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Biosourced polymers: reality or just a hype?

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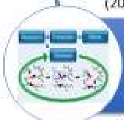
PCR
5

From ***polymer functionalisation*** to ***absolute control***

Click chemistry
Controlled polymerisations
Sequence control

Prog. Polym. Sci. (2018), Macromolecules **51**, (2018); *JACS* **138**, (2016), *Chem. Rev.* **116**, (2016), *Angew. Chem*, **54**, (2015); *Nat. Chem.*, **6**(9), 815 (2014), ...



Dynamic and ***self-healing*** polymeric materials

Self-healing polymers
Microcapsules
Vitrimers

Nat. Comm. (2017), Chem. Sci (2017), Prog. Polym. Sci. **49–50**, (2015) *Adv. Funct. Mat.* **25**, (2015); *Polym. Chem.*, **6**, (2015); ...

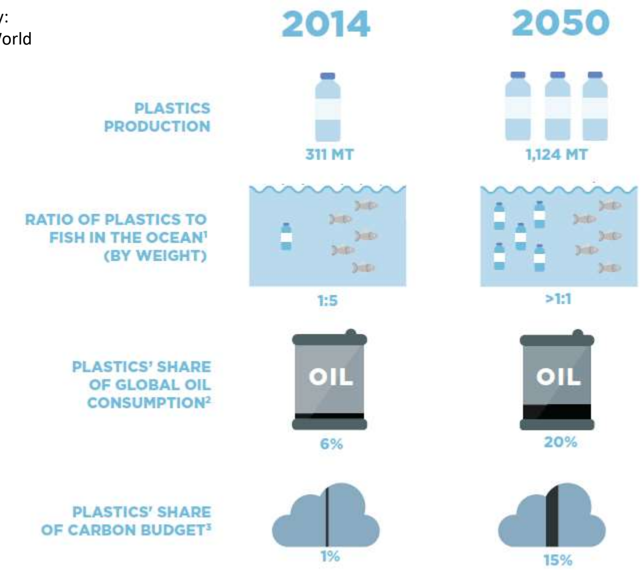
Giving ***renewable materials*** function(ality)

Plant foils
Thiolactones
Polymers from fatty acids

Macromolecules (2017), Green Chemistry (2017), ACS Macro Lett. , **5**, (2016), *Green Chemistry*, **17**, (2015), *Polym. Chem*, **5**, (2014); ...

Some remarkable facts about polymers …

Source: "The New Plastics Economy: Rethinking the future of plastics", World Economic Forum, January 2016



Polymers from Renewable Resources – Prof. Dr. F. Du Prez

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A plastic age?

Decomposition rates of common marine debris items

What are bio-polymers?

Bio-based ⟷ **Bio-degradable**

- ***Bio-based*** or ***bio-sourced*** means that the product has been made from a biological (living) or renewable source, such as corn or sugar cane.
- Bio-degradable means a material may be broken down by other living organisms, such as bacteria, that exist in nature.
- Being bio-based does not mean a material is bio-degradable, and vice-versa.

