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# Poly(lactic acid) Degradation into Methyl Lactate Catalyzed by a Well-Defined Zn(II) Complex

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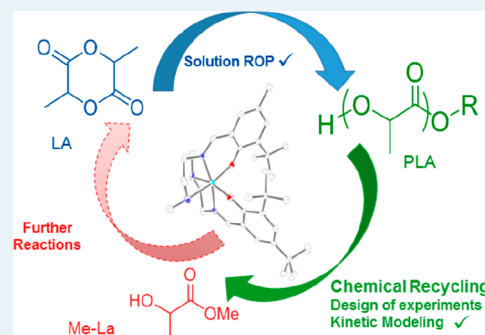
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## Supporting Information

**ABSTRACT:** Poly(lactic acid) (PLA) was degraded to methyl lactate (Me-La) by an imino monophenolate Zn(II)<sub>2</sub> catalyst in the presence of tetrahydrofuran, as the solvent, and methanol, as the protic source. As well as solution-based polymerization and degradation, catalyst stability was assessed and discussed. The chemical degradation of four different commercial samples of PLA, varying in molecular weight, was studied. The effect of PLA concentration (0.05–0.2 g mL<sup>-1</sup>), reaction temperature (40–130 °C), and catalyst concentration (4–16 wt %) on conversion, yield, and selectivity were studied and results statistically analyzed. Mass-transfer limitations were assessed by utilizing two different PLA particle sizes and altering the stirring speed. Results revealed that the main variables affecting PLA degradation are temperature and catalyst concentration. It was possible to observe Me-La formation even at 40 °C, although the reaction times were significantly longer when compared to the highest temperatures. Conversions of 100%, as determined by <sup>1</sup>H NMR spectroscopy and gel permeation chromatography, were possible in short times (<15 min) depending on temperature and catalyst concentration. A reaction mechanism for the production of Me-La from PLA, which considers the formation of chain-end groups as intermediates is presented and values for the kinetic constants are determined from the model. The activation energy for the initial degradation step was in the range 39–65 kJ mol<sup>-1</sup>, decreasing with increasing catalyst loading.

**KEYWORDS:** homogeneous catalysis, polymer degradation, poly(lactic acid), chemical recycling, design of experiments, kinetic modeling



## INTRODUCTION

Although oil-derived synthetic polymers have become indispensable to our daily life, their characteristically long life span have unfortunately also resulted in one of the most acute worldwide environmental problems, plastic pollution, particularly in the oceans.<sup>1,2</sup> Additional concerns are realized when looking at the oil demand for plastic production which is expected to grow to 20% by 2050 from its current value of 6%.<sup>3</sup> Hence, there is a need for more sustainable alternatives that have facile degradation pathways. Potential candidates to replace traditional polymers are biodegradable polymers, considered ecological materials that can degrade in a few months under specific (compostable) conditions<sup>4</sup> and that can be prepared from renewable sources.<sup>5</sup> Poly(lactic acid) (PLA) is a biodegradable polymer whose market demand has grown in recent years as its physical properties resemble those of current synthetic plastics, being suitable in packaging applications.<sup>6,7</sup> However, PLA may still be a source of pollution if not disposed properly because biodegradability occurs only under specific environmental conditions.<sup>8,9</sup> Another barrier to widespread PLA use is the cost of production which includes fermentation of lactic acid and prepolymerization steps to form the monomer, lactide (LA).<sup>10</sup> Recent efforts to address this issue include the use of shape-

selective catalysts and gas-phase reactions, which can reduce the energy and material input of the monomer synthesis.<sup>11–13</sup> A reduction in costs, and pollution, could also be achieved through the chemical recycling of PLA, regeneration of monomers and monomer precursors, or production of valuable chemicals, leading to a circular economy approach.<sup>14,15</sup>

Possible routes for the chemical recycling of PLA include thermal degradation,<sup>16–22</sup> hydrolytic degradation,<sup>23–25</sup> and enzymatic processes.<sup>4,26</sup> However, the first two cases involve high temperatures (200–400 °C), increasing the operating costs, whereas the latter presents possible scalability issues.<sup>27</sup> An alternative method for PLA chemical recycling is the transesterification with alcohols to lactate esters. This process is predicted to be economically and environmentally sustainable on an industrial scale, particularly when PLA production increases.<sup>28</sup> Low-molecular-weight lactate esters are touted as green solvents because of their biodegradability and low toxicity.<sup>29,30</sup> These serve as substitutes to hydrocarbon-based solvents with applications ranging from industrial and house cleaning, paints formulations, agricultural chemicals,

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polymer manufacturing, to pharmaceuticals.<sup>31–33</sup> There is the potential for transformation of lactate esters into LA, allowing for polymer reformation, therefore resulting in a circular economy.<sup>3,12,34</sup>

