



# Reductive Depolymerization of Plastic Waste Catalyzed by $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$

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Plastic pollution is one of the biggest problems all over the world. Beyond change/awareness of consumer behavior, there is an urgent need to search for efficient, economical and environmentally friendly catalysts for the valorization of plastic waste to value-added compounds. This work describes the reductive depolymerization of several types of plastic waste into value-added compounds, including 1,6-hexanediol, 1,2-propanediol, *p*-xylene and tetrahydrofuran, in good yields using the eco-friendly, air-stable, commercially available and very

cheap catalyst  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ . This is the first example of the reductive depolymerization of polyester waste catalyzed by a zinc catalyst. Moreover, the catalytic system silane/ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was successfully applied to the reduction of polycaprolactone (PCL) on the gram scale with good yield and also to the selective reductive depolymerization of plastic mixtures. Finally, this work demonstrated that the catalyst  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  can be used in at least 7 cycles with good yields.

## Introduction

Plastics make our lives much more convenient. The excellent properties of plastics in terms of low cost of manufacturing, light weight and durability have enhanced their applications and led to a displacement of traditional materials, such as wood, metals and ceramics.<sup>[1]</sup> They are used in many sectors such as packaging, construction, automotive manufacture, furniture, toys, shoes, household appliances, electrical and electronic goods, agriculture and medicine. As consequence, the enormous plastic consumption has led in parallel to the generation of plastic waste, which has become one of the biggest problems all over the world.<sup>[2–5]</sup>

Different kinds of plastics can degrade at different times, but the average time for one single-use plastic bottle to completely degrade is at least 450 years. It can even take some bottles 1000 years to biodegrade.<sup>[6]</sup>

More than eight billion tons of plastic waste has accumulated worldwide over the past 50 years.<sup>[7]</sup> As of 2015, approximately 6300 Mt of plastic waste had been generated, around 9% of which had been recycled, 12% was incinerated, and 79% was accumulated in landfills or the natural environment.<sup>[7]</sup> At the current rate, we will end up having more plastic than fish in the ocean by 2050.<sup>[8]</sup>

Traditional plastics are derived from fossil feedstock and difficult to be degraded naturally. Biodegradable polymers are seen as a suitable alternative to commodity plastics. The most

common form of bioplastic is poly(lactic acid) (PLA), which is made out of corn. Unfortunately, in order for PLA to biodegrade, it needs a certain kind of bacteria at just the right temperature (60 °C).<sup>[9]</sup> These conditions are not found in landfills, where most plastics end up. In good conditions, PLA will show signs of biodegradation in 6 months. Under ambient conditions, PLA will endure for hundreds of years and is basically non-degradable in seawater. Moreover, the degradation of plastic waste in landfills typically leads to no recovery of the materials' value.

In parallel with the consumer behavioral change/awareness-raised behavior regarding the use of plastics, it is also urgent to develop new methodologies for the valorization of plastic waste into value-added compounds.

In the literature, various methodologies for recycling plastic waste have been reported,<sup>[10–13]</sup> including mechanical recycling,<sup>[14]</sup> pyrolysis,<sup>[15]</sup> and chemical recycling (e.g., hydrolysis, glycolysis, alcoholysis and aminolysis)<sup>[16–26]</sup> and biochemical degradation.<sup>[27,28]</sup>

In recent years, reductive depolymerization of plastic waste has emerged as an efficient alternative methodology for converting plastic waste into value-added compounds employing ruthenium,<sup>[29–31]</sup> boron<sup>[32]</sup> or iridium<sup>[33]</sup> catalysts and  $\text{H}_2$  or silanes as reducing agents. However, one of the disadvantages of these methods is the price of catalysts. For sustainable industrial application of plastic recycling processes, the catalysts should be highly active, inexpensive, air-stable, and contain ecological or earth abundant metals.

