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Monomers and Polymers derived from Biological Sources

Opportunities and Challenges

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Overview

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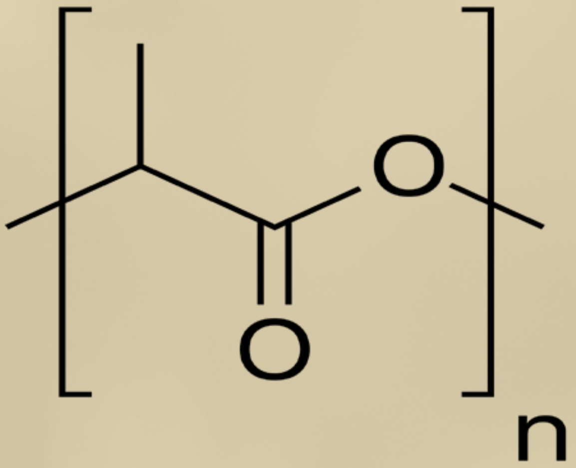
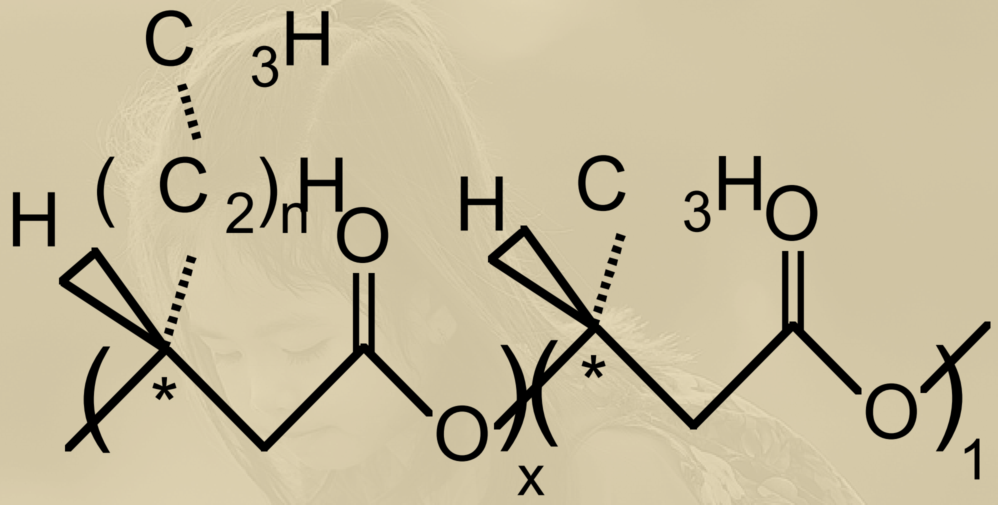
- We are all familiar with the news about plastic waste
  - Biodegradable is more important than biorenewable
  - Bio-based plastics cannot sacrifice on performance
- Biomass purification versus bio-organism production
  - Biomass products take existing natural materials and react/purify to obtain specified monomers/polymers
  - Bio-synthetic routes synthesize monomers or polymers via a metabolic pathway (purification still necessary)

- Biodegradable plastics
  - Microbes in the environment will break down the plastic and use it as a food source
  - Can occur in many environments including terrestrial and marine
- Compostable
  - Products will degrade in municipal and industrial composting facilities
  - Require inputs such as moisture and heat to disintegrate materials

PLA/PHA



PLA



PHA

- Biodegradable in an industrial compost environment
- Will de-polymerize via hydrolysis given enough impetus
- Monomer (lactide) produced via bio-synthesis
- Plastic then produced via polymerization

- 100% biodegradable
- Produced via bio-synthesis
- Micro-organisms create polymers; not monomers
- Polymers then processed/compounded to produce plastics and polymers for specific applications

