Transforming Polylactide into Value-Added Materials

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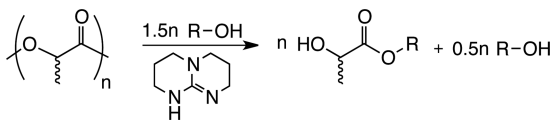
ABSTRACT: The production of chemical building blocks and polymer precursors from biorenewable and sustainable resources is an attractive method to bypass traditional fossil fuel derived materials. Accordingly, we report the organocatalytic recycling of post-consumer polylactide (PLA) into value-added small molecules. This strategy, using the highly active transesterification catalyst triazabicyclodecene, is shown to completely depolymerize PLA in the presence of various alcohols into valuable lactate esters. Using previously used PLA packaging material, the depolymerization is complete in minutes at room temperature and fully retains the stereochemistry of the lactate species. Further, the modularity and utility of this methodology with respect to polyester substrate is detailed by using a variety of functional alcohols to depolymerize both PLA and polyglycolide, with the corresponding ester small-molecules being used to make new polymeric materials. The opportunities to transform waste streams into value-added chemicals and new materials through simple and versatile chemistry hold significant potential to extend the lifecycle of renewable chemical feedstocks. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 4814–4822, 2012

KEYWORDS: biodegradable; depolymerization; glycolate ester; lactate ester; organic catalysis; polyesters; polyglycolide; polylactide; recycling; transesterification

INTRODUCTION As society increasingly deals with inherently limited natural resources, the utilization of 7% of fossil fuels for the production of plastics is a significant drain on petrochemical feedstocks.[1] With the demand for polymeric materials increasing, it is imperative to develop building blocks based on renewable and sustainable resources.[2] The conversion of biomass to value-added small molecules and polymer precursors is an attractive method to bypass traditional fossil fuel-based chemical production.[3–5] For example, polylactide (PLA) has emerged as one of the most promising biorenewable and biodegradable polymers due to its utility in packaging, textile, and biomedical applications.[6–9] The recent addition of Natureworks™ LLC facility in the US has put annual production capacity of PLA at over 150,000 tons, making it a high-volume commodity material.[10–12] This large-scale production and the predicted annual growth rate of 19% for bioplastics[13] assures that many new PLA derived products will enter the marketplace in the coming decades.

Beyond being derived from renewable resources, PLA has distinct advantages over other plastics in terms of waste management. Polyethylene terephthalate (PET), which currently dominates the market for packaging materials, is traditionally mechanically recycled into lower grade materials and repurposed.[14] Although chemical recycling of PET and advanced "bottle-to-bottle" mechanical processes have been developed, they are often overly costly and complex. PLA, however, is compostable and biodegrades into soil-enriching compounds.[11] Further, large-volume waste is ideal for chemical recycling, as the ester bonds in the backbone of PLA can by hydrolyzed.[15] Modern PLA recycling, however, relies on harsh acidic or basic conditions and high temperatures, making these processes unattractive due to their high energy input and difficulty controlling the stereochemistry of the resulting lactate species.[16–18] More complex hydrolysis mechanisms using enzymes[19–21] or heterogeneous catalysis[22–24] can overcome some of these limitations, but alternative, scalable methods for recycling PLA remain underdeveloped.

Lactic acid derived from fermentation of biomass is not only a valuable chemical feedstock for the production of bioplastics, but it is also employed for the production of ethyl lactate and other lactate esters that are found in everyday products such as wine, cosmetics, perfumes, degreasers, and can be used as food additives, solvents, fragrances, and plasticizers.[25–30] A significant opportunity, therefore, exists for repurposing commodity PLA into value-added small molecules through a simple and versatile strategy. Traditionally, acid-catalyzed reactions of lactic acid and an alcohol produce lactate esters in an equilibrium process, with the alkyl lactate being recovered by distillation.[25,31] These batch processes are inherently low yielding and inefficient.



SCHEME 1 The depolymerization of commodity PLA using a variety of alcohols is catalyzed by TBD to produce small-molecule lactate esters.

Alternatively, the transformation of PLA into lactate esters provides a number of potential advantages, including starting materials derived from recycled waste, a high yield of lactate ester from PLA, simple purification, and retention of stereochemistry. Further, this recycling process adds value to the PLA supply chain, as the market price of commodity PLA is about $1.00 per pound compared with almost $2.00 per pound for ethyl lactate.[25]

We report the recycling of PLA into value-added small molecule lactate esters through rapid and quantitative transesterification using triazabicyclodecene (TBD)[32] as an organocatalyst. TBD and other organocatalysts have been used in the ring-opening polymerization of cyclic esters, carbonates, and siloxanes and have advantages including high activity, lack of metal contamination, and control over polymer molecular weight and polydispersivity (PDI).[33–38] Seminal work by Hedrick described the selective chain scission of PLA through transesterification into end-functional, lower molecular weight polymers and oligomers.[38(b)] Further, Hedrick and Waymouth demonstrated the utility of these organocatalysts for the depolymerization of PET at high temperatures.[39,40] Herein, we show that commodity PLA can be quickly and completely broken down at room temperature to yield industrially valuable lactate esters. Special attention is given to the scope of these reactions, with optimized conditions providing quantitative breakdown and isolation of useful lactate esters at room temperature with full retention of stereochemistry. This methodology is further used on polyglycolide (PG), displaying its generality toward polyester starting material and its utility in making novel small molecules.

