Chem 466 Leepve # // 02/20/2014 · No office hours Monday, 02/24/14

Frontiers in Chemical Research

# Krzysztof Matyjaszewski Carnegie Mellon University

# "Macromolecular Engineering by Controlled Radical Polymerization"

# Monday, February 24

"Atom Transfer Radical Polymerization- from Mechanism and Synthesis to Materials and Applications"

> 5:00-6:00 Room 2104

# Tuesday, February 25

"Precise Polymer Architecture by Macromolecular Engineering"

5:00-6:00 Room 2104

Wednesday, February 26 \*\*Note change in time\*\*

"Functional Hybrid and Bioconjugate Materials by ATRP"

**4:00-5:00** Room 2104

Hosted by Drs. Wooley and Fang

III. Polymer Characterization (in brief) (A) molecular weight determination (189 8 9 4 9 (D chain end analysis (text 1.8.2) o gives Mn (counts It ends vs. repeat units) · by 'H NMR spectroscopy ALSO SEE # chain ends - slide eng. from US. reprat D. H. Bolton + K. L. Wooley PROBLEM #2. from Examit 02/24/2011 unit 4 J. Polym. Sci. Part A: Polym. Chem. 1997, 35, 1133-1137. DPn Mn o by titration of end groups (e.g. if acidie or basic) + other techniques detin that can droppuish & quarting It mols of chair ends ( the end group cone. us. the for siver mass of poly remainder of the polymer material (backbone repeat units) • limited to DPn's of ~100-200 (~1% end groups) mol (2) chromatography (text 9.8) - gel permeation chromatography (GPC) got also called size exclusion chromotography (SEC) & CTUPAC ogives Mw + Mn + .: PDI ∘ allows for separation of polys by size ⇒ visualization of mol. wt. distribution



P

Scheme 3. Polymerization of the A<sub>2</sub>B Monomer, 2, To Produce the Hyperbranched Polycarbonate, 9, and Reaction of the Chain End Groups of 9 To Give 1 and Then 10



Scheme 4. Degradation of 10, by Reduction with LiAlH<sub>4</sub> To Give the Three Different Repeat Units for Determination of the Degree of Branching of the Hyperbranched Polymers



precipitation into ether. Cleavage of the carbonylimidazolide groups gave the phenol-terminated material, in which the oligomers were soluble in methanol and were separated by precipitation, resulting in recovery of higher molecular weight material and a decreased yield for 1. The GPC chromatogram of 1 showed a high molecular weight shoulder, which was not observed for 10. Therefore, the  $M_w$  values for 1, determined using LALLS and SEC,<sup>3</sup> were much larger than those measured for 10 even though the overall GPC chromatograms of 1 and 10 were nearly identical.

Comparable retention volumes were observed for each of the products, demonstrating that there was no attraction of the phenol-terminated sample to the GPC column packing material.<sup>15</sup> The samples behaved as highly-branched macromolecules, giving a large signal by light scattering at the high molecular weight prepeak where the RI detector shows very low concentration, and weaker signals in both the LALLS and in the viscometry chromatograms at longer retention times (lower molecular weights).<sup>16</sup>

<sup>1</sup>H NMR end group analysis was also used for the calculation of the number average molecular weights for 1 and 9, which were found to be in agreement with the GPC results. Integration of the resonances due to the methyl and *tert*-butyl groups of the single *tert*-butyldimethylsilyl chain end that is present on each of the polymer molecules, and comparison with the remainder of the protons in the structure gave calculated  $M_n$ 's of 14 300 and 6700 for 1 and 9, respectively.

Each of the polymers were soluble in common organic solvents. However, expected differences were observed corresponding to the differences in chain end functionalities. THF and acetone were solvents for 9, 1, and 10; 9 and 10 were additionally soluble in chloroform while 1 required more polar solvents such as pyridine and *N*-methylpyrrolidinone.

The thermal stability of the polymers was determined by thermogravimetric analysis in air. The phenolterminated polycarbonate, **1**, is thermally stable in air up to 350 °C. After loss of the thermally labile carbonylimidazolide functionality of **9** at 150-200 °C, **9** and **1** show similar thermal behavior. Differential scanning calorimetry (DSC) demonstrated slight differences between the hyperbranched materials with different chain

+ det m. of mono-modality or higher Computer s duent detector pump vaservor ·RI · UV-vis · LS " manual / Syringe · viscometry autorijector 百十百 なき音が porticle (e.s. Xlonled Styrene + divingthenge · smaller molecules (hydrodynamic volume) diffuse in + out of larger # of pones : experiencing longer residence/retention time/ vetn. volume in the column larger # of larger molecules are excluded from pores = 2 SEC vet'n. \* experience shorter residence/retention times/volumes \* defectors seral signals to computer, measuring Signal US. America to show My Min Det. 1 = Epoly) response retention time / volume > mw ->

ARTICLE

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### Transforming Polylactide into Value-Added Materials

#### Frank A. Leibfarth,<sup>1</sup> Nicholas Moreno,<sup>1</sup> Alex P. Hawker,<sup>2</sup> Justin D. Shand<sup>2</sup>