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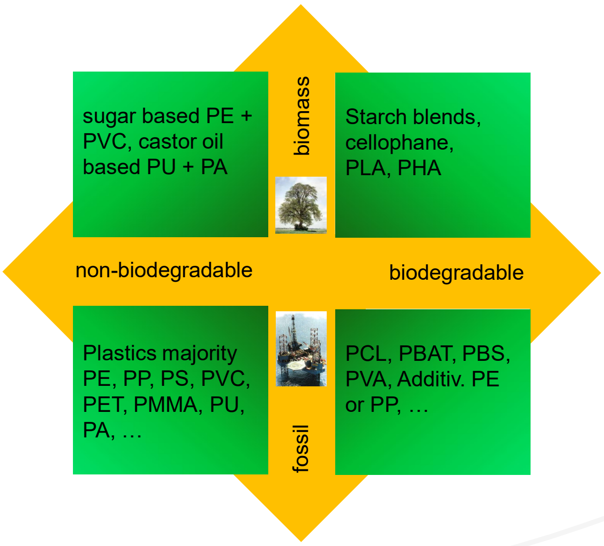
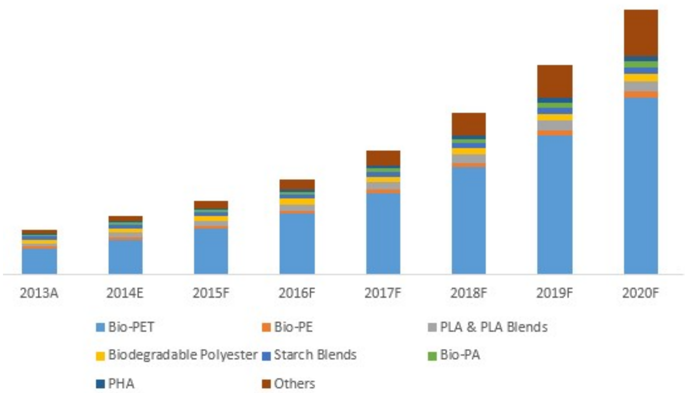
What are bio-polymers?



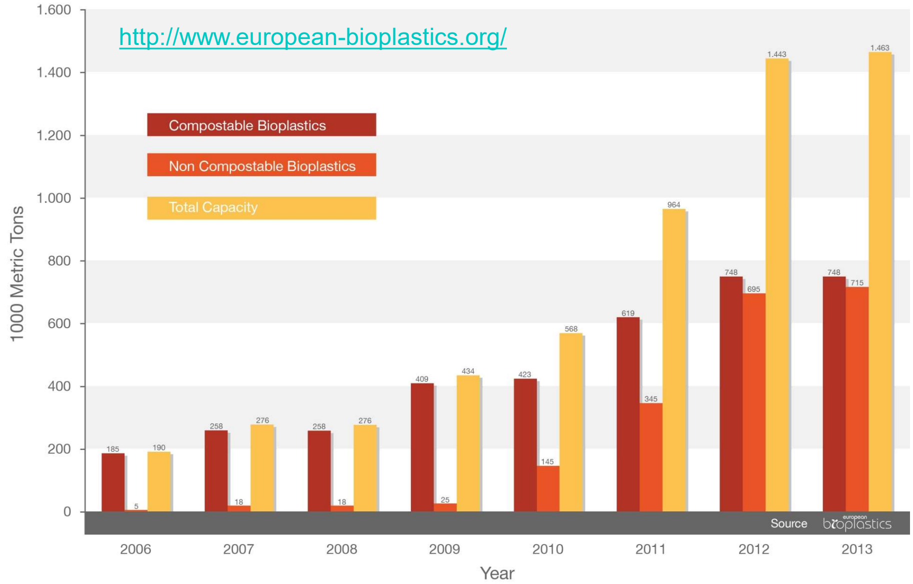
Production capacity: 0.5 to 1% of all plastics only…



1.5 M ton bioplastics

300 M ton synthetic polymers

Compostable vs non compostable



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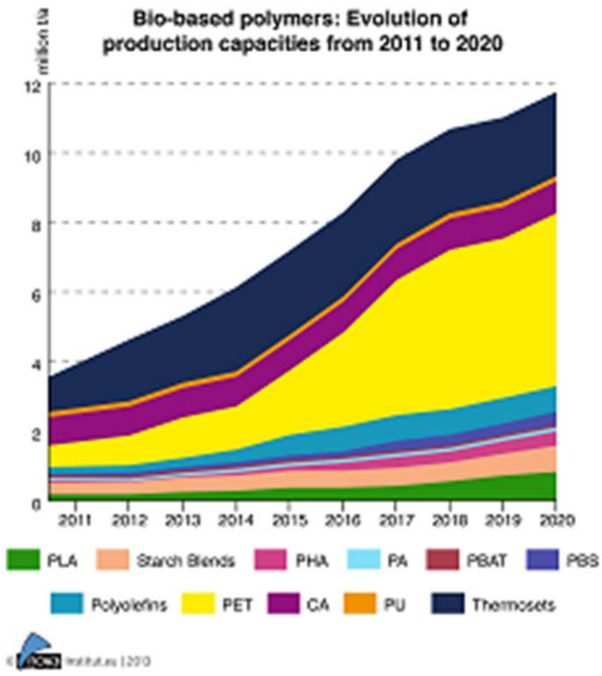


