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## Solvent-Assisted Poly(lactic acid) Upcycling under Mild Conditions

Dion Hubble,<sup>#</sup> Sarah Nordahl,<sup>#</sup> Tianyu Zhu,<sup>#</sup> Nawa Baral, Corinne D. Scown,<sup>\*</sup> and Gao Liu<sup>\*</sup>Cite This: *ACS Sustainable Chem. Eng.* 2023, 11, 8208–8216

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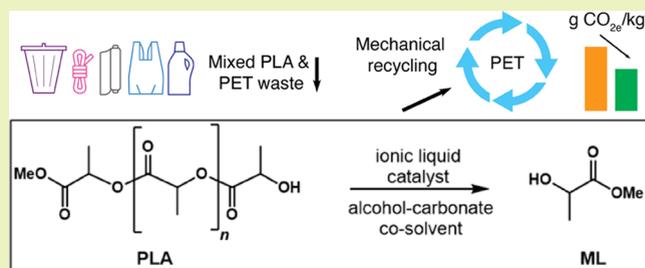
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Supporting Information

**ABSTRACT:** Poly(lactic acid) (PLA) is a biosourced green plastic derived from natural sources that can replace polyolefins in many applications; however, it is seldom recycled. PLA is a prime candidate for chemical recycling by depolymerization, which produces valuable commodity chemicals and/or fresh monomer for new production, compared to mechanical/thermal reprocessing which produces lesser-quality resin. A scalable, low-cost depolymerization process could render PLA the premier choice for designed-to-be-recycled products in a future circular plastics economy. Here, we report a novel process for depolymerization of PLA under mild conditions using alcoholysis with ionic liquid catalysts in the presence of dimethyl (or diethyl) carbonate as a green solvent, along with critical technoeconomic analysis of the potential impact of this process. The effects of catalyst structures, the solvent system, and PLA resin type on conversion and yield were studied. The reaction kinetics were statistically analyzed with experimental and modeling data, suggesting a fast first-order reaction in PLA degradation. Predictive modeling results based on empirical data further guide the design of scenarios and potential for practical application.

**KEYWORDS:** greenhouse gases, polylactic acid, advanced recycling, circular economy, PLA, ionic liquids, organic base, carbonate solvent



## INTRODUCTION

Polymers are ubiquitous for nearly any technology in our daily life, but most of them are disposed of after their service life regardless of the substantial feedstock consumed for the production.<sup>1–6</sup> Biobased polymers derived from renewable resources are emerging as promising replacements for traditional petroleum-based plastics in a sustainable society.<sup>7–15</sup> Design-for-recycling of plastic material has garnered tremendous interest in polymer research in the past decade due to increasing environmental concerns over the lack of recycling for existing plastics. Polylactide, *a.k.a.* poly(lactic acid) or “PLA,” is a biodegradable polymer naturally derived from organic feedstock that has gained increasing ground in the race to replace petrochemical-based plastics.<sup>16,17</sup> However, although it is biodegradable, polylactide has not been widely viewed as recyclable despite possessing the necessary properties for a design-for-recycling polymer material, including renewable feedstock, favorable engineering properties, and chemical bonds that withstand ordinary use conditions but are easily cleaved under readily achieved process conditions. We hope that this work will attract attention to the recycling potential for biodegradable plastics, both in terms of process chemistry and in the technoeconomic aspects.

Possible routes for the chemical recycling of PLA include thermal depolymerization, hydrolytic degradation, and enzymatic reactions.<sup>18–20</sup> An alternative method for PLA chemical recycling is *via* alcoholysis to lactate esters. PLA methanolysis, even with the best catalysts, typically requires a temperature above the boiling point of the alcohol, necessitating long hold

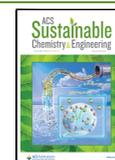
times in pressure vessels which add safety concerns and complexity to scale-up attempts.<sup>21,22</sup> Some studies have circumvented this issue by pre-dissolving PLA in an inert solvent, which speeds up the reaction and allows lower depolymerization temperatures.<sup>23</sup> However, most organic solvents used for PLA methanolysis exhibit potential safety and/or environmental concerns of their own (*e.g.*, chlorinated solvents (like dichloromethane), tetrahydrofuran (THF), *N*-methyl-2-pyrrolidone (NMP), *etc.*) which preclude such processes from being truly “green” and sustainable.<sup>24</sup> Moreover, typical catalysts for this process (*e.g.*, tin(II) salts) tend to be moisture-sensitive and/or toxic.<sup>25</sup> Alternative catalysts based on ionic liquids have shown some promise in this area, but to our knowledge, no study has demonstrated a catalyst system that can achieve high methanolysis yields in a reasonable time at a mild temperature.<sup>26–30</sup>

Previous literature has cited dimethyl carbonate (DMC), a green solvent that can be synthesized renewably from carbon dioxide, as an excellent solvent for PLA electrospinning.<sup>31,32</sup> In this work, we have demonstrated using DMC as a solvent for PLA chemical recycling which allows high concentrations of PLA to be solubilized with methanol at temperatures near the

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boiling point of the mixture. At the same time, several novel basic ionic liquid catalysts were developed for this system. This green catalyst and solvent system has allowed us to demonstrate >90% PLA conversion to methyl lactate (on a 10 s of grams scale) in only 3 h at 70 °C and atmospheric pressure, opening the door to a sustainable and economically feasible chemical recycling process for PLA.