PLA/PHA: Fermentation basics

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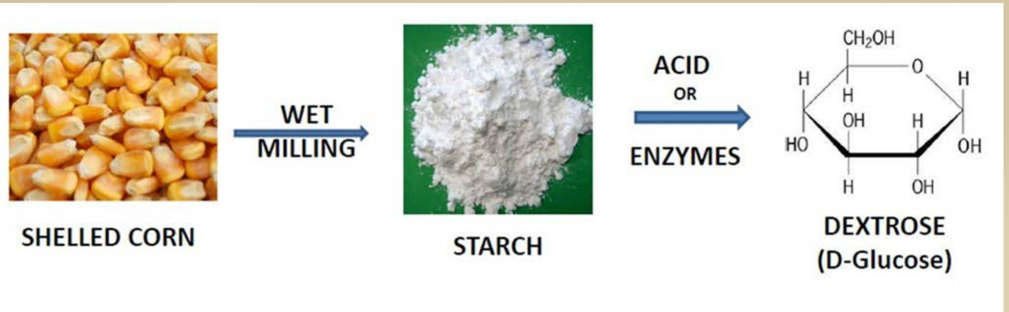
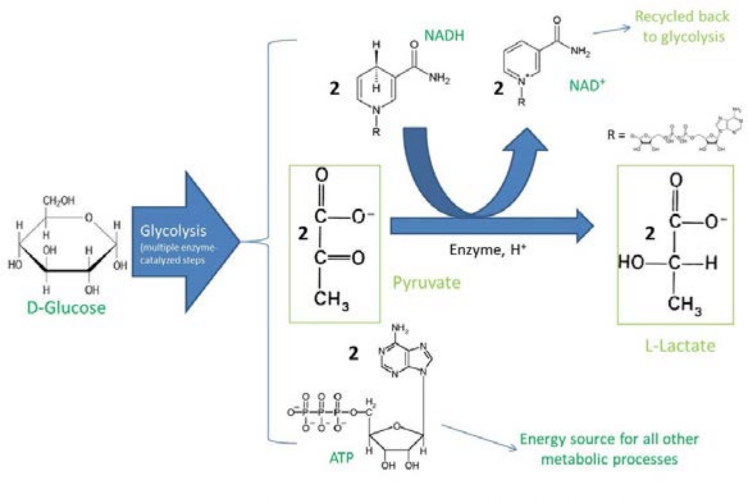
- Common PLA pathway is *Lactobacillus* genus such as *L. delbrueck*ii, *L. amylophilus* and *L. leichmanii*[1]
- Most common monomer produced is L-lactic acid
- Corn is converted to corn sugar (starch); commonly dextrose
- Starch is then heated with acid or enzymes to completely hydrolyze to dextrose
- The dextrose is then subjected to glycolysis to pyruvate, ATP and NADH
- The pyruvate is then metabolized to lactate and the lactic acid





Fermentation of dextrose (D-glucose) to lactic acid

- PHA is synthesized via microorganism *E. coli*
- Substrate is commonly sugars from sugarcane or beet
- Batch processing very common
- End product is PHA polymer; not monomer

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PLA/PHA: Purification and Processing