RESULTS AND DISCUSSION

To illustrate the utility of this strategy, the breakdown of PLA catalyzed by TBD was performed on Natureworks™ Ingeo™ commodity material obtained from both fiber resin or previously used vegetable packaging. Typical samples had a number average molecular weight (M_n) of 76.7 kg/mol, a PDI of 1.38, a glass transition temperature (T_g) of 54 °C, and a melting temperature (T_m) of 164 °C. In a typical experiment, the polymer sample and previously dried alcohol were dissolved in a solution of methylene chloride under inert atmosphere at room temperature and TBD was added (Scheme 1). All reactions could also be done without the addition of solvent at temperatures above 100 °C. The reactions were quenched by the addition of amberlyst H-form resin, decanted, and the solvent and excess alcohol removed to obtain the desired lactate ester. The depolymerization products were monitored using a variety of techniques including gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), infrared spectroscopy (IR), mass spectroscopy, and gas chromatography (GC).

Because of ethyl lactate's prominence as an industrial solvent and food/fragrance additive,[25,28] we first carried out the transesterification of commercial PLA with ethanol using catalytic TBD. Using 1.0 mol % of TBD (~2 wt %) and 1.5 equivalents of alcohol per ester bond, complete polymer depolymerization to small molecules was observed by GPC in only 2 min at room temperature by tracking the polymer molecular weight with respect to time (Fig. 1). Two control experiments, one using alcohol and no catalyst and the other using catalyst and no alcohol, displayed no polymer degradation over a 24-h period under the same conditions. These results demonstrate the efficiency of TBD as a transesterification catalyst, as even low loadings can depolymerize high molecular weight commodity polymers in a short time at room temperature. Subsequently, the concentration of both the catalyst and alcohol were independently varied to probe their individual contributions to the rate and efficiency of the recycling process. Using 1.1, 1.5, 3.0, and 5.0 equivalents of alcohol per ester, all gave identical results as assessed by GPC, indicating that the amount of alcohol present had no discernable effect on the depolymerization kinetics. Conversely, the concentration of catalyst had a significant influence on the kinetics of depolymerization. Increasing the catalyst concentration from 0.5 to 1.0 to 2.5 mol % compared with polymeric ester, the time to complete depolymerization decreased from 10 to 2.0 to $<$ 1.0 min.

After gaining a general understanding of the depolymerization process, the scope of this chemistry was investigated by exploring a range of different alcohols for PLA transesterification. Using standard conditions of 1.0 mol % (~2 wt %) of TBD and three equivalents of alcohol per ester, a wide variety of primary alcohols provided fast and efficient depolymerization. The readily available alcohols methanol, ethanol, and butanol enabled depolymerization of PLA in under 2 min as assessed by GPC (Table 1, entries 1–3), whereas allylic alcohols, benzylic alcohols, and those with branching at the β-carbon required slightly increased reaction times (3 min) to affect polymer depolymerization (Table 1, entries 4, 5, and 7). Gratifyingly, the catalyst system also proved highly functional group compatible, producing a number of functional α-hydroxyesters containing alkenes, alkyl halides, and

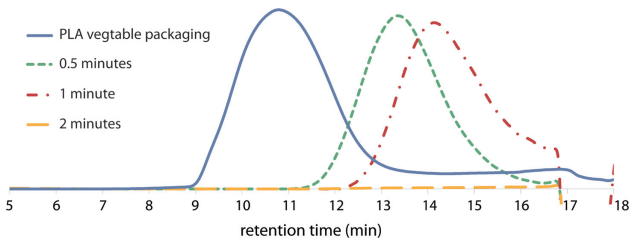
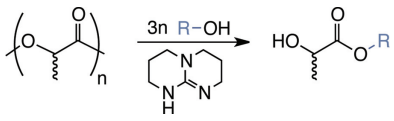
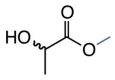
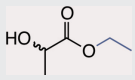
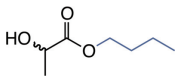
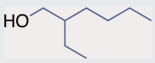
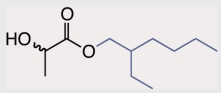
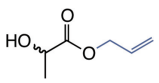
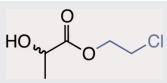
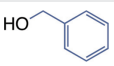
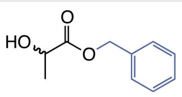
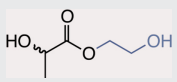


FIGURE 1 GPC traces over time for the depolymerization of PLA using 3 equiv of ethanol and 1.0 mol % of TBD per ester group.

