated without traces of other depolymerization products, but a clear reaction mixture was obtained after the given reaction time indicating complete depolymerization of PET.^gRemoval of MeLa and MeOH after complete depolymerization of PLA at 60°C.

temperatures. However, the methanolysis of PCL seems to be hindered in the presence of PLA, MeLa, PET, and/or DMT. Furthermore, the methanolysis of ternary polymer mixes was strongly influenced by the physical form of PLA. An in-depth evaluation of this study is provided in Section S8.1 in the Supporting Information. To improve the PCL conversion, first, we depolymerized PLA from the PLA, PCL, and PET mix at 60°C. After 95 min, complete conversion of PLA to MeLa (Y_{MeLa} = 100%) was observed and all volatile components (MeLa, MeOH) were removed. To start the depolymerization of PCL, MeOH (4 mL) was added and the reaction tube was placed in an oil bath at 100°C. After 2 h at 100°C, we could only detect a Y_{MeHe} of 12%. Thus, we increased the temperature to 180°C to start the depolymerization process of PET. After 5 h, the reaction mixture was turbid and yellow. ¹H NMR spectroscopic analysis showed slow depolymerization of PCL (Y_{MeHe} = 19%) as well as depolymerization of PET to DMT. PET particles were still clearly visible in the reaction mixture. Thus, we prolonged the reaction time to 22.5 h, after which a clear solution was observed. Resonances for PCL were still observable in the ¹H NMR spectrum (Y_{MeHe} = 41%), but PET was depolymerized completely to DMT and oligomeric species. The oligomeric species were not further identified and are likely the cause of the discoloration as observed during the glycolysis of PET. The isolation process of DMT was performed by adding deionized water to the obtained off-white solid after cooling the reaction down to room temperature. The mixture was filtered, washed with deionized water, and dried in high vacuum. The obtained colorless DMT was contaminated with PCL, MeHe, and oligomeric species of

PET. These results suggest that the catalyst is deactivated and/or removed during the isolation process of MeLa and MeOH. A possible way to prevent the severe activity loss could be the immobilization of the catalyst [88]. Based on the results obtained, we developed the temperature-controlled cascade recycling approach displayed in Figure 5.

Here, the addition of TMG₂e after the removal of MeLa and MeOH compensates the previously described activity loss: After 1 h, complete depolymerization of PLA was observed. MeLa and MeOH were removed in high vacuum, MeOH (4 mL) and TMG₂e (2 mol% regarding the PCL ester bonds) were added to the remaining reaction mixture, and the reaction was started at 100°C. After 1 h, PCL was depolymerized completely to MeHe (Y_{MeHe} = 100%). The high conversion of PCL in the presence of PET, might be due to the increased catalyst concentration in the reaction mixture. After 5 h at 180°C, DMT could be isolated in high purity from MeHe and MeOH in a good yield (Y_{DMT} = 60%) following the previously described isolation process. The procedure displayed in Figure 5 allows selective, temperature-controlled alcoholysis of specific polymers from plastic mixes. The separation of PLA from PET and other polymers could facilitate effective mixed waste stream treatment and recycling. For example, after the chemical recycling of PLA at mild reaction conditions, PET can be easily separated and reintroduced into the mechanical recycling cycle [63]. Further improvements on the isolation of MeLa and MeOH after the depolymerization of PLA or the immobilization of the catalyst could prevent the second addition of catalyst.

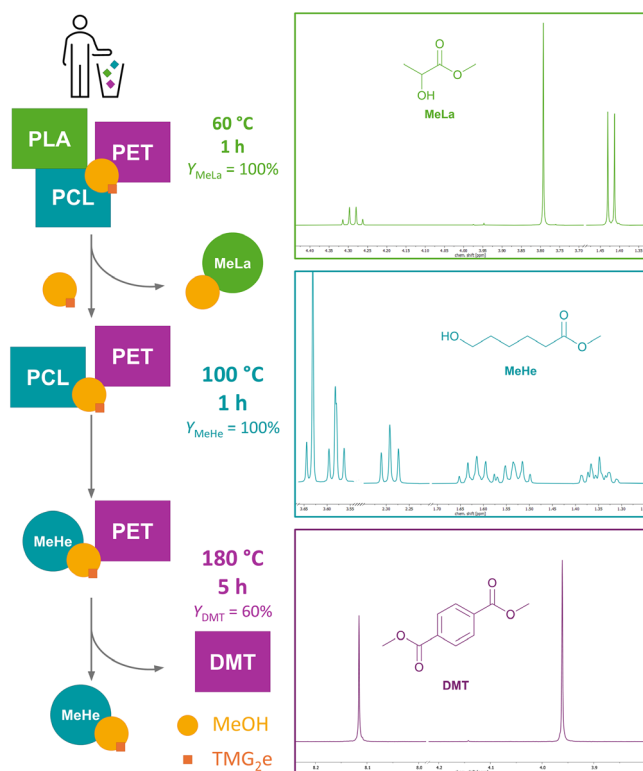


FIGURE 5 | Temperature-controlled cascade recycling of a PLA, PCL, and PET mix at 60, 100, and 180 °C.