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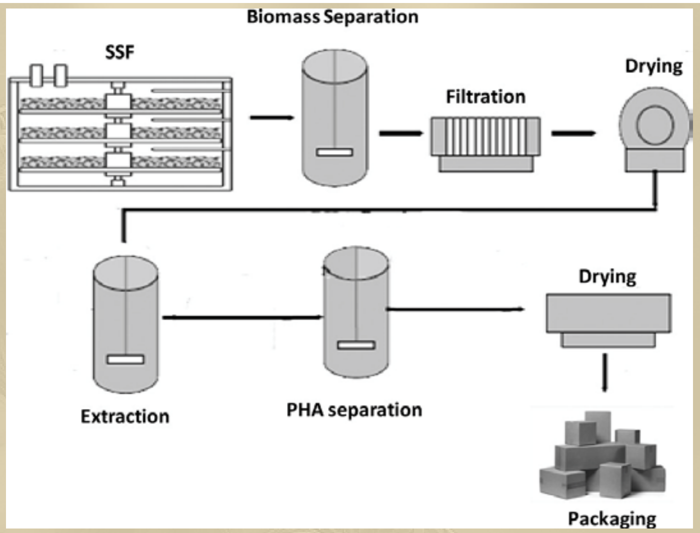
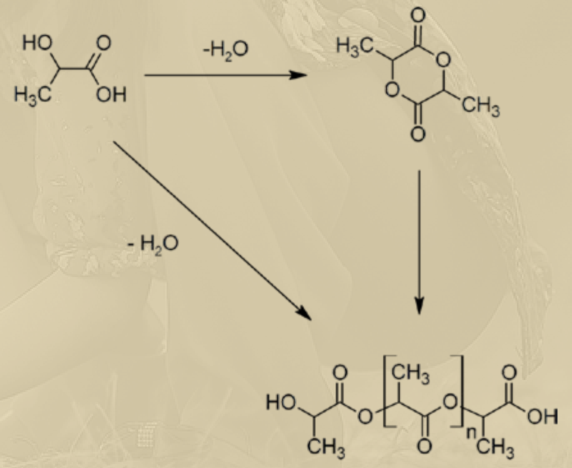
- Common processing in all fermentation processes:
  - Monomer(s) and/or polymer(s) are in an aqueous solution of brine, protein, biomass and contaminants
  - End product must be separated and purified via filtration and similar unit operations
  - Invariably, there is also a drying step
  - Lower yields = higher costs and more by-products, thereby increasing costs
  - More/difficult separations also increase cost
  - Analogous process: crude oil to monomers via distillation
- For PLA, once you have the monomer, the plastic is made via homo-polymerization
- PHA is purified as a polymer
- The polymers are then further compounded to create plastic of desired properties





PLA/PHA: Downstream Applications

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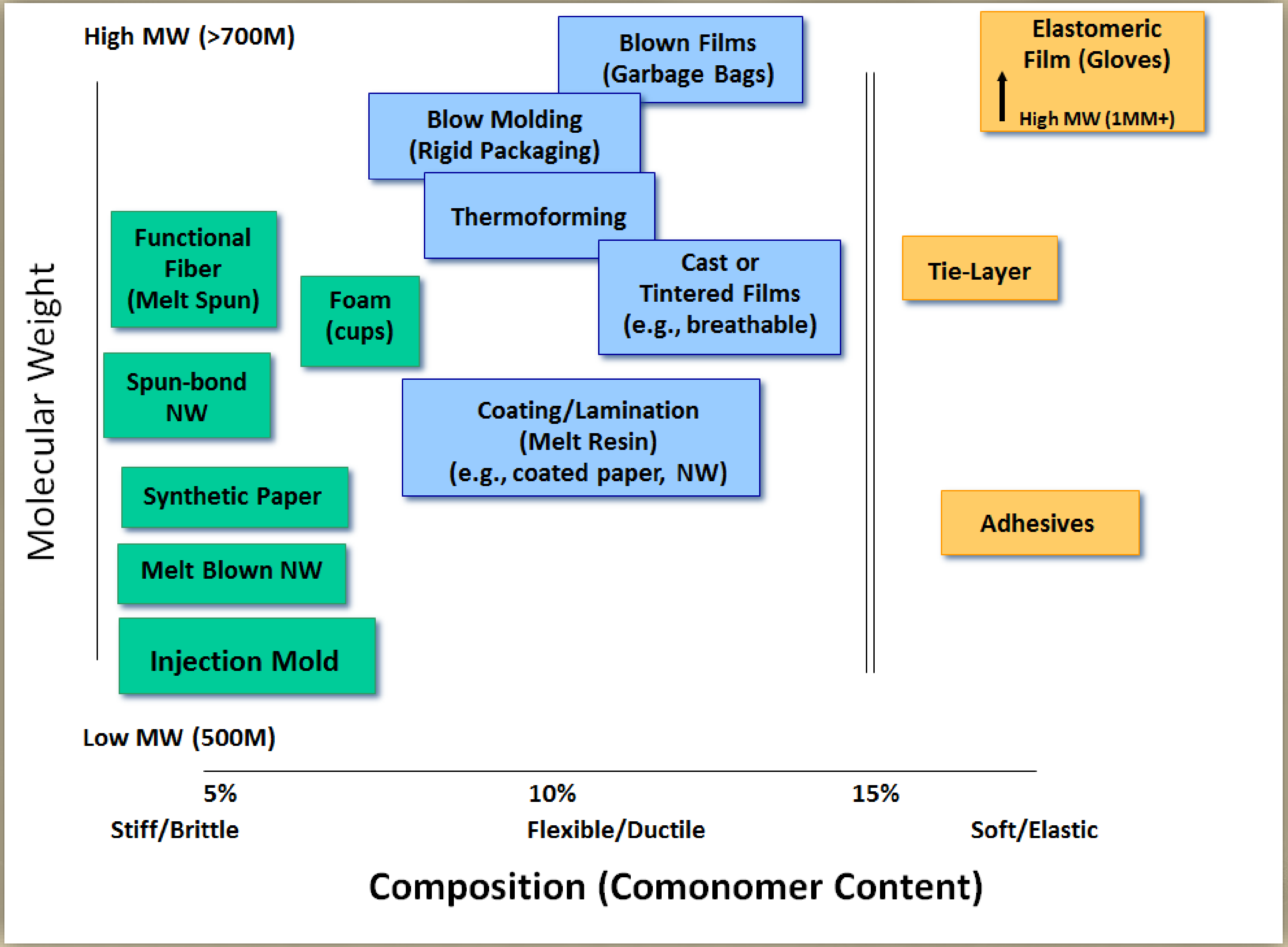
- PLA is one of the most common bio plastics available currently
  - Mainly due to cost
- PLA has application limitations due to a lack of ductility
- Commonly used in injection molding, extrusion and thermoforming
- PHA is a rapidly growing polymer due to biodegradability combined with flexible properties
- Widespread applications
- Traditionally, price has been major drawback
- Volume combined with processing technologies has taken the price down to competitive levels