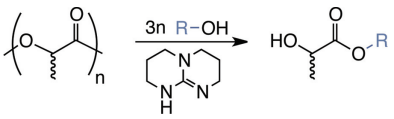
TABLE 1 Screening of Primary Alcohols in the Organocatalytic Depolymerization of PLA

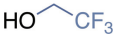
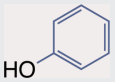
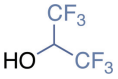
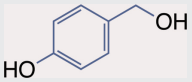


Entry	Alcohol	Product	Degradation Time(min)
1			2
2			2
3			2
4			3
5			3
6			2
7			3
8[a]			10

Standard reaction condition: 1 mol % TBD, three equivalents of alcohol per ester, room temperature in methylene chloride. [a]5 equivalents of alcohol no solvent, 150°C.

TABLE 2 Degradration Conditions for the Orgnocatalytic Depoloymerization of PLA Empolying Sterically Hindered and/or Acidic Alcohols

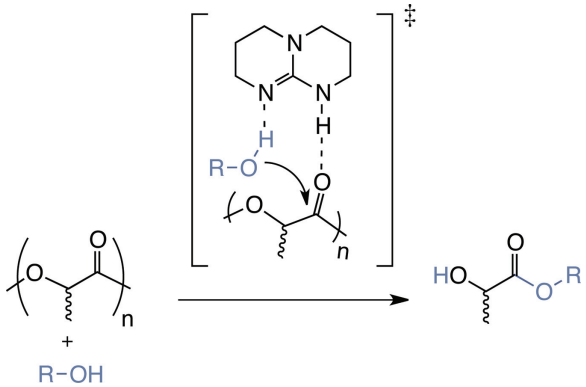


Entry	Alcohol	Degradation conditions
9		30 min 25°C
10		ND
11		30 min 100°C
12		ND
13		ND
14		ND

No depolymerization is signified by ND.

alcohols in a synthetically simple manner. Lastly, for alcohol derivatives that lack complementary solubility with PLA, such as ethylene glycol, performing the reaction solvent free at elevated temperatures (150 °C) provided complete depolymerization in 10 min.

The success of this catalyst system with primary alcohols prompted examination of a wider range of substrates including sterically hindered and acidic alcohols (Table 2). Steric bulk alpha to the alcohol had a significant effect on depolymerization kinetics, evidenced by an increase in polymer depolymerization time to 30 min for isopropanol (Table 2, entry 9). Further increasing steric hindrance to *tert*-butanol resulted in a complete loss of transesterification activity even at temperatures up to 150 °C (Table 2, entry 10). The significant effect of sterics on TBD catalyzed transesterification is presumably a consequence of the proposed dual-activation mechanism (Scheme 2),[41,42] which would hinder sterically demanding substrates from accessing the crowded, three-component intermolecular complex. Also, acidity was predicated to have an effect on substrate scope, as protonation of the highly basic TBD catalyst ($pK_a = 26$ in acetonitrile[43]) would destroy its catalytic activity. Screening the mildly acidic 2,2,2-trifluoroethanol (TFE), a lack of catalytic activity was observed at room temperature. Using chloroform as a solvent and heating the reaction mixture to 100 °C



SCHEME 2 The depolymerization transition state proposed[41,42] for TBD catalyzed transesterification. The crowded intermolecular assembly and basicity of TBD determines the scope of polymer depolymerization.