In continuation of the research work of this group using dioxomolybdenum complexes as catalysts,<sup>[34–36]</sup> very recently we reported a novel and very efficient methodology for the reductive depolymerization of polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polycaprolactone (PCL), poly(lactic acid) (PLA) and polydioxanone (PDO) plastic waste.<sup>[37]</sup> This method allowed the recycling of these polyesters into value-added compounds and fuels, including 1,6-hexanediol, *p*-xylene and propane in good yields using the eco-friendly, cheap and

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air-stable dioxomolybdenum complex  $\text{MoO}_2\text{Cl}_2(\text{H}_2\text{O})_2$  as the catalyst and silanes as the reducing agents. After the publication of our article, Marks and co-workers reported the depolymerization of PET into terephthalic acid and ethylene using a carbon-supported single-site dioxomolybdenum compound as the catalyst.<sup>[38]</sup>

In the literature is reported that  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  is an efficient catalyst for reducing esters,<sup>[39]</sup> however, this catalyst has never been used in the reductive depolymerization of plastic waste.

Due to the high importance of the development of cost-efficient processes for the reductive depolymerization of plastic waste, in this work the reductive depolymerization of plastic waste is investigated, catalyzed by the environmentally friendly, commercially available and very cheap catalyst  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .

## Results and Discussion

The reductive depolymerization of PCL was initially studied in the presence of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  employing several silanes as the reducing agents (Table 1). The depolymerization of PCL using  $(\text{EtO})_2\text{MeSiH}$  (3 equiv.) in THF at refluxing temperature gave 1,6-hexanediol with 98% yield in the presence of 10 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  after 24 h (Table 1, entry 1). When this reaction was performed using only 5 mol% of catalyst, 1,6-hexanediol was obtained with 72% yield after 24 h (Table 1, entry 2) and with 97% yield after 48 h (Table 1, entry 3). This diol was also produced with excellent yield (98%) in the presence of 5 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  employing toluene as the solvent at 110 °C (Table 1, entry 4).

The reductive depolymerization of PCL using only 5 mol% of catalyst and 2 equiv. of  $\text{PhSiH}_3$  as the reducing agent in toluene at 110 °C gave 1,6-hexanediol with 98% yield (Table 1,

entry 5). In contrast, at 65 °C, this reaction produced 1,6-hexanediol with only 61% yield, showing the influence of temperature on the reaction (Table 1, entry 6).

However, when this reduction was performed in the presence of 3 mol% of catalyst, the diol was obtained in moderate yield (52%) after 48 h (Table 1, entry 7). The reaction with the reducing agent polymethylhydrosiloxane (PMHS, 3 equiv.), a byproduct of the silicone industry that is cheap, easy to handle and environmentally friendly, was also performed in the presence of 10 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in reflux of THF or toluene, producing 1,6-hexanediol in 30 and 68% yields, respectively (Table 1, entries 8 and 9). Low yields were obtained employing the silanes dimethylphenylsilane (DMPHS) or triethylsilane (Table 1, entries 10 and 11). Finally, no reactions were observed using the sterically hindered  $\text{Ph}_3\text{SiH}$  (Table 1, entry 12) and in the absence of catalyst (Table 1, entry 13) or silane (Table 1, entry 14). We also tested a reductive depolymerization of PCL using other commercially available zinc compounds including  $\text{ZnCl}_2$ ,  $\text{ZnBr}_2$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ , but the depolymerization of PCL did not occur.

Based on previous work reported in the literature by Beller and co-workers<sup>[40]</sup> the reduction of the polyester with the system  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ /silane should initially involve the activation of the silane by  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  with the formation of species **A** (Scheme 1). Then, this species reacts with the polyester to produce the silyl acetal intermediate **B**. After adding another equivalent of the silane, the silyl acetal is further reduced to disilyl ether **C** in a similar pathway. Finally, the corresponding diol is obtained after hydrolysis.

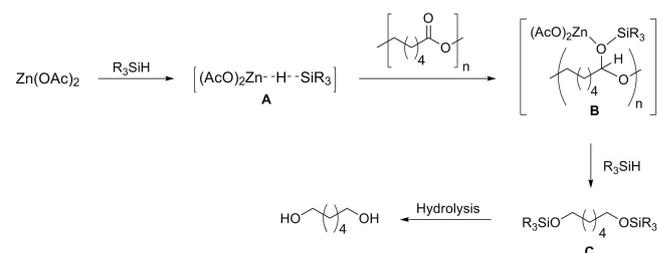
The reaction of PCL in gram scale was also performed with  $(\text{OEt})_2\text{MeSiH}$  (3 equiv.) in the presence of 10 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  using toluene as the solvent at 110 °C (see the Supporting Information). 1,6-Hexanediol was obtained with 65% yield after 24 h. This yield increased to 79% yield after 48 h. This result is interesting since 1,6-hexanediol is a valuable intermediate compound for the chemical industry and finds applications, for example, in the production of coating, polyurethane and polyester plasticizers.