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Polyester Building Blocks

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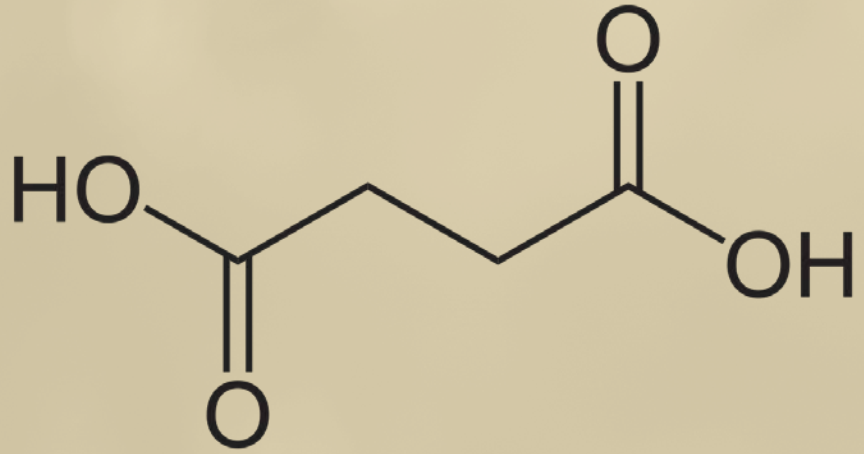
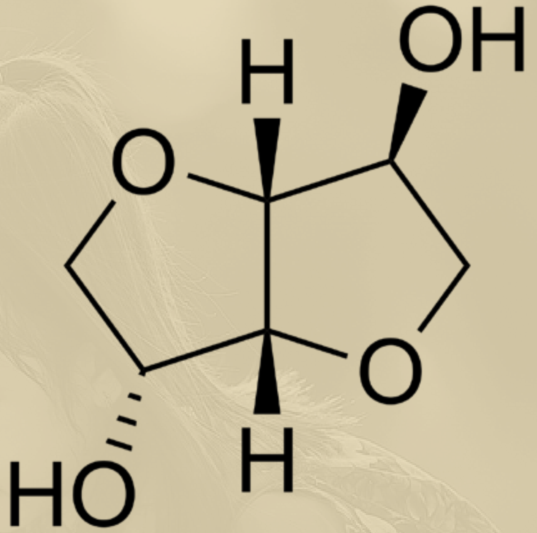
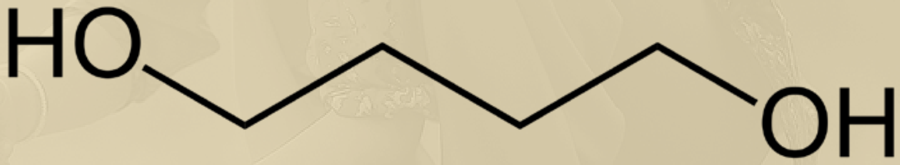