## EXPERIMENTAL SECTION

**Materials.** All chemicals were used as received. Reagents used for ionic liquid synthesis were stored and used in a moisture- and oxygen-free glovebox. Methanol (anhydrous, 99.8%), dimethyl carbonate (anhydrous, ≥99%), imidazole (≥99%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (98%), sodium hydroxide (ACS reagent, ≥98.0%), and tetramethylsilane (NMR grade, ≥99.9%) were purchased from Sigma-Aldrich. Ethanol (200 proof, anhydrous, ≥99.5%) and diethyl carbonate (anhydrous, ≥99%) were purchased from Acros Organics. *N,N*-Dimethylglycine (>98.0%) and methyl *L*-lactate (>98.0%) were purchased from TCI America. Dimethyl sulfoxide-*d*<sub>6</sub> (99.9 atom % D) and deuterium oxide (99.9 atom % D) were purchased from Cambridge Isotope Laboratories. 1,8-Diazabicyclo[5.4.0]undec-7-ene (99%) was purchased from Beantown Chemical. Sodium methoxide solution (~30% in methanol) was purchased from Fluka. Amorphous poly(lactic acid) (Ingeo 6361D) was received as a research sample from NatureWorks, and semicrystalline poly(lactic acid) (ME346310, nominal granule size: 3–5 mm) was received as a research sample from Goodfellow. PET granules were received as a research sample from Goodfellow.

**Synthesis of BMIM Ionic Liquids (1-Butyl-3-methylimidazolium *N,N*-Dimethylglycinate).** [BMIM][OdmGly] was produced by ion metathesis between [BMIM]Cl and NaOdmGly. To an ethanolic solution of NaOH (33.33 mmol) was added an ethanolic solution of 1% molar excess *N,N*-dimethylglycine, causing a white precipitate of sodium *N,N*-dimethylglycinate (NaOdmGly) to appear. A molar equivalent of 1-butyl-3-methylimidazolium (BMIM) chloride was likewise dissolved in ethanol, then this solution was added to the NaOdmGly. The combined solution was stirred vigorously overnight at 70 °C to ensure complete ion exchange. Then, the solution was chilled in a refrigerator and vacuum-filtered cold to remove the sodium chloride precipitate, followed by rotary evaporation to remove ethanol. To the resulting translucent light yellow liquid was added acetone, and the mixture was stirred for 30 min to precipitate additional sodium chloride. The mixture was then chilled and vacuum-filtered cold, followed by rotary evaporation to remove acetone. Finally, the ionic liquid was vacuum-dried with stirring overnight at 60 °C to remove any residual solvent, moisture, or excess amino acid. The product appeared as a faint yellow, slightly viscous liquid.

**1-Butyl-3-methylimidazolium Imidazolidide.** [BMIM][Im] was similarly produced by ion metathesis between [BMIM]Cl and NaIm. Sodium imidazolidide was produced by adding a methanolic solution of sodium methoxide (33.33 mmol) to a 5% molar excess of imidazole. A molar equivalent of 1-butyl-3-methylimidazolium (BMIM) chloride was likewise dissolved in ethanol, then this solution was added to the NaIm solution with stirring. A white precipitate of sodium chloride appeared immediately. The solution was diluted with acetone, then stirred at room temperature for 30 min. Then, the combined solution was vacuum-filtered to remove the sodium chloride precipitate, followed by rotary evaporation to remove the solvent. The resulting amber liquid was diluted again with acetone, causing additional precipitation of sodium chloride. This mixture was chilled in a refrigerator, then vacuum-filtered cold, and acetone was removed by rotary evaporation. The product was extracted three times with diethyl ether to remove any excess imidazole and then vacuum-dried with stirring overnight at 60 °C to remove any residual solvent, moisture, or excess reagent. The product appeared as a dark amber, moderately viscous liquid.

**Synthesis of HDBU Ionic Liquids.** Both [HDBU][OdmGly] and [HDBU][Im] were produced by a simple acid-base reaction.<sup>33</sup> In a

moisture- and oxygen-free glovebox, the solid acid (*N,N*-dimethylglycine [HOdmGly] or imidazole [HIm], 20 mmol) was weighed into a clean glass vial, then a single molar equivalent of liquid 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added and the mixture was stirred with mild heating until all solids dissolved. The resulting protic ionic liquid was then vacuum-dried with stirring overnight at room temperature to remove any trace moisture or excess reagents. The faintly yellow, moderately viscous products were stored and dispensed in a glovebox.

**Synthesis of [HTBD][OdmGly].** In a water- and oxygen-free glovebox, solid 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 20 mmol) and *N,N*-dimethylglycine (HOdmGly, 20 mmol) were weighed into a clean glass vial, then 3 mL of methanol was added. The mixture was stirred with mild heating until all solids dissolved. Methanol was then removed by rotary evaporation. The resulting protic ionic liquid was vacuum-dried with stirring overnight at 70 °C to remove any remaining methanol, trace moisture, or excess reagents. The product appeared as a light yellow, highly viscous liquid, and was stored/dispensed in a glovebox.

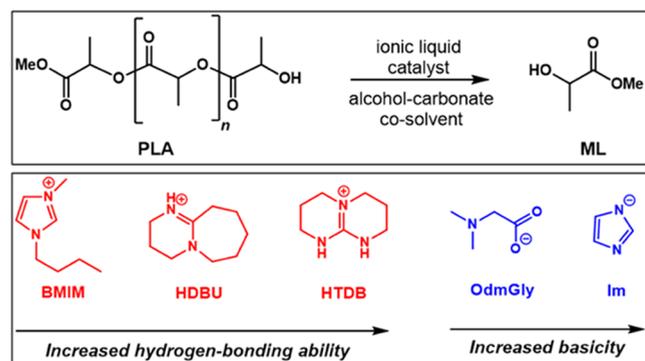
**Characterization.** Nuclear magnetic resonance (NMR) spectra were collected on a Bruker Avance II 500 MHz NMR spectrometer in DMSO-*d*<sub>6</sub> solvent (Figures S3–S5). Fourier transform infrared spectra were collected on a Thermo Fischer Nicolet iS50 FTIR spectrometer in attenuated total reflectance (ATR) mode (Figures S6 and S7). Gel permeation chromatography (GPC) was performed using tetrahydrofuran eluent on a Waters 1515 Isocratic HPLC Pump equipped with a Styragel column and Waters 2414 Refractive Index Detector.

