

Review

The Chemical Recycling of PLA: A Review

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Abstract: Plastics are an indispensable material with numerous benefits and advantages compared to traditional materials, such as glass and paper. However, their widespread use has caused significant environmental pollution and most plastics are currently nonrenewable. Biobased polymers represent an important step for tackling these issues, however, the end-of-life disposal of such materials needs to be critically considered to allow for a transition to a circular economy for plastics. Poly(lactic acid) (PLA) is an important example of a biobased polymer, which is also biodegradable. However, industrial composting of PLA affords water and carbon dioxide only and in the natural environment, PLA has a slow biodegradation rate. Therefore, recycling processes are important for PLA, particularly chemical recycling, which affords monomers and useful platform chemicals, maintaining the usefulness and value of the material. This review covers the different methods of PLA chemical recycling, highlighting recent trends and advances in the area.

Keywords: poly(lactic acid); plastic recycling; chemical recycling; circular economy

1. Introduction

The majority of plastics, that as a society we rely on, are sourced from petroleum-based resources, with only a fraction currently being derived from renewable feedstocks. In 2015, 380 million metric tons of plastic was produced globally, with less than 1% of this production being derived from a bio-based source [1]. This is of particular concern as the use of petroleum resources is associated with global pollution and climate change, as well as being a finite resource [2]. To mitigate these issues, a transition towards bio-based plastics is needed, especially considering the increasing demand for such materials. Based on the present rate of growth, plastic production is predicted to double within the next 20 years [3]. A further issue currently associated with plastic usage is the pollution that is caused by end-of-life mismanagement. Plastic pollution is particularly a problem in marine environments, where it has a tendency to accumulate and persist [4–6]. The application of plastics in everyday life has undeniable advantages and societal benefits [7–9], however, their concerns need to be urgently addressed to make plastic usage sustainable. Therefore, as well as a shift towards biobased materials, there is a necessity to consider the end-of-life treatment of these materials and ensure there are efficient routes of disposal available. The current use of plastics follows a linear model, whereby plastics are prepared, used, and disposed, and this is especially true, as well as problematic, for single-use plastics [10,11]. The future of plastic use needs to be based on a circular model, whereby the value of the material is retained after its useful lifetime [10,12,13].

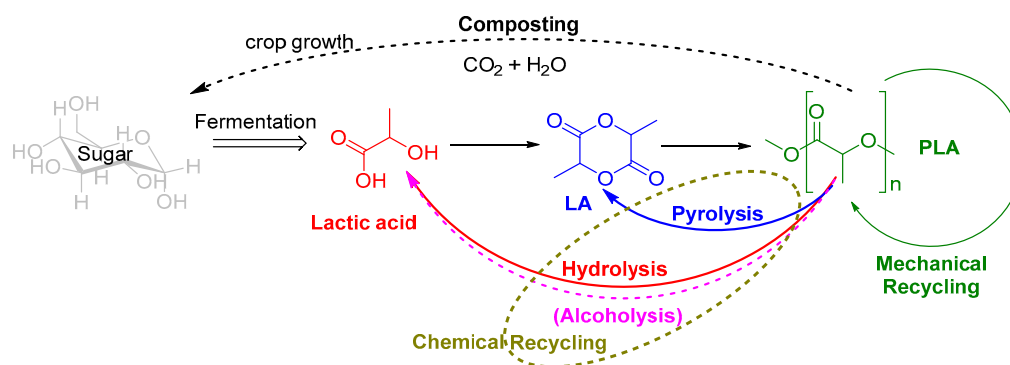
Poly(lactic acid) (PLA) is a bio-based polymer, which has received extensive attention, both in academia and industrially in the last 20 years. The main constituent, lactic acid, is derived, through fermentation, from renewable feedstocks such as food crops (corn) as well as waste sugars (cellulosic material) [14,15]. Compared to petroleum-based plastics, PLA is currently more expensive due to increased production costs associated with the fermentation and purification of LA, which accounts for approximately 50% of the total cost [16,17]. The polymerisation to PLA

is preferentially achieved from the cyclic dimer, lactide (LA), rather than the polycondensation of lactic acid, which is limited by the need to remove water and generally leads to the isolation of PLA with inferior qualities. The formation of LA from lactic acid is traditionally a two-step process, requiring oligomerisation prior to depolymerisation and “backbiting” processes, which generates the cyclic molecule. This process can contribute up to 30% of the total cost of the preparation of PLA [17]. Therefore, to reduce the PLA cost, research has been devoted to the formation of LA, with the aim to produce the dimer directly, in one step [18–24]. The ring opening polymerisation (ROP) of LA has the benefit of not releasing water during propagation, potentially allowing for a high molecular weight (M_n) PLA to be formed. A common mechanism of ROP is the coordination-insertion pathway, typically facilitated by a metal alkoxide complex [25–28]. Both lactic acid and LA possess chirality, which is an important consideration in both their respective production and the preparation of PLA [16].

The properties of PLA make it useful for applications such as food and packaging materials [29–32]. The stability of PLA, towards hydrolysis, has recently been assessed for use in food packaging applications [33]. PLA is also considered biocompatible, and has found use as biomedical implants such as stents [34–38]. PLA is a commercially available polymer, being produced on a large scale with a low carbon footprint [39–42].

Despite the advantageous property of being renewably sourced, the mismanagement of end-of-life PLA still contributes to plastic pollution. The reports of PLA being biodegradable often lead to a misunderstanding that such material will degrade readily in the natural environment. The issue is complicated by the variable test conditions and environments, that can lead to contradictory reports as to the biodegradability of PLA [43]. In soil or domestic composters, degradation can take up to a year with temperatures of 20 °C, however, higher local temperatures (>25 °C) can lead to degradation within 12 weeks [44,45]. The degradation of PLA in marine environments can also be challenging to study due to a wide range of variables and conditions that need to be considered. Under laboratory conditions to mimic static seawater no degradation of PLA was observed within a year [46–48], however, in a simulated dynamic seawater environment, polymer weight loss was observed via mechanical processes [49]. Under accelerated conditions to mimic an extended time in landfill, PLA does not degrade at ambient temperatures, and therefore, does not contribute to methane gas emission [50].

When collected for end-of-life disposal, there are various options for PLA (Scheme 1). However, the first step is the identification and separation of PLA from other plastics. A common issue is the contamination of polyethylene terephthalate (PET) and PLA waste streams as these plastics can be indistinguishable to the naked eye. For PET, the presence of PLA during the recycling process can severely reduce the resultant material properties of the reformed PET [51–53]. Near infrared imaging is a potential solution to differentiate between these materials [54].



Scheme 1. Poly(lactic acid) (PLA) formation and potential end-of-life scenarios. Note: alcoholysis generates an alkyl lactate (A-La).

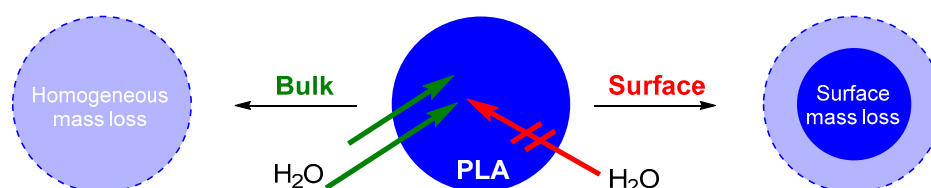
PLA can be efficiently composted under industrial conditions, requiring temperatures around that of the polymer's T_g (60 °C) and high relative humidity [55–58]. Degradation can take as little as 30 days under such conditions [55,59]. The products of composting are CO₂ and water, the amount of carbon dioxide emitted being offset by the initial uptake in the production of PLA feedstocks [40]. The mechanical recycling of PLA is a process in which the material is collected, washed, and reprocessed with the aim of maintaining the original properties. Reprocessing is typically achieved thermally and this can impair the properties of the next generation of the material [60–62]. Through thermo-chemical degradation pathways, the molecular weight of the polymer is often reduced, preventing the use of the material in the same application and therefore, downgrading to a less demanding use. A recent study has considered the reuse of 3D printed PLA material in a closed-loop recycling process [63]. After two use and reprocessing cycles, it was demonstrated that the material had deteriorated sufficiently to prevent further use as a printing material. The blending of virgin PLA could allow for further reuse, but the number of cycles remains limited.

A further option is the chemical recycling of PLA. This process breaks the polymer down into constituent parts, either for direct repolymerisation or for other applications. An immediate benefit of this compared to composting is the recovery of valuable chemicals, which would have otherwise been lost as CO₂ [64]. A study has shown that it is more energetically favourable to attain lactic acid from chemical depolymerisation rather than to produce virgin feedstock from the costly fermentation route [65]. While mechanical recycling can extend the life of manufactured PLA, an efficient chemical recycling process could potentially immortalise it, allowing for consistent material properties from consecutive recycling. A further benefit of chemical recycling methods is that the process can be tolerant to contamination with other plastics, reducing the need for costly separation. For chemical recycling processes, an important consideration is the stereochemistry of the product. Most studies concern the use of enantiopure PLA based on the more common *L*-LA isomer (giving PLLA). It is vitally important that this stereochemistry is maintained in the product to avoid further separation/purification steps, which would increase the potential cost of the process. Despite the importance of stereochemistry, the optical purity of the products is not always measured. Where data is available, the stereochemical outcome will be highlighted.

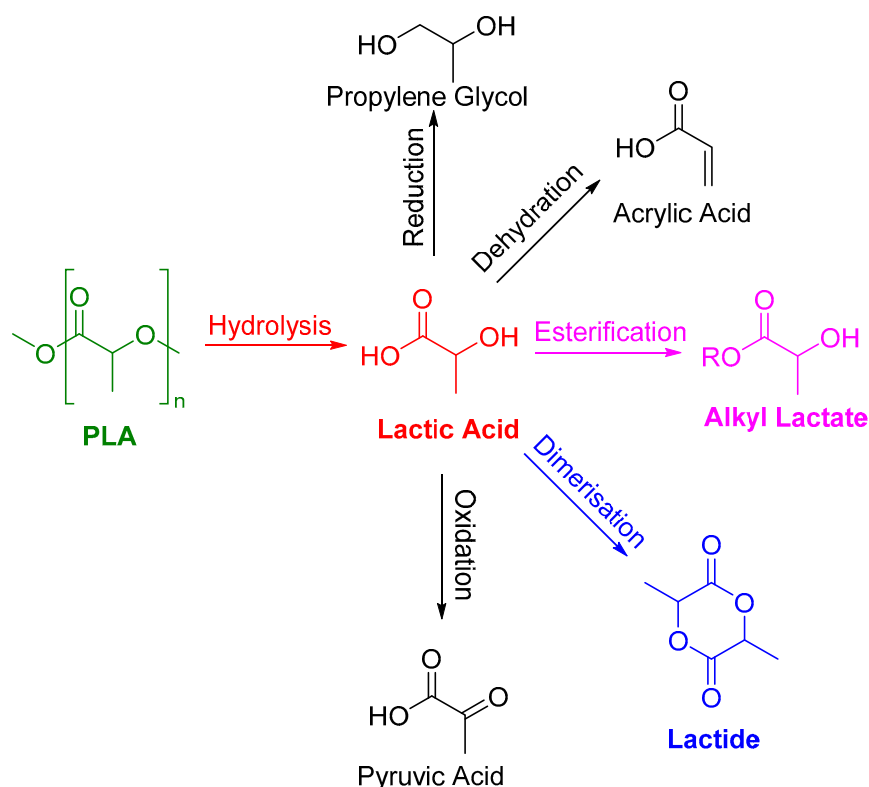
This review seeks to summarise the chemical recycling of PLA, with emphasis on the catalysts and conditions used. The transformations to lactic acid by hydrolysis and alkyl lactates by alcoholysis are highlighted, as well as transformations to other degradation products.

2. PLA Hydrolysis—To Lactic Acid

Due the solubility of PLA in aqueous media, hydrolysis can require high temperatures and/or strongly acidic/basic conditions. In aqueous systems, in which PLA has poor solubility, the hydrolysis can be achieved by bulk or surface erosion (Scheme 2) [66]. Which mechanism operates is dictated by the rate of water diffusion relative to bond breaking, which in-turn depends on molecular weight, polymer dimensions, pH, and temperature. For bulk erosion, in which water diffusivity is high, the polymer loses mass or molecular weight homogeneously across the whole sample whereas surface erosion involves increased degradation on the surface only. The product, lactic acid, is a platform chemical that can be transformed into a range of other valuable feedstocks (Scheme 3) [67].



Scheme 2. Mechanisms of heterogeneous hydrolysis of PLA. Adapted from [66].



Scheme 3. Hydrolysis of PLA and examples of further transformations. Note: similar transformations are possible from alkyl lactates. Adapted from [67].