Succinic Acid



Isosorbide

1,3 Propanediol



1,4 Butanediol

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Polyester Building Block Fermentation

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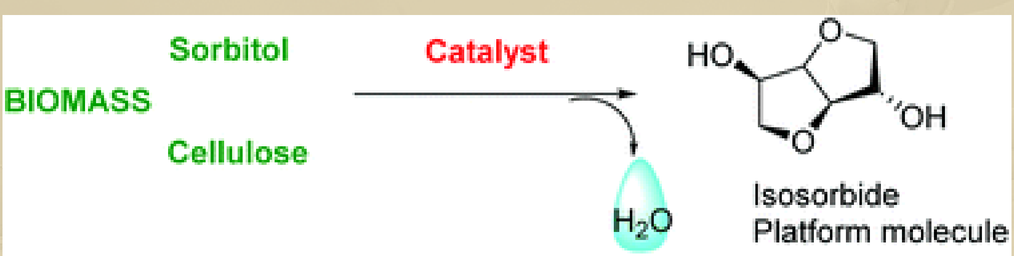
- Succinic acid fermentation from *Actinobacillus succinogenes,* recombinant *Escherichia coli*, *Anaerobiospirillum succiniciproducens* and *Mannheimia succiniciproducens*[2]
- The bioproduction of 1,3-propanediol by bacterial species *Klebsiella pneumoniae*, *Citrobacter freundii*, *Enterobacter agglomerans* and *Clostridium butyricum* have been investigated by batch fermentation[3]
- The bio-based BDO manufacture process is not performed worldwide on large scale yet. It can either take place via hydrogenation of succinic acid or direct fermentation of sugars through experimental metabolic engineered bacterial platform[4]
- The synthesis of isosorbide is still a technical challenge, as several competitive reactions must be simultaneously handled to promote a high molar yield and avoid side reactions, like degradation and polymerization[5]
- Isosorbide is derived from biomass, where as others are typically bio organism production