Thermal gravimetric analysis (TGA) was performed on a TA Instruments SDT650 (Figures S1 and S2). Ionic liquid (or pure PLA polymer) samples (~20 mg) were weighed into alumina pans inside of a moisture- and oxygen-free glovebox, then transported to the instrument inside of a sealed vial. Single pans were then loaded and run immediately under flowing N<sub>2</sub> (100 mL/min). Samples were heated to 80 °C and held for 30 min to remove any adventitious moisture, then allowed to cool to 50 °C, and this weight was taken to be 100%. Finally, samples were heated to 800 °C at 10 °C/min and weight loss was recorded. Polymer samples (~20 mg) were weighed in atmospheric conditions and heated directly to 800 °C at 10 °C/min from room temperature.

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC2500. Ionic liquid samples (~10 mg) were loaded into aluminum pans and hermetically sealed inside a moisture- and oxygen-free glovebox.

**General Methanolysis Procedure.** In a typical experiment, a magnetic stir bar and 18 g of PLA (0.25 mol) were added to a preweighed 250 mL round-bottom flask, followed by 35 g of MeOH and 45 g of DMC. The flask was stoppered and the reaction mixture was stirred for 2 h in a 70 °C oil bath to form a clear solution. Concurrently, 5 mmol of the desired ionic liquid catalyst was dissolved in 5 g of hot MeOH. To begin the reaction, the hot catalyst solution was added into the PLA solution with stirring; the final molar ratio of MeOH/DMC/PLA/catalyst was 5:2:1:0.02. A water-cooled reflux condenser (open to atmosphere) was fitted onto the flask, and the reaction was stirred in a 70 °C oil bath at 300 rpm for 3 h. Over the course of the reaction, solution viscosity and vapor pressure notably decreased. The chemical structures of reactants and catalysts are shown in Figure 1.

Once the designated reaction time had concluded, the flask was removed from the oil bath and allowed to cool for several minutes. Excess MeOH and DMC solvents were then removed from the reaction mixture using a rotary evaporator with a 30 °C water bath, gradually decreasing the pressure from 150 to 70 torr until no more liquid came over. Finally, the reaction flask was transferred back to a 70 °C oil bath and a short-path distillation apparatus was fitted. Any remaining DMC was removed at 25 torr and discarded, then ML product was collected by fractional distillation at 5 torr (b.p. ~31 °C). The reaction flask containing the remaining viscous liquid was allowed to cool and then weighed to determine the amount of unreacted PLA plus catalyst, from which conversion was calculated.



**Figure 1.** Chemical structures of ionic liquid catalysts used for PLA degradation reactions.

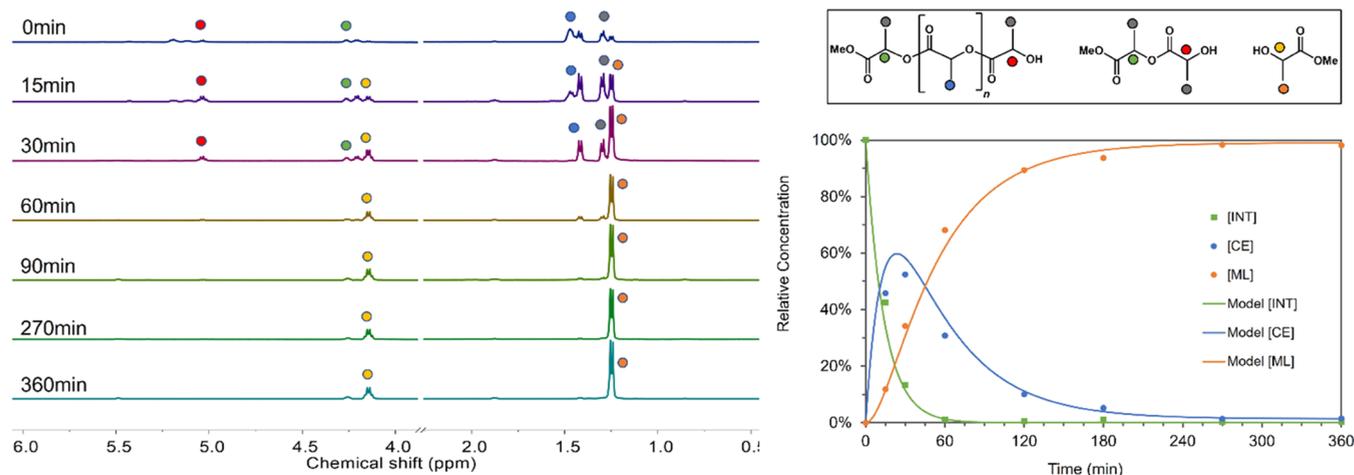
Methyl lactate yield was calculated based on the theoretical amount produced by 100% conversion of PLA

**Kinetic Study Procedure.** To study the kinetics of solvent-assisted PLA methanolysis, a reaction was set up as described above, except using a two-neck round-bottom flask with a water-cooled reflux condenser fitted to the top neck and a rubber septum on the second neck. Samples were extracted from the reaction mixture through the septum at designated times and added directly to vials containing appropriate amounts of DMSO- $d_6$ , then immediately placed in a refrigerator to halt any ongoing reaction. These samples were analyzed by  $^1\text{H}$  NMR to determine the relative concentrations of methine protons belonging to “internal” PLA groups, “chain-end” PLA groups, and ML groups (Figure 2).<sup>34,35</sup> These concentrations were fitted to an established kinetic model for PLA methanolysis, which was analytically solved using Wolfram  $\alpha$ . Kinetic rate constants were then extracted using Microsoft Excel’s solver function.