Biodegradable polymers: definition

Dictionary definition:

« Biodegradable is said for an industrial product that, when discarded, is destroyed by bacteria and other biological agents »

→ *Definition by far too broad, it does not take into account:*

- *the location of occurring biodegradation (soil, water, garbage dump, compost)*
- *the composition and shape of materials, and degradation time*
- *the biodegradation testing methods*
- *the ultimate impact on environment*

More than 15 years (of debates and controversies) have been necessary to reach a consensus …

Biodegradable polymers: definition

« **Environmentally Degradable Plastics 'EDPs'**
is defined as polymeric material-based items that :

✓ retain the same performances as conventional plastics during use;

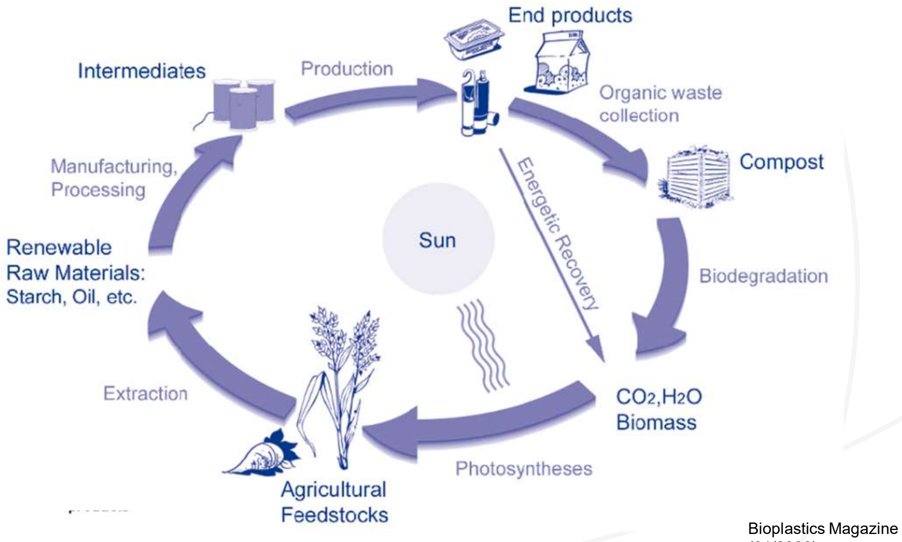
✓ degrade after use into low molecular weight compounds by combination of biological stimuli (*by the action of naturally occurring micro-organisms, such as bacteria, fungi and algae, and/or enzymes*) and/or chemical/physical stimuli (*including light, heat, oxygen and water*) in the environment;

✓ ultimately degrade into CO_2 and/or CH_4, H_2O, and biomass at comparable and commensurable rate and extent as known for environmentally degradable materials like yard waste and paper, and leave no persistent or toxic residues. »

from *- American Society of Testing and Materials (ASTM),*
- International Standard Organization (ISO)
- Comité Européen de Normalisation (CEN)

(AIM Magazine, Vol. 55, suppl. 1, 2001, p. 66- 71)

Life cycle of biodegradable polymers



Bioplastics Magazine (01/2006)