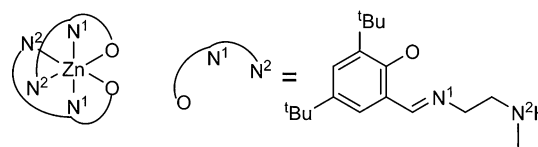
PLA chemical recycling to lactates can be realized via acid–base catalysis. DuPont, for instance, has patented a process for the degradation of PLA in the presence of H<sub>2</sub>SO<sub>4</sub> with temperatures between 150 and 190 °C, demonstrating high conversion to various alkyl lactates within 2 h.<sup>35</sup> Coszach et al.<sup>36</sup> have reported the hydrolysis of PLA to lactic acid; the use of alkyl lactates as solvent aided PLA dissolution with the added benefit of removing other polymers. Hydrolysis was then achieved with or without NaOH at 80–180 °C with pressures of up to 10 bar. Some studies have shown that the PLA hydrolysis mechanism is pH-dependent.<sup>37–40</sup> Song et al.<sup>41</sup> have reported the use of ionic liquids for the methanolysis of PLA, avoiding the need for acid–base catalysis.

Jones and co-workers have reported the relatively mild degradation of PLA in solution to give methyl lactate (Me-La).<sup>42</sup> In their study, Zr(IV)/Hf(IV) salalen complexes were used to both prepare and degrade PLA at 25 and 80 °C. Degradation was observed regardless of polymer tacticity, and a 75% conversion to Me-La was reported for a high-molecular-weight commercial PLA sample in 24 h at room temperature. However, the complexity in ligand preparation excludes this as a large-scale option. Fliedel et al.<sup>43</sup> have also demonstrated catalysts capable of the production and degradation of PLA. The addition of methanol (MeOH) to a binuclear Zn(II) N-heterocyclic carbene-mediated polymerization was observed to reduce polymer molecular weight and to generate Me-La. This system degraded low-molecular-weight PLLA to oligomers, achieving up to 28% Me-La after 24 h at room temperature. Organocatalysts such as 4-(dimethylamino)pyridine (DMAP) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) have also been shown to be feasible catalysts for the degradation of PLA or controlled chain scission.<sup>44,45</sup> More recently, Petrus et al.<sup>32</sup> obtained a wide range of lactate esters from the reaction of PLA with different alcohols and a series of metal-based catalysts. Reaction temperatures were as low as 80 °C in the presence of catalyst or as high as 260 °C for the uncatalyzed reactions; up to 1.5 kg of PLLA was processed in the presence of metallic magnesium at 200 °C.

Despite the need for facile, controlled degradation pathways, literature examples are scarce, particularly concerning the use of discrete metal complexes. Herein, we report the use of Zn(II) complexes for the transesterification reaction of industrial grades of PLA to Me-La. These complexes have the advantage of a simple preparation and a straightforward large-scale production unlike some other literature examples. Initial studies of stability and degradation were carried out on a small scale (0.25 g of PLA) after which the process was scaled up (50 g). To scale the process to the industrial level, it is necessary to further understand the role of operating conditions, catalyst and polymer concentration, mass transport, and kinetic effects, motivating the current study. The effects of different operating conditions on the Me-La formation were studied by means of a design of experimental approach. Furthermore, a reaction mechanism which explains the PLA degradation is proposed and values of the kinetic constants provided. To the best of our knowledge, this is the first example of a kinetic model to explain PLA degradation using a metal complex.

## RESULTS AND DISCUSSION

**Catalyst Introduction and Polymerization.** A Zn(II) complex, Zn(1)<sub>2</sub> (Figure 1), was prepared and characterized



**Figure 1.** Structure of the Zn(1)<sub>2</sub> catalyst used for the polymer degradation reactions.

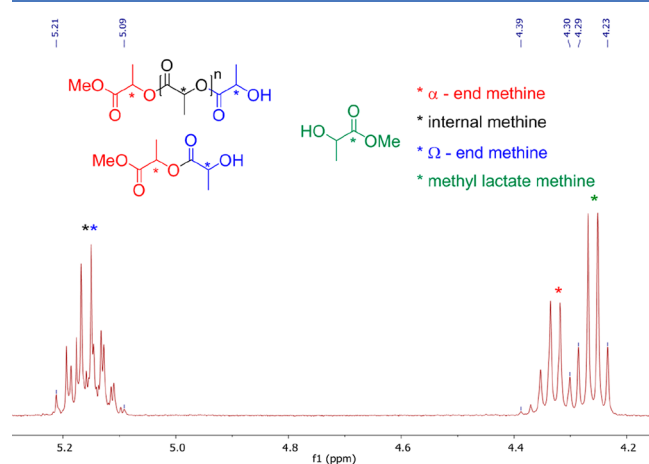
according to literature methods.<sup>46</sup> This complex was found to be highly active toward the solvent-free ring-opening polymerization (ROP) of LA and was synthesized on a large scale (25 g).<sup>46</sup> This complex was active for the solution polymerization of LA (80 °C, [LA]:[Zn]:[BnOH] = 100:1:1) (Table S2, Supporting Information). Under these conditions, polymerization was fast, with high conversion achieved within 5 min (*L*-LA, *k*<sub>app</sub> = 0.25 ± 0.02 min<sup>-1</sup>) (Figure S1). However, this is unremarkable compared to other Zn(II) complexes featured in the literature.<sup>47–52</sup> Analogous activity was observed for the polymerization of *rac*-LA, with atactic PLA being prepared. Good molecular weight control is achieved for both LA monomers, with narrow distributions being observed (*D* = 1.04–1.11). There is also a linear increase of molecular weight with conversion, further demonstrating controlled polymerization (Figure S2).