In order to study the possible use of the catalyst  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in several catalytic cycles, we also carried out the reductive depolymerization of PCL in toluene at 110 °C by successive additions of PCL and  $\text{PhSiH}_3$  to the reaction mixture, without separating the catalyst at the end of each catalytic cycle (see the Supporting Information). The yield of each cycle

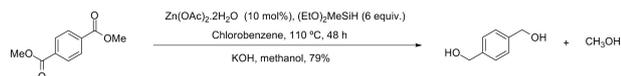
**Table 1.** Reductive depolymerization of PCL catalyzed by  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  using different silanes.<sup>[a]</sup>

Entry	Catalyst [mol%]	Silane (equiv.)	Solvent	T [°C]	t [h]	Yield <sup>[b]</sup> [%]
1	10	$(\text{EtO})_2\text{MeSiH}$ (3)	THF	65	24	98 (92) <sup>[c]</sup>
2	5	$(\text{EtO})_2\text{MeSiH}$ (3)	THF	65	24	72 (23) <sup>[d]</sup>
3	5	$(\text{EtO})_2\text{MeSiH}$ (3)	THF	65	48	97
4	5	$(\text{EtO})_2\text{MeSiH}$ (3)	toluene	110	24	98
5	5	$\text{PhSiH}_3$ (2)	toluene	110	24	98
6	5	$\text{PhSiH}_3$ (2)	toluene	65	24	61 (36) <sup>[d]</sup>
7	3	$\text{PhSiH}_3$ (2)	toluene	110	48	52 (40) <sup>[d]</sup>
8	10	PMHS (3)	THF	65	48	30 (68) <sup>[d]</sup>
9	10	PMHS (3)	toluene	110	48	68 (31) <sup>[d]</sup>
10	10	DMPHS (3)	THF	65	24	20 (79) <sup>[d]</sup>
11	10	$\text{Et}_3\text{SiH}$ (3)	THF	65	48	12 (88) <sup>[d]</sup>
12	10	$\text{Ph}_3\text{SiH}$ (3)	THF	65	48	n.r.
13	–	$\text{PhSiH}_3$ (3)	THF	65	48	n.r.
14	10	–	THF	65	48	n.r.

[a] The reactions were carried out with 0.5 mmol of PCL. [b] Yields were determined by <sup>1</sup>H NMR spectroscopy using mesitylene as internal standard. [c] Isolated yield by column chromatography. [d] Yield of PCL. n.r. = no reaction.



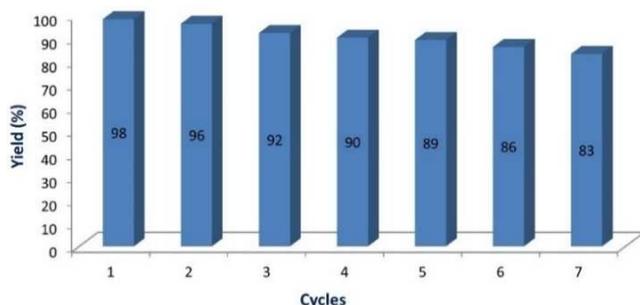
**Scheme 1.** Proposed mechanism for the reduction of PCL with the system silane/ $\text{Zn}(\text{OAc})_2$ .



**Scheme 2.** Reduction of dimethyl terephthalate with the system  $(\text{EtO})_2\text{MeSiH}/\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .

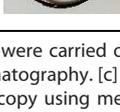
was determined by  $^1\text{H}$  NMR spectroscopy using mesitylene as internal standard. We found that  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  catalyzed at least 7 cycles with excellent activity (Figure 1).

