Chem 466
Lecture #11
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

1. Chain end analysis (text 1.8.2)
   - Gives $M_n$ (counts # ends vs. repeat units)
   - By $^1$H NMR spectroscopy

2. Titration of end groups (e.g. if acidic or basic) + other techniques
   - That can distinguish + quantify the end group conc. vs. the remainder of the polymer material (i.e. backbone repeat units)
   - Limited to $DP_n$'s $\approx 100-200$ ($\approx 1\%$ end groups)

3. Chromatography (text 9.8)
   - Gel permeation chromatography (GPC)
   - Also called size exclusion chromatography (SEC)

   - Gives $M_w + M_n + \ldots$ PDI
   - Allows for separation of polys by size → visualization of mol. wt. distribution
'H NMR
Poly(1,4-cyclohexanecarbonate)

\[
\begin{align*}
\text{Calculation of } M_n \text{ from end group analysis:} \\
\text{6 Hg} &= 2 \\
\text{Hg} &= 0.33 \\
\text{2 Hd} &= 20 \\
\text{Hd} &= 10 \\
\Rightarrow \text{ratio of } \frac{\text{Hd}}{\text{Hg}} &= \frac{10}{0.33} = D_p = 30 \\
M_n &= 30(142) + 67 + 135 \\
\Rightarrow M_n &= 4500 \text{ Da}
\end{align*}
\]

Repeat MW = 142 Da
End group MW's = 67 Da and 135 Da
(C₇H₁₀O₃) (C₅H₃N₂) (C₈H₁₁Si)
2. For the polycarbonate structure and $^1$H NMR spectrum given:

(a) Determine the degree of polymerization. [15 points]

- Use $9H_a$ or $6H_b$ for determining chain end relative to $H_d$.
- For $9H_a$: $9H_a = 40\text{ mm}$ $\Rightarrow H_a = 0.44$
- Use $3H_c$ or $1H_d$ for determining repeat units (Hd complicated by 1 chain end too).
- For $3H_c$: $3H_c = 19\text{ mm}$ $\Rightarrow H_c = 6.33$

\[
\frac{H_c}{H_a} = 14.4 \Rightarrow DP_n = 14
\]

(b) Calculate the number-average molecular weight. [10 points]

Repeat unit is $C_{25}H_{18}N_2O_5$; ignoring isotopic abundance.

Repeat unit mass = 426 g/mol $\Rightarrow M_n = 14(426 \text{ g/mol}) + 115 \text{ g/mol} + 67 \text{ g/mol}$

$\Rightarrow M_n = 6146 \text{ g/mol}$

\[
\frac{w}{2} \approx 6100 \text{ g/mol}
\]
Scheme 3. Polymerization of the A₂B Monomer, 2, To Produce the Hyperbranched Polycarbonate, 9, and Reaction of the Chain End Groups of 9 To Give 1 and Then 10

Hyperbranched Polycarbonate Repeat Unit:

Hyperbranched Polymer Repeat Unit:

Scheme 4. Degradation of 10, by Reduction with LiAlH₄, 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 $M_n$ values for 1, determined using LALLS and SEC, 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. The samples behaved as highly-branched macromolecules, giving a large signal by light scattering at the high molecular weight pre-peak 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).

$^1$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-butylidimethylsilyl 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 phenol-terminated 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

- manual/syringe or autoinjector

- smaller molecules (hydrodynamic volume) diffuse in and out of larger # of pores
  - experiencing longer residence/retention time/retention volume in the volume, large # of

- larger molecules are excluded from pores, SEC, retention volume, shorter residence/retention times/volume

- detectors send signals to computer, measuring

Signal vs. time make these more symmetric to show asymmetry

Det. response:
- high
- low

PS calibration curve (explain) vs. MW

Det. response:
- high
- low
Transforming Polylactide into Value-Added Materials

Frank A. Leibfarth, Nicholas Moreno, Alex P. Hawkner, Justin D. Shand

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 transetherification 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 esters of simple monofunctional alcohols being used to make new polymeric materials. The opportunities to transform waste streams into valuable-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

ARTICLE

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 natural resources, the utilization of 7% of fossil fuels for the production of plastics is a significant drain on petrochemical feedstocks. With the demand for polymeric materials increasing, it is imperative to develop building blocks based on renewable and sustainable resources. The conversion of biomass to value-added small molecules and polymer precursors is an attractive method to bypass traditional fossil fuel-based chemical production. For example, polylactide (PLA) has emerged as one of the most promising biobased polymers to be used as packaging, textile, and biomedical applications. 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. This large-scale production and the predicted annual growth rate of 10% for bioplastics 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 respun. Although chemical recycling of PET and advanced "bottle-to-bottle" mechanical processes have been developed, they are often costly and complex. PLA, however, is compostable and biodegradable in soil-enriching compounds.1-5 Further, large-volume waste is ideal for chemical recycling, as the ester bonds in the backbone of PLA can be hydrolyzed.6 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 their limited ability to control the stereochemistry of the resulting lactate species.6,9,10 More complex hydrolysis mechanisms using enzymes6,11-16 or heterogeneous catalysts17-22 have 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, deodorizers, and preservatives.23,24 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.25,26 These batch processes are inherently low yielding and inefficient.

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 (Mn) of 76.7 kg/mol, a PDI of 1.38, a glass transition temperature (Tg) 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 including gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), infrared spectroscopy (IR), mass spectrometry, and gas chromatography (GC).

Because of ethyl lactate's prominence as an industrial solvent and food/fragrance additive, 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 depolymerization process, the scope of this chemistry was investigated 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; poly lactide; recycling; transetherification

© 2012 Wiley Periodicals, Inc.