Typically, at the end of the polymerization, reactions are quenched and washed with MeOH to deactivate the catalyst and remove unreacted monomer. The washing of polymer derived from *rac*-LA (amorphous P-*D/L*-LA), yielded a viscous liquid rather than the expected solid polymeric material. Analysis by gel permeation chromatography (GPC) showed a broadening of the distribution toward lower molecular weight, demonstrating the degradation activity of Zn(1)<sub>2</sub> (Figure S3). The increase in crystallinity of polymers derived from *L*-LA (semicrystalline PLLA) meant that washing with MeOH afforded only a slight broadening in dispersity with no shift in peak position. This is attributable to the reduced solubility of this polymer. However, dissolution of polymer in CH<sub>2</sub>Cl<sub>2</sub> and addition of MeOH caused degradation as indicated by GPC analysis (Figure S4). <sup>1</sup>H NMR spectroscopic analysis identified degradation products, with assignments based on previous work.<sup>32,53,54</sup> Resonances due to Me-La were identifiable in the <sup>1</sup>H NMR spectra as well as an increased number of resonances due to chain-end groups (Figure S7 for a representative spectrum). GC analysis revealed the degradation of PLA into several intermediates (Figure S20) presumed to be oligomers of varying chain lengths.

**Catalyst Stability.** The stability of Zn(1)<sub>2</sub> with respect to degradation products (Me-La and MeOH) was assessed via <sup>1</sup>H NMR spectroscopy (Figures S5 and S6). The stability of Zn(1)<sub>2</sub> toward LA and PLA has previously been demonstrated.<sup>46</sup> The addition of reactants were carried out in air, to mimic the large-scale testing. To test the stability of Zn(1)<sub>2</sub> to atmospheric conditions, a solid sample was stored under ambient conditions for 2 days before a <sup>1</sup>H NMR spectrum was recorded. The resonances of the complex were unchanged after exposure to air, suggesting Zn(1)<sub>2</sub> is stable to moisture/oxygen in the solid-state. Upon the addition of MeOH to Zn(1)<sub>2</sub>(2 equiv), a slight shift in resonances was observed but there was

no evidence of alcoholysis or formation of ligand (Figure S5). The MeOH resonances were very slightly shifted upfield relative to a spectrum of pure MeOH, suggesting no significant interactions with the Zn(II) center. A similar observation is noted for LA in the presence of Zn(1)<sub>2</sub>.<sup>46</sup> Addition of Me-La had a similar result with a slight shift in resonances of the complex. Once more, the Me-La resonances are slightly shifted upfield, suggesting no major interactions with the metal complex. These results indicate that Zn(1)<sub>2</sub> remains intact in the presence of both MeOH and Me-La. We therefore suggest that the ligand remains coordinated to the zinc center; however, there is the potential for the amine to become uncoordinated from the metal during degradation.

**Preliminary Laboratory-Scale Studies.** Different commercial samples of PLA have been used to further test the application of Zn(1)<sub>2</sub> to control the degradation. As shown by attempts to degrade laboratory-prepared PLLA, solvent choice is crucial. Tetrahydrofuran (THF), acetone, and 2-methyl-THF (2-MeTHF) were screened, whereas MeOH was used as the alcohol for transesterification. The use of chlorinated solvents was discounted to increase the *green* credentials of the process. Initial experiments were performed using a Vegware PLA cup sample (Table S1), which represents a relatively low molecular weight, yet commercially applicable, polymer ( $M_n = 45\,150$ ). For these experiments, an inert atmosphere (Ar) was used. Polymer (0.25 g) and catalyst (8 wt %) were dissolved in solvent (4 mL) and degradation was carried out initially at 40 °C with MeOH (1 mL) added at the temperature; this corresponds to 7 equiv of MeOH per ester linkage. Gentle heating was required to aid polymer dissolution. At room temperature a decrease in molecular weight was observed via GPC, but only small amounts of degradation products were produced according to <sup>1</sup>H NMR spectroscopy. At 40 °C, degradation required more than 15 h to achieve a high yield of Me-La. Reaction progress was assessed by taking aliquots for <sup>1</sup>H NMR spectroscopic (CDCl<sub>3</sub>) analysis. A virtual concentration of methine functional groups was measured as a relative percentage. The methine protons were considered to be in one of three different environments: methyl lactate (Me-La) (4.23–4.29 ppm), chain-end (CE) (4.30–4.39 ppm/5.09–5.21 ppm), and internal (Int) (5.09–5.21 ppm) (Figure 2, Figure S7). Because of the high molecular weight of the polymer samples tested, it is initially assumed that the polymer