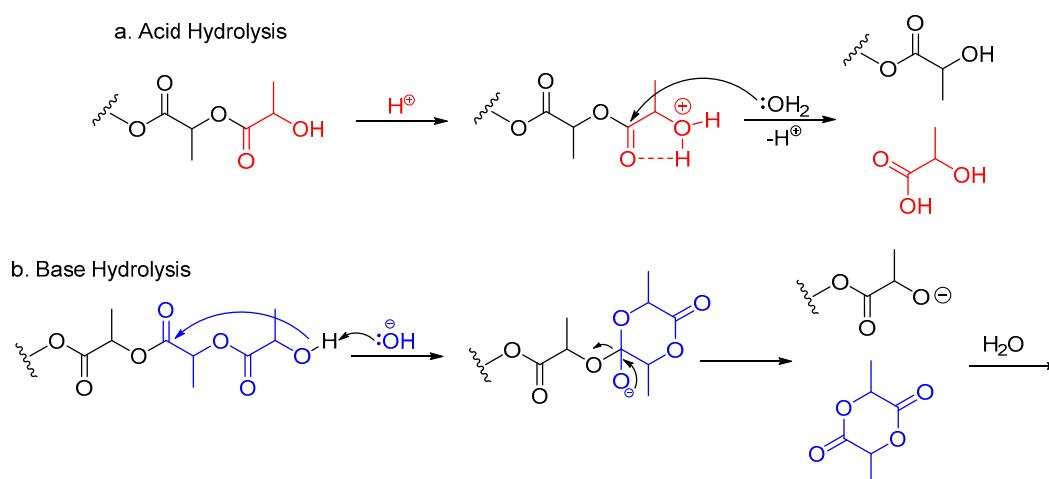
An initial study by Piemonte et al. considered the solubility of PLA in conventional organic solvents [68]. Between acetone and ethyl acetate, it was suggested that acetone was the most effective for solubilising the polymer. However, as water concentration increased, dissolution was reduced for both solvents.

Tsuji et al. have extensively studied the hydrolysis of PLA [69–75]. The initial investigation considered the hydrolysis of PLLA at a temperature range of 180–350 °C with a 5 wt% solution of PLA ($M_n = 170,000 \text{ g mol}^{-1}$) [69]. The optimum temperature for *L*-lactic acid yield was found to be 250 °C, achieving around 90% within 20 min. Between 180–250 °C, the activation energy for hydrolysis was 51.0 kJ mol^{−1}. Above this temperature, racemisation became more severe, being complete within 30 min at 300 °C. At 350 °C, there is evidence of lactic acid decomposition to give gases (CO₂, CO, CH₄). Regardless of temperature (120–250 °C) and the PLA state, (melt or solid), degradation is via bulk erosion mechanism, in which the rate of degradation is uniform throughout the material and not limited to the surface [70]. The activation energies for hydrolysis in the solid phase (120–160 °C, $E_a = 69.6 \text{ kJ mol}^{-1}$) and melt phase (170–250 °C, $E_a = 49.6 \text{ kJ mol}^{-1}$) have been evaluated. The degradation of stereoblock PLA and the effect of average block length has also been investigated [72]. This revealed rapid degradation of atactic segments with a decreased rate of hydrolysis for increasing stereoblock length. The temperature of hydrolysis could be reduced to 170 °C by the application of microwave heating, as demonstrated by Ohara et al. [76]. With conventional heating, 800 min are required to achieve the maximum lactic acid yield, which is achieved within 120 min with microwave irradiation. Under these conditions, however, only 45% yield of lactic acid is achievable before racemisation reduced its optical purity. A relatively concentrated solution of PLA was used ($M_n = 96,000 \text{ g mol}^{-1}$, 75 wt%). The hydrolysis of PLA ($M_n = 23,700 \text{ g mol}^{-1}$) using high pressure steam has also been investigated [77]. At relatively lower temperatures (100–130 °C), kinetic parameters were calculated based on different size exclusion chromatography analyses, with a universal calibration method giving the most reliable results ($E_a = 87.2 \text{ kJ mol}^{-1}$).

Piemonte and Gironi have further studied the kinetics of hydrolytic degradation of PLA from 140–180 °C, with PLA concentrations of 5–50 wt% [78,79]. It is surmised that 95% of PLA is converted to lactic acid within 120 min between 160–180 °C. A further finding was that the kinetic reaction rate was not dependent on the PLA concentration. The data collected suggests two distinct reaction mechanisms, the first being related to a two phase reaction ($E_a = 53.2 \text{ kJ mol}^{-1}$) and the second due to an autocatalytic effect ($E_a = 36.9 \text{ kJ mol}^{-1}$) of having increased carboxylic acid groups as the depolymerisation proceeds. This effect has been previously noted for PLA hydrolysis and decreases the pH of the solution [80]. Further work by this group has modeled the hydrolysis of PLA at higher temperatures (170–200 °C) [81]. The bulk erosion of PLA and subsequent aqueous oligomer hydrolysis is described by the kinetic model, allowing conversion and oligomer concentrations to be accurately predicted. A complete PLA conversion could be achieved within 90 min under these conditions.

The use of water-ethanol mixtures as a medium for PLA hydrolysis has been studied by Auras et al. [82,83]. This study was carried out above the T_g of PLA (40–90 °C) with a 50% ethanol solution. The inclusion of ethanol causes the polymer to swell, facilitating the sorption of water for hydrolysis. Hydrolytic degradation occurred by bulk hydrolysis with the activation energy being lower than for the use of water alone (EtOH/H₂O, $E_a = 93.4 \text{ kJ mol}^{-1}$; H₂O, $E_a = 101.4 \text{ kJ mol}^{-1}$). It was estimated that 41 h would be required to achieve a 95% yield of lactic acid at 90 °C, whereas to form oligomers suitable for repolymerisation, 29 h should be sufficient.

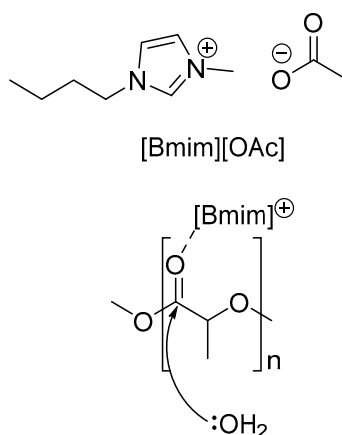
The pH dependence on PLA hydrolysis has also been reported [71,84–91]. The use of acid and base provides alternative mechanisms for the depolymerisation (Scheme 4a,b). Under acidic conditions, the PLA hydrolysis has been shown to be dominated by a chain-end scission, whereby the terminal hydroxyl group is activated by protonation and is hydrolysed directly to lactic acid [84,87,88]. In keeping with this mechanism, the rate of degradation was observed to be independent of chain length and this preference was due to the hydrophobicity of the polymer chain compared to the increased hydrophilicity of the chain end. In contrast, the use of basic conditions leads to a random chain scission via back biting reactions to generate LA, which is subsequently hydrolysed [86,89]. Accordingly, the nature of the hydroxyl terminal can dictate the kinetics of this process, with capping of the alcohol preventing this mechanism from operating. In acidic conditions, hydrolysis has been described by bulk erosion and for basic conditions, by surface erosion [91].



Scheme 4. Mechanisms for PLA hydrolysis via (a) acid catalysis and (b) base catalysis [86].

Relatively mild hydrolysis conditions have been achieved by Fusheng Liu et al., employing a range of ionic liquids as both solvent and catalyst [92]. [Bmim][OAc] was found to be the best candidate, allowing for a high conversion to lactic acid (up to 94%) at 130 °C within 2 h (Scheme 5). This ionic liquid has also been demonstrated for the glycolysis of PET [93]. The ionic liquid could partially solubilise the PLA (up to 40%; $M_n = 102,000 \text{ g mol}^{-1}$) with the ions potentially assisting

in the hydrolysis mechanism. To isolate the product, calcium carbonate was added to precipitate calcium lactate (up to 76%) and the ionic liquid could be reused up to seven times with no decrease in performance. This hydrolysis of PLA in the presence of [Bmim][OAc] had a relatively high activation energy (120–135 °C, $E_a = 133.9 \text{ kJ mol}^{-1}$).

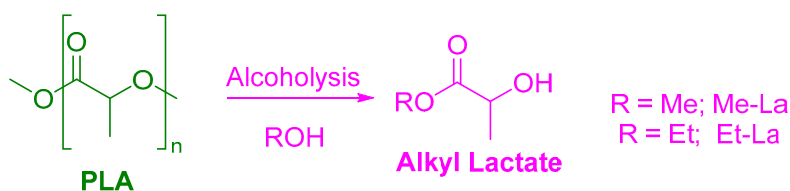


Scheme 5. Structure of [Bmim][OAc] used for PLA hydrolysis and activation of PLA [92].

Several patents with respect to PLA hydrolysis have been filed, the first example being in 1993. These have recently been reviewed by Niaounakis [94]. The reported procedures generally involve acid (H_2SO_4) or basic (NaOH , $\text{Ca}(\text{OH})_2$) catalyst, which can allow for depolymerisation under 100 °C. In the absence of catalyst, temperature can be as high as 350 °C. Water/alcohol mixtures and alkyl lactates are also reported as solvents.

3. Alcoholysis—To Alkyl Lactates

Alcoholysis of PLA has been most commonly performed with methanol to give methyl lactate (Me-La) (Scheme 6). Ethyl lactate is afforded by the alcoholysis of PLA with ethanol, and therefore, has the potential to be fully renewable. Methyl and ethyl lactate can be used as green solvents [95–100], with good biodegradability and low toxicity, [101] or as a potential platform to other chemicals. For example, alkyl lactates can be transformed into lactide [18,21,22], thus “closing the loop” on the PLA life-cycle. Indeed, transformations that can be applied to lactic acid can also be applied to alkyl lactates (Scheme 3) and in some cases better yields can be afforded by the initial use of esters [67].



Scheme 6. Alcoholysis of PLA to give alkyl lactates.

In the patent literature, there are several examples of alcoholysis reactions of PLA [94]. Examples of catalysts include acid (H_2SO_4) and solid acids (Montmorillonite K10, Nafion-H, CaO). A range of solvents have been disclosed including ionic liquids, alcohols, toluene, alkyl lactates, and chloroform.

The utility of degrading PLA to lactates has been noted as early as 1945 [102]. In this study, a range of acid catalysts were used as well as ZnCl_2 with temperatures up to 150 °C. In the absence of catalyst, Ohara et al. have demonstrated the alcoholysis of PLLA ($M_n = 96,000 \text{ g mol}^{-1}$) with the assistance of microwave heating [103]. Both ethanol and butanol were used to produce ethyl and butyl lactate, respectively with a temperature range of 130–210 °C. A greater reaction rate was achieved compared

to conventional heating, but the activation energies and mechanisms are judged to be identical (EtOH, $E_a = 113.1 \text{ kJ mol}^{-1}$). While increasing the rate, the use of microwave irradiation did not increase the amount of racemisation.

A range of studies have been performed using commercially available metal salts for the alcoholysis of PLA. Carné Sánchez and Collinson have demonstrated the use of $\text{Zn}(\text{OAc})_2$ for the alcoholysis of PLA [104]. Both methanolysis and ethanolysis were performed at the boiling point of the respective alcohols. The formation of Me-La was observed to be more facile, with a 70% yield after 16 h. The formation of $\text{Zn}(\text{lactate})_2$ during the degradation was indicated by IR spectroscopy. In the presence of an equal mass of PET, the degradation of PLA proceeded to a similar yield (65%) with PET remaining unreacted and amenable to separation by filtration.

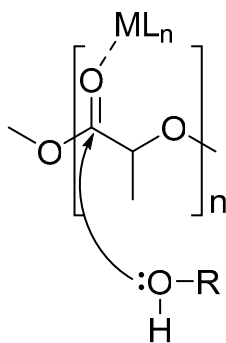
Fusheng Liu et al. have applied ferric chloride (FeCl_3) to the methanolysis of PLA pellets ($M_n = 102,000 \text{ g mol}^{-1}$) [105]. The process was performed in the absence of solvent at 130°C for 4 h. After removal of methyl lactate by distillation, the catalyst residue was reused directly. The PLA conversion and Me-La yield was maintained with up to six reuses of the catalyst. A relatively low activation energy was found for this system ($110\text{--}135^\circ\text{C}$, $E_a = 32.4 \text{ kJ mol}^{-1}$). The authors also report the use of ZnCl_2 , $\text{Zn}(\text{OAc})_2$, $\text{Zn}(\text{Octanoate})_2$, AlCl_3 , NaOAc , NaOH , and NaOMe under identical conditions and these catalysts also generally achieve a high PLA conversion and lactate yield. Sobota et al. have also tested a range of commercial metal catalysts for the solvothermal alcoholysis of PLA ($M_n = 64,200\text{--}115,700 \text{ g mol}^{-1}$) [106]. In the first instance, the reaction was performed in the absence of a catalyst, with a temperature range of $220\text{--}260^\circ\text{C}$ being recommended for efficient alcoholysis in the presence of 4 equivalents of ethanol per repeat unit. The authors note that the residual tin content (up to 16.5 mg/kg PLA), from polymer synthesis, could have mediated this degradation. With magnesium reagents, magnesium metal or $\text{Mg}(\text{tBu})_2$, efficient alcoholysis is achieved at lower temperatures (200°C) with a wide range of linear and branched alcohols. Further to this, the alcoholysis with ethanol could be scaled up to 1.5 kg and the polymer stereochemistry was retained for the resultant lactates, as measured by optical rotation measurements. At 200°C with a reaction time of 1 h, ethanolysis was performed with a range of commercial reagents including alkali/alkaline metals (Li–K/Mg–Ba) and selected alkoxides $\{\text{Na}(\text{OEt}), \text{K}(\text{OEt}), \text{Ca}(\text{OMe})_2\}$, as well as organometallic/chlorido zinc, tin, and aluminium reagents. All reagents demonstrated the activity for this process. The formation of calcium lactate was observed for calcium mediated alcoholysis, potentially implicating such complexes as the active species for other metal precursors.