**Process Modeling and Systems Analysis.** Using the experimental data from this study, we model three different scenarios in SuperPro Designer and subsequently conduct life cycle assessments (LCAs) to understand the life cycle greenhouse gas (GHG) implications of commercial-scale PLA upcycling with and without PET recovery (Figure 3). When a full life cycle inventory cannot be done, other sustainability metrics used in green chemistry, such as E factor (mass of waste/mass of product), may be useful as a preliminary mechanism for comparing individual reactions or multistep processes. However, these simple mass-based metrics are not applicable when applied to entire supply chains and lack standardization in their use,<sup>36</sup> so we have chosen not to apply them in this study. The system boundary begins with the transportation of waste plastics from a material recovery facility (MRF) or waste

transfer station to a PLA upcycling facility and ends with the production of lactide (and in scenarios 2 and 3, PET recycling). All PLA and PET processing was assumed to occur at the same facility. Scenario 1 is focused on recycling PLA from a stream that is 99% PLA with 1% PET contamination. The waste is treated with DMC and the IL ([HDBU][OdmGly]) to produce methyl lactate, which is then converted to lactide. Scenario 1 is most relevant in a case where either an MRF recovers PLA or a specific source, such as a sports stadium or other controlled facility, collects and aggregates waste that is homogeneous by design. Scenarios 2 and 3, alternatively, depict an incoming stream, in which a recovered PET stream is contaminated with small amounts of PLA (10%). While even trace amounts of PLA (0.1%) can impede PET recycling, we model these mixed cases with higher PLA contamination to understand how our process could impact both PET and PLA recycling streams as biopolymer production increases.<sup>37</sup> In these scenarios, the outputs are both lactide and mechanically recycled PET. The distinguishing difference between these two scenarios is an additional DMC wash step to separate PET and PLA before entering the reactor in Scenario 3 (see Figure 3). Relative to Scenario 1, the PLA conversion rate in Scenario 2 is reduced by  $\sim 25\%$  because of the increased PET contamination entering the PLA reactor. The DMC wash in Scenario 3 can prevent some of this conversion loss by separating PET from the PLA stream prior to entering the reactor. This scenario was modeled to understand the trade-offs between an additional process step, the DMC wash, and an improved PLA conversion rate in the reactor. All parameters and assumptions relevant for this process modeling work, including experimental data, are presented in Tables S2–S6 in the Supporting Information. All three scenarios are modeled twice: first assuming current state conditions and again assuming optimal technical parameters for a hypothetical, improved future case. We assume a processing capacity of 50 tonnes per day for the current state case and 100 tonnes per day in the optimal case.

The process simulation models created in SuperPro Designer for each scenario provide both mass and energy balance data for the life cycle greenhouse gas inventory of the PLA upcycling reaction and lactide synthesis. The mass and energy balance data for mechanical PET recycling is based on data drawn from previously published literature.<sup>38</sup> The net life cycle GHG footprint, including all upstream and downstream impacts, is assessed through a physical units-based input–output life cycle inventory model called Agile-Cradle-to-Grave (Agile-C2G).<sup>38</sup> Relevant emission factor data and input–output data are available in Tables S7 and S8 in the Supporting Information. Because inputs and outputs vary across scenarios, no material-specific functional unit was used. Instead, the results presented here use two functional units: (1) 1 kg of total dry waste input and (2) 1 kg of total scalable outputs, also providing details on input and output compositions.