Classification biodegradable polymers

Biodegradable polymers

- **Biomass products** From agro-resoures → Agro-polymers
  - **Polysaccharides**
    - *Starches Wheat Potatoes Maize,…..*
    - *Ligno-cellulosic products: Wood Straws,…..*
    - *Others: Pectins Chitosan/Chitin Gums,……..*
  - **Proteins, Lipids**
    - *Animals: Casein Whey Collagen/Gelatin*
    - *Plant : Zein Soya Glutten*
- **From micro-organisms** (obtained by extractions)
  - **Polyhydroxyalkanoates (PHA)**
    - *Poly(hydroxybutyrate) (PHB) Poly(hydroxybutyrate co-hydroxyvalerate) (PHBV)*
- **From biotechnology** (conventional synthesis from bio-derived monomers)
  - **Polylactides**
    - *Poly(lactic acid) (PLA)*
- **From petrochemical products** (conventional synthesis from synthetic monomers)
  - **Polycaprolactones (PCL)**
  - **Polyesteramides (PEA)**
  - **Aliphatic co-polyesters (e.g. PBSA)**
  - **Aromatic co-polyesters (e.g. PBAT)**

Ref: *Progress in Polymer Science*, **34**, 125-155 (2009)

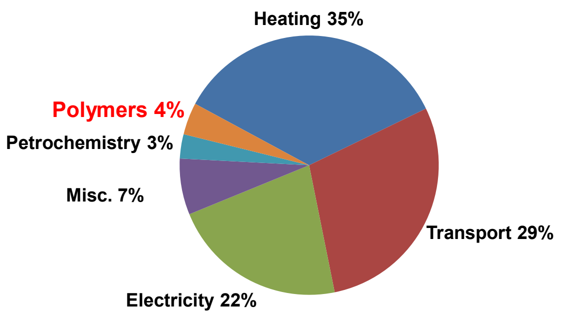
Why?

- Decrease oil dependence; price & availability
- Improve the environmental image of polymers
- To be prepared for political decisions
- Demand from customers
- Recycling via energy recovery (bio fuel)

Why?

- Today's polymers are made from fossile feed stock

Usage of oil in West Europe



Why?

Polymers and the environment – opinion

What is the answer if you ask the public about their opinion on the combination plastics – environment???

Negative!!!

Why?

- ??
- it pollutes
- too many unnecessary plastics
- plastics are made from oil

⇨ Polymers from renewable resources are perceived much more positively!

Why?

Political measures

Driving forces:

- CO_2 – greenhouse effect
- Fossil feed stock is limited

Actions:

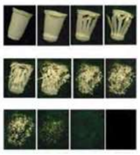
- Ecotax on plastic bags (2007)
- Eu directives on renewable feed stock
  - Already existing for fuel:2005 – 2%; 2010 – 5,75%
  - When does it arrive for polymers??
- PE made of renewable feed stock can be viewed as bio fuel. Energy recovery can be done without CO_2 tax.

⇨ The mind of politicians is changing

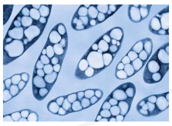
Bio-plastics

- **Natural polymers**
  Starch, protein, cellulose, chitosan

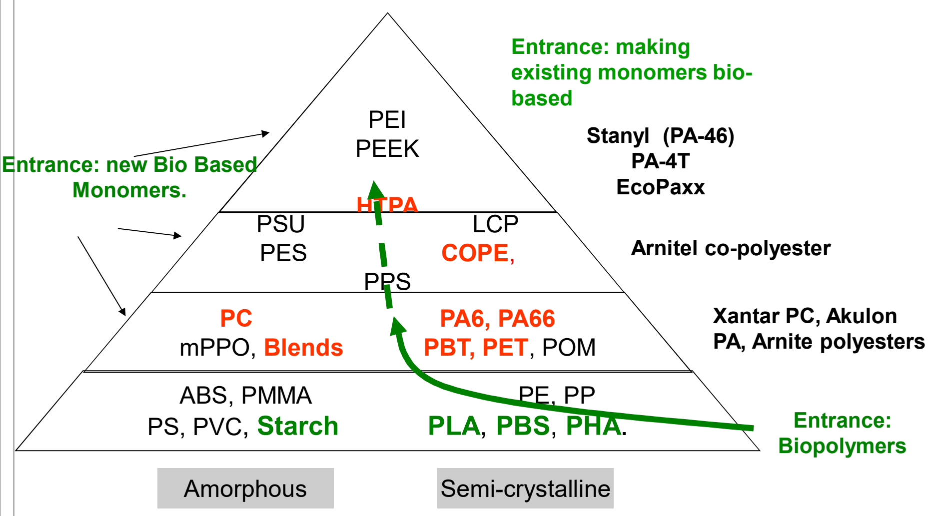
- **Synthetic Polymers from natural monomers**
  Polylactic acid (PLA)