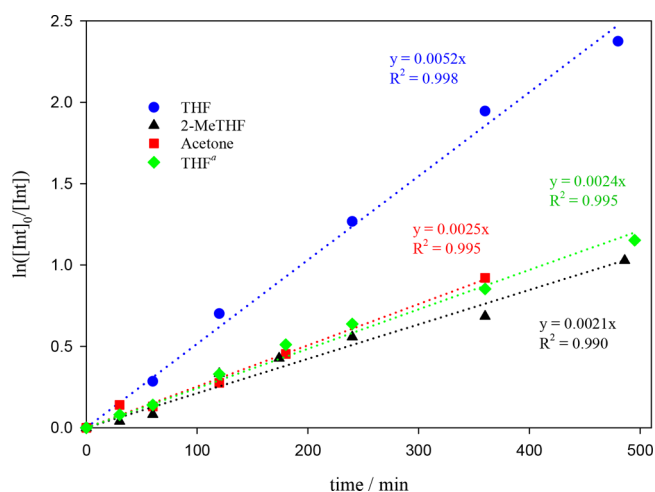
**Figure 2.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) assignment of internal, chain-end, and methyl lactate methine groups.

can be represented exclusively by internal methine groups. Accordingly, as degradation proceeds, there is an initial increase in chain-end methine concentration concomitant with a decrease in internal methine concentration. Because of further reaction to Me-La, this chain-end concentration generally achieves a maximum value followed by a reduction period consistent with an intermediate reaction profile. After 6 h of reaction, THF achieved the highest percentage of desired product Me-La ( $Y_{\text{Me-La}} = 29\%$ ). Acetone and Me-THF yielded a similar conversion to lactate ( $Y_{\text{Me-La}} = 16\text{--}18\%$ ). The consumption of internal methine groups, Int, could be described by first-order kinetics (Table 1, Figure 3). The

**Table 1.** PLA Cup Degradation with Zn(1)<sub>2</sub> in Different Solvents<sup>a,b,c</sup>

solvent	$X_{\text{Int}}$ (%)	$S_{\text{Me-La}}$ (%)	$Y_{\text{Me-La}}$ (%)	$k_{\text{app}} \times 10^3$ (min <sup>-1</sup> )
THF	86	33	29	5.2 ± 0.3
2-MeTHF	50	36	18	2.1 ± 0.2
acetone	60	27	16	2.5 ± 0.2
THF <sup>d</sup>	27	38	10	
THF <sup>e</sup>	57	22	12	2.4 ± 0.1
none <sup>f</sup>	97	61	63	

<sup>a</sup>Reaction conditions: 0.25 g of PLA cup (Vegware), 40 °C,  $V_{\text{Solvent}}:V_{\text{MeOH}} = 4:1$ ,  $[\text{Zn}(1)_2] = 8$  wt % = 1 mol % relative to ester linkages,  $n_{\text{MeOH}}:n_{\text{ester}} = 7:1$ . <sup>b</sup>Internal methine group conversion ( $X_{\text{Int}}$ ), Me-La selectivity ( $S_{\text{Me-La}}$ ), and Me-La yield ( $Y_{\text{Me-La}}$ ) determined at 360 min by <sup>1</sup>H NMR. <sup>c</sup>Apparent rate constant ( $k_{\text{app}}$ ) obtained from concentration versus time plot (Figure 3). <sup>d</sup> $[\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}] = 8$  wt % = 3 mol % relative to ester linkages. <sup>e</sup> $[\text{Zn}(1)_2] = 4$  wt % = 0.5 mol % relative to ester linkages. <sup>f</sup>130 °C,  $V_{\text{MeOH}} = 1$  mL, 30 min,  $[\text{Zn}(1)_2] = 16$  wt % = 2 mol % relative to ester linkages.



**Figure 3.** Pseudo-first-order plots for the degradation of a PLA Vegware cup with Zn(1)<sub>2</sub> in different solvents (Table 1). <sup>a</sup> $[\text{Zn}(1)_2] = 4$  wt %. NB. Line of best fit constrained to pass through origin; it is noted that there is negligible induction period.

relative rate constants for this process also indicate degradation in THF to be the most efficient solvent for this process (Table 1). As a comparison, the degradation was carried out using Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O under identical conditions (8 wt %); the conversion of PLA and yield of Me-La were significantly lower compared to Zn(1)<sub>2</sub> ( $X_{\text{Int}} = 27\%$ ,  $Y_{\text{Me-La}} = 10\%$ ) (Table 1). The activity of Zn(1)<sub>2</sub> is superior despite the fact that the concentration of Zn(II) is almost one-third of that for Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O. Kinetic analysis was attempted using time-

dependent GPC measurements. However, for the majority of conditions, oligomers are generally produced within the first or second recorded samples. However, for an experiment with a low catalyst loading (4 wt % Zn(1)<sub>2</sub> using the PLA cup) the reduction of molecular weight could be followed by GPC. These results demonstrated a fast initial decrease of molecular weight followed by a period of slower molecular weight reduction (Figure S8). This is likely related to the increasing number of (smaller) chains formed as degradation proceeds. This technique has not been used further as subsequent degradation conditions cause a more rapid decrease in molecular weights which were not readily measured. Also from these conditions (40 °C, 4 wt %), MALDI-ToF was also used to demonstrate the presence of oligomers ( $n \sim 8$ ), which had the expected MeO-/-H end groups due to transesterification (Figure S10).