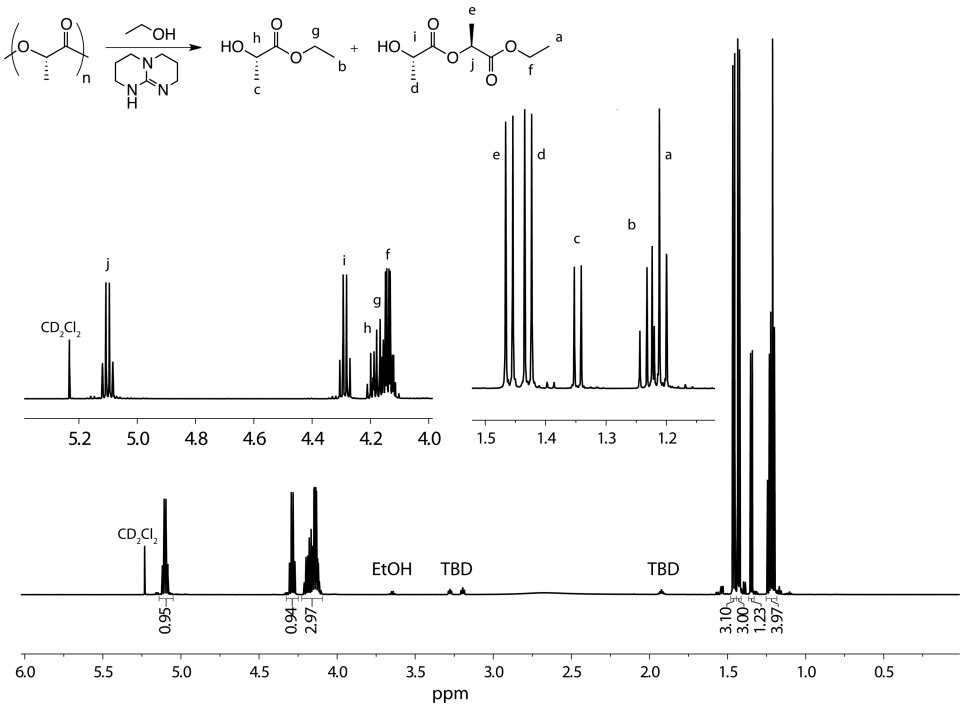


FIGURE 2 ^{1}H NMR of reaction mixture after polymer depolymerization with 1 mol % TBD and 3 equiv of ethanol after 3 min showing ethyl lactate and the ethyl lactate dimer as the two exclusive products.

in a closed reactor, TFE was able to depolymerize PLA in 10 min to provide a new fluorinated α-hydroxyester (Table 2, entry 11). In contrast, the more acidic substrates phenol and hexafluoroisopropanol displayed no transesterification activity even at elevated temperatures. To determine if this observed trend was an acidity effect of phenol as opposed to a consequence of its diminished nucleophilicity compared with primary alcohols, the difunctional derivative 4-hydroxybenzyl alcohol was used (Table 2, entry 14). This molecule contains a sufficiently nucleophilic benzyl alcohol known to work well in this depolymerization process (Table 1, entry 7) along with an acidic phenolic proton. 4-Hydroxybenzyl alcohol showed no activity for transesterification in this system even at elevated temperatures, suggesting that the acidic nature of the phenol deactivates TBD even when a primary alcohol is present.

Stereodefined lactate esters and oligomers are useful small molecules and synthetic intermediates in the pharmaceutical and biomedical fields;[26,27,44,45] therefore, to complete our understanding of the scope of TBD catalyzed PLA recycling, the stereochemistry of the commercial polymer and the resulting lactate esters was investigated. Circular dichroism (CD) was used to determine the stereochemistry of commodity materials obtained from recycled packaging and fiber resin. Samples of poly(L-lactide) and poly(D,L-lactide) purchased commercially were used as references. As expected, poly(L-lactide) displayed a positive response in the CD spectra,[46] whereas poly(D,L-lactide) displayed no response. Subsequently, both samples of the Natureworks™ Ingeo™ polymers were analyzed and displayed identical positive responses to that of poly(L-lactide) at the same concentration, indicating that commercial Ingeo™ polymers are comprised of poly(L-lactide). Subsequently, the materials were depolymerized using benzyl alcohol and the products were analyzed by chiral high-performance liquid chromatography (HPLC). Depolymerization of achiral poly (D,L-lactide) into benzyl lactate showed the expected set of two peaks in a 1:1 ratio corresponding to the *R* and *S* enantiomers of the small molecule. Depolymerization of the commodity samples of poly(L-lactide), conversely, displayed a drastic stereoenrichment of one enantiomer, providing $>$ 95% *S*-benzyl lactate. These results demonstrate that the TBD catalyst does not significantly racimize the polymer or the resulting lactate ester during the recycling process. Further, obtaining highly enantiomerically pure small molecules from commodity polymers has significant implications for the potential uses of these materials in downstream applications.

In addition to stereochemical purity, it was important to determine the final product distribution of these depolymerization reactions from a purity standpoint. ^{1}H NMR spectroscopy of the degradation products after 3 min of reaction of PLA with ethanol and catalytic TBD at room temperature showed the presence of two distinct products: ethyl lactate and the ethyl ester of the lactic acid dimer, hereafter referred simply as "dimer" (Fig. 2), with no higher order oligomers detectable. GC confirmed the presence and ratio of these two products. To further probe the origin of this finding, a time-dependant study of the ethyl lactate to dimer ratio after polymer depolymerization was accomplished by independently varying both the concentration of alcohol and TBD (Fig. 3). Using 1.0 mol % TBD and three equivalents of