Enthaler et al. have explored the use of tin (II) ethylhexanoate for the methanolysis of end-of-life PLA samples ($M_n = 43,600\text{--}150,400 \text{ g mol}^{-1}$), with up to 50 g of a cup degraded in one experiment [107]. High yields of Me-La were achieved between $140\text{--}180^\circ\text{C}$ with a low catalyst loading (0.05–0.25 mol%). The amount of MeOH was critical, with the yield going from quantitative to negligible when reducing equivalents from 15.4 to 11.6. At 180°C , a turnover number of $39,600 \text{ h}^{-1}$ was reported. Plichta et al. have described the partial alcoholysis of PLA ($M_w = 217,000 \text{ g mol}^{-1}$) with various protic reagents including diols, di-acids, and macromolecules [108]. Tin(II) ethylhexanoate was used as a catalyst with temperatures of up to 200°C applied. The aim of this study was to reduce the molecular weight of the initial PLA sample with the further aim of creating block copolymers. Butane-1,4-diol, propane-1,3-diol, dipentaerythritol, and adipic acid were successfully used, as well as PEG, poly adipates, and terephthalates, the latter macromolecules generating triblock copolymers.

Enthaler et al. have tested simple alkali halide salts for the methanolysis of PLA ($M_n = 43,600\text{--}150,400 \text{ g mol}^{-1}$) [109]. With microwave assisted heating ($140\text{--}160^\circ\text{C}$), potassium fluoride, KF, was shown to facilitate high yields of Me-La within 10 min. The potassium cation was suggested to activate the carbonyl group to attack with the fluoride anion assisting proton transfer. The catalyst residue could be used up to three times before a noticeable decrease in the Me-La yield. A range of end-of-life PLA samples were tested, without rigorous cleaning, and moderate to high yields (43%–97%) were generally achieved. The presence of plastic contaminants was also

considered. Poly(bisphenol A carbonate) underwent concomitant degradation with PLA whereas PET and polyamide 6 remained intact under the degradation conditions but did reduce the yield of Me-La.

Fusheng Liu et al. have also tested a range of ionic liquids for the methanolysis of PLA ($M_w = 400,000 \text{ g mol}^{-1}$) [110]. As for PLA hydrolysis, [Bmim][OAc] was found to be the most efficient for this process (Scheme 5, with MeOH). At 115°C , a high PLA conversion (97%) was achieved within 3 h and the ionic liquid could be reused up to six times without a reduction in activity. The activation energy was also evaluated for this system ($90\text{--}115^\circ\text{C}$, $E_a = 38.3 \text{ kJ mol}^{-1}$). A combination of the ionic liquid and metal salts has been shown to enhance the activity of both components, allowing for milder degradation conditions for PLA ($M_n = 79,850 \text{ g mol}^{-1}$) [111]. With $2[\text{Bmim}][\text{OAc}]\text{-Zn}(\text{OAc})_2$, efficient methanolysis is achieved after 1–2 h (110°C). A lower activation energy was calculated compared to using just the ionic liquid ($90\text{--}105^\circ\text{C}$, $E_a = 21.0 \text{ kJ mol}^{-1}$). This catalyst was also amenable to recycling, able to perform five further reactions with no loss of activity. Similarly, [Bmim][FeCl₄] was demonstrated to have a superior activity for PLA methanolysis ($M_n = 159,566 \text{ g mol}^{-1}$; 3 h, 120°C) than the component groups, FeCl₃ and [Bmim][Cl] [112]. Compared to FeCl₃, a lower activation energy was observed ($100\text{--}125^\circ\text{C}$, $E_a = 21.3 \text{ kJ mol}^{-1}$). These enhancements are likely due to the ionic liquids acting to solubilise the PLA, allowing for the Lewis acidic metals to activate the carbonyl group more readily (Scheme 7).



Scheme 7. General activation of PLA via Lewis acidic metal centres.

Organocatalysts have also been applied to the alcoholysis of PLA [113]. Hedrick et al. demonstrated the use of 4-pyrrolidinopyridine (PPY) and 4-dimethylaminopyridine (DMAP) for PLA transesterification, though the target of this work was to controllably reduce molecular weight rather than complete degradation to lactates (Figure 1a,b) [114]. Enthaler et al. have recently revisited DMAP for PLA methanolysis with microwave assisted heating (Figure 1b) [115]. In the absence of solvent, at 180°C , high yields of Me-La could be achieved within 20 min. In this study, a range of PLA waste samples were investigated, and the catalytic system demonstrates a reasonable tolerance to plastic contaminants and additives. 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) was also shown to afford a good yield of Me-La under the same conditions (Figure 1c) [115].

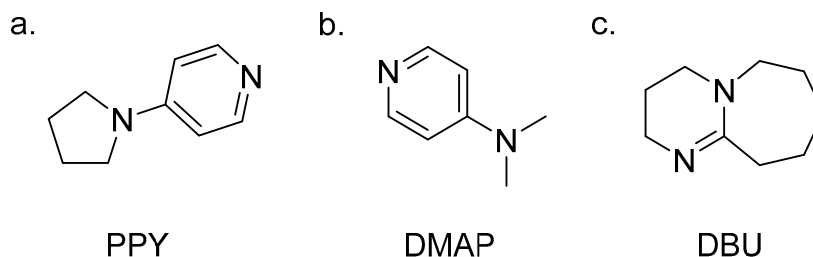


Figure 1. Organocatalysts for PLA alcoholysis; (a) PPY, (b) DMAP, (c) DBU [114,115].

In the same year, Fusheng Liu et al. reported the use of DBU-based protic ionic liquids for the degradation of PLA ($M_w = 400,000 \text{ g mol}^{-1}$) [116]. Protonated DBU cations with carboxylate anions such as acetate, lactate, and propionate allowed for higher degradation yields under milder conditions (100°C , 5 h) compared to using DBU alone (Figure 2a). A range of alkyl alcohols were tested and the potential for catalyst reuse was demonstrated. A proposed mechanism involved the [DBU-H] cation activating the polymer carbonyl with the attack of the alcohol assisted by the carboxylate anion through hydrogen bonding/transfer. The use of imidazole-based anions in conjugation with [DBU-H] afforded a versatile system ([DBU-H][Im]) capable of degrading a range of polyesters and polycarbonates (Figure 2b) [117]. At a reduced temperature of 70°C , a complete PLA degradation to Me-La was achieved in 1 h.

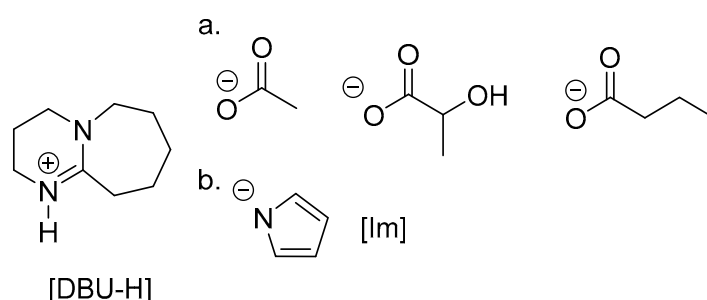
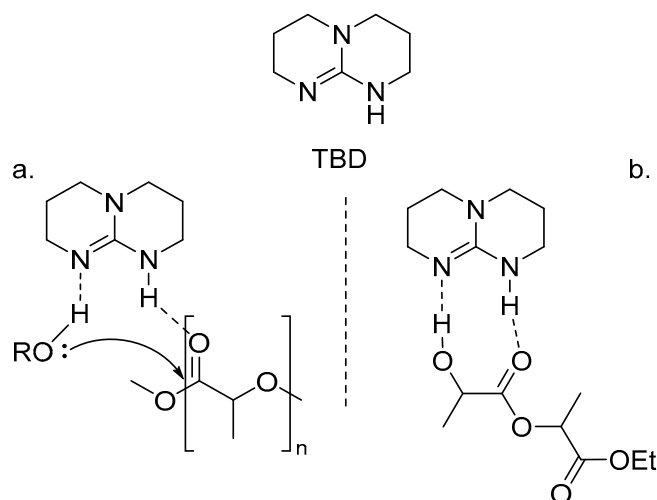


Figure 2. DBU-based protic ionic liquids used of PLA alcoholysis; (a) carboxylate anions, (b) imidazole anion [116,117].

1,5,7-Triazabicyclo[4.4.0] dec-5-ene (TBD) was shown to be an extremely efficient catalyst for PLA degradation at room temperature in CH_2Cl_2 (Scheme 8) [118]. Leibfarth et al. employed TBD with a range of primary alcohols (including MeOH, EtOH, BuOH, and BnOH), achieving complete degradation within minutes ($M_n = 76,700 \text{ g mol}^{-1}$). The organocatalyst is predicted to facilitate degradation via a dual-activation mechanism (Scheme 8a), with both incoming alcohol and PLA carbonyl groups being hydrogen bonded to TBD in the transition state. Interestingly, the transesterification of an ethyl lactate dimer was found to be much slower than expected based on the efficient degradation of PLA. This was suggested to be due to intramolecular binding of this dimer to TBD, preventing the activation of a further ethanol molecule (Scheme 8b). On degradation, the stereochemistry was shown to be maintained, with $>95\%$ enantiomeric excess (ee) measured for the lactate product formed from PLLA.



Scheme 8. TBD catalyst for PLA alcoholysis. (a) Dual-activation of alcohol and polymer; (b) intramolecular binding of lactate dimer to TBD, hindering reaction [118].

Perhaps the less studied area of PLA is the alcoholysis by discrete metal complexes. This is despite the fact that a wide range of complexes are reported for the ROP of lactide, which requires similar reaction characteristics to alcoholysis. Whitelaw et al. reported zirconium and hafnium (IV) salalen complexes, which facilitate both lactide polymerisation and PLA degradation (Figure 3). During the preparation of PLA, it is common to add catalytic amounts of methanol to remove the growing polymer chain from the metal centre and terminate the reaction. Excess methanol is often added to purify the polymer by removing unreacted monomer and catalytic species. With the group 4 salalen complexes, such a polymer purification procedure afforded Me-La rather than PLA, as confirmed by NMR spectroscopy and GC-MS analysis. The excess MeOH is suggested to form a bismethoxide complex, which catalyses extensive degradation of the PLA. Controlled degradation of PLA samples (various tacticities; $M_n = 10,000\text{--}200,000\text{ g mol}^{-1}$) was demonstrated for the Hf(IV) salalen analogue ($R = \text{Me}$) at room temperature in CH_2Cl_2 within 24 h.

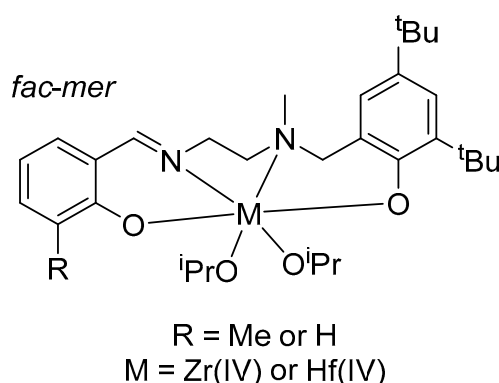


Figure 3. Group 4 salalen complexes for PLA methanolysis [119].

Zinc complexes are perhaps currently the most studied for PLA recycling. Fliedel et al. reported the use of a dinuclear zinc-carbene complex for both the ROP of lactide and the first example of Zn(II) complexes for the controlled degradation of PLA (Figure 4) [120]. On the quenching of the ROP with methanol, ^1H NMR resonances were observed for Me-La suggesting further extensive transesterification reactions to be occurring. The authors then sought to demonstrate this in a controlled manner, degrading a commercial sample of PLLA ($M_n = 18,410\text{ g mol}^{-1}$). After 24 h at room temperature, only oligomeric PLA ($M_n \sim 2000\text{ g mol}^{-1}$) and methyl lactate ($\sim 30\%$) were present in the solution. Under these degradation conditions, the benzyl alkoxide (Figure 4a) at the zinc centre is substituted with a methoxide (Figure 4b) with minor degradation of the carbene complex. With the initial $(\text{NHC})\text{ZnEt}(\text{Cl})$ complex, protonolysis of the zinc ethyl group occurred on addition of PLA, affording a Zn-PLA species (Figure 4c).