The degradation of PLA by Zn(1)<sub>2</sub> was also carried out under solvent-free conditions, with a catalyst loading of 16 wt %. In this case it was necessary to use a temperature of 130 °C to completely dissolve the polymer in only MeOH. High conversion of PLA was observed within 30 min with reasonable selectivity to Me-LA ( $X_{\text{Int}} = 97\%$ ,  $Y_{\text{Me-LA}} = 63\%$ ), further demonstrating the applicability of this system.

Nevertheless, THF was the solvent of choice for the purposes of carrying out experimental design and reaction kinetics. An additional experiment at 50 °C, to aid polymer dissolution, was performed. Degradation of the PLA cup was faster under these conditions ( $\{k_{\text{app}} = (8.9 \pm 0.2) \times 10^{-3} \text{ min}^{-1}\}$  (Table 2). With the aim to demonstrate the versatility

**Table 2. Degradation of Different PLA Samples with Zn(1)<sub>2</sub>**<sup>ab,c,d</sup>

PLA sample	$X_{\text{Int}}$ (%)	$S_{\text{Me-LA}}$ (%)	$Y_{\text{Me-LA}}$ (%)	$k_{\text{app}} \times 10^3$ (min <sup>-1</sup> )
cup (45 150)	85	45	38	10 ± 1
2500HP (71 900)	83	39	32	9.1 ± 1.3
4043D (61 900)	86	48	41	12 ± 1
6060D (71 700)	88	39	35	11 ± 2
6202D (44 350)	82	39	32	8.2 ± 0.9

<sup>a</sup>The numbers in parentheses represent the experimental (GPC) recorded molecular weight ( $M_n$ ) of the polymer. <sup>b</sup>Reaction conditions: 0.25 g of PLA, 50 °C,  $V_{\text{THF}}:V_{\text{MeOH}} = 4:1$ ,  $[\text{Zn}(1)_2] = 8 \text{ wt \%} = 1 \text{ mol \%}$  relative to ester linkages,  $n_{\text{MeOH}}:n_{\text{ester}} = 7:1$ . <sup>c</sup>Internal methine group conversion ( $X_{\text{Int}}$ ), Me-LA selectivity ( $S_{\text{Me-LA}}$ ), and Me-LA yield ( $Y_{\text{Me-LA}}$ ) determined at 180 min by <sup>1</sup>H NMR. <sup>d</sup>Apparent rate constant ( $k_{\text{app}}$ ) obtained from semilogarithm plot.

of the degradation process using Zn(1)<sub>2</sub>, four different PLA commercial samples from NatureWorks (Table S1) comprising different molecular weights and a wide spectrum of industrial applications (extrusion, thermoforming, films, and fibers) were utilized. The samples were ground to reduce their particle size to 3 mm to assist dissolution. GPC analysis after particle size reduction showed no change to the molecular weight and dispersity of the polymer samples. Initially, the rate of degradation was determined and was found to be independent of the polymer molecular weight (Table 2). For the concentration time plots there is a small induction period before the production of Me-LA. GPC sampling early in the reaction shows a rapid decrease in molecular weight, which also prevents the measurement of kinetics from this technique. It is therefore suggested that the degradation reaction occurs via a random chain scission rather than scission at the chain

end. This is also supported by the increase in percentage of chain-end groups, as measured by <sup>1</sup>H NMR spectroscopy, in the initial stages of degradation.

**Design of Experiments.** Since the preliminary studies showed a dependency of reaction variables, a Taguchi design of experiments<sup>55</sup> was employed to explore the effect of operating parameters on the degradation of PLA and the production of Me-LA. All reactions were performed in a 300 mL reactor, as detailed in the Supporting Information, with the aim to demonstrate scalability of the process. The main variables (factors) identified for the study were as follows: (i) PLA grade, corresponding to the four different PLA commercial samples from NatureWorks; (ii) PLA concentration (0.05–0.2 g mL<sup>-1</sup>); (iii) reaction temperature (40–130 °C); and (iv) catalyst concentration (4–16 wt % with respect to PLA concentration). Additionally, and to determine any mass-transfer limitations, the following factors were also studied: (v) PLA particle size (two sizes were tested, the ~5 mm size of the polymer beads, as received, and 3 mm size); and finally (vi) stirring speed (300 and 700 rpm). The factors and their corresponding levels can be found in Table S3. The resulting orthogonal array was a mixed level L16 design (Table 3). The responses (outcomes) were as follows: (i) PLA conversion, as represented by the concentration of internal methine groups; (ii) Me-LA selectivity; (iii) Me-LA yield; and (iv) maximum concentration of Me-LA (Table 3). The first three responses were determined after 60 min of reaction to set a frame for comparison.

