

Chem 466

Lecture # 4

01/23/2014

Ⓟ Recommended text problems from

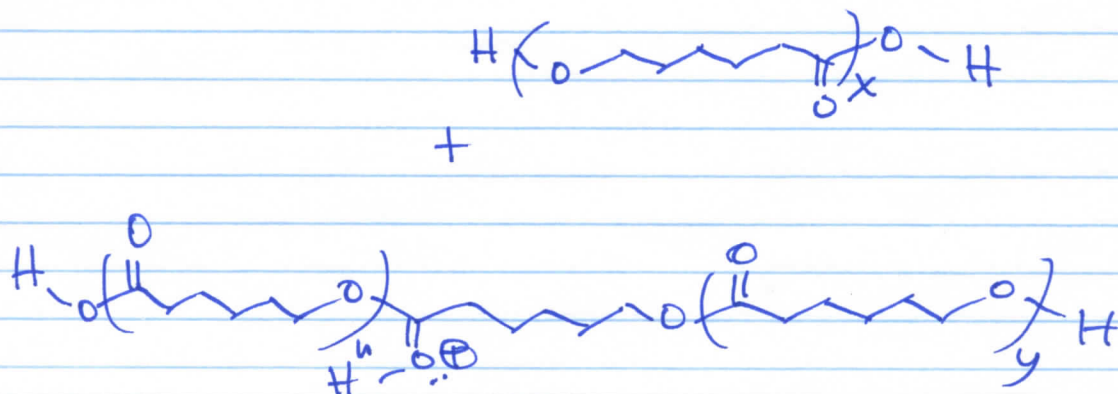
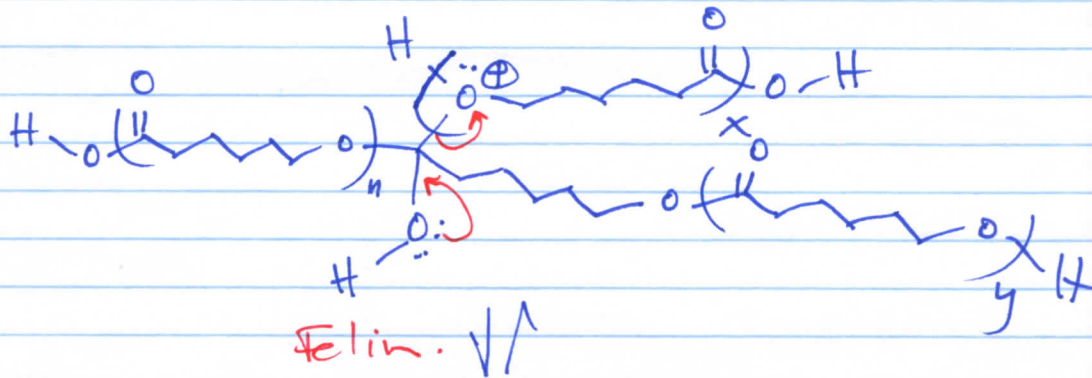
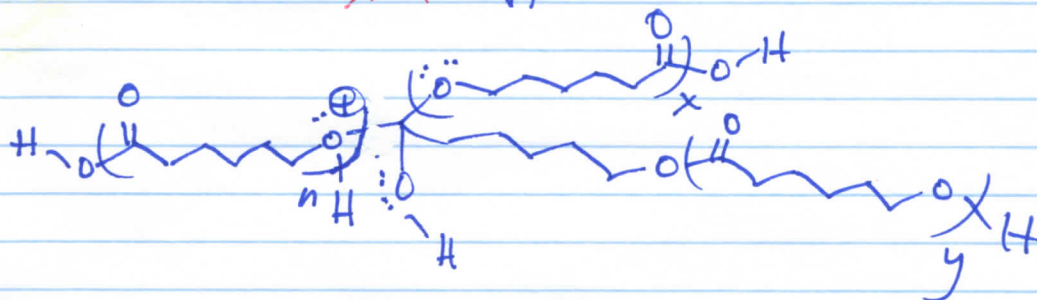
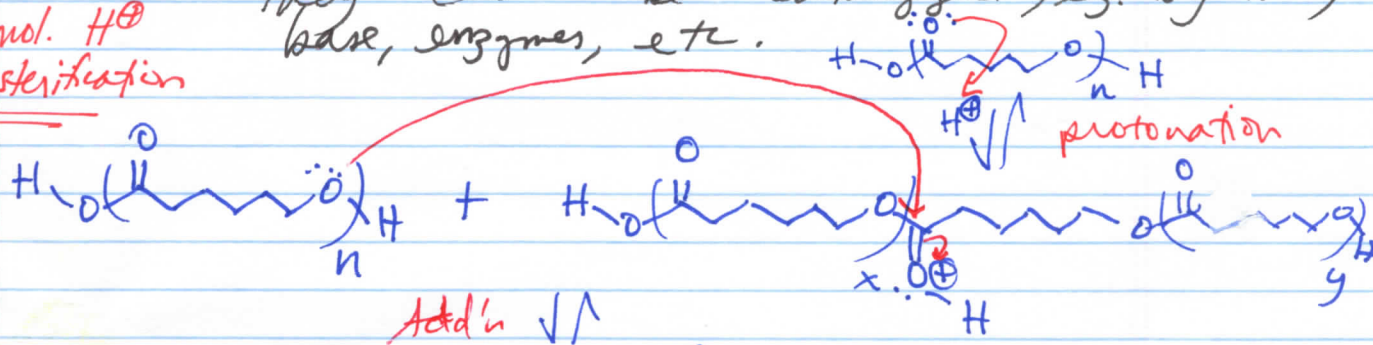
Chapter 1 : # 5, 6, 8, 12, 15, 16