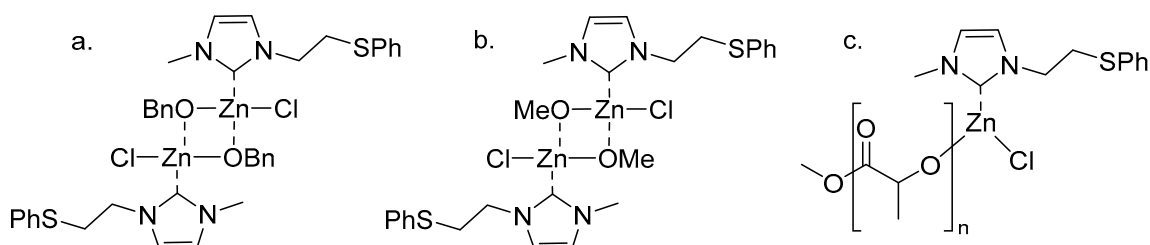


Figure 4. Dinuclear zinc N-heterocyclic carbene complexes active in PLA methanolysis; (a) Benzyl alkoxide species, (b) methoxide species, (c) coordinated PLA species [120].

In 2015, Ejfler et al. described a homoleptic $\text{Zn}\{\text{ON}\}_2$ complex for the controlled synthesis of a low molecular weight PLA (Figure 5a) [121]. The precipitation of the oligomers by alcohol after

reaction led to transesterification to lactate products. However, it is noted that this degradation was not evident for the higher molecular weight PLA. Payne et al. have reported Schiff base Zn{ON} complexes for lactide polymerisation and PLA methanolysis (Figure 5b,c) [122]. In THF at 80 °C, a PLA cup ($M_n = 45,150 \text{ g mol}^{-1}$) could be degraded to high Me-La yields after 8 h. The rate of consumption of PLA was observed to follow a first order kinetic profile. For this system, the activation of the carbonyl group of PLA by the Lewis acidic Zn(II) centre is anticipated (Scheme 7).

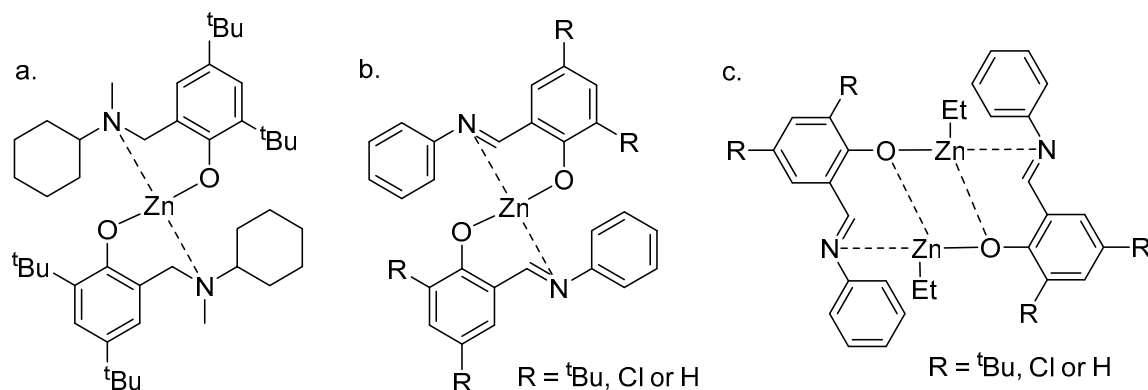


Figure 5. Zn(II) {ON} complexes for PLA alcoholysis; (a) Zn{ON}₂ complex for synthesis of low molecular weight PLA, (b) monomeric Zn{ON}₂ complex for PLA degradation, (c) dimeric ({NO}ZnEt)₂ complex for PLA degradation [121,122].

McKeown et al. studied a series of aminopiperidine-based {ONN} Zn(II) and Mg(II) complexes for LA polymerisation (Figure 6a) [123]. As with previous polymerisation catalysts, polymer purification was observed to cause extensive transesterification, with the reduction of PLA molecular weights being caused by both complexes. Due to the complexity of the ligand system, a full degradation study was not performed. Román-Ramírez et al. have performed an in-depth kinetic study of PLA degradation with a homoleptic Zn(II) complex (Figure 6b) [124]. This complex demonstrated high activity towards the ROP of LA, displaying robustness and immortal characteristics, which are good properties for a degradation catalyst [125]. The stability of the Zn(II) complex towards the degradation medium was demonstrated through NMR spectroscopy and commercial PLA samples, including a cup, were systematically degraded ($M_n = 44,350\text{--}71,900 \text{ g mol}^{-1}$). Of the solvents tested, THF was found to give the best results in terms of PLA conversion and Me-La formation. Experimental design suggested there was no dependence on the PLA type/molecular weight with temperature (40–130 °C) and catalyst loading (4–16 wt%) being the main reaction variables. Kinetic parameters for a consecutive reaction mechanism, with equilibration between Me-La and lactate oligomers, and activation energies were also reported ($E_a = 39\text{--}65 \text{ kJ mol}^{-1}$). A minor variation in the ligand backbone afforded Zn(II) complexes, which demonstrated different coordination geometries (Figure 6c; R = N(H)Me or N(H)Me) [126]. Rapid degradation was observed at 50 °C in THF and methanol, with a complete PLA consumption within 1 h. The reaction was also successfully demonstrated for up to 12.5 g of PLA. Ethyl lactate could also be produced, albeit with a slight reduction in activity, requiring 1.5 h. This Zn(II) system was also demonstrated to be tolerant to the contamination of other plastics, such as PET. The kinetics of these complexes has also been studied, with kinetic parameters and activation energies being calculated for PLA methanolysis [127]. These complexes demonstrated an unusual behaviour, with a curved Arrhenius plot and variable activation energies, with the formation of MeLa being observed at −20 °C.

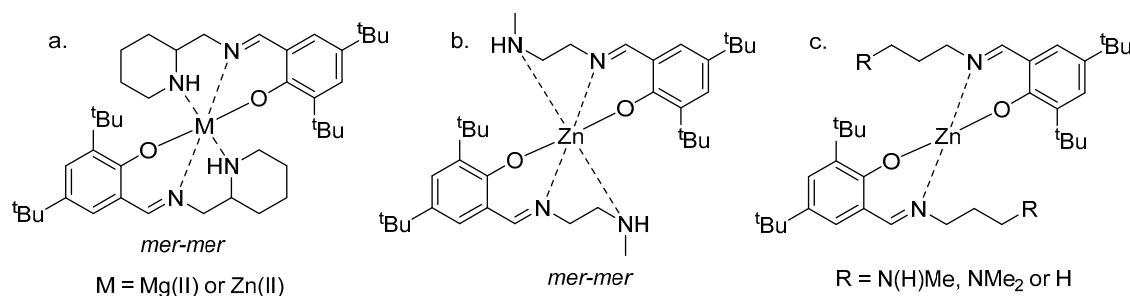


Figure 6. Zn(II) and Mg(II) homoleptic {ONN} complexes for PLA alcoholysis; (a) aminopiperidine Zn(II)/Mg(II) complexes, (b) Ethylenediamine Zn(II) complex, (c) propylamine Zn(II) complexes [123–127].

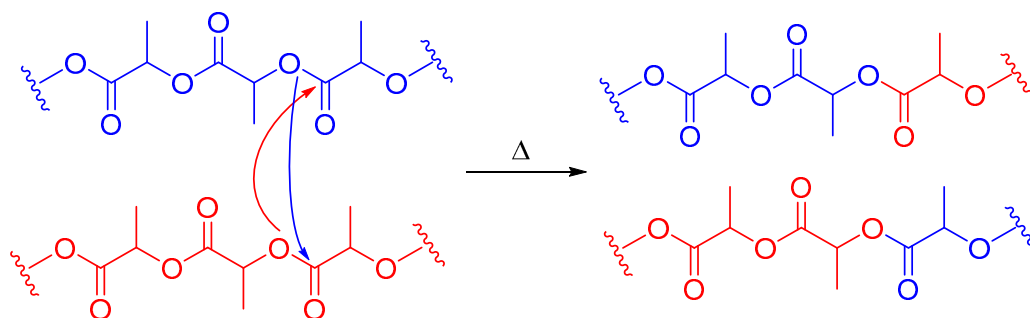
For comparison, a Zn-{ON}₂ Schiff base analogue was prepared and tested for degradation activity (Figure 6c; R = H) [126]. A much reduced activity under identical conditions potentially implicates the additional amine group as having a role in the reaction, possibly activating the incoming alcohol while the Zn(II) centre activates the carbonyl group.

4. To Other Products

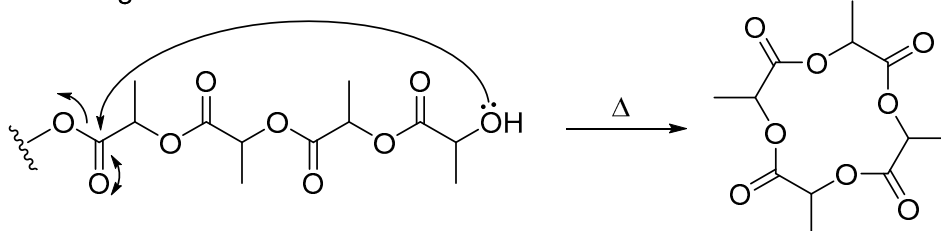
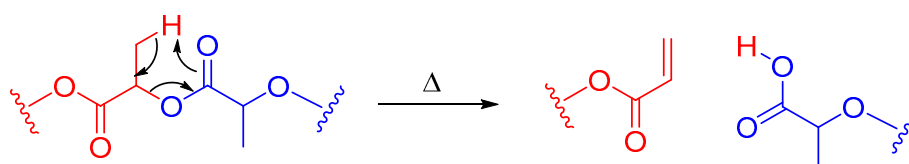
The chemical recycling of PLA can also be achieved thermally, in the absence of exogenous reagents. While potentially affording depolymerisation products such as LA, high temperatures are required, which can lead to racemisation/epimerisation and side reactions to products other than LA. Early work was performed by McNeill and Leiper, heating PLA samples up to 450 °C [128,129]. Under programmed heating conditions (10 °C min^{−1}), PLA breaks down in one step between 250–450 °C [128]. Carbon dioxide is the main product, with lactide and cyclic oligomers also being observed. Isothermal studies demonstrated different product distributions at different temperatures [129]. As well as lactide and oligomers, acetaldehyde is observed at 230 °C through *cis* elimination (Scheme 9), with CO₂, ethylene, propylene, and methyl ketene being observed at higher temperatures. Capping the hydroxyl group with an acetyl group stabilised the polymer towards thermal degradation, suggesting the operation of a backbiting mechanism (Scheme 9).

Subsequent work has focused on the addition of metal salts with the aim of controlling the selectivity and determining the effect of a residual metal catalyst during polymer processing [130–141]. The presence of metal contaminants often decreases the thermal stability, reducing the onset temperature for degradation. Tin complexes are very common for the ROP of LA, therefore, residual Sn(II) species in the polymeric material is a possibility. Nishida et al. demonstrated that the presence of tin favoured extensive intramolecular unzipping depolymerisation of PLLA to selectively give *L*-LA rather than the random intermolecular transesterification (Scheme 9) [131,140]. The presence of Sn(II) carboxylate end groups and the operation of this mechanism caused a reduction in the activation energy (from 175 to 85 kJ mol^{−1}, depending on the amount of tin) and therefore, an earlier onset of weight loss with respect to temperature (150 °C). In the absence of Sn(II), the depolymerisation was less controlled with oligomers being the major products and with *meso*-LA also being formed. The same group have also studied the effect of calcium and magnesium oxides on this process, demonstrating a similar trend in activation energies and the operation of an unzipping mechanism facilitated by the metal centres [135,137,139]. The extent of racemisation was highly dependent on temperature, with CaO causing extensive formation of *meso*-LA below 250 °C but being more selective to *L*-LA at higher temperatures (<300 °C). For MgO, racemisation was less prevalent and a high selectivity towards *L*-LA could be achieved at temperatures lower than 270 °C. The effect of Zn(II), Fe(III), and Al(III) cations has also been tested for PLA pyrolysis [133,141]. The partial pyrolysis of PLA with a residual organocatalyst, DBU, has also been investigated [142].