An analysis of variance (ANOVA) for the means of the responses showed a high relationship between the chosen parameters and the responses as values of  $R^2 > 99.5\%$  were obtained for all the dependent variables (shown in the Supporting Information).

The means effects plots (Figures S11 and S13–S15) and their corresponding Tables (Tables S7, S10, S13, and S16) present the influence of the operating parameters on the responses. In conjunction with ANOVA, it can be concluded that the strongest associations ( $F_{\text{critical-value}} > 6.25$ ) on yield of Me-LA are temperature and catalyst concentration (the statistical significance was set to  $P < 0.1$ ). Selectivity of Me-LA is associated with only temperature whereas conversion is mainly affected by temperature (60% contribution effect) followed by catalyst concentration and PLA particle size (11% and 13% respectively) (Figure S12). The PLA grade used only show statistical association on this response (8%). For the case of the maximum Me-LA concentration (Table S15), the only determining factor is the initial concentration of PLA, as expected. The stirring speed and the size of the polymer particles do not have any influence on Me-LA selectivity and yield at the conditions tested, suggesting no mass-transfer limitations of the process.

The PLA particle size influenced only two experiments at 40 °C (entries 1 and 16 in Table 3) for which the largest particle size was used. The reaction at this temperature is relatively slow; the Me-LA plateau was reached after 171 and 98 h for entries 1 and 16, respectively (Table S4). Although Me-LA was in fact detected after just 60 min of reaction by GC, it is possible that not all the PLA was completely dissolved at this time and therefore the sample is not representative of the PLA concentration. The concentrations for these two entries were estimated from the kinetic model to be detailed in the next section. Conversely, certain reactions were relatively fast as

**Table 3. Experimental Design (L16) for the Study of PLA Grade, PLA Concentration ([PLA]), Temperature (T), Catalyst Concentration ([Cat.]), Stirring Speed (Stir.), and Their Effects on Int Conversion<sup>a</sup> (X<sub>Int</sub>), Me-La Selectivity<sup>a</sup> (S<sub>Me-La</sub>), Me-La Yield<sup>a</sup> (Y<sub>Me-La</sub>), and Maximum Me-La Concentration (Max. [Me-La])<sup>b</sup>**

entry	PLA grade	[PLA] (g mL <sup>-1</sup> )	T (°C)	[Cat.] (wt %)	PLA size (mm)	Stir. (rpm)	X <sub>Int</sub> (%)	S <sub>Me-La</sub> (%)	Y <sub>Me-La</sub> (%)	Max. [Me-La] (g mL <sup>-1</sup> )
1	2500HP	0.05	40	4	5	300	3	2	0	0.05
2	2500HP	0.1	60	8	5	700	71	38	27	0.13
3	2500HP	0.15	90	12	3	300	100	90	90	0.17
4	2500HP	0.2	130	16	3	700	100	92	92	0.21
5	6060D	0.05	60	12	3	700	93	51	47	0.06
6	6060D	0.1	40	16	3	300	76	32	24	0.12
7	6060D	0.15	130	4	5	700	100	92	92	0.19
8	6060D	0.2	90	8	5	300	98	73	72	0.21
9	4043D	0.05	90	16	5	700	100	100	100	0.07
10	4043D	0.1	130	12	5	300	100	96	96	0.12
11	4043D	0.15	40	8	3	700	62	27	17	0.15
12	4043D	0.2	60	4	3	300	45	20	9	0.21
13	6202D	0.05	130	8	3	300	100	100	100	0.06
14	6202D	0.1	90	4	3	700	92	52	48	0.14
15	6202D	0.15	60	16	5	300	80	45	36	0.17
16	6202D	0.2	40	12	5	700	8	7	1	0.22

<sup>a</sup>Determined at 60 min of reaction. <sup>b</sup>X<sub>Int</sub>, S<sub>Me-La</sub>, and Y<sub>Me-La</sub> for entries 1 and 16 were computed from the kinetic model.

shown for instance in entry 13, where 100% conversion was reached before 15 min (Table S4).

**Kinetic Modeling.** The results of the preliminary laboratory-scale studies and the design of experiments revealed a first-order reaction in PLA decomposition and a characteristic profile for a reversible reaction for the intermediate. A reaction mechanism was therefore proposed consisting of two consecutive first-order reactions: in the first step, internal methine groups undergo transesterification to become chain-end groups; in a second step, the chain-end groups convert to Me-La through a reversible reaction (eq 1) in agreement with literature studies on the conversion of lactides into ethyl lactates.<sup>53</sup> The excess alcohol was not included in the model. The rate equations (presented in the Supporting Information) were solved numerically coupled with a nonlinear square fitting procedure to compute the kinetic constants at the conditions tested (Table 4).