2.9 | Post-Consumer Plastic Waste Depolymerization

To further confirm the applicability of TMG_{2e} in industry, post-consumer plastic waste was investigated. For PLA, we tested the methanolysis of single-use poly-L-lactide (PLLA) cups (Figure S19) [21]. The PLLA cups contained water, cola, and cold coffee. After use, the PLLA cups were not cleaned and cut into small pieces (0.5×0.5 cm). Using 0.5 mol% TMG_{2e} , we were able to depolymerize PLA to MeLa within 60 min ($Y_{\text{MeLa}} = 98\%$) under standard reaction conditions (3.47 mmol PLA, 0.5 mol% TMG_{2e} , 7.1 equiv MeOH, 4 mL THF, 60 °C, 260 rpm). TMG_{2e} showed no significant activity loss due to the remains of the beverages. To obtain a more realistic insight into post-consumer waste depolymerization, we investigated the glycolysis and methanolysis of PET from waste material collected in Spain and Denmark (Figure S20). Four different post-consumer waste sources with varying amounts of PET were tested (Table 5): Mixed plastic waste from Spain containing no PET (AIMPLAS), mixed plastic waste from Denmark (VFB, 30% PET, 41% polyethylene, 3% polystyrene, 9% polypropylene, 8% multilayer brick, 9% nonplastic material), PET trays (AIMPLAS, 87% PET, 11% PE), and PET bottles (AIMPLAS, 100% PET). Using MeOH, TMG_{2e} depolymerized the waste material from PET trays to DMT ($Y_{\text{DMT}} = 52\%$) and from mixed plastic waste (VFB, $Y_{\text{DMT}} = 54\%$) within 5 h at 180 °C. We obtained a lower amount of DMT compared to pristine PET ($Y_{\text{DMT}} = 73\%$) and discoloration of the product was observable. Nonetheless, ^1H NMR spectroscopic analysis suggests we obtained DMT in high purity. During the isolation of DMT from the remaining plastic particles for the mixed plastic waste material (VFB), we were able to obtain DMT as crystalline

colorless powder by performing additional purification steps, which decreased the amount of obtained DMT significantly. Thus, more advanced technical purification processes as done in industry need to be applied to enhance the color and yield of the obtained DMT. Besides discoloration of the product, the waste material leads to a discoloration of the reaction mixture; thus, we could not observe a clear solution indicating complete PET consumption. Therefore, we choose elongated reaction times for the glycolysis compared to pristine PET material to ensure the complete depolymerization of PET.

The results listed in Table 5 show that waste materials could influence the activity of TMG_{2e} . The mixed plastic waste from VFB shows a lower yield of BHET than PET waste from plastic bottles or plastic trays. The low PET content and the high content of other materials and impurities aggravate the isolation process further, as described for the isolation of DMT. Another factor impacting the BHET yields is the crystallinity of the PET. PET bottles have a higher crystallinity than the PET used in the trays, which could lead to lower conversion of PET. We could further increase the BHET yield by increasing the catalyst loading to 1.0 or 1.3 mol% regarding the PET ester bonds. Hot filtration of the reaction mixture improved the BHET yield by up to 55%. The glycolysis of the PET trays showed the highest BHET yield under the given reaction conditions. We successfully scaled up the PET glycolysis of the PET trays reaching $Y_{\text{BHET}} = 55\%$ from 3 g of post-consumer PET waste and 49% BHET from 7.0 g of post-consumer PET waste. The produced recycled BHET was successfully used as a monomer for PET production as described previously [84]. We demonstrated that TMG_{2e} is a versatile and robust catalyst applicable in the chemical recycling of post-consumer PET waste and other post-consumer polyester waste: closing the loop of PET production, consumption, and recycling to monomers for new PET production.

3 | Conclusions

In this study, we investigated three robust bisguanidine organo-catalysts for their applicability in a sustainable, circular plastics economy. Evaluation of the structure-reactivity relationship between the length of the linker between two guanidine functionalities and the activity of the catalysts in the methanolysis and ethanolysis of PLA established the ethylene-bridged TMG_{2e} as the most active guanidine organocatalyst depolymerizing PLA within 3 min under mild reaction conditions ($k_{\text{dp}} = 10.3 \cdot 10^{-1} \text{ mol}^{-1} \text{ min}^{-1}$). At elevated temperatures (150 °C) and under solvent-free conditions, we achieved a complete methanolysis of PLA to MeLa ($Y_{\text{MeLa}} = 98\%$) within 5 min. Thus, we studied TMG_{2e} under industrially relevant conditions by applying the principles of Green Chemistry. The scalability of the methanolysis and ethanolysis was demonstrated as well as the recyclability of the nucleophiles used. Besides PLA, TMG_{2e} depolymerized other polyesters (PCL, PET) efficiently. Further, TMG_{2e} was successfully applied in the depolymerization of not only pristine polymers and challenging polymer mixes (PLA, PCL, PET) but also in the depolymerization of post-consumer plastic waste, thus proving its high robustness and activity. However, we see a decrease in the activity using post-consumer

waste. The influence of the varying composition of the waste material needs to be addressed and further studied to identify and possibly circumvent the loss in catalytic activity. Overall, the herein presented straightforward and robust process to transform even hard-to-recycle mixed materials into a source for new, value-added chemicals or into a new feedstock for monomers makes TMG₂e a key enabler for a circular plastics economy.

4 | Experimental

4.1 | Resynthesis of Bis(*N,N,N',N'*-tetramethylguanidino)ethane (TMG₂e)

TMG₂e was synthesized according to literature [67]. The synthesis was performed with synthesis-grade reagents and without a protective atmosphere. A solution of tetramethylchloroformamidinium chloride Vilsmeier salt (11.0 g, 64.3 mmol, 2.17 equiv) in MeCN (80 mL) was added dropwise to a solution of ethane-1,2-diamine (1.80 g, 2.00 mL, 29.7 mmol, 1.00 equiv) and NEt₃ (8.80 mL, 63.1 mmol, 2.13 equiv) in MeCN (100 mL) at 0°C. The mixture was treated to reflux conditions for 3 h at 110°C. After cooling to room temperature, a solution of sodium hydroxide (2.50 g, 62.5 mmol, 2.11 equiv) in water (30 mL) was added and the solvent was removed under reduced pressure. The residue was transferred to a separating funnel using MeCN (75 mL) and deionized water (55 mL). A solution of potassium hydroxide (30.3 g, 540 mmol, 18.2 equiv) in deionized water (30 mL) was added. The phases were separated, and the aqueous phase was extracted with MeCN (3 × 50 mL). Remaining water in the combined organic phases was removed over Na₂SO₄ and filtered over activated charcoal and celite. The solvent was removed under reduced pressure. Tetramethyl urea was removed under high vacuum at 60°C. The product was further purified by sublimation (stationary vacuum at 4·10⁻² mbar, 135°C). TMG₂e was obtained as a colorless crystalline solid (*Y* = 71%, *Y*_{Lit.} = 72% [67]). The obtained FAIR data is provided under: doi: [10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZCBQJRXSMA-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ](https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZCBQJRXSMA-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ).