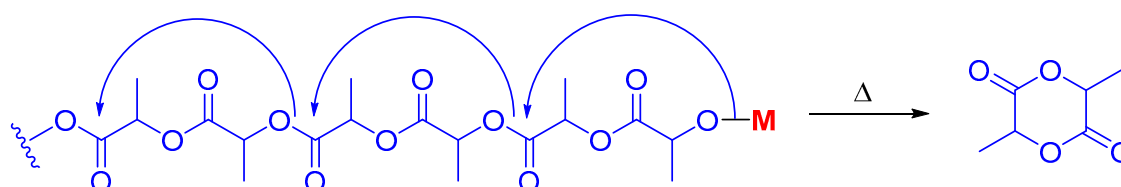
Random Intermolecular Transesterification



Backbiting

*cis*-elimination

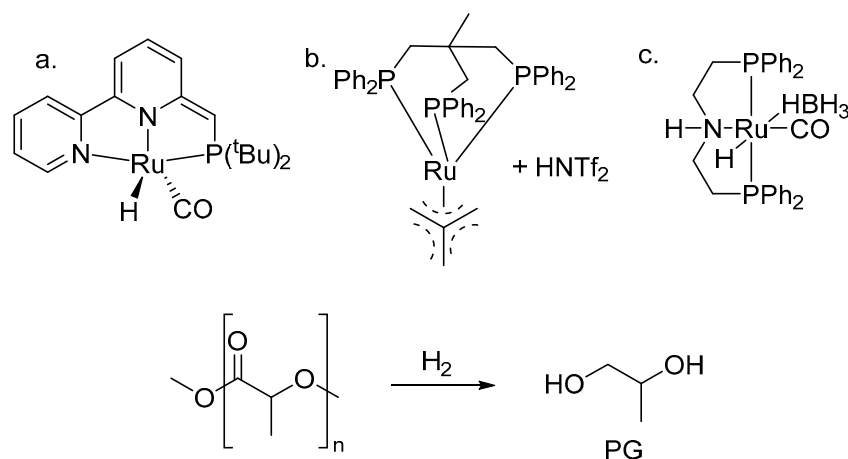
Unzipping depolymerisation



M = Metal salt
= Sn(II), Mg(II), Zn(II), Fe(III), Al(III)

Scheme 9. Possible thermal degradation mechanisms [130,131].

The above examples of PLA degradation maintain the carbonyl functionality, either as a carboxylic acid or ester group. However, there is scope to reduce this functionality and form alcohols and alkanes. Krall et al. have employed ruthenium (II) PNN pincer complexes for the hydrogenative degradation of polyesters and polycarbonates (Scheme 10a) [143]. In this study, a PLA cup was successfully degraded to propylene glycol (PG) in the presence of a catalyst and H_2 (55 bar). The reaction was performed at 160 °C with a solvent mixture of THF and anisole. The quantitative conversion to PG was achieved after 24 h.

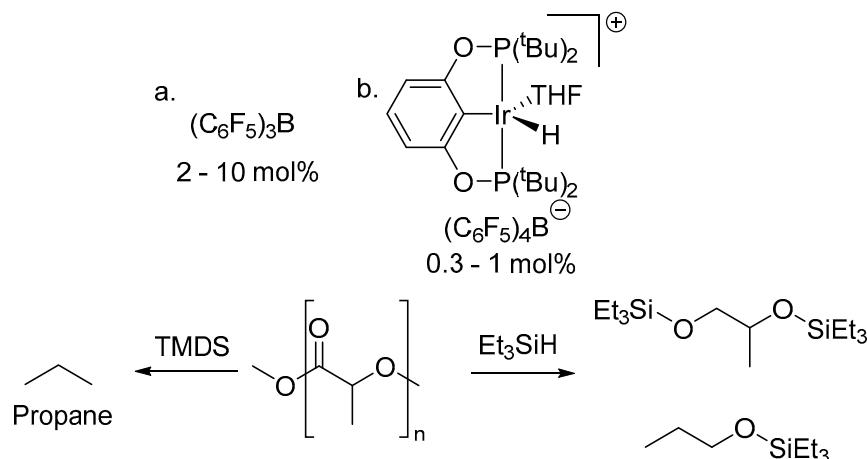


Scheme 10. Ruthenium (II) complexes used for PLA hydrogenation and degradation to propylene glycol (PG); (a) Ru(II) PNN pincer complex, (b) Ru(II) triphos complex, (c) Ru-MACHO-BH complex [143–145].

More recently, Klankermayer et al. have applied a Ru(II) triphos complex to the recycling of polyesters and polycarbonates (Scheme 10b) [144]. Under relatively milder conditions (100 bar H_2 , 140 °C, 16 h) a PLA cup could be quantitatively and selectively transformed into PG. Either 1,4-dioxane or PG was used as the solvent in this process with a bis(trifluoromethane)sulfonimide (HNTf_2) co-catalyst. Investigations were also carried out into the selective degradation of PLA in the presence of PET (achieved by choice of solvent and temperature) and the potential for reaction scale up (up to 11.4 g PLA). Enthaler et al. have applied a commercially available Ru-MACHO-BH complex for this process (Scheme 10c) [145]. In this work, milder conditions are used with a shorter reaction time (120–140 °C, 30–45 bar H_2 , <6 h). A range of used PLA samples were successfully degraded to PG despite the presence of dyes and additives. Polycarbonates were also degraded by this system, with a mixture of PLA and poly(propylene carbonate) affording PG and MeOH. The degradation of PLA was coupled with the breakdown of poly(oxyethylene) to give a cyclic acetal with the second process being catalysed by $\text{Bi}(\text{OTf})_3$.

Shuklov et al. investigated the heterogeneous transformation of PLA and lactide into PG using barium promoted copper chromite (Cu/Cr/Ba) and H_2 (150 bar) [146]. The process is described as a tandem reaction whereby the Me-La is formed by methanolysis followed by hydrogenation to the diol. The reaction in the presence of ethanol was reported to be much slower. The process was performed at temperatures up to 150 °C, however, severe racemisation of the stereocentre was observed. At 100 °C, a 90% ee was measured for the PG, but a reduced yield resulted (50%). A high catalyst loading was employed (133 wt%), however, the catalyst was readily separated from the reaction mixture by centrifugation and catalyst reuse was demonstrated for the lactide transformations.

Cantat et al. have utilised both an organocatalyst and Brookhart's iridium (III) hydrosilylation catalyst on a range of polymers including PLA (coloured 3D printing material) to give silyl ethers or propane (Scheme 11a,b) [147,148]. With $\text{B}(\text{C}_6\text{F}_5)_3$, this could be achieved at room temperature, in CH_2Cl_2 , with triethylsilane (Et_3SiH) giving silylated propylene glycol (16 h, <65% yield) and 1,1,3,3-tetramethyldisiloxane (TMDS) yielding propane (1 h, >99%) [147]. For the Ir(III) catalyst, a mixture of silylated propylene glycol and propanol were formed at 65 °C in chlorobenzene after 60 h [148]. At 90 °C with excess silane, silylated propanol was selectively formed. PLA degradation was observed to occur despite the presence of additives such as dye and with a lower catalytic loading compared to $\text{B}(\text{C}_6\text{F}_5)_3$ alone (<1 mol%). In the presence of a hydridic silane source (TMDS), PLA could be further degraded and reduced to propane (110 °C, 12 h). The formation of polydimethoxysilane (PDMS) as a by-product can add further value to the process.



Scheme 11. Catalysts used for hydrosilylation of PLA and degradation products; (a) Organocatalyst, (b) Brookhart's Ir(III) complex_ [147,148].

Recently, Fernandes et al. have demonstrated the use of an air-stable oxo bridged molybdenum complex for PLA reductive degradation [149]. In the presence of reductive silanes (polymethylhydroxysilane or $PhSiH_3$) and $MoO_2Cl_2(H_2O)_2$, PLA was transformed into propane (toluene, 110 °C, 20–40 h). The authors demonstrated PG to be a possible intermediate in the reaction, which would be further reduced under the reaction conditions. The degradation of 3D printing material and a PLA cup were demonstrated in the study.

5. Conclusions

Renewable bio-based polymers represent an important step towards a circular economy for plastics. However, it is equally important that the end-of-life scenarios are critically assessed and infrastructure is in place to dispose of these materials efficiently. PLA is a promising bio-based polymer, which is applicable to packaging and biomedical uses. Despite being compostable under high temperature, industrial conditions, there is greater incentive for the chemical recycling of PLA, which could potentially reduce production costs to a level competitive with petrochemical-based plastics. The chemical recycling of PLA can be achieved by three main methods: Hydrolysis, alcoholysis, and pyrolysis. The hydrolysis of PLA yields lactic acid in a process, which could potentially be more cost effective than the fermentation of sugars. Lactic acid is a biobased platform to other value-added chemicals and a precursor to the PLA monomer, lactide. High temperatures (100–200 °C) are required for this heterogeneous process, which is also influenced by pH and PLA morphology. Alcoholysis affords alkyl lactates, which can be transformed to useful chemicals or useful as benign solvents. Methyl or ethyl lactate are degradation products via methanolysis or ethanolysis, respectively. The use of a cosolvent and catalyst can allow for this process to occur at ambient temperatures. A range of commercial metal salts and organocatalysts have been applied to the alcoholysis of PLA. More recently, the use of discrete metal complexes have been demonstrated for methanolysis, with Zn(II) catalysts being the most common. In the absence of protic reagents, PLA can be thermally depolymerised by pyrolysis (200–300 °C). The addition of metal catalysts, for example Sn(II), is necessary for the selective formation of lactide via an unzipping depolymerisation mechanism. The selective, one-step transformation of PLA into alcohols and alkanes is a relatively new direction of PLA recycling. Several Ru(II) complexes have been demonstrated for the formation of PG via hydrogenation reactions. An organocatalyst and complexes of Ir(III) and Mo(VI) have also been used to convert PLA to silyl alcohols and propane.

To be successful, chemical recycling processes need to be efficient and quantitative to compete with other disposal methods. A further advantage to chemical recycling is the potential to act selectively on a mixture of different plastics and allow for polymer additive separation. The use of chemical recycling methods strongly aligns with a circular economy approach. For PLA, as the scale of demand

and production increases, warranting increased attention to the recycling of end-of-life products, it is imperative that such processes are available in the near future.

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References

1. Geyer, R.; Jambeck, J.R.; Law, K.L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **2017**, *3*, e1700782. [[CrossRef](#)] [[PubMed](#)]
2. Shafiee, S.; Topal, E. When will fossil fuel reserves be diminished? *Energy Policy* **2009**, *37*, 181–189. [[CrossRef](#)]
3. Lebreton, L.; Andrady, A. Future scenarios of global plastic waste generation and disposal. *Palgrave Commun.* **2019**, *5*, 1–11. [[CrossRef](#)]
4. Bonanno, G.; Orlando-Bonaca, M. Ten inconvenient questions about plastics in the sea. *Environ. Sci. Policy* **2018**, *85*, 146–154. [[CrossRef](#)]
5. Jambeck, J.R.; Geyer, R.; Wilcox, C.; Siegler, T.R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K.L. Plastic waste inputs from land into the ocean. *Science (80-.)* **2015**, *347*, 768–771. [[CrossRef](#)]
6. Lebreton, L.; Slat, B.; Ferrari, F.; Sainte-Rose, B.; Aitken, J.; Marthouse, R.; Hajbane, S.; Cunsolo, S.; Schwarz, A.; Levivier, A.; et al. Evidence that the Great Pacific Garbage Patch is rapidly accumulating plastic. *Sci. Rep.* **2018**, *8*, 1–15. [[CrossRef](#)]
7. Andrady, A.L.; Neal, M.A. Applications and societal benefits of plastics. *Philos. Trans. R. Soc. B Biol. Sci.* **2009**, *364*, 1977–1984. [[CrossRef](#)]
8. Thompson, R.C.; Swan, S.H.; Moore, C.J.; Vom Saal, F.S. Our plastic age. *Philos. Trans. R. Soc. B Biol. Sci.* **2009**, *364*, 1973–1976. [[CrossRef](#)]
9. Millet, H.; Vangheluwe, P.; Block, C.; Sevenster, A.; Garcia, L.; Antonopoulos, R. The Nature of Plastics and Their Societal Usage. In *Plastics and the Environment*; The Royal Society of Chemistry: London, UK, 2019; pp. 1–20. [[CrossRef](#)]
10. Payne, J.; McKeown, P.; Jones, M.D. A circular economy approach to plastic waste. *Polym. Degrad. Stab.* **2019**, *165*, 170–181. [[CrossRef](#)]
11. Hopewell, J.; Dvorak, R.; Kosior, E. Plastics recycling: Challenges and opportunities. *Philos. Trans. R. Soc. B Biol. Sci.* **2009**, *364*, 2115–2126. [[CrossRef](#)]
12. Kaur, G.; Uisan, K.; Ong, K.L.; Ki Lin, C.S. Recent Trends in Green and Sustainable Chemistry & Waste Valorisation: Rethinking Plastics in a circular economy. *Curr. Opin. Green Sustain. Chem.* **2018**, *9*, 30–39. [[CrossRef](#)]
13. Huysman, S.; De Schaepmeester, J.; Ragaert, K.; Dewulf, J.; De Meester, S. Performance indicators for a circular economy: A case study on post-industrial plastic waste. *Resour. Conserv. Recycl.* **2017**, *120*, 46–54. [[CrossRef](#)]
14. Abdel-Rahman, M.A.; Tashiro, Y.; Sonomoto, K. Recent advances in lactic acid production by microbial fermentation processes. *Biotechnol. Adv.* **2013**, *31*, 877–902. [[CrossRef](#)] [[PubMed](#)]
15. Abdel-Rahman, M.A.; Tashiro, Y.; Sonomoto, K. Lactic acid production from lignocellulose-derived sugars using lactic acid bacteria: Overview and limits. *J. Biotechnol.* **2011**, *156*, 286–301. [[CrossRef](#)] [[PubMed](#)]
16. VanWouwe, P.; Dusselier, M.; Vanleeuw, E.; Sels, B. Lactide Synthesis and Chirality Control for Polylactic acid Production. *ChemSusChem* **2016**, *9*, 907–921. [[CrossRef](#)] [[PubMed](#)]
17. Shen, L.; Haufe, J.; Patel, M.K. *Product Overview and Market Projection of Emerging Bio-Based Plastics*; Utrecht University: Utrecht, The Netherlands, 2009; p. 74.
18. De Clercq, R.; Dusselier, M.; Poleunis, C.; Debecker, D.P.; Giebler, L.; Oswald, S.; Makshina, E.; Sels, B.F. Titania-Silica Catalysts for Lactide Production from Renewable Alkyl Lactates: Structure–Activity Relations. *ACS Catal.* **2018**, *8*, 8130–8139. [[CrossRef](#)]
19. Ghadamyari, M.; Chaemchuen, S.; Zhou, K.; Dusselier, M.; Sels, B.F.; Mousavi, B.; Verpoort, F. One-step synthesis of stereo-pure l, l lactide from l-lactic acid. *Catal. Commun.* **2018**, *114*, 33–36. [[CrossRef](#)]

20. Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Jacobs, P.A.; Sels, B.F. Shape-selective zeolite catalysis for bioplastics production. *Science* (80-.). **2015**, *349*, 78–80. [[CrossRef](#)]
21. De Clercq, R.; Dusselier, M.; Makshina, E.; Sels, B.F. Catalytic Gas-Phase Production of Lactide from Renewable Alkyl Lactates. *Angew. Chem. Int. Ed.* **2018**, *57*, 3074–3078. [[CrossRef](#)]
22. Upare, P.P.; Hwang, Y.K.; Chang, J.-S.; Hwang, D.W. Synthesis of Lactide from Alkyl Lactate via a Prepolymer Route. *Ind. Eng. Chem. Res.* **2012**, *51*, 4837–4842. [[CrossRef](#)]
23. Upare, P.P.; Yoon, J.W.; Hwang, D.W.; Lee, U.H.; Hwang, Y.K.; Hong, D.Y.; Kim, J.C.; Lee, J.H.; Kwak, S.K.; Shin, H.; et al. Design of a heterogeneous catalytic process for the continuous and direct synthesis of lactide from lactic acid. *Green Chem.* **2016**, *18*, 5978–5983. [[CrossRef](#)]
24. Heo, S.; Park, H.W.; Lee, J.H.; Chang, Y.K. Design and Evaluation of Sustainable Lactide Production Process with an One-Step Gas Phase Synthesis Route. *ACS Sustain. Chem. Eng.* **2019**, *7*, 6178–6184. [[CrossRef](#)]
25. Thomas, C.M. Stereocontrolled ring-opening polymerization of cyclic esters: synthesis of new polyester microstructures. *Chem. Soc. Rev.* **2010**, *39*, 165–173. [[CrossRef](#)] [[PubMed](#)]
26. Platel, R.H.; Hodgson, L.M.; Williams, C.K. Biocompatible Initiators for Lactide Polymerization. *Polym. Rev.* **2008**, *48*, 11–63. [[CrossRef](#)]
27. Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. FeA Controlled Ring-Opening Polymerization of Lactide and Glycolide. *Chem. Rev.* **2004**, *104*, 6147–6176. [[CrossRef](#)] [[PubMed](#)]
28. Stanford, M.J.; Dove, A.P. Stereocontrolled ring-opening polymerisation of lactide. *Chem. Soc. Rev.* **2010**, *39*, 486–494. [[CrossRef](#)]
29. Rabnawaz, M.; Wyman, I.; Auras, R.; Cheng, S. A roadmap towards green packaging: the current status and future outlook for polyesters in the packaging industry. *Green Chem.* **2017**, *19*, 4737–4753. [[CrossRef](#)]
30. Auras, R.; Harte, B.; Selke, S. An overview of polylactides as packaging materials. *Macromol. Biosci.* **2004**, *4*, 835–864. [[CrossRef](#)]
31. Ahmed, J.; Varshney, S.K. Polylactides-chemistry, properties and green packaging technology: A review. *Int. J. Food Prop.* **2011**, *14*, 37–58. [[CrossRef](#)]
32. Viera, J.S.C.; Marques, M.R.C.; Nazareth, M.C.; Jimenez, P.C.; Castro, Í.B. On replacing single-use plastic with so-called biodegradable ones: The case with straws. *Environ. Sci. Policy* **2020**, *106*, 177–181. [[CrossRef](#)]
33. Rocca-Smith, J.R.; Whyte, O.; Brachais, C.H.; Champion, D.; Piasente, F.; Marcuzzo, E.; Sensidoni, A.; Debeaufort, F.; Karbowski, T. Beyond Biodegradability of Poly(lactic acid): Physical and Chemical Stability in Humid Environments. *ACS Sustain. Chem. Eng.* **2017**, *5*, 2751–2762. [[CrossRef](#)]
34. Pawar, R.P.; Tekale, S.U.; Shisodia, S.U.; Totre, J.T.; Domb, A.J. Biomedical Applications of Poly(Lactic Acid). *Rec. Pat. Regen. Med.* **2014**, *4*, 40–51. [[CrossRef](#)]
35. Lasprilla, A.J.R.; Martinez, G.A.R.; Lunelli, B.H.; Jardini, A.L.; Filho, R.M. Poly-lactic acid synthesis for application in biomedical devices - a review. *Biotechnol. Adv.* **2012**, *30*, 321–328. [[CrossRef](#)] [[PubMed](#)]
36. Singhvi, M.S.; Zinjarde, S.S.; Gokhale, D.V. Polylactic acid: synthesis and biomedical applications. *J. Appl. Microbiol.* **2019**, *127*, 1612–1626. [[CrossRef](#)] [[PubMed](#)]
37. Ghalia, M.A.; Dahman, Y. Biodegradable poly(lactic acid)-based scaffolds: synthesis and biomedical applications. *J. Polym. Res.* **2017**, *24*. [[CrossRef](#)]
38. Nampoothiri, K.M.; Nair, N.J.; John, R.P. An overview of the recent developments in polylactide (PLA) research. *Bioresour. Technol.* **2010**, *101*, 8493–8501. [[CrossRef](#)] [[PubMed](#)]
39. Castro-Aguirre, E.; Iñiguez-Franco, F.; Samsudin, H.; Fang, X.; Auras, R. Poly(lactic acid)-Mass production, processing, industrial applications, and end of life. *Adv. Drug Deliv. Rev.* **2016**, *107*, 333–366. [[CrossRef](#)]
40. Vink, E.T.H.; Davies, S. Life Cycle Inventory and Impact Assessment Data for 2014 Ingeo™ Polylactide Production. *Ind. Biotechnol.* **2015**, *11*, 167–180. [[CrossRef](#)]
41. Gu, W.; Xu, P.; Wang, Y.; Yao, Y.; Yuan, D.; Shen, Q. Synthesis and Characterization of Yttrium and Ytterbium Complexes Supported by Salen Ligands and Their Catalytic Properties for rac-Lactide Polymerization. *Organometallics* **2015**, *34*, 2907–2916. [[CrossRef](#)]
42. Shen, L.; Worrell, E.; Patel, M. Present and future development in plastics from biomass. *Biofuels Bioprod. Biorefining* **2010**, *4*, 25–40. [[CrossRef](#)]
43. Haider, T.P.; Völker, C.; Kramm, J.; Landfester, K.; Wurm, F.R. Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society. *Angew. Chem. Int. Ed.* **2019**, *58*, 50–62. [[CrossRef](#)] [[PubMed](#)]

44. Ho, K.L.G.; Pometto, A.L.; Hinz, P.N.; Gadea-Rivas, A.; Briceño, J.A.; Rojas, A. Field exposure study of polylactic acid (PLA) plastic films in the banana fields of Costa Rica. *J. Environ. Polym. Degrad.* **1999**, *7*, 167–172. [[CrossRef](#)]
45. Rudnik, E.; Briassoulis, D. Degradation behaviour of poly(lactic acid) films and fibres in soil under Mediterranean field conditions and laboratory simulations testing. *Ind. Crops Prod.* **2011**, *33*, 648–658. [[CrossRef](#)]
46. Bagheri, A.R.; Laforsch, C.; Greiner, A.; Agarwal, S. Fate of So-Called Biodegradable Polymers in Seawater and Freshwater. *Glob. Chall.* **2017**, *1*, 1700048. [[CrossRef](#)]
47. Tsuji, H.; Suzuyoshi, K. Environmental degradation of biodegradable polyesters 1. Poly(ϵ -caprolactone), poly[(R)-3-hydroxybutyrate], and poly(L-lactide) films in controlled static seawater. *Polym. Degrad. Stab.* **2002**, *75*, 347–355. [[CrossRef](#)]
48. Nazareth, M.; Marques, M.R.C.; Leite, M.C.A.; Castro, Í.B. Commercial plastics claiming biodegradable status: Is this also accurate for marine environments? *J. Hazard. Mater.* **2019**, *366*, 714–722. [[CrossRef](#)]
49. Tsuji, H.; Suzuyoshi, K. Environmental degradation of biodegradable polyesters 2. Poly(ϵ -caprolactone), poly[(R)-3-hydroxybutyrate], and poly(L-lactide) films in natural dynamic seawater. *Polym. Degrad. Stab.* **2002**, *75*, 357–365. [[CrossRef](#)]
50. Kolstad, J.J.; Vink, E.T.H.; De Wilde, B.; Debeer, L. Assessment of anaerobic degradation of IngeoTM polylactides under accelerated landfill conditions. *Polym. Degrad. Stab.* **2012**, *97*, 1131–1141. [[CrossRef](#)]
51. Alaerts, L.; Augustinus, M.; Van Acker, K. Impact of bio-based plastics on current recycling of plastics. *Sustainability* **2018**, *10*, 1487. [[CrossRef](#)]
52. La Mantia, F.P.; Botta, L.; Morreale, M.; Scaffaro, R. Effect of small amounts of poly(lactic acid) on the recycling of poly(ethylene terephthalate) bottles. *Polym. Degrad. Stab.* **2012**, *97*, 21–24. [[CrossRef](#)]
53. Cornell, D.D. Biopolymers in the existing postconsumer plastics recycling stream. *J. Polym. Environ.* **2007**, *15*, 295–299. [[CrossRef](#)]
54. Ulrici, A.; Serranti, S.; Ferrari, C.; Cesare, D.; Foca, G.; Bonifazi, G. Efficient chemometric strategies for PET-PLA discrimination in recycling plants using hyperspectral imaging. *Chemom. Intell. Lab. Syst.* **2013**, *122*, 31–39. [[CrossRef](#)]
55. Danyluk, C.; Erickson, R.; Burrows, S.; Auras, R. Industrial Composting of Poly(Lactic Acid) Bottles. *J. Test. Eval.* **2010**, *38*, 717–723. [[CrossRef](#)]
56. Kale, G.; Auras, R.; Singh, S.P.; Narayan, R. Biodegradability of polylactide bottles in real and simulated composting conditions. *Polym. Test.* **2007**, *26*, 1049–1061. [[CrossRef](#)]
57. Ahn, H.K.; Huda, M.S.; Smith, M.C.; Mulbry, W.; Schmidt, W.F.; Reeves, J.B. Biodegradability of injection molded bioplastic pots containing polylactic acid and poultry feather fiber. *Bioresour. Technol.* **2011**, *102*, 4930–4933. [[CrossRef](#)]
58. Emadian, S.M.; Onay, T.T.; Demirel, B. Biodegradation of bioplastics in natural environments. *Waste Manag.* **2017**, *59*, 526–536. [[CrossRef](#)]
59. Kale, G.; Kijchavengkul, T.; Auras, R.; Rubino, M.; Selke, S.E.; Singh, S.P. Compostability of bioplastic packaging materials: An overview. *Macromol. Biosci.* **2007**, *7*, 255–277. [[CrossRef](#)]
60. Pillin, I.; Montrelay, N.; Bourmaud, A.; Grohens, Y. Effect of thermo-mechanical cycles on the physico-chemical properties of poly(lactic acid). *Polym. Degrad. Stab.* **2008**, *93*, 321–328. [[CrossRef](#)]
61. Badia, J.D.; Ribes-Greus, A. Mechanical recycling of polylactide, upgrading trends and combination of valorization techniques. *Eur. Polym. J.* **2016**, *84*, 22–39. [[CrossRef](#)]
62. Beltrán, F.R.; Lorenzo, V.; Acosta, J.; de la Orden, M.U.; Martínez Urreaga, J. Effect of simulated mechanical recycling processes on the structure and properties of poly(lactic acid). *J. Environ. Manag.* **2018**, *216*, 25–31. [[CrossRef](#)]
63. Zhao, P.; Rao, C.; Gu, F.; Sharmin, N.; Fu, J. Close-looped recycling of polylactic acid used in 3D printing: An experimental investigation and life cycle assessment. *J. Clean. Prod.* **2018**, *197*, 1046–1055. [[CrossRef](#)]
64. Hong, M.; Chen, E.Y.X. Chemically recyclable polymers: A circular economy approach to sustainability. *Green Chem.* **2017**, *19*, 3692–3706. [[CrossRef](#)]
65. Piemonte, V.; Sabatini, S.; Gironi, F. Chemical Recycling of PLA: A Great Opportunity Towards the Sustainable Development? *J. Polym. Environ.* **2013**, *21*, 640–647. [[CrossRef](#)]
66. Von Burkersroda, F.; Schedl, L.; Göpferich, A. Why degradable polymers undergo surface erosion or bulk erosion. *Biomaterials* **2002**, *23*, 4221–4231. [[CrossRef](#)]

67. Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Makshina, E.; Sels, B.F. Lactic acid as a platform chemical in the biobased economy: The role of chemocatalysis. *Energy Environ. Sci.* **2013**, *6*, 1415–1442. [\[CrossRef\]](#)
68. Gironi, F.; Frattari, S.; Piemonte, V. PLA Chemical Recycling Process Optimization: PLA Solubilization in Organic Solvents. *J. Polym. Environ.* **2016**, *24*, 328–333. [\[CrossRef\]](#)
69. Tsuji, H.; Daimon, H.; Fujie, K. A new strategy for recycling and preparation of poly(L-lactic acid): hydrolysis in the melt. *Biomacromolecules* **2003**, *4*, 835–840. [\[CrossRef\]](#)
70. Tsuji, H.; Saeki, T.; Tsukegi, T.; Daimon, H.; Fujie, K. Comparative study on hydrolytic degradation and monomer recovery of poly(l-lactic acid) in the solid and in the melt. *Polym. Degrad. Stab.* **2008**, *93*, 1956–1963. [\[CrossRef\]](#)
71. Tsuji, H.; Ogiwara, M.; Saha, S.K.; Sakaki, T. Enzymatic, alkaline, and autocatalytic degradation of poly(L-lactic acid): Effects of biaxial orientation. *Biomacromolecules* **2006**, *7*, 380–387. [\[CrossRef\]](#)
72. Rahaman, M.H.; Tsuji, H. Hydrolytic degradation behavior of stereo multiblock and diblock poly(lactic acid)s: Effects of block lengths. *Polym. Degrad. Stab.* **2013**, *98*, 709–719. [\[CrossRef\]](#)
73. Tsuji, H. Poly(lactide) Stereocomplexes: Formation, Structure, Properties, Degradation, and Applications. *Macromol. Biosci.* **2005**, *5*, 569–597. [\[CrossRef\]](#) [\[PubMed\]](#)
74. Tsuji, H.; Ikada, Y. Blends of crystalline and amorphous poly(lactide). III. Hydrolysis of solution-cast blend films. *J. Appl. Polym. Sci.* **1997**, *63*, 855–863. [\[CrossRef\]](#)
75. Tsuji, H. Hydrolytic Degradation. In *Poly(Lactic Acid)*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2010; pp. 343–381. [\[CrossRef\]](#)
76. Hirao, K.; Shimamoto, Y.; Nakatsuchi, Y.; Ohara, H. Hydrolysis of poly(l-lactic acid) using microwave irradiation. *Polym. Degrad. Stab.* **2010**, *95*, 86–88. [\[CrossRef\]](#)
77. Mohd-Adnan, A.-F.; Nishida, H.; Shirai, Y. Evaluation of kinetics parameters for poly(l-lactic acid) hydrolysis under high-pressure steam. *Polym. Degrad. Stab.* **2008**, *93*, 1053–1058. [\[CrossRef\]](#)
78. Piemonte, V.; Gironi, F. Kinetics of Hydrolytic Degradation of PLA. *J. Polym. Environ.* **2013**, *21*, 313–318. [\[CrossRef\]](#)
79. Piemonte, V.; Gironi, F. Lactic Acid Production by Hydrolysis of Poly(Lactic Acid) in Aqueous Solutions: An Experimental and Kinetic Study. *J. Polym. Environ.* **2013**, *21*, 275–279. [\[CrossRef\]](#)
80. Siparsky, G.L.; Voorhees, K.J.; Miao, F. Hydrolysis of polylactic acid (PLA) and polycaprolactone (PCL) in aqueous acetonitrile solutions: Autocatalysis. *J. Environ. Polym. Degrad.* **1998**, *6*, 31–41. [\[CrossRef\]](#)
81. Annesini Maria, C.; Frattari, S.; Gironi, F.; Piemonte, V.; Sabia, R.; Villani, C. Degradation of Post-consumer PLA: Hydrolysis of Polymeric Matrix and Oligomers Stabilization in Aqueous Phase. *J. Polym. Environ.* **2018**, *26*, 4396–4404. [\[CrossRef\]](#)
82. Iñiguez-Franco, F.; Auras, R.; Dolan, K.; Selke, S.; Holmes, D.; Rubino, M.; Soto-Valdez, H. Chemical recycling of poly(lactic acid) by water-ethanol solutions. *Polym. Degrad. Stab.* **2018**, *149*, 28–38. [\[CrossRef\]](#)
83. Auras, R.; Burgess, G.; Holmes, D.; Fang, X.; Rubino, M.; Soto-valdez, H. Concurrent solvent induced crystallization and hydrolytic degradation of PLA by water-ethanol solutions. *Polymer* **2016**, *99*, 315–323. [\[CrossRef\]](#)
84. Lazzari, S.; Codari, F.; Storti, G.; Morbidelli, M.; Moscatelli, D. Modeling the pH-dependent PLA oligomer degradation kinetics. *Polym. Degrad. Stab.* **2014**, *110*, 80–90. [\[CrossRef\]](#)
85. Jung, J.H.; Ree, M.; Kim, H. Acid- and base-catalyzed hydrolyses of aliphatic polycarbonates and polyesters. *Catal. Today* **2006**, *115*, 283–287. [\[CrossRef\]](#)
86. De Jong, S.J.; Arias, E.R.; Rijkers, D.T.S.; Nostrum, C.F. Van New insights into the hydrolytic degradation of poly(lactic acid): participation of the alcohol terminus. *Polymer* **2001**, *42*, 2795–2802. [\[CrossRef\]](#)
87. Shih, C. Chain-end scission in acid catalyzed hydrolysis of poly(d,l-lactide) in solution. *J. Control. Release* **1995**, *34*, 9–15. [\[CrossRef\]](#)
88. Codari, F.; Lazzari, S.; Soos, M.; Storti, G.; Morbidelli, M.; Moscatelli, D. Kinetics of the hydrolytic degradation of poly(lactic acid). *Polym. Degrad. Stab.* **2012**, *97*, 2460–2466. [\[CrossRef\]](#)
89. Van Nostrum, C.F.; Veldhuis, T.F.J.; Bos, G.W.; Hennink, W.E. Hydrolytic degradation of oligo(lactic acid): A kinetic and mechanistic study. *Polymer* **2004**, *45*, 6779–6787. [\[CrossRef\]](#)
90. Lyu, S.P.; Schley, J.; Loy, B.; Lind, D.; Hobot, C.; Sparer, R.; Untereker, D. Kinetics and time-temperature equivalence of polymer degradation. *Biomacromolecules* **2007**, *8*, 2301–2310. [\[CrossRef\]](#)
91. Rodriguez, E.J.; Marcos, B.; Huneault, M.A. Hydrolysis of polylactide in aqueous media. *J. Appl. Polym. Sci.* **2016**, *133*, 1–11. [\[CrossRef\]](#)

92. Song, X.; Wang, H.; Yang, X.; Liu, F.; Yu, S.; Liu, S. Hydrolysis of poly(lactic acid) into calcium lactate using ionic liquid [Bmim][OAc] for chemical recycling. *Polym. Degrad. Stab.* **2014**, *110*, 65–70. [\[CrossRef\]](#)
93. Al-Sabagh, A.M.; Yehia, F.Z.; Eissa, A.M.M.F.; Moustafa, M.E.; Eshaq, G.; Rabie, A.R.M.; Elmetwally, A.E. Glycolysis of poly(ethylene terephthalate) catalyzed by the Lewis base ionic liquid [Bmim][OAc]. *Ind. Eng. Chem. Res.* **2014**, *53*, 18443–18451. [\[CrossRef\]](#)
94. Niaounakis, M. Recycling of biopolymers—The patent perspective. *Eur. Polym. J.* **2019**, *114*, 464–475. [\[CrossRef\]](#)
95. Medina-Gonzalez, Y.; Aimar, P.; Lahitte, J.F.; Remigy, J.C. Towards green membranes: Preparation of cellulose acetate ultrafiltration membranes using methyl lactate as a biosolvent. *Int. J. Sustain. Eng.* **2011**, *4*, 75–83. [\[CrossRef\]](#)
96. Rasool, M.A.; Van Goethem, C.; Vankelecom, I.F.J. Green preparation process using methyl lactate for cellulose-acetate-based nanofiltration membranes. *Sep. Purif. Technol.* **2020**, *232*, 115903. [\[CrossRef\]](#)
97. Aparicio, S. Computational study on the properties and structure of methyl lactate. *J. Phys. Chem. A* **2007**, *111*, 4671–4683. [\[CrossRef\]](#)
98. Planer, S.; Jana, A.; Grela, K. Ethyl Lactate: A Green Solvent for Olefin Metathesis. *ChemSusChem* **2019**, *12*, 4655–4661. [\[CrossRef\]](#)
99. Pereira, C.S.M.; Silva, V.M.T.M.; Rodrigues, A.E. Ethyl lactate as a solvent: Properties, applications and production processes—A review. *Green Chem.* **2011**, *13*, 2658–2671. [\[CrossRef\]](#)
100. Aparicio, S.; Alcalde, R. The green solvent ethyl lactate: An experimental and theoretical characterization. *Green Chem.* **2009**, *11*, 65–78. [\[CrossRef\]](#)
101. Bowmer, C.T.; Hooftman, R.N.; Hanstveit, A.O.; Venderbosch, P.W.M.; van der Hoeven, N. The ecotoxicity and the biodegradability of lactic acid, alkyl lactate esters and lactate salts. *Chemosphere* **1998**, *37*, 1317–1333. [\[CrossRef\]](#)
102. Filachione, E.M.; Lengel, J.H.; Fisher, C.H. Preparation of Methyl Lactate. *Ind. Eng. Chem.* **1945**, *37*, 388–390. [\[CrossRef\]](#)
103. Hirao, K.; Nakatsuchi, Y.; Ohara, H. Alcoholysis of Poly(l-lactic acid) under microwave irradiation. *Polym. Degrad. Stab.* **2010**, *95*, 925–928. [\[CrossRef\]](#)
104. Carné Sánchez, A.; Collinson, S.R. The selective recycling of mixed plastic waste of polylactic acid and polyethylene terephthalate by control of process conditions. *Eur. Polym. J.* **2011**, *47*, 1970–1976. [\[CrossRef\]](#)
105. Liu, H.; Song, X.; Liu, F.; Liu, S.; Yu, S. Ferric chloride as an efficient and reusable catalyst for methanolysis of poly(lactic acid) waste. *J. Polym. Res.* **2015**, *22*, 135. [\[CrossRef\]](#)
106. Petrus, R.; Bykowski, D.; Sobota, P. Solvothermal Alcoholysis Routes for Recycling Polylactide Waste as Lactic Acid Esters. *ACS Catal.* **2016**, *6*, 5222–5235. [\[CrossRef\]](#)
107. Hofmann, M.; Alberti, C.; Scheliga, F.; Meißner, R.R.R.; Enthaler, S. Tin(ii) 2-ethylhexanoate catalysed methanolysis of end-of-life poly(lactide). *Polym. Chem.* **2020**, *1*–5. [\[CrossRef\]](#)
108. Plichta, A.; Lisowska, P.; Kundys, A.; Zychewicz, A.; Dębowski, M.; Florjańczyk, Z. Chemical recycling of poly(lactic acid) via controlled degradation with protic (macro)molecules. *Polym. Degrad. Stab.* **2014**, *108*, 288–296. [\[CrossRef\]](#)
109. Alberti, C.; Damps, N.; Meißner, R.R.R.; Hofmann, M.; Rijono, D.; Enthaler, S. Selective Degradation of End-of-Life Poly(lactide) via Alkali-Metal-Halide Catalysis. *Adv. Sustain. Syst.* **2020**, *4*. [\[CrossRef\]](#)
110. Song, X.; Zhang, X.; Wang, H.; Liu, F.; Yu, S.; Liu, S. Methanolysis of poly(lactic acid) (PLA) catalyzed by ionic liquids. *Polym. Degrad. Stab.* **2013**, *98*, 2760–2764. [\[CrossRef\]](#)
111. Song, X.; Bian, Z.; Hui, Y.; Wang, H.; Liu, F.; Yu, S. Zn-Acetate-Containing ionic liquid as highly active catalyst for fast and mild methanolysis of Poly(lactic acid). *Polym. Degrad. Stab.* **2019**, *168*, 108937. [\[CrossRef\]](#)
112. Liu, H.; Zhao, R.; Song, X.; Liu, F.; Yu, S.; Liu, S.; Ge, X. Lewis Acidic Ionic Liquid [Bmim]FeCl₄ as a High Efficient Catalyst for Methanolysis of Poly (lactic acid). *Catal. Lett.* **2017**, *147*, 2298–2305. [\[CrossRef\]](#)
113. Jehanno, C.; Pérez-Madrugal, M.M.; Demarteau, J.; Sardon, H.; Dove, A.P. Organocatalysis for depolymerisation. *Polym. Chem.* **2019**, *10*, 172–186. [\[CrossRef\]](#)
114. Nederberg, F.; Connor, E.F.; Glausser, T.; Hedrick, J.L. Organocatalytic chain scission of poly(lactides): A general route to controlled molecular weight, functionality and macromolecular architecture. *Chem. Commun.* **2001**, 2066–2067. [\[CrossRef\]](#) [\[PubMed\]](#)
115. Alberti, C.; Damps, N.; Meißner, R.R.R.; Enthaler, S. Depolymerization of End-of-Life Poly(lactide) via 4-Dimethylaminopyridine-Catalyzed Methanolysis. *ChemistrySelect* **2019**, *4*, 6845–6848. [\[CrossRef\]](#)