**Figure 2.** Kinetic study of PLA methanolysis catalyzed by [HTBD][OdmGly].

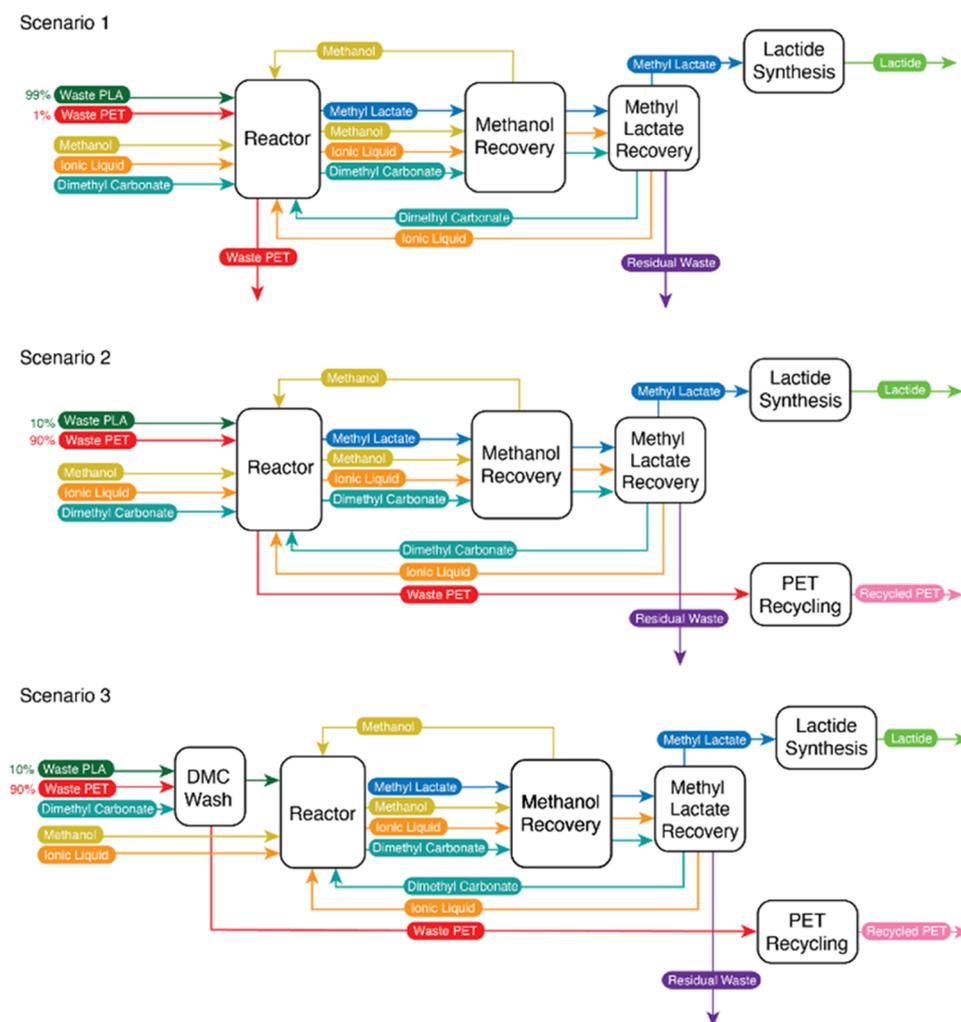


Figure 3. Process flow diagram for TEA and LCA scenarios.

## RESULTS AND DISCUSSION

**Ionic Liquid Catalyst Design.** Previous literature on PLA alcoholysis has found basic ionic liquids to be among the most effective promoters of this process. A two-step catalysis mechanism is usually proposed to explain these results. First, the cation (either a 1,3-dialkylimidazolium or a protonated nitrogenous base) activates PLA for nucleophilic attack through hydrogen bonding to the carbonyl group of the PLA backbone. Second, following nucleophilic attack by methanol, the cation stabilizes the transition state while a mildly basic anion (acetate or another carboxylate) facilitates proton transfer from the oxygen of methanol to the adjacent oxygen of the PLA ester backbone, driving the chain-scission reaction forward. Assuming this mechanism to be correct, it follows that catalytic activity could be improved by (1) increasing the electron-accepting ability of the cation and (2) increasing the proton-accepting ability (*i.e.*, basicity) of the anion. With this in mind, a series of basic ionic liquids were designed using one of three cations (1-butyl-3-methylimidazolium [BMIM], 1,8-diazabicyclo[5.4.0]undec-7-enium [HDBU], or 1,5,7-triazabicyclo[4.4.0]dec-5-enium [HTBD]) with increasing hydrogen-bonding ability, and one of two anions (*N,N*-dimethylglycinate [OdmGly], or imidazolate [Im]) with increasing basicity (Figure 1). *N,N*-Dimethylglycinate was selected as an ideal anion candidate due to the higher  $pK_a$  of

the amino group compared to the carboxylate group relied upon in previous catalyst designs. Additionally, the tertiary amino group cannot undergo nucleophilic addition to PLA, ensuring that the catalyst will not participate in side reactions during methanolysis. Finally, OdmGly is a biologically derived and nontoxic anion, improving the environmental credentials of the catalyst. HTBD was selected as an ideal cation candidate due to the presence of two chemically identical protons which can both participate in hydrogen bonding with PLA carbonyls (Figure 1), along with its high stability and easy synthetic access through simple acid-based neutralization.

The chemical structures of ionic liquid catalysts were characterized by NMR and FT-IR. The heteroatom proton on [HTBD][OdmGly] is visible on  $^1\text{H}$  NMR (Figure S4), indicating that the ionic form is very stable and proton exchange in the deuterated solvent is quite slow. This also supports the designation of this system as a protic ionic liquid rather than a hydrogen-bonded adduct, despite the high basicity of the anion.

**Effect of Catalyst on PLA Methanolysis.** Among ionic liquids with a OdmGly anion, an increase in PLA conversion with increasing hydrogen-bonding strength of the cation (HTBD > HDBU > BMIM) was observed, supporting the hypothesis that carbonyl activation of the PLA ester bond plays a critical role in the reaction mechanism. Notably, all three

Table 1. PLA Alcoholysis Catalyzed by Various Ionic Liquid Catalysts under Different Solvent Conditions

solvent	catalyst	cat./PLA	feedstock	temp. (°C)	time (h)	PLA conv. (%)	ML yield
DMC/MeOH	[BMIM][OdmGly]	1:50 (molar)	amorphous PLA	70	3	71.6	61.1%
DMC/MeOH	[HDBU][OdmGly]	1:50 (molar)	amorphous PLA	70	3	85.2	73.1%
DMC/MeOH	[HTBD][OdmGly]	1:50 (molar)	amorphous PLA	70	3	93.4	69.0%
DMC/MeOH	[BMIM][Im]	1:50 (molar)	amorphous PLA	70	3	87.8	59.0%
DMC/MeOH	[HDBU][Im]	1:50 (molar)	amorphous PLA	70	3	44.4	26.4%
DMC/MeOH	[HTBD][OdmGly]	1:50 (molar)	semicrystalline PLA	70	3	90.1	71.1%
MeOH only	[HTBD][OdmGly]	1:50 (molar)	semicrystalline PLA	65	3	39.3	25.9%
DEC/EtOH	[HTBD][OdmGly]	1:50 (molar)	amorphous PLA	80	3	45.6	21.0%
DMC/MeOH	[HTBD][OdmGly]	1:5 (molar)	amorphous PLA/semicrystalline PET (1:9 by wt)	70	3	68.0	n/a

basic ionic liquids with OdmGly were effective methanolysis catalysts in the mixed-solvent system, producing PLA yields >70% in only 3 h under the mild conditions of 70 °C, atmospheric pressure, and only 2 mol % catalyst relative to PLA. The champion catalyst, [HTBD][OdmGly], was capable of converting 93.4% of PLA under these conditions (see Table 1). The remaining material is expected to be in the form of PLA dimers and oligomers, which could be recycled back to the reactor in an industrial-scale application of the process, improving the overall conversion even more. The measured methyl lactate (ML) yields, while high, do not scale directly with conversion; this is largely a matter of small-scale separation inefficiency, which could be readily optimized on a larger scale.