↑
write e^- arrow-pushing
rxn mechanisms
for each part too

Today, solutions will be posted on
course website

- see text p. 61 — ester interchange w/ alcohol or w/ ester occur
- mechanisms of intramol. + intermol. rxns are the same — we're focusing on only ester interchange rxns of ester + alcohol
- Also, prevalence of intra- and intermolecular transesterifications depends on conditions es. temperature, & they can be catalyzed, eg. by H^+ , base, enzymes, etc.

e.g. intermol. H^+
cat. transesterification



(b) ester interchange/transesterification rxns can also be performed intentionally

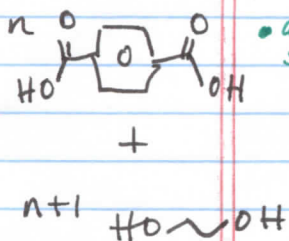
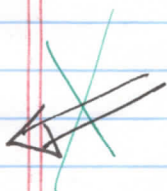
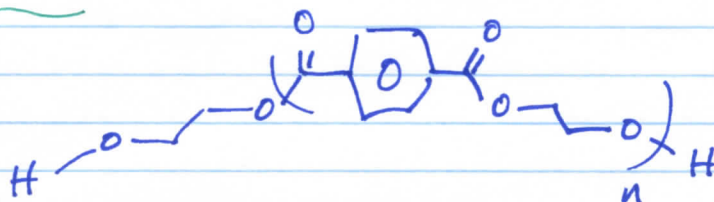
⊗ between polys \rightarrow mixtures of polys with scrambled compositions (e.g. to blend properties)

⊗ between monomers \rightarrow polym processes (e.g. PET)

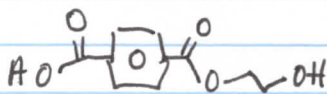
Poly(ethylene terephthalate)

- > 9 billion lbs/yr.
- Tradenames - Mylar, Dacron, others
- Uses - drink bottles, fibers, cloths, films, mag. tapes, etc.

consider 3 retrosyntheses

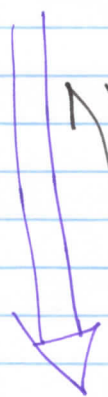


- difficult to solubilize/purify
- stoichiometric balance (may be) required (challenging to achieve)



- stoichiometric balance built-in but, difficult to synthesize (i.e. expensive)

- Industrial prep. involves transesterification



280 °C

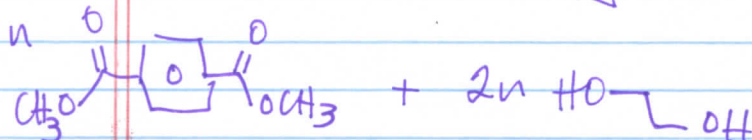
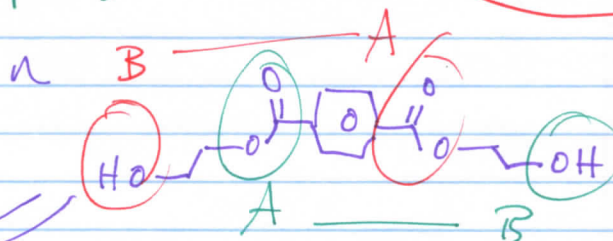
$-(n-1) \text{HO} \sim \text{OH}$

STAGE 2

STAGE 1

150-190 °C

$-2n \text{CH}_3\text{OH}$



- an unusual overlapping A-B monomer (+ oligomers from stage 1)

- equilibria driven toward AB monomer and then poly by removal of CH_3OH

- acid, base, enzyme, transition metals can catalyze transesterification



between polys
+ small molecules



poly recycling via
depolymerization processes
(e.g. PET)

see K. Fukushima et al. J. Polym. Sci.,
Part A: Polym. Chem. 2011, 49, 1273-1281

- as an example of the
depolymerization of PET by
MXr with $\text{HO}-\text{OH}$ in the
presence of an organic base
catalyst