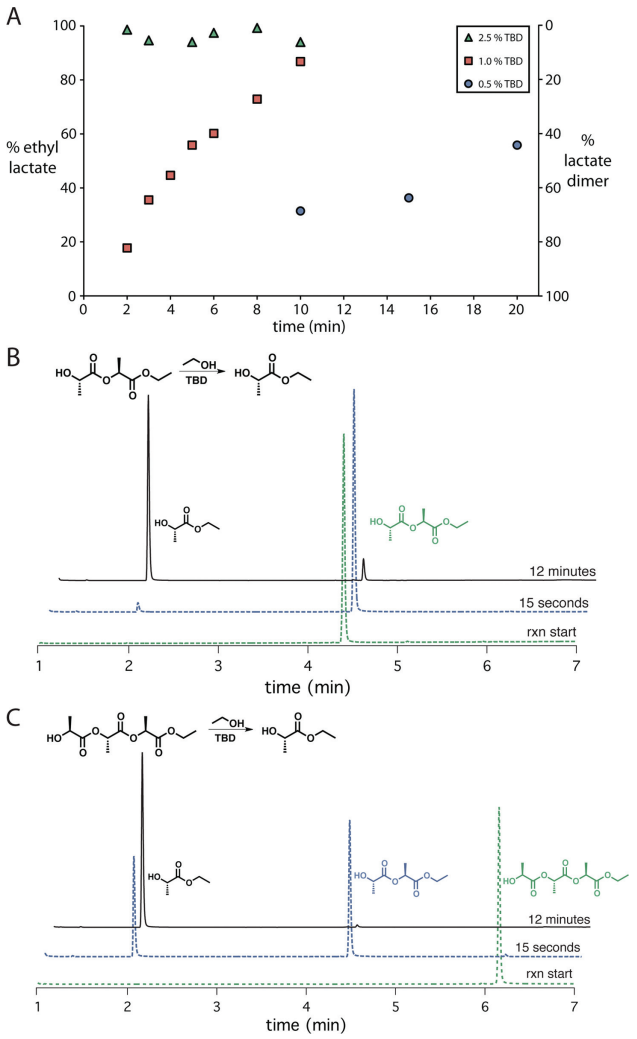
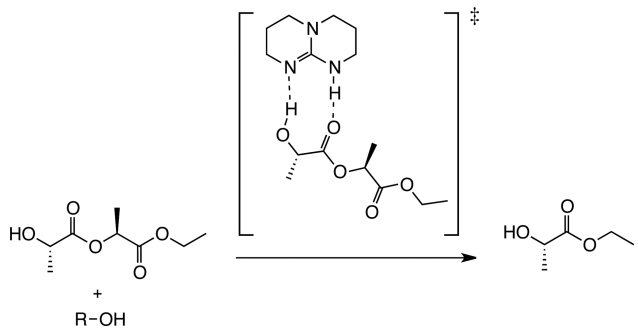


FIGURE 3 A: plot displaying the amount of ethyl lactate compared with the amount of ethyl lactate dimer as monitored by GC after polymer depolymerization. Reactions used 3 equiv of ethanol and varying loadings of TBD. B and C: GC traces following the reaction of 3 equiv of ethanol and 1 mol % TBD with the ethyl lactate dimer (B) and trimer (C). Spectra are offset for clarity.

alcohol per ester, commodity PLA depolymerized completely to a mixture of ~1:5 ethyl lactate to dimer in 2 min, with no higher order oligomers evident by either ^{1}H NMR or GC. Allowing the reaction to proceed resulted in further breakdown of the dimer to pure ethyl lactate, with >90% ethyl lactate observed after 10 min. Increasing the concentration of TBD to 2.5 mol % significantly increased the transesterification rate of the dimer, leading to the production of >95% ethyl lactate in only 2 min. Lastly, decreasing the concentration of TBD to 0.5% per ester decreased the rate of both polymer depolymerization and transesterification of the dimer to ethyl lactate, taking 10 min to depolymerize PLA into small molecules and an hour to break the dimer to >90% ethyl lactate. Independently changing the concentration of ethanol from 1.5 to 3 to 5 equivalents at each catalyst concentration did not change any of the results in a statistically significant manner.

TBD is known to have a high turnover frequency (80 s^{-1})[35,36] and that efficiency is displayed in this work by its ability to depolymerize high molecular weight polymers with over 1000 esters in the backbone in under 2 min at room temperature. The slow transesterification of the resulting ethyl lactate dimer, then, was curious. To confirm this result, isolation of both the ethyl lactate dimer and trimer was accomplished by depolymerizing PLA while using only 0.5 equivalents of ethanol and 1.0 mol % TBD per ester. The ability to simply make these higher order lactates from commodity PLA is significant, as these molecules are traditionally difficult to synthesize[47,48] and are the basis for pioneering work out of the Meyer lab on the tunable biodegradability of polyesters for biomedical applications.[44,45,49] The isolated dimer and trimer were subsequently exposed to the depolymerization conditions (3 equivalents of ethanol and 1.0 mol % TBD to ester) and the product distribution was followed over time by GC [Fig. 3(B,C)]. The trimer was transesterified to a 1:1 mixture of ethyl lactate and the dimer immediately [Fig. 3(C)]. Conversely, when the dimer was exposed to the same reaction conditions, it showed slow transesterification, taking over 12 min to produce >90% ethyl lactate [Fig. 3(B)]. These results clearly demonstrate the large decrease in kinetics of the TBD catalyzed transesterification of the lactate dimer as compared with other lactate ester oligomers. We postulate that this retardation of activity is a result of the dimer's intramolecular alcohol alpha to the ester. This intramolecular alcohol presumably outcompetes intermolecular alcohols in hydrogen bonding to the guanidinium nitrogen in the proposed transition state for TBD (Scheme 3), which would considerably hinder the ability of intermolecular alcohols to be activated for transesterification. Studies are ongoing to confirm this hypothesis.