- **Polymers from microbial fermentation**
  Polyhydroxyalkanoates (PHA)



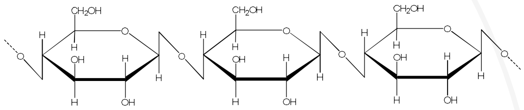
Introduction of bio-based materials



Source:DSM

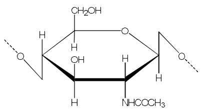
Natural polymers

- Cellulose

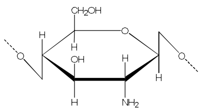


Cellulose-based films
→ transparant, fully degradable, heat sealable

- Chitin

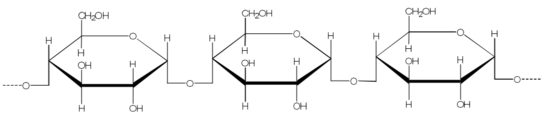


- Chitosan



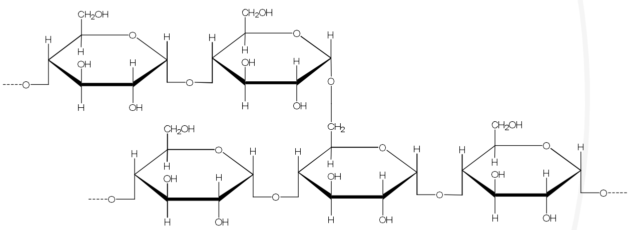
For applications and modifications of cellulose, chitin and chitosan, see Gandini, A *Macromolecules*, **2008**, 41, 9491-9504

Starch: mixture of two polysaccharides



Amylose: *D-glucans with α 1-4 bonds*

Amylopectine: *D-glucans with both α 1-4 bonds and α 1-6 bonds*



→ Can be used as starch granules (~10 µm) or as **thermoplastic starch** (after plastization, e.g. with glycerol)

Starch: commercial applications

- Shopping bags
- Bread bags
- 'Flushable' sanitary product backing materials
- Mulch film
- …

Starch: commercial applications

- Plantic®
  - transparent, dissolvable, water resistance up to 12 weeks and more
  - used for trays, plant pots, …