The catalytic system silane/ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was also tested in the reductive depolymerization of the aliphatic polyester PLA. Initially, this reaction was carried out with a PLA sample obtained from a beverage cup cut into pieces, using  $(\text{EtO})_2\text{MeSiH}$  (3 equiv.) and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (10 mol%) in toluene at  $110^\circ\text{C}$ , leading to the formation of 1,2-propanediol with 65% yield, along with 29% of PLA, after 48 h (Table 2, entry 1). This diol was also produced in 49% yield when this reaction was performed with  $\text{PhSiH}_3$  after 24 h and in 71% yield after 48 h



**Figure 1.** Use of the catalyst  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in multiple cycles. The reactions were carried out by successive addition of PCL (0.25 mmol) and  $\text{PhSiH}_3$  (0.75 mmol) to the reaction mixture. Yields were determined by  $^1\text{H}$  NMR spectroscopy using mesitylene as an internal standard.

**Table 2.** Reductive depolymerization of PLA samples with the catalytic system silane/ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .<sup>[a]</sup>

Entry	PLA sample	Silane	Yield [%]
1		$(\text{EtO})_2\text{MeSiH}$	65 (29) <sup>[b,c]</sup>
2		$\text{PhSiH}_3$	71 (20) <sup>[b,c]</sup>
3		$\text{PhSiH}_3$	60 (33) <sup>[c,d]</sup>

[a] The reactions were carried out with 1.0 mmol of PLA. [b] Isolated yield by column chromatography. [c] Yield of PLA. [d] Yields were determined by  $^1\text{H}$  NMR spectroscopy using mesitylene as internal standard.

(Table 2, entry 2). The production of 1,2-propanediol from PLA waste is also relevant as this diol has wide applications in the chemical, cosmetic and pharmaceutical industry. Finally, the system  $\text{PhSiH}_3/\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was applied to the valorization of filament waste from 3D printer into 1,2-propanediol with 60% yield (Table 2, entry 3).

PET is the most-used polyester in the world. As consequence, the huge amount of PET waste generated from domestic waste or from various industries requires the development of recycling methodologies using cheap, environmentally friendly and air-stable catalysts. With this goal in mind, the reductive depolymerization of PET waste was also studied using  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  as the catalyst. Initially, the reductive depolymerization of PET, obtained from a synthetic pillow filling, was performed in dioxane using  $\text{PhSiH}_3$  (6 equiv.) as the reducing agent in the presence of 10 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  at  $140^\circ\text{C}$  over 4 days. However, the reaction did not occur, probably due to the low solubility of this polyester in dioxane. Changing the solvent of the reaction to chlorobenzene and using  $\text{PhSiH}_3$  (6 equiv.) in the presence of 10 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  at  $160^\circ\text{C}$ , *p*-xylene was obtained in 65% yield, after 4 days, along with 43% yield of ethylene glycol (Table 3, entry 1). The formation of *p*-xylene should occur by deoxygenation of the silylated 1,4-benzenedimethanol intermediate, due to the activation by the aromatic ring. When this reaction was performed in the presence of 5 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , the yield of *p*-xylene decreased to 39% (Table 3, entry 2). The reductive depolymerization of PET was also investigated using  $(\text{EtO})_2\text{MeSiH}$  as the reducing agent, leading to the formation of 1,4-benzenedimethanol with 55% yield and *p*-xylene with only 30% yield (Table 3, entry 3).

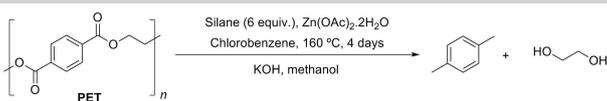
The catalytic system  $\text{PhSiH}_3/\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was also applied to the depolymerization of other PET samples obtained from domestic waste, such as a commercial Evian® water bottle finely ground and a sport jersey, producing *p*-xylene (59–61% yield) and ethylene glycol (36–41%) (Table 3, entries 4 and 5). The production of *p*-xylene from plastic waste is also very important, as it is commonly derived from crude oil and is widely used in several industries.

In this work, the reaction of dimethyl terephthalate was also performed with  $(\text{OEt})_2\text{MeSiH}$  catalyzed by  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in chlorobenzene at  $110^\circ\text{C}$  during 48 h (Scheme 2), leading to the formation of 1,4-benzenedimethanol in 79% isolated yield (see the Supporting Information).