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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 postconsumer polylactide (PLA) into value-added small molecules. This strategy, using the highly active transesterfication 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 is both PLA and polyglycolide, with the corresponding ester smallmolecules being used to make new polymeric materials. The opportunities to transform waste streams into value-added chemies. cals 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 ng Part A: Polym Chem 50: 4814-4822, 2012

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

developed, they are often overly costly and complex. PLA,

however, is compostable and biodegrades into soil-enriching

compounds,<sup>11</sup> Further, large-volume waste is ideal for chemi-

cal 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, mak-

ing these processes unattractive due to their high energy

input and difficulty controlling the stereochemistry of the

resulting lactate species.<sup>16-18</sup> More complex hydrolysis mech-

anisms using enzymes<sup>19-21</sup> or heterogeneous catalysis<sup>22-24</sup>

can overcome some of these limitations, but alternative, scal-

Lactic acid derived from fermentation of biomass is not only

a valuable chemical feedstock for the production of bioplas-

tics but it is also employed for the production of ethyl lac-

tate 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 plas-

ticizers.<sup>25-30</sup> A significant opportunity, therefore, exists for

repurposing commodity PLA into value-added small mole-

cules 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 lac-

tate being recovered by distillation.25,31 These batch proc-

esses are inherently low yielding and inefficient.

able methods for recycling PLA remain underdeveloped.

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**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.<sup>2</sup> 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.<sup>6-9</sup> The recent addition of Natureworks<sup>TM</sup> LLC facility in the US has put annual production capacity of PLA at over 150,000 tons, making it a high-volume commodity material.<sup>10-12</sup> This largescale production and the predicted annual growth rate of 19% for bioplastics13 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.<sup>14</sup> Although chemical recycling of PET and advanced "bottle-to-bottle" mechanical processes have been

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1.5n R-OH n HO O R + 0.5n R-OH

JOURNAL OF Polymer

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.<sup>25</sup>

We report the recycling of PLA into value-added small molecule lactate esters through rapid and quantitative transesterification using triazabicyclodecene (TBD)<sup>32</sup> 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).<sup>33-38</sup> 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 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<sup>TM</sup> Ingeo<sup>TM</sup> 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 (Tm) 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

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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,<sup>25,28</sup> 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 transesterifcation. 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  $\beta$ -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 *x*-hydroxyseters 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.

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# Karen L. Wooley

From: Sent: To: Subject: Carol Moidel <cmoidel@presschem.com> Thursday, February 28, 2013 10:08 AM karen.wooley@mail.chem.tamu.edu **Polymer Standards** 





see text section 9.8 for SEC + details on detectors, 9.8.4

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## Polyethylene Glycol CAS# 25322-68-3

atalog Number	MW MW/MN
PEG200	229 1.11
PEG300	331 1.08
PEG400	445 1.07
PEG600	629 1.10
PEG1000	1,030 1.05
PEG3600	3,662 1.10
PEG5000	5,160 1.04
PEG11000	10,890 1.19
PEG14000	19,683 1.34

### Polyethylene CAS #9002-88-4

Catalog Number	MW MW/MN
PE540	540 1.09
PE750	750 1.18
PE1110	1,110 1.20
PE2100	2,100 1.15
PE7AF	35,700 4.22
PE8AC	41,700 3.70

## Polystyrene CAS #9003-53-6

Catalog Number	MW MW/MN
PS40717	906 1.11
PS31019	1,241 1.07
PS40627	1,300 1.06
PS31116	1,681 1.10
PS50110	2,032 1.06
PS12C	2,200 1.06
PS61223	2,500 1.09
PS30525	4,000 1.06
PS50131	5,200 1.06
PS50828	5,780 1.05
PS30420	13,000 1.06
PS30811	25,000 1.06
PS80317	30,000 1.06
PS7B	37,000 1.07
PS30908	50,000 1.06

3 visusity (text 1.8.1 + 9.1-9.4 (9.3 intrinsic viscosity, [M], is a measure the ability of a polymer (solute) increase the viscosity of a solution when added to a solvert vs. the viscosity of the solvert 5/0 • [n] is related directly to the size of the polymer in the solution (not necessarily the mol. at. - molecular architecture is important) the hydrodynamic volume, V<sub>h</sub> = <u>HTT</u> Rg<sup>3</sup> where Rg = vadius of gyration = vms, mass-weighted disense average distance Vh is cale.'d as h though the poly is a rigid sphere of rootins, Rg C.J. Hawker et al . Chom. Soc. J.Am whit from the 1997 119,9903-9904( poly center of mass • [n] units are volume, typically mass

· Mark- Homimle equation relates ENJ to mol. wt. [n] = le Mu where, k and a are constants that depen on the poly, solvert temperature, + 0.5 = a = 0.8 for a flexible chain are available (in a theta solvert Jobles text and My is the Joan. viscosity average 9.3. mol. wt. preter typically Mn < Mw on good solvent) a > 0.8 for a semi-flex.ble on risid chain