Process of biodegradation in compost

week 1

week 2

week 3

week 4

week 5

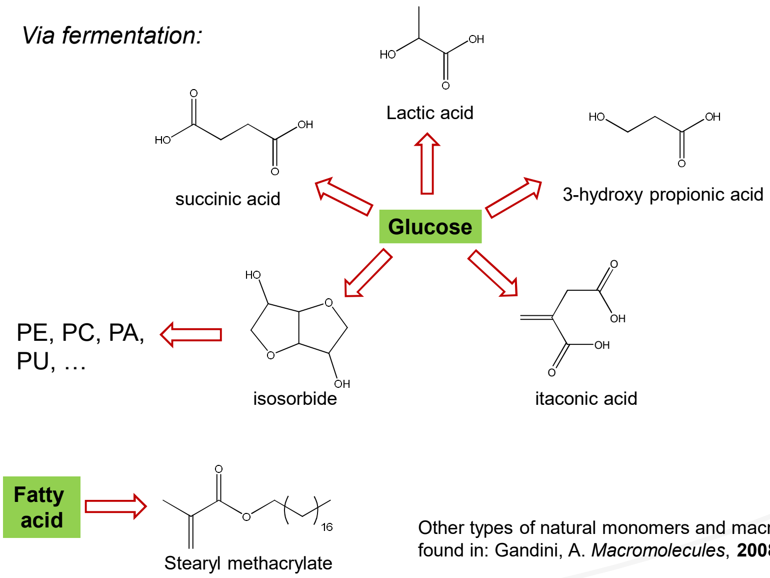
Starch as bioplastic: degradation

- Starch-based bioplastics are mostly degraded by hydrolysis

- Also enzymatic degradation is possible

Monomers from renewable resources

Via fermentation:

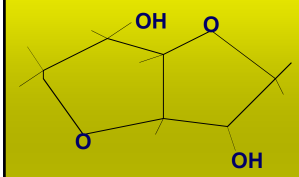


Other types of natural monomers and macromonomers can be found in: Gandini, A. *Macromolecules*, **2008**, 41, 9491-9504

Possible new bio-based monomers

Isosorbide: $C_6H_{10}O_4$

Via dehydration of sorbitol

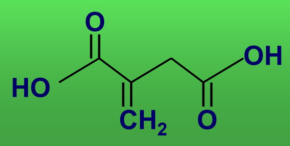


Diol for:
- Polyesters
- Polycarbonates
- Polyurethanes
- Plasticizers

Commercial quantities: 2008/2009

Itaconic Acid: $C_5H_6O_4$

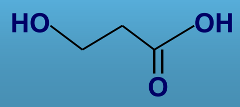
Via fungal fermentation of glucose



Potential use:
- Polymerization monomer
- (Meth)acrylic esters alternative
- Hydrogels for superabsorption

Commercial quantities: 2007

3-Hydroxy Propionic Acid: $C_3H_6O_2$



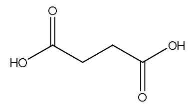
Feedstock for:
- Acrylonitrile
- Acrylic Acid
- Acrylamide

Technically feasible, but not yet cost effective

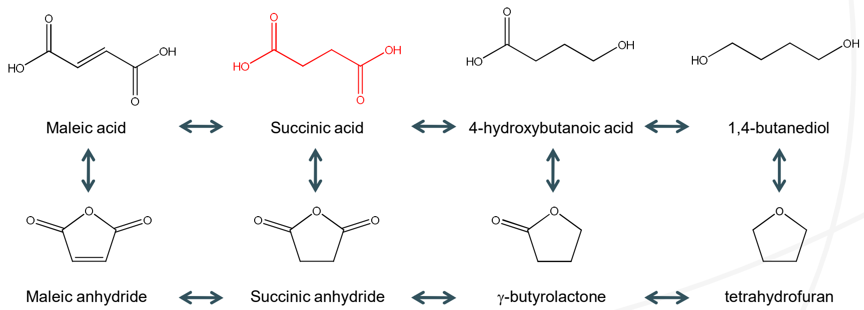
Source: DSM

Succinic acid

Potential use as:



- Diacid for polyesters
- Diacid for alkyds
- Intermediate for manufacturing of maleic acid, butanediol, diaminobutane, adipic acid



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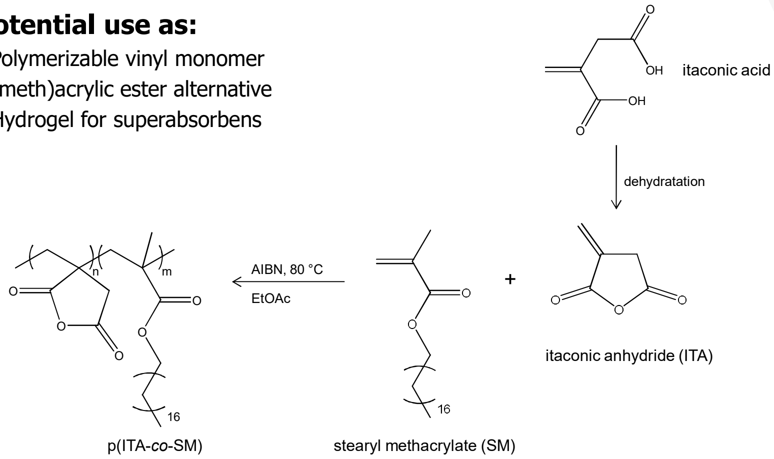
Itaconic acid