When this reaction was performed under the same reaction conditions used for the reductive depolymerization of PET, the deoxygenation of ester groups occurred, confirming the formation of *p*-xylene with 81% yield (see the Supporting Information). This result also suggests that the catalytic system  $\text{PhSiH}_3/\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  can be used to deoxygenate aromatic esters in the corresponding alkyl benzene derivatives (Scheme 3).

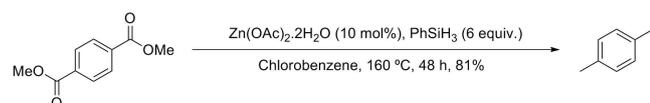
The efficiency of the catalyst  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was also tested in the reductive depolymerization of PBT, which is widely used in packaging and in the electronics and automotive industries. Initially, the reductive depolymerization of PBT was performed using a granulated PBT sample and  $(\text{OEt})_2\text{MeSiH}$  (6 equiv.) as

**Table 3.** Reductive depolymerization of different PET samples using the system silane/ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .<sup>[a]</sup>



Entry	PET sample	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ [mol%]	Silane	<i>p</i> -Xylene yield <sup>[b]</sup> [%]	Ethylene glycol yield <sup>[b]</sup> [%]
1		10	$\text{PhSiH}_3$	65	43
2		5	$\text{PhSiH}_3$	39	16
3		10	$(\text{EtO})_2\text{MeSiH}$	30 (55) <sup>[c]</sup>	11
4		10	$\text{PhSiH}_3$	61	41
5		10	$\text{PhSiH}_3$	59	36

[a] The reactions were carried out with 0.25 mmol of PET. [b] Yields were determined by <sup>1</sup>H NMR spectroscopy using furan as internal standard. [c] Yield of 1,4-benzenedimethanol.

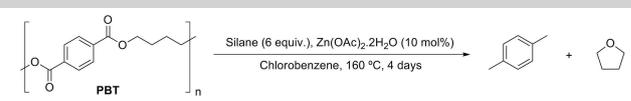


**Scheme 3.** Reduction of dimethyl terephthalate with the system  $\text{PhSiH}_3/\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .

the reducing agent in the presence of 10 mol% of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  in THF or dioxane at 160 °C during 4 days. However, no reaction was observed in these solvents and the granulated PBT remained insoluble in the reaction mixture. Then, the same reaction was also performed in chlorobenzene producing *p*-xylene in only 15% yield, along with of a mixture of several intermediates (Table 4, entry 1). In contrast, when the depolymerization of PBT was carried out using  $\text{PhSiH}_3$  (6 equiv.) instead of  $(\text{OEt})_2\text{MeSiH}$ , a mixture of *p*-xylene (67%) and THF (70%) was obtained (Table 4, entry 2). In addition to the good yield of *p*-xylene, this result is also very interesting since THF is widely used as a solvent and valuable chemical intermediate in the industry, with a world annual production of approximately 200000 tons.<sup>[41]</sup> For example, it is used as an industrial solvent for making polyvinyl chloride (PVC) and can also be used as reaction medium in the pharmaceutical industry. Moreover, the production of THF from plastic waste has never been reported.

In order to expand the applicability of this method, the catalytic system  $\text{PhSiH}_3/\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was also tested into the reductive depolymerization of PBT sample obtained from an

**Table 4.** Reductive depolymerization of different PBT samples using the system silane/ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ .<sup>[a]</sup>



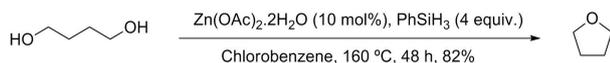
Entry	PBT sample	Silane	<i>p</i> -Xylene yield <sup>[b]</sup> [%]	THF yield <sup>[b]</sup> [%]
1		$(\text{OEt})_2\text{MeSiH}$	15	–
2		$\text{PhSiH}_3$	67	70
3		$\text{PhSiH}_3$	52	53

[a] The reactions were carried out with 0.25 mmol of PBT. [b] Yields were determined by <sup>1</sup>H NMR spectroscopy using furan as internal standard.

engine component (distributor cap) of a car, leading to the formation of *p*-xylene and THF (Table 4, entry 3).

To confirm the synthesis of THF from 1,4-butanediol, the reaction of this diol was carried out with the catalytic system  $\text{PhSiH}_3/\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (see the Supporting Information), leading to the formation of THF in 82% yield (Scheme 4).