To display the generality of the TBD catalyzed depolymerization of commodity polyesters, we sought to apply this methodology to the biomedically relevant thermoplastic PG. PG and PG-*co*-PLA have been widely investigated for *in vivo*



SCHEME 3 The proposed intramolecular complex that explains the retardation of transesterification activity for the ethyl lactate dimer. The hydrogen bonding of the intramolecular alcohol presumably outcompetes intermolecular alcohols to be activated for transesterification.

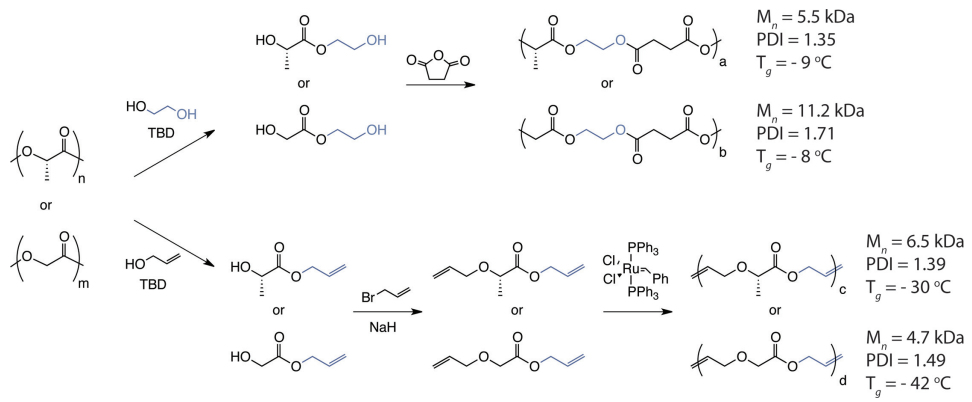


FIGURE 4 Production of functional monomers from the recycling of either PLA or PG and their subsequent polymerization into novel materials.

applications including tissue scaffolds and drug delivery because of their slow degradation and biocompatible degradation byproducts.[50–52] Commercial grade PG resin provided by Purac Biomaterials (PURASORB® PG20) was used as a substrate for recycling studies. Unlike PLA, PG is not soluble in common organic solvents, making room temperature, homogeneous depolymerization impossible. Suspending PG resin in the desired alcohol with 1 mol % of TBD per ester and heating to 120 °C in a closed container lead to complete depolymerization of PG into the corresponding glycolate ester in only 30 min. Similar to PLA, the recycling of PG was most efficient with primary alcohols and displayed the same functional group compatibility to alkenes, alkyl halides, and other alcohols.

Although the commercial value of alkyl lactates is well established, the access to functional lactate and glycolate esters through this recycling strategy provides a number of opportunities in the production of new polymeric materials. The key to this strategy is the orthogonal nature of the TBD catalyst to various functionalities, which allows the introduction of polymerizable groups into the lactate or glycolate ester products during polymer degradation. For example, diol monomers for condensation type polymerizations were generated through the depolymerization of either PLA or PG with ethylene glycol. These diols were successfully condensed with succinic anhydride following the procedure of Xiao et al.[53,54] to produce new polyesters with glass transition temperatures of around −10 °C (Fig. 4). The only observable difference in the two polymers was the higher molecular weight of the glycolate-based material under the same reaction conditions, which can be attributed to the higher reactivity of the primary alcohol alpha to the ester as opposed to the secondary alcohol for the lactate monomer. To further display the opportunities for this recycling process to produce novel monomers, the synthesis of both lactate and glycolate dialkene monomers was accomplished by polymer depolymerization with allyl alcohol and subsequent alkylation of the α-alcohol with allyl bromide. These dialkene monomers were used in acyclic diene methathesis polymerization (ADMET)[55] using the reaction conditions of Grubbs and coworkers[56] and underwent facile polymerization to provide rubbery materials with both an alkene and ester in each monomer repeat unit. In this case, the glycolate and lactate species showed different thermal properties, with glass transition temperatures of −30 °C and −42 °C, respectively. As expected, each unsymmetrical monomer displayed both "head-to-tail" and "head-to-head" coupling, evidenced by the four distinct olefin peaks in the ^{13}C NMR.

CONCLUSIONS

PLA and PG were efficiently and quantitatively transformed into value-added small molecules through organocatalytic depolymerization of commodity polyesters. The mild reaction conditions, generality with respect to both alcohol and polyester starting material, and retention of stereochemistry make this methodology highly applicable in the utilization of biorenewable chemical feedstocks. The opportunities to transform waste into valuable chemicals for cosmetics, food additives, solvents, and the production of new materials contributes to the ultimate goal of reducing industrial reliance on petrochemical feedstocks.