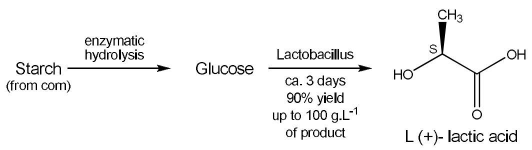
Potential use as:
- Polymerizable vinyl monomer
- (meth)acrylic ester alternative
- Hydrogel for superabsorbens



→ After hydrolysis of the anhydride side chain, the polymer behaves like an ionomer (improvement of thermal and mechanical properties)

Poly(lactic acid) (PLA)

Synthesis of lactic acid



Separation and purification

2 LA + $Ca(OH)_2$ ⟶ $(CH_3\text{-}CH(OH)COO^-)_2Ca^{2+}$ + 2 H_2O

$(CH_3\text{-}CH(OH)COO^-)_2Ca^{2+}$ + H_2SO_4 ⟶ 2 LA + $CaSO_4$ ↓

or

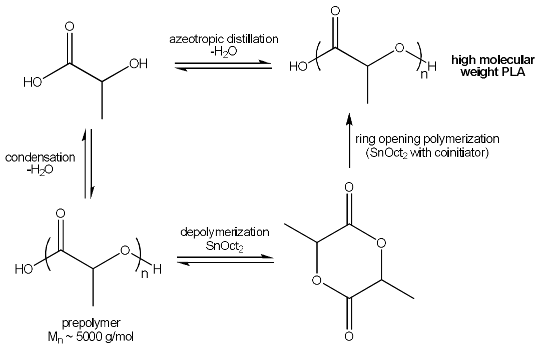
LA + NaOH ⟶ $(CH_3\text{-}CH(OH)COO^-)Na^+$ + H_2O

electrodialysis: $(CH_3\text{-}CH(OH)COO^-)Na^+$ + HCl ⟶ LA + NaCl

Mecking S. *Angew. Chem. Int. Ed.* **2004**, 43, 1078

Poly(lactic acid) (PLA)

Polymerization of lactic acid



Drumwright, R.E.; Gruber, P.R.; Henton, D.E. *Adv. Mater.* **2000**, 12, 1841

Poly(lactic acid): applications

Poly(lactic acid): applications

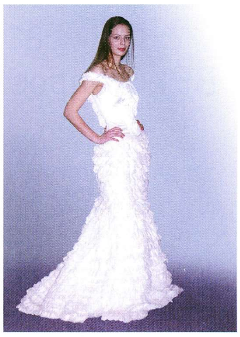
PLA bottles: recyclable & compostable

… complete decomposition in CO_2, water and biomass in less than 60 days

Bioplastics Magazine (04/2009)

Poly(lactic acid): applications

PLA in textile



Applications for Ingeo ® fibers include Versace Sport, Armani Collezioni, and Nadia Fassi

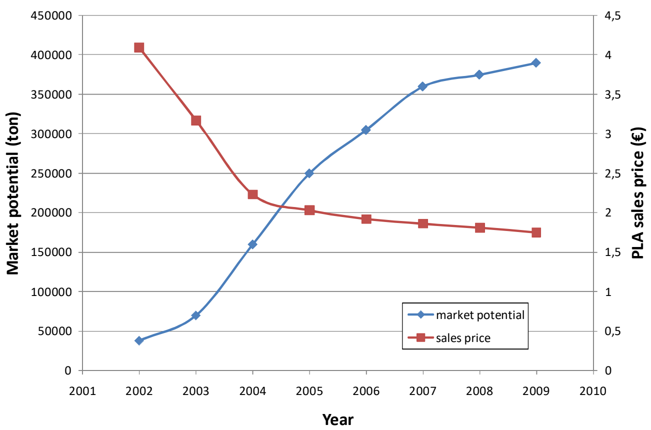
Bioplastics Magazine (01/2007)