Finally, this method was also tested in the depolymerization of mixtures of different polyester waste. The reaction of the mixtures PCL + PET and PCL + PBT with  $(\text{EtO})_2\text{MeSiH}$  and Zn-



**Scheme 4.** Conversion of 1,4-butanediol into THF with the system PhSiH<sub>3</sub>/Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O.

**Table 5.** Selective reductive depolymerization of PCL with the system silane/Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O.<sup>[a]</sup>

Entry	Mixture	Silane (equiv.)	Zn(OAc) <sub>2</sub> ·2H <sub>2</sub> O [mol%]	Product	Yield <sup>[b]</sup> [%]
1	PCL + PET	(EtO) <sub>2</sub> MeSiH (3)	10	1,6-hexanediol	95
2	PCL + PBT	(EtO) <sub>2</sub> MeSiH (3)	10	1,6-hexanediol	93

[a] The reactions were carried out with 0.25 mmol of PCL and 0.25 mmol of PET or PBT. [b] Yields were determined by <sup>1</sup>H NMR spectroscopy using furan as internal standard.

(OAc)<sub>2</sub>·2H<sub>2</sub>O in THF at 65 °C during 24 h (see the Supporting Information), in both cases, led to the selective reduction of PCL and the production of 1,6-hexanediol with excellent yields (Table 5).

## Conclusions

This work reports the first methodology for the reductive depolymerization of plastic waste using a zinc catalyst. The commercially available, very cheap, environmentally friendly and earth-abundant compound Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O proved to be an efficient catalyst for the reductive depolymerization of polycaprolactone (PCL), poly(lactic acid) (PLA), polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) waste into value-added compounds including 1,6-hexanediol, 1,2-propanediol, *p*-xylene and THF in good yields. Moreover, this is the first example of the production of THF by reductive depolymerization of PBT waste. This catalyst was also efficient on a gram scale and can be successfully used in at least 7 catalytic cycles with good yields in the selective reduction of PCL, suggesting the possible industrial application of this method.

Finally, this work demonstrates that it is possible to efficiently recycle plastic waste using a simple, eco-friendly, commercially available and inexpensive catalyst, contributing to reduce the large amount of plastic waste that is released into the environment and into the oceans and also to improve the circular economy and human health. These results can lead to further developments of more cost-effective catalytic systems, which can offer a sustainable alternative to the depolymerization of plastic waste.

## Experimental Section

### Materials

All the reactions were carried out under air atmosphere without using dry solvents. Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O, PhSiH<sub>3</sub>, (EtO)<sub>2</sub>MeSiH, DMPS, Et<sub>3</sub>SiH, Pr<sub>3</sub>SiH, Ph<sub>3</sub>SiH and PMHS were obtained from commercial suppliers and were used without further purification. Polymers such as PCL and PBT were purchased as granulate from Sigma and Aldrich. PLA was obtained from a beverage cup generously donated by C2Catering. PET was obtained from a used Evian® water bottle, a sport jersey and a synthetic pillow filling.

### Reductive depolymerization of PCL with the catalytic system Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O/PhSiH<sub>3</sub>

To a Schlenk flask equipped with a J. Young tap containing PCL (114 mg, 1.0 mmol) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (11.0 mg, 5 mol%) in toluene (3 mL) was added PhSiH<sub>3</sub> (0.25 mL, 2.0 mmol). The reaction mixture was stirred in the closed Schlenk flask at 110 °C during 24 h. After cooling to room temperature, a solution of KOH (20%) in methanol (5 mL) was added and the reaction mixture was stirred overnight, followed by extraction with ethyl acetate (3 × 10 mL). After evaporation, the product was purified by column chromatography.

### Reductive depolymerization of PLA with the catalytic system Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O/PhSiH<sub>3</sub>

To a Schlenk flask equipped with a J. Young tap containing PLA (72 mg, 1.0 mmol), obtained from a beverage cup cut into small pieces, in toluene (3 mL) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (22.0 mg, 10 mol%) was added PhSiH<sub>3</sub> (0.37 mL, 3 mmol). The reaction mixture was stirred in the closed Schlenk flask at 110 °C during 48 h. After cooling to room temperature, a solution of KOH (20%) in methanol (5 mL) was added and the reaction mixture was stirred overnight, followed by extraction with ethyl acetate (3 × 10 mL). After evaporation, the product was purified by column chromatography.