¹H NMR (400 MHz, CDCl₃): 3.30 (s, 4H), 2.76 (s, 12H), 2.67 (s, 12H) ppm.

4.2 | Synthesis of 1,2-Di[2*N*-(1,1,3,3-tetramethylguanidinium)]ethane Dichloride ([TMG₂eH₂)²⁺ 2Cl⁻]

TMG₂e (273 mg, 1.07 mmol, 1.00 equiv) was dissolved in MeCN (2.00 mL). Concentrated hydrochloric acid (1.05 g, 880 μL, 10.6 mmol, 9.98 equiv) was added and the reaction stirred at room temperature for 1.5 h. All volatile components were removed under high vacuum at 60°C. The obtained colorless solid was washed with MeCN and the remaining solvent was removed under reduced pressure. The hydrochloride of TMG₂e was obtained as colorless powder (169 mg, 421 μmol, 40% yield). The obtained FAIR data is provided under: doi: [10.14272/reaction/SA-FUHFF-UHFFFADPSC-LYPYBITZWV-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ](https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-LYPYBITZWV-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ).

¹H NMR (400 MHz, MeCN-*d*₃): δ = 9.17 (s, 2H), 3.52–3.44 (m, 4H), 2.99 (b, 24H) ppm.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 8.10 (s, 2H), 3.39–3.36 (m, 4H), 2.91 (b, 24H) ppm.

¹H NMR (400 MHz, CDCl₃): δ = 8.10 (s, 2H), 3.39–3.36 (m, 4H), 2.91 (b, 24H) ppm.

¹³C NMR (400 MHz, CDCl₃): δ = 162.00 (CN₃), 44.49 (CH₂), 40.65 (CH₃) ppm.

ESI MS: *m/z*: [M-H]⁺: Calculated for [C₁₂H₂₉N₆]⁺: 257.24482 g mol⁻¹. Found for [C₁₂H₂₉N₆]⁺: 257.24442 g mol⁻¹.

4.3 | Synthesis of Bis(*N,N,N',N'*-tetramethylguanidino)pentane (TMG₂pe)

TMG₂pe was synthesized according to literature [67, 68, 69]. Tetramethylchloroformamidinium chloride Vilsmeier salt (5.40 g, 31.5 mmol, 2.07 equiv) was dissolved in absolute MeCN (60 mL). The solution was added dropwise to a solution of pentane-1,5-diamine (1.56 g, 15.2 mmol, 1.00 equiv) and NEt₃ (3.19 g, 4.39 mL, 31.5 mmol, 2.07 equiv) in absolute MeCN (30 mL) at *T* = 0°C. The mixture was heated to reflux conditions (*T*_{oil bath} = 110°C) for 3 h. After cooling down, a solution of NaOH (1.26 g, 31.5 mmol, 2.07 equiv) in water (15 mL) was added. The solvent was removed under reduced pressure. The residue was transferred to a separating funnel using MeCN (40 mL). A solution of KOH (15.0 g, 267 mmol, 17.6 equiv) in water (15 mL) was added. The different layers were separated, and the aqueous layer was extracted twice with MeCN (2 × 40 mL). Remaining water in the organic layer was removed over NaSO₄ and filtered over activated charcoal. The solvent was removed under reduced pressure and tetramethyl urea was removed under high vacuum at 60°C. The crude product was obtained as partly liquid and partly solid slightly yellow product phases. For further purification, recrystallization with *n*-hexane was conducted. The product mixture was stored in the fridge for 10 days. Subsequently, the liquid and solid phases were separated. The solid was washed with *n*-pentane several times. TMG₂pe was obtained as colorless oil (*Y* = 40%). The obtained FAIR data is provided under: doi: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-VKARKQYNUZ-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ>.

¹H NMR (400 MHz, CDCl₃): δ = 3.08 (t, *J* = 7.0 Hz, 4H, CH₂), 2.71 (s, 12H, CH₃), 2.68 (s, 12H, CH₃), 1.51–1.47 (m, 4H, CH₂), 1.39–1.26 (m, 2H, CH₂) ppm.

¹³C NMR (400 MHz, CDCl₃): δ = 159.96 (CN₃), 49.84 (CH₂N), 39.76 (CH₃), 38.97 (CH₃), 32.88 (CH₂CH₂N), 25.60 (CH₂CH₂CH₂N) ppm.

ESI-MS *m/z*: [M+H]⁺: Calculated for [C₁₅H₃₅N₆]⁺: 299.29177 g mol⁻¹. Found for [C₁₅H₃₅N₆]⁺: 299.29118 g mol⁻¹.

FTIR (ATR, $\tilde{\nu}$) = 2999 (vw), 2922 (w), 2901 (w), 2859 (w), 2839 (w), 2797 (w), 1616 (vs), 1493 (w), 1449 (w), 1437 (w), 1425 (w),

1402 (vw), 1358 (vs), 1308 (vw), 1233 (w), 1132 (m), 1103 (vw), 1063 (w), 1055 (w), 991 (w), 912 (w), 746 (vw), 579 (vw) cm^{-1} .

4.4 | PLA Alcoholysis

4.4.1 | General Procedure

Catalyst (1.0 mol%) and THF (4 mL) were provided in a Young-type Schlenk tube. PLA (250 mg, 3.47 mmol, 1.00 equiv) was added. The reaction mixture was dissolved using an external heat source, placed in a heated oil bath ($T = 60^\circ\text{C}$), and stirred at 260 rpm. The reaction was started ($t = 0$ min) by addition of MeOH (1.0 mL, 7.1 equiv) or EtOH (1.4 mL, 6.9 equiv). The reaction process was monitored using ^1H NMR spectroscopy.

4.4.2 | Determination of k_{dp} , E_{A} , $\Delta S^\ddagger$, and $\Delta H^\ddagger$

The alcoholysis was performed under inert conditions using Schlenk techniques. The catalyst (0.1–2.0 mol%) and THF (4 mL) were provided in a Young-type Schlenk tube. PLA (film (0.5×0.5 cm), 250 mg, 3.47 mmol, 1.00 equiv) was added in an Ar counterflow. The reaction mixture was dissolved using an external heat source, placed in a heated oil bath ($T = 30$ – 60°C), and stirred at 260 rpm. The reaction was started by addition of the nucleophile ($t = 0$ min): MeOH (1.0 mL, 7.1 equiv) or EtOH (1.4 mL, 6.9 equiv). The reaction process was monitored using ^1H NMR spectroscopy. Samples were taken in appropriate time intervals.