To test whether increasing the anion  $pK_a$  beyond that of OdmGly could improve catalytic performance even further, imidazolate anion was selected for study considering ionic liquids based on Im are already known. Between [BMIM]-[OdmGly] and [BMIM][Im], the latter does indeed result in higher catalytic activity (87.8 vs 71.6% conversion, as shown in Table 1), as expected by the higher basicity of imidazolate. Curiously, however, the opposite is true for [HDBU][Im], which gives worse performance than [HDBU][OdmGly] (44.4 vs 85.2% conversion, Table 1). It was hypothesized that DBU (conjugate acid  $pK_a \sim 13.5$  in water) is not a strong-enough base to completely deprotonate imidazole ( $pK_a \sim 14$  in water). This is supported by the poor thermal stability of [HDBU][Im] (Figure S1) and, anecdotally, its much lower viscosity than the other ionic liquids. Indeed, this material is probably more accurately described as a hydrogen-bonded adduct or deep eutectic solvent rather than a protic ionic liquid, which explains its poorer catalytic performance. In comparison, [HTBD][OdmGly] has the highest thermal stability of all catalyst candidates, even more so than those based on the traditionally stable BMIM cation. We therefore conclude that full ionization, strong hydrogen-bonding ability of the cation, and ability of the anion to facilitate rapid intramolecular proton exchange—all characteristics possessed by [HTBD]-[OdmGly]—are critical characteristics for successful catalytic performance in PLA methanolysis. As a final comment, we note that high thermal stability is also desirable for the industrial application of this catalyst so that it may be separated from methyl lactate with high efficiency and recycled back to the reactor.

**Effect of PLA Crystallinity.** While the majority of the experiments were performed with an amorphous grade of PLA (Ingeo 6361D), commercial samples of this material are often semicrystalline. Therefore, the process was repeated with a semicrystalline grade of PLA (Goodfellow ME346310) to

ensure that the reaction design is applicable to nonamorphous materials. When added to the DMC/MeOH solvent mixture, the semicrystalline PLA took slightly longer to dissolve prior to catalyst addition; however, the reaction itself proceeded without any notable differences. With [HTBD][OdmGly] catalyst under identical process conditions, a PLA conversion of 90.1% and a methyl lactate yield of 71.1% were measured, both of which are nearly identical to the results achieved with amorphous PLA. Therefore, it was concluded that the solvent-assisted PLA methanolysis process is applicable regardless of the feedstock crystallinity.

**Effect of DMC Solvent.** In order to demonstrate the critical role played by DMC, the reaction was also attempted using [HTBD][OdmGly] catalyst and methanol in identical molar ratios to semicrystalline PLA, but without DMC solvent. While the nominal PLA concentration of this mixture is higher, omitting DMC makes the reaction suspension heterogeneous, as PLA is totally insoluble in methanol under these conditions; therefore, the reaction can only occur at the surface of PLA. Methanolysis still occurs but conversion/yield is much worse after 3 h (39.3 and 25.9%, respectively, as shown in Table 1), confirming that DMC as a green solvent is critical to the success of the process.

**Ethanolysis vs Methanolysis.** Following the success of the novel catalyst [HTBD][OdmGly] in PLA methanolysis with DMC solvent, it was considered whether the process was generalizable to other alcohols such as ethanol. In order to avoid *in situ* generation of methanol from the transesterification of DMC, the solvent was switched to diethyl carbonate (DEC). It was found that PLA does indeed dissolve in DEC and a DEC/EtOH 2:5 molar mixture, although less readily than with their methyl variants. Both solvents have higher boiling points, however, which allowed the reaction to be run at 80 °C without requiring a pressurized vessel.

With ethanol as a protic source, DEC as the solvent, and [HTBD][OdmGly] as the catalyst, the alcoholysis reaction still proceeds but with lower efficiency (45.6% conversion and 21.0% ethyl lactate yield). It was hypothesized that this is due to the lower acidity of ethanol compared to methanol, but further study is required to clarify the origin of this effect and determine optimized process conditions for ethanolysis.

**Selective Methanolysis of PLA in Mixtures with PET.** Poly(ethylene terephthalate) (PET) is a ubiquitous engineering plastic commonly found in drink containers. PET and PLA are notoriously difficult to separate in recycling streams, as their densities are nearly identical and there is no obvious visual difference.<sup>39</sup> Furthermore, PLA contamination leads to diminished optical, surface, and mechanical properties during PET recycling (Gere and Czigany, McLaughlin and