EXPERIMENTAL

General Methods

PLA for degradation studies was obtained from Natureworks™ Ingeo™ packaging materials from Trader Joe's© roma tomatoes or from Natureworks™ Ingeo™ fiber resin provided by Cornfinger, and PG was generously provided by Purac Biomaterials. Dry methylene chloride, DMF, and THF was obtained from a dry solvent system.[57] Dry chloroform, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), NaH, and allyl bromide were purchased from Aldrich and used without further purification. All alcohol reagents were purchased from Aldrich, dried over CaH_2 and distilled before use. Storage of compounds and reaction assembly was performed in an inert atmosphere glovebox. Analytical thin layer chromatography (TLC) was carried out on Merck silica gel 60 F_{254} glass plates and flash column chromatography was performed on Merck silica gel 60 (70–230 mesh) or on a Biotage SP1 Flash Purification System using FLASH 40+M cartridges and FLASH 40+ sample cartridges. ^{1}H and ^{13}C solution-state NMR were recorded on a Varian VNMRS 600 (600 MHz for

^{1}H and 150 MHz for ^{13}C) spectrometer. Chemical shifts are reported relative to residual solvent peaks (δ 7.26 for $CDCl_3$ or δ 5.32 for CD_2Cl_2 in ^{1}H NMR and δ 77.2 for $CDCl_3$ or δ 54.0 for CD_2Cl_2 in ^{13}C NMR). IR spectra were obtained using a Thermo-Nicholet Avatar-330 IR spectrometer with single-bounce attenuated total reflection (Ge crystal) accessory (Smart MIRacle). GPC was performed in chloroform (with 0.25% triethylamine) on a Waters 2695 Separation Module equipped with a Waters 2414 Refractive Index Detecter and a Waters 2996 Photodiode Array Detector. Molecular weights of polymers were calculated relative to linear polystyrene standards. Differential scanning calorimetry (DSC) data was acquired on a TA Instruments Q2000 modulated DSC at a heating rate of 5 °C/min. Data presented are from the second heating after a single cycle from −75 to 180 °C. Mass spectral data were collected on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer. TGA data was collected on a Mettler 851e TG. Chrial HPLC data was obtained on a Shimadzu LC-6AD pumps with a 254 nm detector and employing a Chiralpak® IB column with 5 μM beads and dimensions of 4.6 × 250 mm^2. A 5% isopropanol solution in hexane was used as the eluent at a flow rate of 1 mL/min. CD spectra were collected on an Olis Rapid Scanning Monochromator with a 150 W Photon Technology International light source. The polymer samples were dissolved in a solution of acetonitrile at a concentration of 0.05 mg/mL. GC was performed on a Shimadzu GC-2014 GC with a heating rate of 30 °C per minute from 40 to 280 °C.

General Procedure for Degradation of PLA Using TBD

PLA (300 mg, 4.16 mmol of ester) and desired alcohol (12.5 mmol) was dissolved in 10 mL methylene chloride and TBD (5.8 mg, 0.0416 mmol) was added to the stirring solution. The reaction was capped and allowed to stir for the desired timed, after which excess acid resin was added and the solution was decanted. Removal of solvent and excess alcohol by distillation provided the desired lactate ester typically in >95% yield. Methyl lactate,[58] ethyl lactate,[58] butyl lactate,[58] ethylhexyl lactate,[59] allyl lactate,[58] 2-chloroethyl lactate,[60] benzyl lactate,[59] 2-hydroxyethyl lactate,[54] and isopropyl lactate[61] are known molecules.

2,2,2-Trifluoro 2-Hydroxypropanoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.61 (m, 1H), 4.52 (m, 1H), 4.41 (q, J = 6.6 Hz, 1H), 1.48 (d, J = 6.6 Hz, 3H); ^{19}F NMR (564 MHZ, $CDCl_3$) δ −73.98 (t, J = 9 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1, 123.5 (q, J = 270 Hz), 66.7, 61.1 (q, J = 37 Hz), 20.2; IR 3420, 2994, 2929, 2856, 1763, 1671, 1456, 1418, 1283, 1167, 1128, 977, 738 cm^{-1}; MS (TOF-ESI) calcd. for $C_5H_7F_3O_3$ [M + Na]: 195.03, found [M + Na]: 195.04.

General Procedure for Degradation of PG Using TBD

PG (300 mg, 5.17 mmol of ester) was suspended in a solution of the desired alcohol (15.5 mmol), and TBD (7.2 mg, 0.0517 mmol) in a thick-walled round-bottom flask. The flask was sealed with a Teflon stopper and heated at 120 °C for 30 min with magnetic stirring, upon which time all visible solids had dissolved into a homogeneous solution. The reaction was quenched by addition of acid resin, decanted, and removal excess alcohol by distillation provides the desired glycolate ester typically in >95% yield. Both 2-hydroxyethyl glycolate[62] and allyl glycolate[63] are known molecules.