4.4.3 | Solvent-Free Methanolysis

PLA (250 mg, 3.47 mmol, 1.00 equiv), TMG₂e (8.9 mg, 35 μmol , 0.010 equiv), and MeOH (1.00 mL, 24.7 mmol, 7.13 equiv) were placed in a preheated oil bath at 150°C ($t = 0$ min) and stirred at 260 rpm. The reaction process was monitored using ^1H NMR spectroscopy. After 5 min, $Y_{\text{MeLa}} = 98\%$ was determined using ^1H NMR spectroscopic analysis. Additional information on the reaction procedure and original analysis data files are available via the Chemotion repository: [10.14272/reaction/SA-FUHFF-UHFFFADPSC-LPEKGGXMPW-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.8](https://chemotion.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-LPEKGGXMPW-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.8).

4.4.4 | Scale-up of PLA Alcoholysis

PLA film (0.5×0.5 cm) and TMG₂e (0.5–1.0 mol%) were provided in a Schlenk flask, excess alcohol was added and the reaction heated to 60°C for the methanolysis or 60 – 100°C for the ethanolysis. The reaction was stopped after all polymer particles were dissolved. All volatile components were removed under high vacuum and collected in a cooling trap. The alcohol was removed from the obtained clear solution using rotary evaporation. The alkyl lactates were obtained as clear, colorless liquids.

4.5 | PCL Methanolysis

PCL (pellets ($\varnothing = 3$ mm), 396 mg, 3.47 mmol, 1.00 equiv) and TMG₂e (17.8 mg, 69.4 μmol , 1.99 mol%) were provided in a Young-type Schlenk tube. MeOH (4 mL) was added and the tube placed in a preheated oil bath at 100°C ($t = 0$ min). The reaction process was monitored using ^1H NMR spectroscopy. The tube was

cooled to room temperature to take samples in appropriate time intervals. Afterward, the tube was placed in the oil bath again.

4.6 | PET Methanolysis

4.6.1 | Pristine PET

PET (powder ($\varnothing = 0.75$ mm), 667 mg, 3.47 mmol, 1.00 equiv) and TMG₂e (17.8 mg, 69.4 μmol , 2.00 mol%) were provided in a Young-type Schlenk tube. MeOH (4 mL) was added and the tube placed in a preheated oil bath at 180°C ($t = 0$ min). The tube was cooled to room temperature to take samples in appropriate time intervals. Afterward, the tube was placed in the oil bath again. After a clear solution was obtained, the reaction was cooled to room temperature upon which a colorless solid formed; deionized water (10 mL) was added. The mixture was stored at 4°C . The colorless solid was filtered and washed with deionized water. Dimethyl terephthalate was obtained as colorless solid.

4.6.2 | Post-Consumer PET Waste

Post-consumer waste material (0.67 g) and TMG₂e (2.3 mol%) were provided in a Young-type Schlenk tube. MeOH (4.0 mL) was added, and the tube was placed in a preheated oil bath at 180°C ($t = 0$ min). After 5 h, the reaction was cooled to room temperature, and deionized water (10 mL) was added. The mixture was filtered and the resulting solid was dried under high vacuum. The obtained dimethyl terephthalate was obtained as gray to colorless solid.

4.7 | PET Glycolysis

4.7.1 | Pristine PET

PET (powder ($\varnothing = 0.75$ mm), 667 mg, 3.47 mmol, 1.00 equiv) and TMG₂e (17.8 mg, 69.4 μmol , 2.00 mol%) were provided in a Young-type Schlenk tube. Ethylene glycol (4 mL) was added, and the tube was placed in a preheated oil bath at 180°C ($t = 0$ min). After the desired reaction time, the reaction was cooled to room temperature, and deionized water (10 mL) was added. The mixture was rapidly filtered, and the filtrate was stored at 4°C . Bis(2-hydroxyethyl) terephthalate was obtained in moderate yield as light gray solid.

4.7.2 | Post-Consumer PET Waste

Post-consumer waste material and TMG₂e were provided in a Young-type Schlenk tube. Ethylene glycol (2.0 mL) was added, and the tube was placed in a preheated oil bath at 180°C ($t = 0$ min). After the desired reaction time, the reaction was cooled to room temperature, and deionized water (10 mL) was added. The mixture was filtered, and the filtrate was stored at 4°C . Bis(2-Hydroxyethyl) terephthalate was obtained in low to good yield as gray solid.

4.7.3 | Scale-up of PET Glycolysis

Pristine PET (powder ($\varnothing = 0.75$ mm)) or post-consumer waste PET and TMG₂e (1–2 mol%) were provided in a Schlenk flask. Ethylene glycol was added, and the flask was placed in a preheated oil bath at 180°C ($t = 0$ min). After a certain reaction time, the reaction was

cooled down and deionized water was added. The mixture was rapidly filtered, and the filtrate was stored at 4°C. Bis(2-hydroxyethyl) precipitated as brown solid. It was filtered and dried in high vacuum. Bis(2-hydroxyethyl) was obtained in a good yield as gray solid.

4.8 | Methanolysis of Polymer Mixes

4.8.1 | Without Removal of Volatile Components

The mixes were prepared from PLA (film (0.5 × 0.5 cm), 3.5 mmol, 1.0 equiv) or PLA (powder (Ø = 0.75 mm), 3.5 mmol, 1.0 equiv), PCL (pellets (Ø = 3 mm), 3.5 mmol, 1.0 equiv), and PET (powder (Ø = 75 mm), 3.5 mmol, 1.0 equiv) accordingly. TMG₂e (17.8 mg, 69.4 µmol, 1.98 mol% of PLA ester bonds) and MeOH (4 mL) were added. The reaction was heated to 60°C (t_1 = 0 min), 100°C (t_2 = 0 min), and/or 180°C (t_3 = 0 min) for appropriate time intervals. The reaction was monitored using ¹H NMR spectroscopy. Methyl lactate and methyl hexanoate were not further isolated. If PET was used, the reaction was cooled to room temperature, and the formation of a colorless solid was observed. The mixture was filtered. The obtained colorless solid was washed with MeOH or deionized water. Dimethyl terephthalate was dried in high vacuum and obtained as colorless solid.