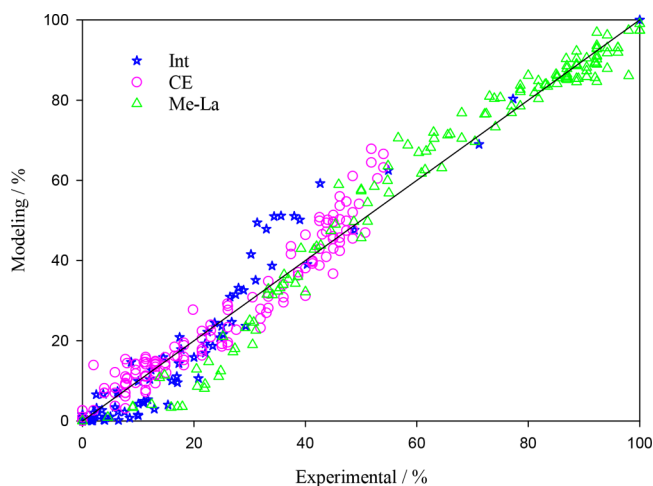


A parity plot for the experimental and modeling data is presented in Figure 4, whereas examples of the modeling predictions are displayed in Figure 5. Both figures show a good agreement between experimental and modeling data. The representation was best for the PLA degradation, for which the overall mean absolute errors was estimated as 2.56 (Table S17). The model also represents well the intermediates concentration (absolute error of 3.48) considering that all intermediate products were just grouped into this category. Although a more robust kinetic model can be obtained by determining the nature of other intermediates, and by proposing for instance side reactions, the mechanism presented here could be considered as a suitable approximation for engineering purposes.

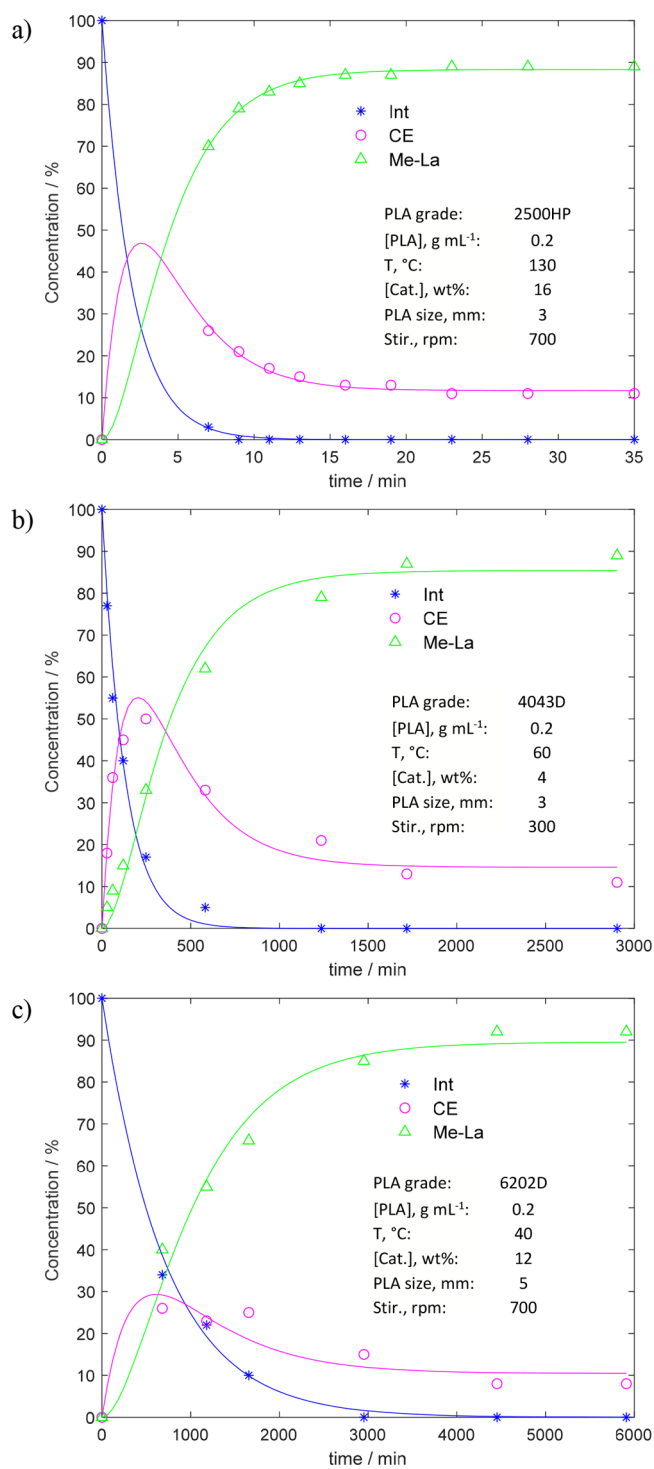
Figure 5 also exemplifies how the reaction rate changes under different conditions. For instance, while the reaction at the conditions given in entry 4, Table 3 (Figure 5a) is completed in around 25 min, at the settings given in entry 12 (Figure 5b) the reaction seems to be completed at around 2000 min.