- a collaboration between industry +
academia in the U.S., Belgium +
Saudi Arabia

⊗⊗ see notes on 1st page of the
hand-out article

Organocatalytic Depolymerization of Poly(ethylene terephthalate)

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ABSTRACT: We describe the organocatalytic depolymerization of poly(ethylene terephthalate) (PET), using a commercially available guanidine catalyst, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). Postconsumer PET beverage bottles were used and processed with 1.0 mol % (0.7 wt %) of TBD and excess amount of ethylene glycol (EG) at 190 °C for 3.5 hours under atmospheric pressure to give bis(2-hydroxyethyl) terephthalate (BHET) in 78% isolated yield. The catalyst efficiency was comparable to other metal acetate/alkoxide catalysts that are commonly used for depolymerization of PET. The BHET content in the glycolysis product was subject to the reagent loading. This

catalyst influenced the rate of the depolymerization as well as the effective process temperature. We also demonstrated the recycling of the catalyst and the excess EG for more than 5 cycles. Computational and experimental studies showed that both TBD and EG activate PET through hydrogen bond formation/activation to facilitate this reaction. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 49: 1273–1281, 2011

KEYWORDS: catalysis; degradation; depolymerization; glycolysis; organocatalyst; poly(ethylene terephthalate); recycling

INTRODUCTION Advances in technology continue to present many environmental issues making waste management a significant challenge. Landfill space is at a premium, even if the total amount of municipal solid waste (MSW) going to landfills in US has dropped since 1990. The plastic refuse generated in US constitutes 12% of the MSW in 2008; while relatively modest as a percentage, plastic waste is the 4th major component of the MSW after paper, food, and yard trimmings.¹ Poly(ethylene terephthalate) (PET), a widely used commodity-grade thermoplastic contributes several billion pounds of waste to landfills every year, and the amount of PET needed is unlikely to diminish any time soon.² Recycling of petroleum-based plastics has recently attracted enormous attention to promote effective use of limited fossil resources to mitigate impacts on solid waste. According to the American Plastics Council, now only 27% of the PET bottles and jars are recycled and the PET market for packaging continues to grow due to the popularity of PET-packaged products, such as bottled water.³

The challenge for PET recycling is to achieve a closed-loop, bottle-to-bottle process, similar to the aluminum cans (48%

recycled).¹ Two major conventional methods of recycling postconsumer PET exist: mechanical recycling and chemical recycling.^{4–7} The former is most commonly practiced and involves sorting, washing and drying postconsumer PET before melt-processing to produce a new material. The organometallic catalysts used to synthesize PET such as antimony, titanium or germanium⁸ remain permanently in the fabricated item, leading to significant property deterioration during the secondary melt fabrication process.⁹ As a consequence, mechanically-recycled PET generally ends up in secondary products such as fiber for clothing or carpeting, and engineering resins for reinforced automobile components.^{2,10} Ultimately these all find their way to the landfill. The problem was, however, solved by solid state polymerization technique where the catalysts in the waste PET are applied to increase/maintain the molecular weight high enough for the fabrication.¹¹ Mechanical methods for bottle-to-bottle recycling are being established, but there still are some practical concerns especially when colored bottles are used as raw materials;¹² variation in the amounts and types of residual catalysts in the waste PETs create additional challenges.

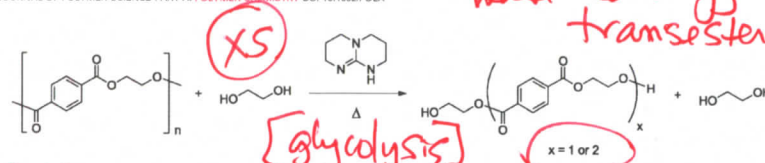
Additional Supporting Information may be found in the online version of this article. Correspondence to: K. Fukushima (E-mail: kazukifu@us.ibm.com) or J. E. Rice (E-mail: julia@almaden.ibm.com) or J. L. Hedrick (E-mail: hedrick@almaden.ibm.com)
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ORGANOCATALYTIC DEPOLYMERIZATION OF PET, FUKUSHIMA ET AL.

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@ 190 °C, glycolysis degradation time decreased, from > 300 min. w/out TBD to 8 min w/ 10% TBD vs. PET, due to base-catalyzed transesterification

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$n > 10$

SCHEME 1 Glycolysis of poly(ethylene terephthalate) catalyzed by TBD.