Polyester Building Block Purification and Polymer Synthesis

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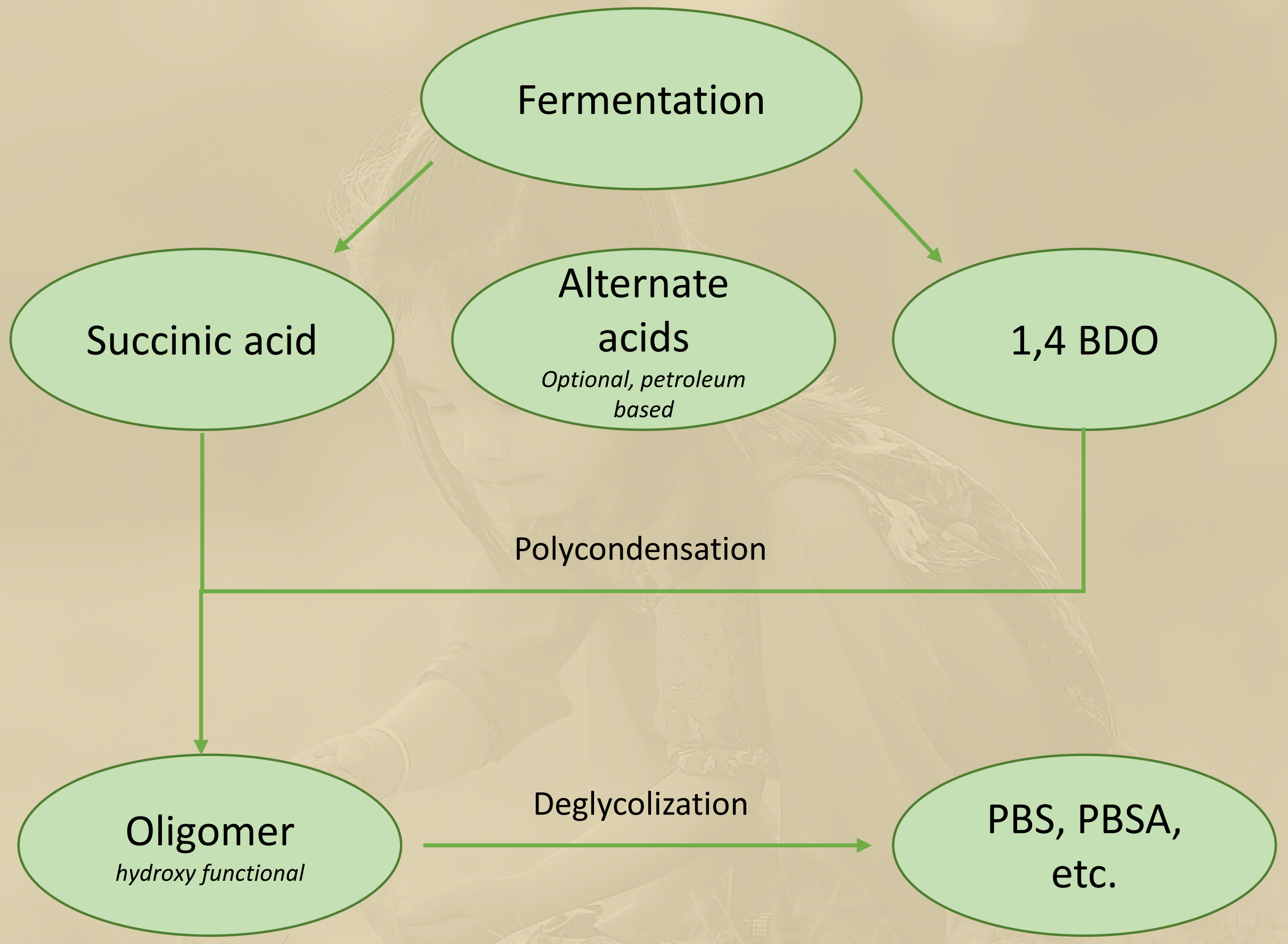
- SAC, BDO, PDO and BDO are subject to typical post synthetic purifications
- Isosorbide subject to separation and purification from biomass
- Once isolated, all can be used as polyester monomers via typical esterification techniques
- Replacement into petroleum at levels up to 100%
- Common polyester plastics include PBS, PBSA, PBAT



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Polyester Applications

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- Extremely diverse; across many industries
- Hydroxy functional oligomers used as building blocks into polyurethanes for foams, coatings, adhesives, PUDs and TPUs
- Unsaturated oligomers as resin component of free radically cured composites
  - Unsaturation also lends itself to UV curing
- High MW PBS, PBSA, PBT can be used in packaging, thermoforming, and many other plastic applications including blown films
- Anywhere conventional petroleum based monomers can be used, bio based can be substituted

NOT A DROP IN!

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Polyester Building Blocks: Newer Bio-based Monomers