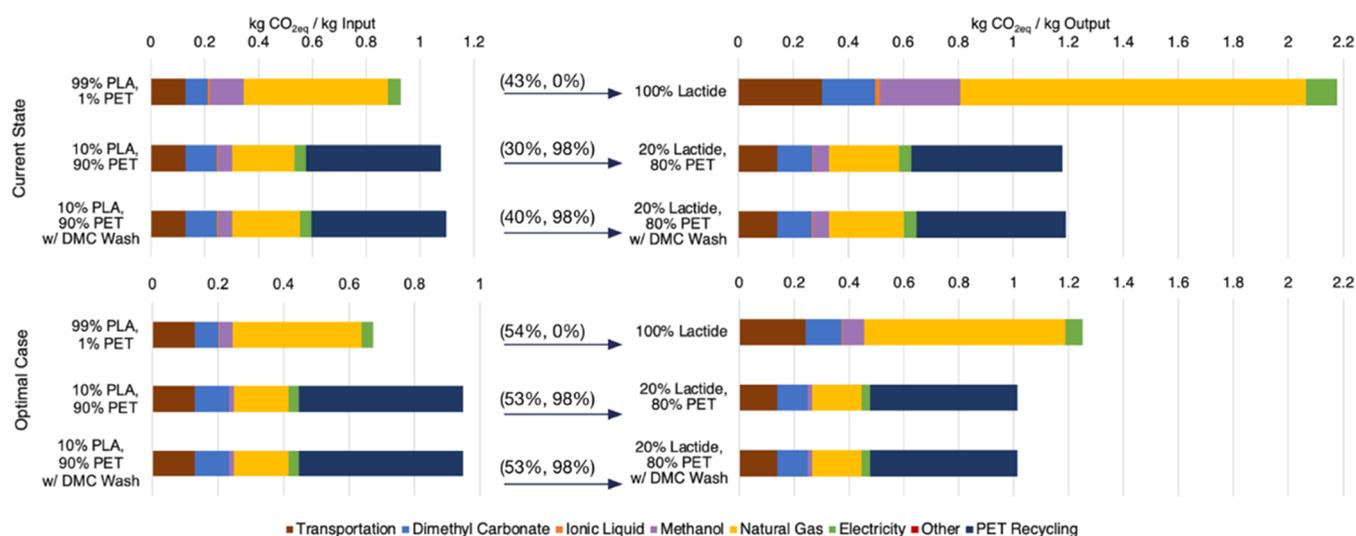


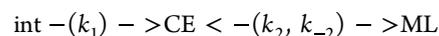
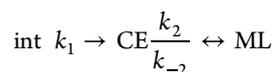
Figure 4. Life cycle greenhouse gas impacts from PLA upcycling.

Ghita).<sup>39,40</sup> However, unlike PLA, PET is insoluble in DMC, and it also requires much higher temperatures for methanolysis. This presents an opportunity to chemically separate these resins.<sup>40</sup>

If a mixed stream of 90% PET and 10% PLA is fed into our process with [HTBD][OdmGly] catalyst, PLA is selectively methanolized while PET is left behind. In fact, the weight of PET actually increased slightly (0.18%) after recovering it and vacuum drying, likely due to minor absorption of ionic liquid catalyst. However, PLA conversion is negatively affected (68.0%). Additionally, ionic liquid uptake by PET represents a single-cycle loss of 2.4% which partially undermines catalyst reusability, not to mention raising concerns about the purity of resin produced. A better implementation of this process for mixed PET/PLA streams would be to pre-separate by selectively dissolving PLA in DMC, then feeding this solution into a reactor with methanol and catalyst to perform methanolysis as usual (Figures S7 and S8).

#### Methanolysis Kinetics with [HTBD][OdmGly] Catalyst.

Kinetics for PLA depolymerization in the presence of excess methanol is well described by a simplified two-step reaction mechanism: internal PLA repeat units (“Int”) are irreversibly converted to dimers *a.k.a.* chain-end units (“CE”), followed by a reversible reaction of dimers into methyl lactate (“ML”).



The methine protons of each group have distinct <sup>1</sup>H chemical shifts in DMSO-*d*<sub>6</sub>, allowing the relative concentrations of each chemical species to be followed using NMR. The kinetic equations of this reaction can be represented as a linear system of first-order ordinary differential equations, which has an analytic solution. Nonlinear least-squares fitting of the relative concentration data (obtained under representative process conditions using [HTBD][OdmGly] catalyst) to the kinetic equation gives the following values:

$$k_1 = 7.23 \times 10^{-2} \text{ min}^{-1}$$

$$k_2 = 2.21 \times 10^{-2} \text{ min}^{-1}$$

$$k_{-2} = 2.09 \times 10^{-4} \text{ min}^{-1}$$

These values are comparable to those reported by Román-Ramírez et al. but under milder conditions and with a simpler catalyst system.<sup>22</sup> It was found that the forward reaction of oligomers into methyl lactate was 2 orders of magnitude faster than the reverse reaction, which is unsurprising considering the excess of methanol and the reduced reactivity of the secondary alcohol group of methyl lactate compared to the primary alcohol group of methanol. This kinetic analysis confirms that our catalyst and green solvent system are highly effective at chemically depolymerizing PLA and that the overall reaction rate is primarily limited by conversion of low-molecular-weight species. The possible methanolysis mechanism with ionic liquid catalyst developed in this work is shown in Figure S14.

**Life Cycle Assessment.** A simplistic metric, such as the energy economy coefficient, which divides mass yield by the product of time (in minutes) and temperature (in degrees Celsius) can be used to compare all of the process conditions and yields shown in Table 1, which would produce values ranging from  $2.2 \times 10^{-5}$  to  $5.8 \times 10^{-5}$ .<sup>41</sup> However, such values offer minimal value since they ignore actual system-level energy use as upstream energy and emissions embedded in material inputs. This is why, we make use of life cycle assessment. Based on currently demonstrated operating conditions and performance, upcycling of a 99% pure PLA input waste stream emits ~2.2 kg of CO<sub>2eq</sub> per kg of lactide produced (Scenario 1, Figure 4). If the process can be further optimized (see Tables S1–S6), this emission factor can be reduced by around half to ~1.3 kg CO<sub>2eq</sub> per kg lactide. Regardless of whether the process has been optimized, the emissions are driven primarily by the consumption of natural gas to supply thermal energy at the facility. Because natural gas use accounts for over half of the GHG impacts from PLA upcycling, these results are sensitive to the carbon footprint of natural gas production; using renewable energy as an alternative could reduce impacts. Relative to natural gas, electricity, materials (including methanol, DMC, and the IL catalyst), and transportation are minor contributors to the global warming potential of PLA upcycling, each accounting for no more than 15% of the total impact. A source of uncertainty is the residence time modeled in these scenarios.