4.8.2 | With Removal of Volatile Components

The mixes were prepared from PLA (film (0.5 × 0.5 cm), 3.5 mmol, 1.0 equiv), PCL (pellets (Ø = 3 mm), 3.5 mmol, 1.0 equiv), and PET (powder (Ø = 75 mm), 3.5 mmol, 1.0 equiv). TMG₂e (17.8 mg, 69.4 µmol, 1.98 mol% of PLA ester bonds) and MeOH (4 mL) were added. The reaction was heated to 60°C (t_1 = 0 min). After depolymerization of PLA, all volatile components were removed in high vacuum. Methyl lactate and MeOH were collected in a cooling trap. TMG₂e (17.8 mg, 69.4 µmol, 1.98 mol%) and MeOH (4 mL) were added to the reaction flask which was placed in an oil bath at 100°C (t_2 = 0 min), and/or 180°C (t_3 = 0 min) for appropriate time intervals. The reaction was monitored using ¹H NMR spectroscopy. After a homogeneous reaction mixture was observed, the reaction was cooled to room temperature, and the formation of a colorless solid was observed. The mixture was filtered. The obtained colorless solid was washed with MeOH or deionized water. Dimethyl terephthalate was dried in high vacuum and obtained as colorless solid. Methyl hexanoate in the filtrate was not further isolated.

Acknowledgments

The authors thank bio-mi Ltd. (Croatia), AIMPLAS (Spain), and Vestforbrænding (Denmark) for the supply of pristine polymers and/or post-consumer polymer waste. The authors thank the European Commission under H2020 Grant Agreement no. 953073 (acronym: UPLIFT) and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – Cluster of Excellence 2186 “The Fuel ScienceCenter” ID: 390919832 for funding. Further, the authors thank NFDI4Chem for funding the repositories Chemotion Repository and RADAR4Chem.

Open Access funding enabled and organized by Projekt DEAL.

Funding

This work was supported by European Commission (953073), Deutsche Forschungsgemeinschaft (ID: 390919832) and Fuel Science Cluster.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Original NMR data for the kinetic experiments performed are available via the RADAR4Chem repository by FIZ Karlsruhe – Leibniz Institut für Informationsinfrastruktur and are published under an Open Access model (CC BY-NC-SA 4.0 Attribution-NonCommercial-Share Alike: <https://www.radar-service.eu/radar/en/dataset/2ejvm338fzgukrrr>). The data for all other experiments can be found in the Chemotion Repository: https://dx.doi.org/10.14272/collection/LB_2024-12-11.

References

1. A. Metz, A. Hoffmann, K. Hock, and S. Herres-Pawlis, “Katalysatoren Für Die Produktion Von Biokunststoffen,” *Chemie in Unserer Zeit* 50 (2016): 316–325.
2. OECD, Global Plastics Outlook: Policy Scenarios to 2060 (OECD, 2022).
3. L. Milà i Canals, A. Cairns, P. Lefort, et al., Turning Off the Tap. How the World Can End Plastic Pollution and Create a Circular Economy (UNEP, 2023).
4. OECD, Global Plastics Outlook: Economic Drivers, Environmental Impacts and Policy Options (OECD, 2022).
5. R. Geyer, J. R. Jambeck, and K. L. Law, “Production, Use, and Fate of All Plastics Ever Made,” *Science Advances* 3 (2017): e1700782.
6. J. Brizga, K. Hubacek, and K. Feng, “The Unintended Side Effects of Bioplastics: Carbon, Land, and Water Footprints,” *One Earth* 3 (2020): 45–53.
7. I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, et al., “Beyond Mechanical Recycling: Giving New Life to Plastic Waste,” *Angewandte Chemie International Edition* 59 (2020): 15402–15423.
8. S. Shafiee and E. Topal, “When Will Fossil Fuel Reserves be Diminished?,” *Energy Policy* 37 (2009): 181–189.
9. R. Meys, A. Katelhon, M. Bachmann, et al., “Achieving Net-Zero Greenhouse Gas Emission Plastics by a Circular Carbon Economy,” *Science* 374 (2021): 71–76.
10. S. M. Al-Salem, P. Lettieri, and J. Baeyens, “Recycling and Recovery Routes of Plastic Solid Waste (PSW): A Review,” *Waste Management* 29 (2009): 2625–2643.
11. M. Lackner, A. Mukherjee, and M. Koller, “What Are “Bioplastics”? Defining Renewability, Biosynthesis, Biodegradability, and Biocompatibility,” *Polymers* 15 (2023): 4695.
12. P. M. Schäfer and S. Herres-Pawlis, “Robust Guanidine Metal Catalysts for the Ring-Opening Polymerization of Lactide under Industrially Relevant Conditions,” *ChemPlusChem* 85 (2020): 1044–1052.
13. M. J. Stanford and A. P. Dove, “Stereocontrolled Ring-Opening Polymerisation of Lactide,” *Chemical Society Reviews* 39 (2010): 486–494.
14. J. Payne, M. Kamran, M. Davidson, and M. D. Jones, “Versatile Chemical Recycling Strategies: Value-Added Chemicals from Polyester and Polycarbonate Waste,” *ChemSusChem* 15 (2022): e202200255.
15. J. Payne, P. McKeown, and M. D. Jones, “A Circular Economy Approach to Plastic Waste,” *Polymer Degradation and Stability* 165 (2019): 170–181.
16. J. Payne and M. D. Jones, “The Chemical Recycling of Polyesters for a Circular Plastics Economy: Challenges and Emerging Opportunities,” *ChemSusChem* 14 (2021): 4041–4070.