116. Liu, F.; Guo, J.; Zhao, P.; Gu, Y.; Gao, J.; Liu, M. Facile synthesis of DBU-based protic ionic liquid for efficient alcoholysis of waste poly(lactic acid) to lactate esters. *Polym. Degrad. Stab.* **2019**, *167*, 124–129. [[CrossRef](#)]
117. Liu, M.; Guo, J.; Gu, Y.; Gao, J.; Liu, F. Versatile Imidazole-Anion-Derived Ionic Liquids with Unparalleled Activity for Alcoholysis of Polyester Wastes under Mild and Green Conditions. *ACS Sustain. Chem. Eng.* **2018**, *6*, 15127–15134. [[CrossRef](#)]
118. Leibfarth, F.A.; Moreno, N.; Hawker, A.P.; Shand, J.D. Transforming Polylactide into Value-Added Materials. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 4814–4822. [[CrossRef](#)]
119. Whitelaw, E.L.; Davidson, M.G.; Jones, M.D. Group 4 salalen complexes for the production and degradation of polylactide. *Chem. Commun.* **2011**, *47*, 10004–10006. [[CrossRef](#)]
120. Fliedel, C.; Vila-Viçosa, D.; Calhorda, M.J.; Dagorne, S.; Avilés, T. 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* **2014**, *6*, 1357–1367. [[CrossRef](#)]
121. Jędrzkiewicz, D.; Czełusniak, I.; Wierzejewska, M.; Szafert, S.; Ejfler, J. Well-controlled, zinc-catalyzed synthesis of low molecular weight oligolactides by ring opening reaction. *J. Mol. Catal. A Chem.* **2015**, *396*, 155–163. [[CrossRef](#)]
122. Payne, J.; McKeown, P.; Mahon, M.F.; Emanuelsson, E.A.C.; Jones, M.D. Mono- and dimeric zinc(ii) complexes for PLA production and degradation into methyl lactate—A chemical recycling method. *Polym. Chem.* **2020**. [[CrossRef](#)]
123. McKeown, P.; Brown-Humes, J.; Davidson, M.G.; Mahon, M.F.; Woodman, T.J.; Jones, M.D. Ligands and complexes based on piperidine and their exploitation of the ring opening polymerisation of rac-lactide. *Dalton Trans.* **2017**, *46*, 5048–5057. [[CrossRef](#)]
124. Román-Ramírez, L.A.; McKeown, P.; Jones, M.D.; Wood, J. Poly(lactic acid) Degradation into Methyl Lactate Catalyzed by a Well-Defined Zn(II) Complex. *ACS Catal.* **2019**, *9*, 409–416. [[CrossRef](#)]
125. McKeown, P.; McCormick, S.N.; Mahon, M.F.; Jones, M.D. Highly active Mg(ii) and Zn(ii) complexes for the ring opening polymerisation of lactide. *Polym. Chem.* **2018**, *9*, 5339–5347. [[CrossRef](#)]
126. McKeown, P.; Román-Ramírez, L.A.; Bates, S.; Wood, J.; Jones, M.D. Zinc Complexes for PLA Formation and Chemical Recycling: Towards a Circular Economy. *ChemSusChem* **2019**, 5233–5238. [[CrossRef](#)] [[PubMed](#)]
127. Román-Ramírez, L.A.; McKeown, P.; Jones, M.D.; Wood, J. Kinetics of Methyl Lactate Formation from the Transesterification of Polylactic Acid Catalyzed by Zn(II) Complexes. *ACS Omega* **2020**, *5*, 5556–5564. [[CrossRef](#)] [[PubMed](#)]
128. McNeill, I.C.; Leiper, H.A. Degradation studies of some polyesters and polycarbonates—1. Polylactide: General features of the degradation under programmed heating conditions. *Polym. Degrad. Stab.* **1985**, *11*, 267–285. [[CrossRef](#)]
129. McNeill, I.C.; Leiper, H.A. Degradation studies of some polyesters and polycarbonates-2. Polylactide: Degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. *Polym. Degrad. Stab.* **1985**, *11*, 309–326. [[CrossRef](#)]
130. Kopinke, F.; Remmler, M.; Mackenzie, K.; Moder, M.; Wachsen, O. Thermal decomposition of biodegradable polyesters -II. Poly (lactic acid). *Polym. Degrad. Stab.* **1996**, *53*, 329–342. [[CrossRef](#)]
131. Nishida, H.; Mori, T.; Hoshihara, S.; Fan, Y.; Shirai, Y.; Endo, T. Effect of tin on poly(L-lactic acid) pyrolysis. *Polym. Degrad. Stab.* **2003**, *81*, 515–523. [[CrossRef](#)]
132. Wachsen, O.; Platkowski, K.; Reichert, K.H. Thermal degradation of poly-L-lactide -studies on kinetics, modelling and melt stabilisation. *Polym. Degrad. Stab.* **1997**, *57*, 87–94. [[CrossRef](#)]
133. Cam, D.; Marucci, M. Influence of residual monomers and metals on poly (l-lactide) thermal stability. *Polymer* **1997**, *38*, 1879–1884. [[CrossRef](#)]
134. Fan, Y.; Nishida, H.; Shirai, Y.; Tokiwa, Y.; Endo, T. Thermal degradation behaviour of poly(lactic acid) stereocomplex. *Polym. Degrad. Stab.* **2004**, *86*, 197–208. [[CrossRef](#)]
135. Fan, Y.; Nishida, H.; Mori, T.; Shirai, Y.; Endo, T. Thermal degradation of poly(L-lactide): Effect of alkali earth metal oxides for selective L,L-lactide formation. *Polymer* **2004**, *45*, 1197–1205. [[CrossRef](#)]
136. Nishida, H.; Fan, Y.; Mori, T.; Oyagi, N.; Shirai, Y.; Endo, T. Feedstock Recycling of Flame-Resisting Poly(lactic acid)/Aluminum Hydroxide Composite to L,L-lactide. *Ind. Eng. Chem. Res.* **2005**, *44*, 1433–1437. [[CrossRef](#)]
137. Fan, Y.; Nishida, H.; Hoshihara, S.; Shirai, Y.; Tokiwa, Y.; Endo, T. Pyrolysis kinetics of poly(L-lactide) with carboxyl and calcium salt end structures. *Polym. Degrad. Stab.* **2003**, *79*, 547–562. [[CrossRef](#)]

138. Feng, L.; Feng, S.; Bian, X.; Li, G.; Chen, X. Pyrolysis mechanism of Poly(lactic acid) for giving lactide under the catalysis of tin. *Polym. Degrad. Stab.* **2018**, *157*, 212–223. [[CrossRef](#)]
139. Fan, Y.; Nishida, H.; Shirai, Y.; Endo, T. Control of racemization for feedstock recycling of PLLA. *Green Chem.* **2003**, *5*, 575–579. [[CrossRef](#)]
140. Mori, T.; Nishida, H.; Shirai, Y.; Endo, T. Effects of chain end structures on pyrolysis of poly(L-lactic acid) containing tin atoms. *Polym. Degrad. Stab.* **2004**, *84*, 243–251. [[CrossRef](#)]
141. Abe, H.; Takahashi, N.; Kim, K.J.; Mochizuki, M.; Doi, Y. Thermal degradation processes of end-capped poly(L-lactide)s in the presence and absence of residual zinc catalyst. *Biomacromolecules* **2004**, *5*, 1606–1614. [[CrossRef](#)]
142. Coulembier, O.; Moins, S.; Raquez, J.M.; Meyer, F.; Mespouille, L.; Duquesne, E.; Dubois, P. Thermal degradation of poly(l-lactide): Accelerating effect of residual DBU-based organic catalysts. *Polym. Degrad. Stab.* **2011**, *96*, 739–744. [[CrossRef](#)]
143. Krall, E.M.; Klein, T.W.; Andersen, R.J.; Nett, A.J.; Glasgow, R.W.; Reader, D.S.; Dauphinais, B.C.; Mc Ilrath, S.P.; Fischer, A.A.; Carney, M.J.; et al. Controlled hydrogenative depolymerization of polyesters and polycarbonates catalyzed by ruthenium(ii) PNN pincer complexes. *Chem. Commun.* **2014**, *50*, 4884. [[CrossRef](#)]
144. Westhues, S.; Idel, J.; Klankermayer, J. Molecular catalyst systems as key enablers for tailored polyesters and polycarbonate recycling concepts. *Sci. Adv.* **2018**, *4*, eaat9669. [[CrossRef](#)] [[PubMed](#)]
145. Kindler, T.; Alberti, C.; Fedorenko, E.; Santangelo, N.; Enthaler, S. Ruthenium-Catalyzed Hydrogenative Degradation of End-of-Life Poly(lactide) to Produce 1,2-Propanediol as Platform Chemical. *ChemistryOpen* **2020**, *9*, 401–404. [[CrossRef](#)] [[PubMed](#)]
146. Shuklov, I.A.; Dubrovina, N.V.; Schulze, J.; Tietz, W.; Kühlein, K.; Börner, A. Propane-1,2-diols from Dilactides, Oligolactides, or Poly-L-lactic Acid (PLLA): From Plastic Waste to Chiral Bulk Chemicals. *Chem. A Eur. J.* **2014**, *20*, 957–960. [[CrossRef](#)] [[PubMed](#)]
147. Feghali, E.; Cantat, T. Room Temperature Organocatalyzed Reductive Depolymerization of Waste Polyethers, Polyesters, and Polycarbonates. *ChemSusChem* **2015**, *8*, 980–984. [[CrossRef](#)] [[PubMed](#)]
148. Monsigny, L.; Berthet, J.-C.; Cantat, T. Depolymerization of Waste Plastics to Monomers and Chemicals Using a Hydrosilylation Strategy Facilitated by Brookhart's Iridium(III) Catalyst. *ACS Sustain. Chem. Eng.* **2018**, *6*, 10481–10488. [[CrossRef](#)]
149. Nunes, B.F.S.; Oliveira, M.C.; Fernandes, A.C. Dioxomolybdenum complex as an efficient and cheap catalyst for the reductive depolymerization of waste plastics into value-added compounds and fuels. *Green Chem.* **2020**, 13–16. [[CrossRef](#)]