General Procedure for Alkylation of α-Hydroxyester with Allyl Bromide

To a dry 250-mL round-bottom flask equipped with a magnetic stir bar was added allyl lactate (1.0 equiv) and dry THF (50 mL) and cooled to 0 °C. NaH (1.5 equiv) was added in 4 equal aliquots over 10 min, after which the solution was warmed to room temperature and allowed to stir for 30 min. The reaction mixture was cooled to 0 °C and allyl bromide (1.2 equiv) was added dropwise. The solution was warmed to room temperature and stirred an additional 4 h. The reaction was quenched with 100 mL saturated NH_4Cl, extracted ×3 with 75 mL Et_2O, the organic layers were combined and washed with brine, dried over $MgSO_4$, and concentrated. The mixture was purified by flash column chromatography on silica gel (5% EtOAc:Hex) to yield the desired product as a clear liquid.

Allyl 2-(Allyloxy)propanoate

1.11 g, 79% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (m, 2H), 5.25 (m, 4H), 4.62 (m, 2H), 4.02 (q, J = 6.6 Hz, 1H), 3.93 (ddd, J = 5.4, 12.6, and 121 Hz, 2H), 1.36 (d, J = 6.6 HZ, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 134.2, 132.0, 118.7, 117.8, 74.1, 71.2, 65.5, 18.8; IR: 3093, 2992, 2945, 2890, 1750, 1459, 1378, 1272, 1195, 1137, 1132, 925 cm^{-1}; HR-MS (TOF-ESI) calcd. for $C_9H_{14}O_3Na$ [M + Na]: 193.0841, Found: [M + Na]: 193.0824.

Allyl 2-(Allyloxy)acetate

2.02 g, 51% yield; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90 (m, 2H), 5.25 (m, 4H), 4.65 (d, J = 6.0 Hz, 2H), 4.101 (s, 2H), 4.09 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.24, 133.9, 131.9, 119.0, 118.4, 72.6, 67.3, 65.6; IR 3097, 3001, 2954, 2900, 1755, 1429, 1275, 1195, 1131, 1126, 989, 926 cm^{-1}; HR-MS (TOF-ESI) calcd. for $C_8H_{12}O_3Na$ [M + Na]: 179.0684, Found: [M + Na]: 179.0661.

ADMET Polymerization

ADMET polymerization was accomplished with Grubb's generation I catalyst using the procedure of Momčilović et al.[56] The polymers were purified by precipitation in 10% MeOH in Hexane to yield dark oils.

Poly(allyl 2-(allyloxy)propanoate

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.9–5.7 (—*H*C=C*H*—CH_2—O—), 4.7–4.5 (—COO—C*H*$_2$—), 4.2–3.8 (—HC=CH—C*H*$_2$—O—C*H*(—CH_3)—COO—CH_2—), 1.5–1.3 (CH_2—O—CH(—C*H*$_3$)—COO—); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7, 130.7, 129.3, 128.2, 126.7, 74.3, 69.7, 64.5, 18.7; GPC M_n = 6.5 kg mol^{-1}, M_w = 9.0 kg mol^{-1}, PDI =1.39. T_g = −30 °C, T_d = 174 °C.

Poly(allyl 2-(allyloxy)acetate

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.9–5.7 (—*H*C=C*H*—CH_2—O—), 4.8–4.6 (—COO—C*H*$_2$—), 4.2–4.0 (—HC=CH—C*H*$_2$—O—C*H*$_2$—COO—CH_2—); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 130.5, 129.5, 128.3, 127.1, 71.3, 71.1, 67.4, 64.5, 64.2; GPC M_n = 4.7 kg mol^{-1}, M_w = 7.0 kg mol^{-1}, PDI = 1.49. T_g = −42 °C, T_d = 200 °C.

Polymerization of Diols with Succinic Anhydride

Polyester polymerization using 2-hydroxyethyl lactate or glycolate was performed by the procedure of Xiao et al. The polymers were purified by precipitation into MeOH to yield clear oils.

Poly(2-hydroxyethyl 2-hydroxypropanoate)

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.2–5.0 (—O—C*H*(—CH_3)—COO—), 4.4–4.2 (—COO—CH_2—CH_2— OOC—), 2.7–2.5 (—OOC—CH_2—CH_2—COO—) 1.6–1.4 (—O—CH(—CH_3)—COO—); ^{13}C NMR 171.8 (m), 170.1, 68.6, 62.3 (m), 28.6, 16.8; IR 2996, 2975, 1733, 1377, 1152, 1098, 755 cm^{-1}; GPC M_n = 5.5 kg mol^{-1}, M_w = 7.4 kg mol^{-1}, PDI = 1.35. T_g = −9 °C, T_d = 220 °C.

Poly(2-hydroxyethyl 2-hydroxyacetate)

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.8–4.6 (—O—CH_2—COO—), 4.4–4.2 (—COO—CH_2—CH_2—OOC—), 2.8–2.6 (—OOC—CH_2—CH_2—COO—); ^{13}C NMR 172.0 (m), 167.5, 62.3 (m), 60.5, 28.6; IR 2971, 1732, 1425, 1391, 1144, 1060 cm^{-1}; GPC M_n = 11.2 kg mol^{-1}, M_w = 19.1 kg mol^{-1}, PDI = 1.71. T_g = −10 °C, T_d = 235 °C.

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