17. P. McKeown, M. Kamran, M. G. Davidson, M. D. Jones, L. A. Román-Ramírez, and J. Wood, "Organocatalysis for Versatile Polymer Degradation," *Green Chemistry* 22 (2020): 3721–3726.
18. P. McKeown and M. D. Jones, "The Chemical Recycling of PLA: A Review," *Sustainable Chemistry* 1 (2020): 1–22.
19. F. M. Lamberti, L. A. Román-Ramírez, and J. Wood, "Recycling of Bioplastics: Routes and Benefits," *Journal of Polymers and the Environment* 28 (2020): 2551–2571.
20. F. A. Leibfarth, N. Moreno, A. P. Hawker, and J. D. Shand, "Transforming Polylactide into Value-Added Materials," *Journal of Polymer Science Part A: Polymer Chemistry* 50 (2012): 4814–4822.
21. M. Hofmann, C. Alberti, F. Scheliga, R. R. R. Meissner, and S. Enthaler, "Tin(ii) 2-Ethylhexanoate Catalysed Methanolysis of End-of-Life Poly(Lactide)," *Polymer Chemistry* 11 (2020): 2625–2629.
22. E. Cheung, C. Alberti, S. Bycinskij, and S. Enthaler, "Zinc-Catalyzed Chemical Recycling of Poly(ϵ -caprolactone) Applying Transesterification Reactions," *ChemistrySelect* 6 (2021): 8063–8067.
23. F. Liguori, C. Moreno-Marrodan, and P. Barbaro, "Valorisation of Plastic Waste via Metal-Catalysed Depolymerisation," *Beilstein Journal of Organic Chemistry* 17 (2021): 589–621.
24. E. L. Whitelaw, M. G. Davidson, and M. D. Jones, "Group 4 Salalen Complexes for the Production and Degradation of Polylactide," *Chemical Communications* 47 (2011): 10004–10006.
25. L. A. Roman-Ramirez, P. McKeown, M. D. Jones, and J. Wood, "Kinetics of Methyl Lactate Formation from the Transesterification of Poly(lactic Acid) Catalyzed by Zn(II) Complexes," *ACS Omega* 5 (2020): 5556–5564.
26. J. Payne, P. McKeown, M. F. Mahon, E. A. C. Emanuelsson, and M. D. Jones, "Mono- and Dimeric Zinc(ii) Complexes for PLA Production and Degradation into Methyl Lactate—A Chemical Recycling Method," *Polymer Chemistry* 11 (2020): 2381–2389.
27. J. Payne, P. McKeown, O. Driscoll, G. Kociok-Köhn, E. A. C. Emanuelsson, and M. D. Jones, "Make or Break: Mg(ii)- and Zn(ii)-Catalen Complexes for PLA Production and Recycling of Commodity Polyesters," *Polymer Chemistry* 12 (2021): 1086–1096.
28. P. McKeown, L. A. Roman-Ramirez, S. Bates, J. Wood, and M. D. Jones, "Zinc Complexes for PLA Formation and Chemical Recycling: Towards a Circular Economy," *ChemSusChem* 12 (2019): 5233–5238.
29. A. Hermann, T. Becker, M. A. Schäfer, A. Hoffmann, and S. Herres-Pawlis, "Effective Ligand Design: Zinc Complexes with Guanidine Hydroquinoline Ligands for Fast Lactide Polymerization and Chemical Recycling," *ChemSusChem* 15 (2022): e202201075.
30. M. Fuchs, M. Walbeck, E. Jagla, A. Hoffmann, and S. Herres-Pawlis, "Guanidine Carboxy Zinc Complexes for the Chemical Recycling of Renewable Polyesters," *ChemPlusChem* 87 (2022): e202200029.
31. M. Fuchs, P. M. Schäfer, W. Wagner, et al., "A Multitool for Circular Economy: Fast Ring-Opening Polymerization and Chemical Recycling of (Bio)polyesters Using a Single Aliphatic Guanidine Carboxy Zinc Catalyst," *ChemSusChem* 16 (2023): e202300192.
32. C. Conrads, L. Burkart, S. Soerensen, et al., "Understanding Structure-Activity Relationships: Iron(II) Complexes of "Legacy Guanidines" as Catalysts for the Synthesis of Polylactide," *Catalysis Science & Technology* 13 (2023): 6006–6021.
33. L. Burkart, A. Eith, A. Hoffmann, and S. Herres-Pawlis, "Open Loop Recycling - Guanidine Iron(II) Polymerization Catalyst for the Depolymerization of Polylactide," *Chemistry—An Asian Journal* 18 (2023): e202201195.
34. T. Becker, A. Hermann, N. Saritas, A. Hoffmann, and S. Herres-Pawlis, "Open- and Closed-Loop Recycling: Highly Active Zinc Bisguanidine Polymerization Catalyst for the Depolymerization of Polyesters," *ChemSusChem* 17 (2024): e202400933.