**Table 4. Kinetic Constants and Calculated Time Required for 99% PLA Conversion (tx<sub>PLA=99%</sub>)**

entry	k <sub>1</sub> × 10 <sup>1</sup> (min <sup>-1</sup> )	k <sub>2</sub> × 10 <sup>2</sup> (min <sup>-1</sup> )	k <sub>-2</sub> × 10 <sup>3</sup> (min <sup>-1</sup> )	tx <sub>PLA=99%</sub> (min)
1	0.005 ± 0.0008	0.07 ± 0.02	0.11 ± 0.09	9044
2	0.19 ± 0.03	0.95 ± 0.21	1.72 ± 0.98	246
3	1.53 ± 0.13	7.5 ± 0.5	8.72 ± 2.57	30
4	5.17 ± 0.79	30.5 ± 2.6	37.9 ± 4.38	9
5	0.84 ± 0.14	1.6 ± 0.30	2.22 ± 1.47	55
6	0.23 ± 0.05	0.45 ± 0.1	0.72 ± 0.53	196
7	1.60 ± 0.15	11.3 ± 1.15	10.1 ± 3.5	29
8	1.05 ± 0.13	4.0 ± 0.5	6.59 ± 2.38	44
9	1.92 ± 0.13	10.9 ± 0.75	0.66 ± 0.17	24
10	3.01 ± 0.27	87.8 ± 24.7	65.6 ± 23.7	15
11	0.11 ± 0.03	0.23 ± 0.06	0.20 ± 0.19	411
12	0.08 ± 0.008	0.31 ± 0.05	0.54 ± 0.18	587
13	3.94 ± 1.07	28.9 ± 5.4	7.62 ± 5.28	12
14	0.41 ± 0.03	2.4 ± 0.3	4.92 ± 2.01	112
15	0.31 ± 0.04	1.5 ± 0.3	2.53 ± 1.20	150
16	0.01 ± 0.002	0.23 ± 0.05	0.27 ± 0.12	3293



**Figure 4.** Parity plot for the experimental and modeling data.



**Figure 5.** Experimental (symbols) and modeling (lines) results for conditions in Table 3: (a) entry 4, (b) entry 12, and (c) entry 16.

To further exemplify the differences between the operating parameters tested, the time necessary to convert 99% of PLA was estimated from the kinetic model (Table 4). This high level of conversion can be achieved in less than 12 min under appropriate combinations of temperature and catalyst concentration (as shown in entries 4 and 13). In a comparison of entry 4 with the preliminary laboratory-scale studies in which no solvent was employed, it is appreciated that the use of a solvent reduces considerably the time needed to reach a desired yield. An estimated  $Y_{\text{Me-La}} = 78\%$  is obtained at 9 min,

compared to 63% achieved at 30 min without solvent under the same conditions.

An initial estimation of the activation energy ( $E_a$ ) for the degradation step ( $k_1$ ) was calculated for the low, high, and intermediate catalyst concentrations considering that the main contributions to the process are given by temperature and catalyst concentration and assuming an Arrhenius-type temperature dependency. The  $E_a$  values were 65, 44, and 39 kJ mol<sup>-1</sup> for the 4, 8, and 16 wt % concentrations, respectively (Figure S16). The measured activated energies are of the same magnitude as those found for hydrolytic degradation despite the use of milder conditions.<sup>23–25</sup> The results of the calculated activation energies serve to validate the results of the experimental design showing no mass-transfer limitations.<sup>56</sup> A decrease in activation energy by increasing the amount of catalyst is observed.

## CONCLUSIONS

Zn(1)<sub>2</sub>, an initiator that has previously shown to be active for the production of PLA, is employed in this study for the production of Me-La from the degradation of PLA, therefore providing an opportunity for the chemical recycling of end-of-life PLA. The PLA samples studied were commercial samples covering a wide range of applications, demonstrating the versatility of the system. The main operating parameters affecting the process were temperature and catalyst concentration, which were identified through a design of experiments with further statistical analysis. The overall process did not show mass-transfer limitations due to particle size or stirring speed. A kinetic model for the formation of Me-La that takes into account the formation of intermediates showed a good agreement with the experimental data. The computed kinetic constants of the model can be used for reactor design and scale-up of this process. Estimates of the activation energy for the degradation step were calculated and were found to be competitive with those derived from hydrolytic degradation.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b04863.

General considerations, polymerization procedure and data, catalyst stability, small-scale degradation reactions, large-scale degradation reactions, experimental data, ANOVA results (Int conversion, Me-La selectivity, Me-La yield, and maximum Me-La concentration), kinetic model, and further degradation characterization PDF)

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## Notes

The authors declare no competing financial interest. Data sets associated with this work are available free of charge at <http://epapers.bham.ac.uk>.

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