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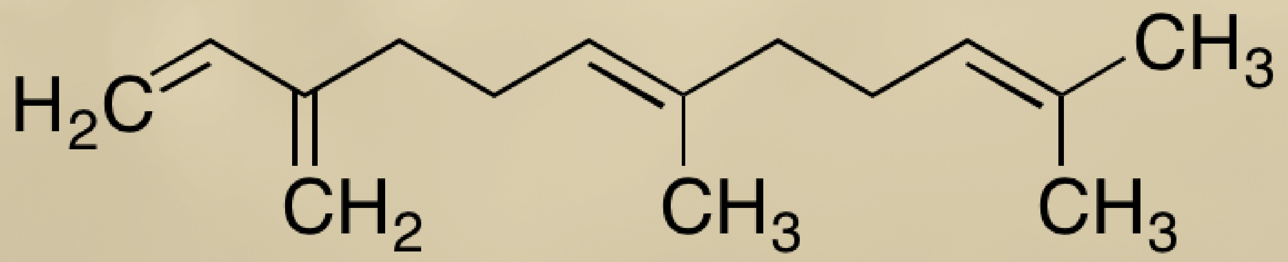
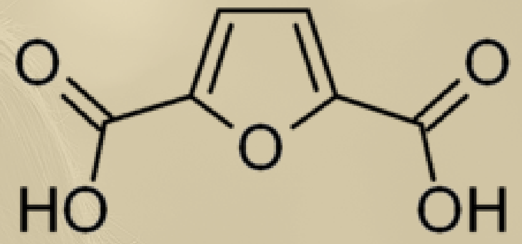
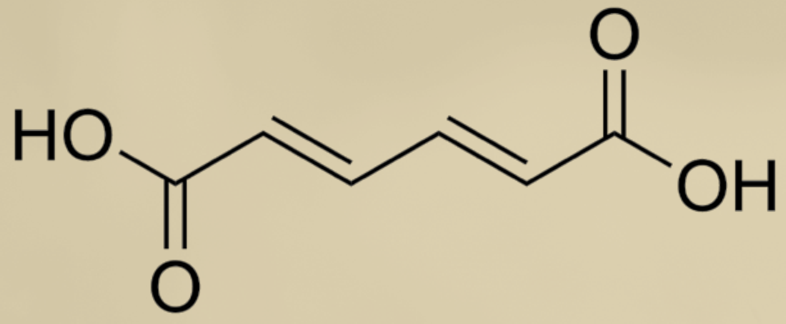


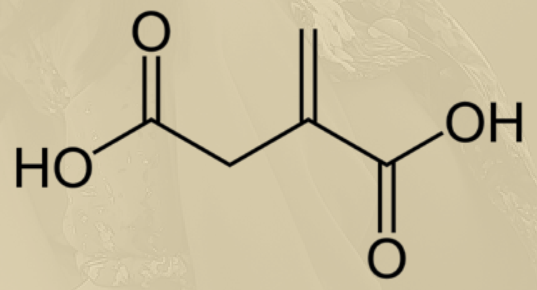
- Farnesene
- CAS # 18794-84-8
- Easily made into diol for polyurethane



- FDCA
- CAS # 3238-40-2
- “the next PET”



- Muconic acid
- CAS # 3588-17-8
- Possible precursor to bio adipic



- Itaconic acid
- CAS # 97-65-4
- Labile unsaturation opens many possibilities

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Advantages and Challenges

- Advantages are clear; no need to re-state public convention
- Challenges are more covert
  - Price premium: From the obvious point of view, cannot be more expensive than the petroleum based incumbent
  - Price premium: Even more subtle; bio-based/biodegradable offsets that out perform incumbents and are competitively priced still face resistance to change
  - “Green” alone will not sell
- Recycling Challenges: Typical bio-based products will contaminate a petroleum recycle stream

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Advantages and Challenges

- Important challenge: bio sourced versus biodegradable
  - Bio-sourced offers very little incentive on a macro economic scale
  - Biodegradable is more enticing, but some petroleum polymers are considered compostable
- Many degradable plastics such as PLA, PBS and similar should be sent to a commercial facility who use extremely controlled environments speed up decomposition
  - Even in that time, the process is said to take up to 90 days
  - Often, biodegradable products are advertised as such when they are not in a practical sense
  - Counter argument is; why not just recycle petroleum plastic?

Advantages and Challenges

- Marine biodegradable
  - The marine environment offer particular challenges to degradability; especially salt water
  - Salt water tends to act as a preservative
  - Most plastic waste not in controlled landfills or facilities ends up in ocean
- The shelf life required for perishable foods will always be compromised with biodegradable films.
  - Many people fail to see is this unavoidable paradox
  - You want a material to degrade over time, but you also want to keep your produce as fresh as possible

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Thank You!

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References

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4 https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5456926/

5 https://pubs.rsc.org/en/content/articlelanding/2017/gc/c7gc01912b#!divAbstract