35. F. Santulli, D. Pappalardo, M. Lamberti, et al., "Simple and Efficient Zinc Catalysts for Synthesis and Chemical Degradation of Polyesters," *ACS Sustainable Chemistry & Engineering* 11 (2023): 15699–15709.
36. F. Santulli, M. Lamberti, and M. Mazzeo, "A Single Catalyst for Promoting Reverse Processes: Synthesis and Chemical Degradation of Polylactide," *ChemSusChem* 14 (2021): 5470–5475.
37. F. Santulli, M. Lamberti, A. Annunziata, R. C. Lastra, and M. Mazzeo, "The Contribution of Commercial Metal Amides to the Chemical Recycling of Waste Polyesters," *Catalysts* 12 (2022): 1193.
38. E. Cheung, C. Alberti, and S. Enthaler, "Chemical Recycling of End-of-Life Poly(lactide) via Zinc-Catalyzed Depolymerization and Polymerization," *ChemistryOpen* 9 (2020): 1224–1228.
39. C. Alberti, N. Damps, R. R. R. Meißner, M. Hofmann, D. Rijono, and S. Enthaler, "Selective Degradation of End-of-Life Poly(lactide) via Alkali-Metal-Halide Catalysis," *Advanced Sustainable Systems* 4 (2019): 1900081.
40. C. Alberti and S. Enthaler, "Depolymerization of End-of-Life Poly(lactide) to Lactide via Zinc-Catalysis," *ChemistrySelect* 5 (2020): 14759.
41. L. A. Román-Ramírez, P. McKeown, M. D. Jones, and J. Wood, "Poly(Lactic acid) Degradation into Methyl Lactate Catalyzed by a Well-Defined Zn(II) Complex," *ACS Catalysis* 9 (2018): 409–416.
42. F. M. Lamberti, L. A. Román-Ramírez, P. McKeown, M. D. Jones, and J. Wood, "Kinetics of Alkyl Lactate Formation from the Alcoholysis of Poly(Lactic Acid)," *Processes* 8 (2020): 738.
43. L. E. English, M. D. Jones, and D. J. Liptrot, "N-Heterocyclic Phosphines as Precatalysts for the Highly Selective Degradation of Poly(Lactic Acid)," *ChemCatChem* 14 (2022): e202101904.
44. C. Fliedel, D. Vila-Viçosa, M. J. Calhorda, S. Dagorne, and T. Avilés, "Dinuclear Zinc-N-Heterocyclic Carbene Complexes for Either the Controlled Ring-Opening Polymerization of Lactide or the Controlled Degradation of Polylactide Under Mild Conditions," *ChemCatChem* 6 (2014): 1357–1367.
45. S. Liu, L. Hu, J. Y. Liu, Z. S. Zhang, H. Y. Suo, and Y. S. Qin, "Zinc Catalyst for Chemical Upcycling of PLA Wastes: Novel Industrial Monomer Resource Toward Poly(Ester-Amide)," *Macromolecules* 57 (2024): 4662–4669.
46. J. A. Stewart, L. T. W. Powell, M. J. Cullen, G. Kociok-Kohn, M. G. Davidson, and M. D. Jones, "Imino-Pyrrole Zn(II) Complexes for the Rapid and Selective Chemical Recycling of Commodity Polymers" *Angewandte Chemie International Edition* 64 (2025): e202502845.
47. C. Alberti, N. Damps, R. R. R. Meissner, and S. Enthaler, "Depolymerization of End-of-Life Poly(lactide) via 4-Dimethylaminopyridine-Catalyzed Methanolysis," *ChemistrySelect* 4 (2019): 6845–6849.
48. F. M. Lamberti, A. Ingram, and J. Wood, "Synergistic Dual Catalytic System and Kinetics for the Alcoholysis of Poly(Lactic Acid)," *Processes* 9 (2021): 921.
49. X. Y. Song, H. Wang, X. D. Zheng, F. S. Liu, and S. T. Yu, "Methanolysis of Poly(lactic acid) Using Acidic Functionalized Ionic Liquids as Catalysts," *Journal of Applied Polymer Science* 131 (2014): 40817.
50. X. Y. Song, X. J. Zhang, H. Wang, F. S. Liu, S. T. Yu, and S. W. Liu, "Methanolysis of Poly(Lactic Acid) (PLA) Catalyzed by Ionic Liquids," *Polymer Degradation and Stability* 98 (2013): 2760–2764.
51. F. S. Liu, J. Guo, P. H. Zhao, Y. Q. Gu, J. Gao, and M. S. Liu, "Facile Synthesis of DBU-Based Protic Ionic Liquid for Efficient Alcoholysis Of Waste Poly(Lactic Acid) to Lactate Esters," *Polymer Degradation and Stability* 167 (2019): 124–129.
52. J. Stewart, M. Fuchs, J. Payne, et al., "Simple Zn(ii) Complexes for the Production and Degradation Of Polyesters," *RSC Advances* 12 (2022): 1416–1424.