50, 4814-4822
WWW.MATERIALSVIEWS.COM
WWW.MATERIALSVIEWS.COM
JOURNAL OF POLYMER SCIENCE PART A: POLYMER CHEMISTRY ONLINE LIBRARY
JOURNAL OF POLYMER SCIENCE PART A: POLYMER CHEMISTRY ONLINE LIBRARY
Polymer Standards

Since 1964 Pressure Chemical Company has been supplying a broad range of polymer standards for gel permeation chromatography (GPC) including Polystyrene, Polyethylene Fractions and Polyethylene Glycol Standards. Our narrow molecular weight polymer standards have been characterized for number, weight and viscosity average molecular weights, by GPC, light scattering and NMR, where applicable.

Please contact me directly for the low price of US$3.00/g for bulk quantities.

Polyethylene Glycol CAS# 25322-68-3

<table>
<thead>
<tr>
<th>Catalog Number</th>
<th>MW</th>
<th>MW/MN</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG200</td>
<td>229</td>
<td>1.11</td>
</tr>
<tr>
<td>PEG300</td>
<td>331</td>
<td>1.08</td>
</tr>
<tr>
<td>PEG400</td>
<td>445</td>
<td>1.07</td>
</tr>
<tr>
<td>PEG600</td>
<td>629</td>
<td>1.10</td>
</tr>
<tr>
<td>PEG1000</td>
<td>1,030</td>
<td>1.05</td>
</tr>
<tr>
<td>PEG3600</td>
<td>3,662</td>
<td>1.10</td>
</tr>
<tr>
<td>PEG5000</td>
<td>5,160</td>
<td>1.04</td>
</tr>
<tr>
<td>PEG11000</td>
<td>10,890</td>
<td>1.19</td>
</tr>
<tr>
<td>PEG14000</td>
<td>19,683</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Polyethylene CAS #9002-88-4

<table>
<thead>
<tr>
<th>Catalog Number</th>
<th>MW</th>
<th>MW/MN</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE540</td>
<td>540</td>
<td>1.09</td>
</tr>
<tr>
<td>PE750</td>
<td>750</td>
<td>1.18</td>
</tr>
<tr>
<td>PE11100</td>
<td>1,110</td>
<td>1.20</td>
</tr>
<tr>
<td>PE2100</td>
<td>2,100</td>
<td>1.15</td>
</tr>
<tr>
<td>PE7AF</td>
<td>35,700</td>
<td>4.22</td>
</tr>
<tr>
<td>PE8AC</td>
<td>41,700</td>
<td>3.70</td>
</tr>
</tbody>
</table>

Polystyrene CAS #9003-53-6

<table>
<thead>
<tr>
<th>Catalog Number</th>
<th>MW</th>
<th>MW/MN</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS40717</td>
<td>906</td>
<td>1.11</td>
</tr>
<tr>
<td>PS31019</td>
<td>1,241</td>
<td>1.07</td>
</tr>
<tr>
<td>PS40527</td>
<td>1,300</td>
<td>1.06</td>
</tr>
<tr>
<td>PS31116</td>
<td>1,681</td>
<td>1.10</td>
</tr>
<tr>
<td>PS50110</td>
<td>2,032</td>
<td>1.06</td>
</tr>
<tr>
<td>PS12C</td>
<td>2,200</td>
<td>1.06</td>
</tr>
<tr>
<td>PS61223</td>
<td>2,500</td>
<td>1.09</td>
</tr>
<tr>
<td>PS30525</td>
<td>4,000</td>
<td>1.06</td>
</tr>
<tr>
<td>PS50131</td>
<td>5,200</td>
<td>1.06</td>
</tr>
<tr>
<td>PS50828</td>
<td>5,780</td>
<td>1.05</td>
</tr>
<tr>
<td>PS30420</td>
<td>13,000</td>
<td>1.06</td>
</tr>
<tr>
<td>PS30811</td>
<td>25,000</td>
<td>1.06</td>
</tr>
<tr>
<td>PS80317</td>
<td>30,000</td>
<td>1.06</td>
</tr>
<tr>
<td>PS7B</td>
<td>37,000</td>
<td>1.07</td>
</tr>
<tr>
<td>PS30908</td>
<td>50,000</td>
<td>1.06</td>
</tr>
</tbody>
</table>
3. Viscosity (text 1.8.1 + 9.1-9.4 (9.3))

- Intrinsic viscosity \( [\eta] \) is a measure of the ability of a polymer (solute) to increase the viscosity of a solution when added to a solvent vs. the viscosity of the solvent.

- \( [\eta] \) is related directly to the size of the polymer in solution (not necessarily the mol. wt. — molecular architecture is important) — the hydrodynamic volume,

\[
V_h = \frac{4}{3} \pi R_g^3
\]

where \( R_g = \text{radius of gyration} = \text{rms, mass-weighted average distance of monomer repeat units from the poly center of mass} \)

- \( [\eta] \) units are \( \frac{\text{volume}}{\text{mass}} \), typically \( \text{mL/g} \)

Discuss:
- \( V_h \) is calculated as though the poly is a rigid sphere of radius \( R_g \)
Mark-Houwink equation relates $[\eta]$ to mol. wt.

$$[\eta] = k M^\alpha$$

where $k$ and $\alpha$ are constants that depend on the poly, solvent, temperature $T$, and $M_v$ is the viscosity average mol. wt. typically $M_n < M_v < M_w$.

$0.5 \leq \alpha \leq 0.8$

for a flexible chain (in a theta solvent or good solvent)

$\alpha > 0.8$ for a semi-flexible or rigid chain

for the viscosity average mol. wt. $M_v$ are available in tables.