### Reductive depolymerization of PET with the system Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O/PhSiH<sub>3</sub>

To a Schlenk flask equipped with a J. Young tap containing PET (48 mg, 0.25 mmol), obtained from a synthetic pillow filling, and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (5.5 mg, 10 mol%) in chlorobenzene (2 mL) was added PhSiH<sub>3</sub> (0.185 mL, 1.5 mmol). The reaction mixture was stirred in the closed Schlenk flask at 160 °C for 4 days. After cooling to room temperature, a solution of KOH (20%) in methanol (5 mL) was added and the reaction mixture was stirred overnight, followed by extraction with ethyl acetate (3 × 10 mL).

### Reductive depolymerization of PBT with the system Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O/PhSiH<sub>3</sub>

To a Schlenk flask equipped with a J. Young tap containing PBT (55 mg, 0.25 mmol) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (5.5 mg, 10 mol%) in chlorobenzene (2 mL) was added PhSiH<sub>3</sub> (0.185 mL, 1.5 mmol). The reaction mixture was stirred in the closed Schlenk flask at 160 °C during 4 days.

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## Conflict of Interest

There are no conflicts to declare.

**Keywords:** plastic recycling · polyesters · reductive depolymerization · silanes

- [1] A. L. Andrad, M. A. Neal, *Philos. Trans. R. Soc. London Ser. B* **2009**, *364*, 1977–1984.
- [2] H. K. Webb, J. Arnott, R. J. Crawford, E. P. Ivanova, *Polymer* **2013**, *5*, 1–18.
- [3] C. G. Avio, S. Gorbi, F. Regoli, *Mar. Environ. Res.* **2017**, *128*, 2–11.
- [4] Y. Chae, Y.-J. An, *Environ. Pollut.* **2018**, *240*, 387–395.
- [5] A. Chamas, H. Moon, J. Zheng, Y. Qiu, T. Tabassum, J. H. Jang, M. Abu-Omar, S. L. Scott, S. Suh, *ACS Sustainable Chem. Eng.* **2020**, *8*, 3494–3511.
- [6] <https://www.postconsumers.com/2011/10/31/how-long-does-it-take-a-plastic-bottle-to-biodegrade/> (accessed June 2020).
- [7] R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782.
- [8] The new plastics economy: rethinking the future of plastics & catalysing action. Ellen MacArthur Foundation (2017). <https://www.ellenmacarthur-foundation.org/publications/the-new-plastics-economy-rethinking-the-future-of-plastics-catalysing-action> (accessed May 2020).
- [9] J. J. Kolstad, E. T. H. Vink, B. De Wilde, L. Debeer, *Polym. Degrad. Stab.* **2012**, *97*, 1131–1141.
- [10] T. Thiounn, R. C. Smith, *J. Polym. Sci.* **2020**, *58*, 1347–1364.
- [11] C. Jehanno, M. M. Pérez-Madrigal, J. Demarteau, H. Sardon, A. P. Dove, *Polym. Chem.* **2019**, *10*, 172–186.
- [12] A. Rahimi, J. M. García, *Nat. Chem. Rev.* **2017**, *1*, 0046.
- [13] M. Hong, E. Y.-X. Chen, *Green Chem.* **2017**, *19*, 3692–3706.
- [14] I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2020**, *59*, 15402–15423; *Angew. Chem.* **2020**, *132*, 15524–15548.
- [15] R. Miandad, M. Rehan, M. A. Barakat, A. S. Aburiazza, H. Khan, I. M. I. Ismail, J. Dhavamani, J. Gardy, A. Hassanpour, A.-S. Nizami, *Front. Energy Res.* **2019**, *7*, 27.
- [16] S. Ügdüler, K. M. Van Geem, R. Denolf, M. Roosen, N. Mys, K. Ragaert, S. De Meester, *Green Chem.* **2020**, *22*, 5376–5394.