Although we use 3 h, actual residence times in an industrial facility may vary; however, because the residence time primarily impacts electricity (a minor contributor to life cycle GHG emissions), this uncertainty does not substantially impact the results.

To put these results in context, emission factors for lactide and PLA in the peer-reviewed literature and company reports were explored. Reported emission factors for virgin PLA production typically range from 1.5 to 3.5 kg of CO<sub>2eq</sub> per kg of PLA produced.<sup>42–45</sup> The most recent LCA from Ingeo NatureWorks, one of the biggest producers of PLA, reported an emission factor of 0.42 kg of CO<sub>2eq</sub> per kg of lactide produced and a total emission factor of 0.62 CO<sub>2eq</sub> per kg of PLA produced.<sup>42</sup> The reported emission factors from Ingeo may be smaller than other reported emission factors in part because the study assumed high renewable energy penetration in the electricity grid mix and high carbon uptake and sequestration in the polymer. Using the allocation of emissions from Ingeo, we can assume ~68% of PLA production emissions are attributable to lactide. Applying this adjustment factor to the highest reported emissions footprint for PLA, a maximum emission factor of 2.4 kg of CO<sub>2eq</sub> per kg of lactide was calculated. Few peer-reviewed studies have shown LCAs specific to lactide production; Groot and Boren (2010) found that synthesizing 1 kg of L-lactide emitted 0.3–0.8 kg of CO<sub>2eq</sub>. Compared to this range of previously reported values, 0.3–2.4, our results indicate that upcycling PLA with DMC may offer GHG savings relative to the highest-emitting processes, but further improvements will require a shift toward renewable sources of thermal energy (e.g., biogas).

In Figure 4, the top row shows results given current experimental parameters and the bottom row shows results for a potential, future case assuming optimal technical parameters. The first column of figures uses a functional unit of 1 kg of combined dry waste input (PLA and PET), and the second column uses a functional unit of 1 kg of combined valuable outputs (lactide and recycled PET). The arrows in between the first and second columns of figures are labeled with 2 values: the first is the lactide yield (mass of lactide output/mass of waste PLA input), and the second is the recycled PET yield (mass of recycled PET output/mass of waste PET input).

An alternative perspective is to consider PLA upcycling compared to other end-of-life management options on a per-unit-waste basis. With respect to GHG emissions, PLA upcycling with DMC is more emission-intensive than mechanical recycling, which emits less than 0.5 kg of CO<sub>2eq</sub> per kg of waste PLA. Although mechanical recycling has a smaller carbon footprint, the quality of recyclate will vary, as dyes and additives will remain in the recycled material. According to a recent study from Aryan et al., chemical recycling of PLA via hydrolysis and via alcoholysis with either methanol or ethanol all have life cycle nonbiogenic GHG emissions of around 1.5 kg CO<sub>2eq</sub> per kg of PLA waste excluding substitution credits for final products, making PLA upcycling with DMC a slightly less emission-intensive recycling option.<sup>46</sup>

Unlike Scenario 1, Scenarios 2 and 3 consider a stream that is 90% PET with 10% PLA contamination. Both Scenarios 2 and 3 offer the opportunity to produce a higher quality, more pure PET stream for mechanical recycling while also upcycling PLA. The lower GHG impact of the mixed PET/PLA cases on a per-input or per-output basis compared to the pure PLA case is driven by the relatively low carbon footprint of mechanical

PET recycling, approximately 0.6 kg of CO<sub>2eq</sub> per kg waste PET (Figure S15). Because PET dominates the waste stream in these scenarios, PLA upcycling can be viewed as a complementary technology for removing a problematic contaminant (PLA) and upcycling it to a salable product (lactide) rather than paying for its disposal. As shown in Figure 4, the results for Scenario 2 and 3 are nearly the same; the additional DMC wash in Scenario 3 did not provide substantial GHG benefits. Facilities may choose to implement this strategy if it proves beneficial in practice, as the impacts on emissions appear to be negligible.

## CONCLUSIONS

In summary, a chemical process was demonstrated to degrade poly(lactic acid) (PLA) into methyl lactate using a novel dimethyl carbonate solvent system and catalyzed by a class of novel ionic liquid catalysts under mild temperatures. The best-performing catalyst is a protic ionic liquid that can be synthesized by the simple neutralization reaction of an amino acid (*N,N*-dimethylglycine) with an organic superbase (1,5,7-triazabicyclo[4.4.0]dec-5-ene), enabling >93% PLA conversion to methyl lactate in only 3 h at mild temperature (70 °C). Besides, the cost of using such ionic liquid catalysts becomes less a concern considering the high stability and recyclability through vacuum distillation or aqueous extraction (for hydrophilic ionic liquids). The overall process lowers the environmental cost of chemical PLA recycling into a range that is competitive with virgin PLA production. Additionally, it may be deployed as a means to chemically separate PLA from poly(ethylene terephthalate) (PET) while producing a valuable byproduct. Looking forward, any secondary waste generated during the cleaning of ionic liquid catalysts will be the focus for applying this process on a large scale. This work represents a significant advance in the quest for a circular plastics economy using designed-to-be-recycled products.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c06500>.

Detailed experimental data and technoeconomic analyses input and out numbers (PDF)

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## Notes

The authors declare no competing financial interest.

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