53. Y. Li, S. Wang, S. Qian, Z. Liu, Y. Weng, and Y. Zhang, "Depolymerization and Re/Upcycling of Biodegradable PLA Plastics," *ACS Omega* 9 (2024): 13509–13521.
54. C. Jehanno, M. M. Pérez-Madrugal, J. Demarteau, H. Sardon, and A. P. Dove, "Organocatalysis for depolymerisation," *Polymer Chemistry* 10 (2019): 172–186.
55. A. L. Merchan, T. Fiscoeder, J. Hee, et al., "Chemical Recycling of Bioplastics: Technical Opportunities to Preserve Chemical Functionality as Path Towards a Circular Economy," *Green Chemistry* 24 (2022): 9428–9449.
56. P. P. Upare, Y. K. Hwang, J. S. Chang, and D. W. Hwang, "Synthesis of Lactide from Alkyl Lactate via a Prepolymer Route," *Industrial & Engineering Chemistry Research* 51 (2012): 4837–4842.
57. M. Pala, G. Lligadas, and A. Moreno, "Valorization of Lactate Esters and Amides into Value-Added Biobased (Meth)Acrylic Polymers," *Biomacromolecules* 25 (2024): 6338–6356.
58. A. B. Raheem, Z. Z. Noor, A. Hassan, M. K. Abd Hamid, S. A. Samsudin, and A. H. Sabeen, "Current developments in chemical recycling of post-consumer polyethylene terephthalate wastes for new materials production: A review," *Journal of Cleaner Production* 225 (2019): 1052–1064.
59. F. Awaja and D. Pavel, "Recycling of PET," *European Polymer Journal* 41 (2005): 1453–1477.
60. E. Barnard, J. J. R. Arias, and W. Thielemans, "Chemolytic Depolymerisation of PET: A Review," *Green Chemistry* 23 (2021): 3765–3789.
61. R. Weber, N. M. Ashta, N. Aurisano, et al., Chemicals in Plastics: A Technical Report (UNEP, 2023).
62. Z. O. G. Schyns and M. P. Shaver, "Mechanical Recycling of Packaging Plastics: A Review," *Macromolecular Rapid Communications* 42 (2021): e2000415.
63. A. Carné Sánchez and S. R. Collinson, "The Selective Recycling of Mixed Plastic Waste of Polylactic Acid and Polyethylene Terephthalate by Control of Process Conditions," *European Polymer Journal* 47 (2011): 1970–1976.
64. R. López-Fonseca, I. Duque-Ingunza, B. de Rivas, S. Arnaiz, and J. I. Gutiérrez-Ortiz, "Chemical recycling of post-consumer PET wastes by glycolysis in the presence of metal salts" *Polymer Degradation and Stability* 95 (2010): 1022–1028.
65. M. N. Siddiqui, H. H. Redhwi, A. A. Al-Arfaj, D. S. Achilias, "Chemical Recycling of PET in the Presence of the Bio-Based Polymers, PLA, PHB and PEF: A Review," *Sustainability* 13 (2021): 10528.
66. N. Evode, S. A. Qamar, M. Bilal, D. Barceló, and H. M. N. Iqbal, "Plastic Waste and Its Management Strategies for Environmental Sustainability," *Case Studies in Chemical and Environmental Engineering* 4 (2021): 100142.
67. H. Wittmann, A. Schorm, and J. Sundermeyer, "Chelatliganden auf Basis Peralkylierter Bis-Und Tris-Guanidine," *Zeitschrift Für Anorganische und Allgemeine Chemie* 626 (2000): 1583–1590.
68. S. Pohl, M. Harmjan, J. Schneider, W. Saak, and G. Henkel, "1,3-Bis(N,N,N',N'-Tetramethylguanidino)Propane: Synthesis, Characterization and Bonding Properties of the First Bidentate, Peralkylated Guanidine Ligand," *Journal of the Chemical Society, Dalton Transactions* 2000 (2000): 3473–3479.
69. G. Malle, C. Blaise, and X. Radisson, (*L'Oreal*), *EP 1 532 964 A1*, 2006.
70. P. Anastas and N. Eghbali, "Green Chemistry: Principles and Practice" *Chemical Society Reviews* 39 (2010): 301–312.
71. P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice* (Oxford University Press, 1998).
72. A. P. Gupta and V. Kumar, "New emerging trends in synthetic biodegradable polymers – Polylactide: A Critique," *European Polymer Journal* 43 (2007): 4053–4074.
73. C. S. M. Pereira, V. M. T. M. Silva, and A. E. Rodrigues, "Ethyl Lactate as a Solvent: Properties, Applications and Production Processes—A Review," *Green Chemistry* 13 (2011): 2658–2671.
74. R. A. Sheldon, "Green Solvents for Sustainable Organic Synthesis: State of the Art," *Green Chemistry* 7 (2005): 267–278.
75. R. Petrus, D. Bykowski, and P. Sobota, "Solvothermal Alcoholysis Routes for Recycling Polylactide Waste as Lactic Acid Esters," *ACS Catalysis* 6 (2016): 5222–5235.
76. R. Kamaraj, P. K. Ganta, T. Ben Halima, et al., "Organocatalysts for L-Lactide polymerization: 2-alkyl- and 2-aryl-1,1,3,3-tetramethylguanidines" *Molecular Catalysis* 569 (2024): 114580.
77. A. Chuma, H. W. Horn, W. C. Swope, et al., "The Reaction Mechanism for the Organocatalytic Ring-Opening Polymerization of L-Lactide Using a Guanidine-Based Catalyst: Hydrogen-Bonded or Covalently Bound?," *Journal of the American Chemical Society* 130 (2008): 6749–6754.
78. L. Simon and J. M. Goodman, "The Mechanism of TBD-Catalyzed Ring-Opening Polymerization of Cyclic Esters," *The Journal of Organic Chemistry* 72 (2007): 9656–9662.
79. X. Fu and C. H. Tan, "Mechanistic Considerations of Guanidine-Catalyzed Reactions," *Chemical Communications* 47 (2011): 8210–8222.
80. R. C. Pratt, B. G. Lohmeijer, D. A. Long, R. M. Waymouth, and J. L. Hedrick, "Triazabicyclodecene: a Simple Bifunctional Organocatalyst for Acyl Transfer and Ring-Opening Polymerization of Cyclic Esters," *Journal of the American Chemical Society* 128 (2006): 4556–4557.
81. B. Liu, X. M. Lu, Z. Y. Ju, et al., "Ultrafast Homogeneous Glycolysis of Waste Polyethylene Terephthalate via a Dissolution-Degradation Strategy," *Industrial & Engineering Chemistry Research* 57 (2018): 16239–16245.
82. C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez, and H. Sardon, "Organocatalysed Depolymerisation of PET in a Fully Sustainable Cycle Using Thermally Stable Protic Ionic Salt," *Green Chemistry* 20 (2018): 1205–1212.
83. K. Fukushima, O. Coulembier, J. M. Lecuyer, et al., "Organocatalytic Depolymerization of Poly(ethylene terephthalate)," *Journal of Polymer Science Part A: Polymer Chemistry* 49 (2011): 1273–1281.
84. V. Celestre, J. Madsen, C. Siracusa, et al., "Microwave-Assisted Synthesis of Polyethylene Terephthalate as a Fast Screening Method for Catalyst Evaluation and for Evaluating Polymerizability of Monomers Recovered From Degraded Polyesters," *Journal of Applied Polymer Science* 142 (2025): e57688.
85. A. J. Spicer, A. Brandolese, and A. P. Dove, "Selective and Sequential Catalytic Chemical Depolymerization and Upcycling of Mixed Plastics," *ACS Macro Letters* 13 (2024): 189–194.
86. R. Yang, G. Xu, B. Dong, X. Guo, and Q. Wang, "Selective, Sequential, and "One-Pot" Depolymerization Strategies for Chemical Recycling of Commercial Plastics and Mixed Plastics," *ACS Sustainable Chemistry & Engineering* 10 (2022): 9860–9871.
87. J. Sherwood, "Closed-Loop Recycling of Polymers Using Solvents Remaking Plastics For A Circular Economy," *Johnson Matthey Technology Review* 64 (2020): 4–15.
88. F. Fink, F. Grabowski, S. Oden, P. Nisgutski, A. Pich, and S. Herres-Pawlis, "Depolymerization of PLA Catalyzed By Guanidine-Modified Microgels," *Chemical Science* 16 (2025): 19614–19623.

Supporting Information

Additional supporting information can be found online in the Supporting Information section. The authors have cited additional references within the Supporting Information.