- [17] M. J. Kang, H. J. Yu, J. Jegal, H. S. Kim, H. G. Cha, *Chem. Eng. J.* **2020**, *398*, 125655.
- [18] G. P. Tsintzou, D. S. Achilias, *Waste Biomass Valorization* **2013**, *4*, 3–7.
- [19] L. Wang, G. Nelson, J. Toland, J. D. Holbrey, *ACS Sustainable Chem. Eng.* **2020**, *8*, 13362–13368.
- [20] C. A. Fuentes, M. V. Gallegos, J. R. García, J. Sambeth, M. A. Peluso, *Waste Biomass Valorization* **2020**, *11*, 4991–5001.
- [21] C. N. Hoang, T. T. N. Le, Q. D. Hoang, *Polym. Bull.* **2019**, *76*, 23–34.
- [22] V. Jamdar, M. Kathalewar, A. Sabnis, *J. Coat. Technol. Res.* **2018**, *15*, 259–270.
- [23] Q. F. Yue, L. F. Xiao, M. L. Zhang, X. F. Bai, *Polymer* **2013**, *5*, 1258–1271.
- [24] A. P. More, S. R. Kokate, P. C. Rane, S. T. Mhaske, *Polym. Bull.* **2017**, *74*, 3269–3282.
- [25] R. M. Musale, S. R. Shukla, *Int. J. Plast. Technol.* **2016**, *20*, 106–120.
- [26] V. Sharma, P. Shrivastava, D. D. Agarwal, *J. Polym. Res.* **2015**, *22*, 241.
- [27] T. Ahmed, M. Shahid, F. Azeem, I. Rasul, A. A. Shah, M. Noman, A. Hameed, N. Manzoor, I. Manzoor, S. Muhammad, *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 7287–7298.
- [28] D. Danso, J. Chow, W. R. Streit, *Appl. Environ. Microbiol.* **2019**, *85*, e01095.
- [29] E. M. Krall, T. W. Klein, R. J. Andersen, A. J. Nett, R. W. Glasgow, D. S. Reader, B. C. Dauphinais, S. P. Mc Ilrath, A. A. Fischer, M. J. Carney, D. J. Hudson, N. J. Robertson, *Chem. Commun.* **2014**, *50*, 4884–4887.
- [30] J. A. Fuentes, S. M. Smith, M. T. Scharbert, I. Carpenter, D. B. Cordes, A. M. Z. Slawin, M. L. Clarke, *Chem. Eur. J.* **2015**, *21*, 10851–10860.
- [31] S. Westhues, J. Idel, J. Klankermayer, *Sci. Adv.* **2018**, *4*, eaat9669.
- [32] E. Feghali, T. Cantat, *ChemSusChem* **2015**, *8*, 980–984.
- [33] L. Monsigny, J.-C. Berthet, T. Cantat, *ACS Sustainable Chem. Eng.* **2018**, *6*, 10481–10488.
- [34] S. C. A. Sousa, I. Cabrita, A. C. Fernandes, *Chem. Soc. Rev.* **2012**, *41*, 5641–5653.
- [35] R. G. Noronha, A. C. Fernandes, *Curr. Org. Chem.* **2012**, *16*, 33–64.
- [36] S. C. A. Sousa, A. C. Fernandes, *Coord. Chem. Rev.* **2015**, *284*, 67–92.
- [37] B. F. S. Nunes, M. C. Oliveira, A. C. Fernandes, *Green Chem.* **2020**, *22*, 2419–2425.
- [38] Y. Kratish, J. Li, S. Liu, Y. Gao, T. J. Marks, *Angew. Chem. Int. Ed.* **2020**, *59*, 19857–19861; *Angew. Chem.* **2020**, *132*, 20029–20033.
- [39] S. Das, K. Mçller, K. Junge, M. Beller, *Chem. Eur. J.* **2011**, *17*, 7414–7417.
- [40] S. Das, D. Addis, S. Zhou, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 1770–1771.
- [41] L. Karas, W. J. Piel, *Ethers. Kirk-Othmer Encyclopedia of Chemical Technology*, Wiley, **2004**.

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## FULL PAPERS

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Reductive Depolymerization of  
Plastic Waste Catalyzed by Zn-  
(OAc)<sub>2</sub>·2H<sub>2</sub>O



**Waste not, want not:** Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O is used as a cost-effective catalyst for the reductive depolymerization of several types of plastic waste into

value-added compounds including 1,6-hexanediol, 1,2-propanediol, *p*-xylene and THF.

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