Chemical recycling entails degradation of the polymer to its starting monomer, purification, and then subsequent repolymerization to yield high quality plastic.⁷ Depolymerization processes for chemical recycling mainly include hydrolysis, methanolysis, and glycolysis^{13–15} which are generally conducted at high temperature in the presence of catalysts such as metal (zinc, lead, cobalt, manganese) acetate, zeolite, titanium(IV) *n*-butoxide, and sodium/potassium sulfate, and under the pressure in some cases.^{15–20} Hydrolysis and methanolysis are more common because the high crystalline monomers terephthalic acid (TA) and dimethylterephthalate (DMT) are easier to isolate than the glycolysis product bis(2-hydroxyethyl) terephthalate (BHET). In addition, PET is generally prepared by a two step process: the condensation of TA or DMT with excess ethylene glycol (EG) to generate BHET followed by the self-condensation of BHET at high temperatures (270–290 °C) using mixed organometallic catalysts optimized for their reactivity and selectivity for each step of the process.^{5,21} Current processes for the chemical recycling of PET are energy intensive, and consequently suffer from unfavorable economics relative to mechanical recycling, and are therefore not widely practiced.^{5,7} Low monomer costs also contribute to the economic challenges for alternative technologies utilizing postconsumer PET as a monomer feedstock.^{22,23} Moreover, the chemical approach to recycling of PET-based copolyesters^{24,25} has advantages in terms of mechanical properties associated with the final product. It also can be readily extended to other polyesters.^{26,27} Initiatives in the chemical recycling of PET are thus ideally focused on developing an environmentally safe, economically feasible, and industrially applicable process for wide-scale application. Chemical recycling methodologies that are energy efficient and do not involve heavy metals are highly desirable even though the catalysts are usually not contained in the purified monomers.

Organic catalysts are attractive alternatives to traditional organometallic reaction promoters. Organic phase transfer catalysts based on quaternary ammonium salts have been used for hydrolysis of PET where sodium hydroxide was used as a cocatalyst.^{14,28} Organocatalysis has been shown to be a powerful strategy for polymer synthesis. As these catalysts typically operate by different mechanisms than metal alkoxides, they offer a diversity of mechanistic pathways that can provide new opportunities for selective polymerization and depolymerization processes.²⁹ We have developed several organic catalyst platforms for polymerization and transesterification reactions.³⁰ 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), a potent neutral base (pKa = 26 in aceton-

trile)³¹ well-known as a catalyst for a variety of reactions³² is among the most active ring-opening polymerization (ROP) catalysts known. The ROP of lactide with 0.1% TBD in THF exhibits a turnover frequency of 80 s^{−1} at room temperature, a rate comparable to that of the most active metal catalysts reported for ROP of lactide.³³ Computational studies suggest that TBD is such an effective catalyst because it activates both alcohol and monomer through hydrogen-bonds.^{34,35} The high activity of TBD for transesterification reactions stimulated us to extend our investigation to depolymerization, rather than polymerization. Herein, we show that the guanidine TBD is an efficient catalyst for the glycolysis of PET to its monomer bis(2-hydroxyethyl)terephthalate (BHET)^{36,37} and also demonstrate its recyclability (Scheme 1).

EXPERIMENTAL

Materials

PET beverage bottles were washed with water, dried, and shredded to around 3 mm squares prior to use. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), ethylene glycol (EG; anhydrous, 99.8%), and solvents were used as received (Sigma-Aldrich).

Instruments

¹H NMR spectra were obtained on a Bruker Avance 400 Instrument at 400 MHz. Size exclusion chromatography (SEC) was performed in THF at 30 °C using a Waters chromatograph equipped with four 5 μm Waters columns (300 mm × 7.7 mm) connected in series with increasing pore size (10, 100, 1000, 105, 106 Å), a Waters 410 differential refractometer for refractive index (RI) detection, and calibrated with polystyrene standards (750 – (2 × 106) g/mol).

Typical Procedure of Glycolysis

To a 25 mL Schlenk tube containing colorless PET flakes (0.96 g, 5.0 mmol),³⁸ previously dried at 80 °C for 1 h, was charged a mixture of EG (5.00 g, 80.6 mmol) and TBD (70 mg, 0.50 mmol) in a glove box. The tube was immersed in an oil bath heating at 190 °C to conduct the reaction with stirring. After 8 minutes the slurry turned into a clear and homogeneous liquid. The crude solid was purified by either of the following two methods.

A. Extraction: The reaction mixture was cooled to room temperature and dissolved in methylene chloride (100 mL) with slight heating to dissolve the solid. The solution was washed with 0.5 N HCl aqueous solution (100 mL) and extracted with methylene chloride (50 mL). The organic fractions were combined, stirred over MgSO₄, evaporated, and dried in

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(as done for polylactide in F.A. Leibfarth et al. *J. Polym. Sci. Part A: Polym. Chem.* 2012, 50, 4814–4822)

• other diols or other small molecules give new recycled monomers + other by-products