Poly(lactic acid): suppliers

Industry	Location
Cargill - Teijin	USA
Shimadzu	Japan
Mitsui Chemicals	Japan
Chronopol	USA
Dainippon Ink Chem.	Japan
Galactic/Total (Futerro)	Belgium
Toyota	Japan
Treofan	The Netherlands
Purac	The Netherlands
Mitsubishi	Japan
Biomer	Germany

Poly(lactic acid): cost-effectiveness

Is the production profitable?

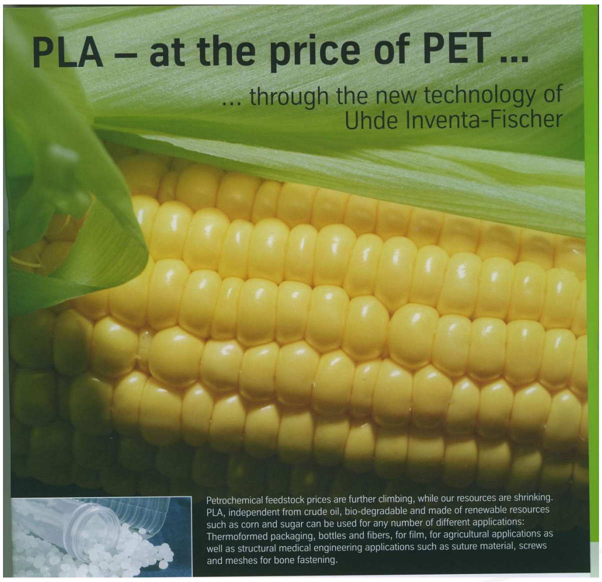


"Best opportunities are anticipated for PLA…

It is now competitive with petroleum-based PET."

"MACPLAS International; March 2005"

Poly(lactic acid): cost effectiveness



Bioplastics Magazine (01/2007)

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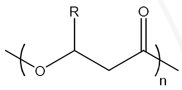
Poly(hydroxyalkanoates)

Synthesis of PHA's

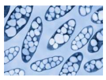


R = Me (PHB)
R = Et (PHV)

Produced via **fermentation** of carbohydrates and fatty acids:

- In plants *(one-step process)*

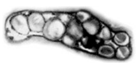
  $CO_2 + H_2O \xrightarrow{\text{plants, algae}}$ polyhydroxyalkanoates



genetically engineered plant cells

- In bacteria *(two-step process)*

  $CO_2 + H_2O \xrightarrow{\text{plants}}$ glucose/vegetal oils $\xrightarrow{\text{bacteria}}$ polyhydroxyalkanoates



genetically engineered *E. Coli* bacteria

In both cases PHA's are stored as intracellular granules for carbon and energy reserve

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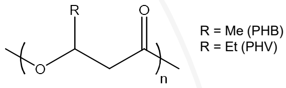
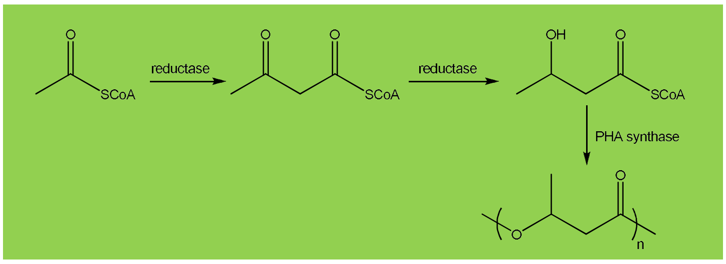
Poly(hydroxyalkanoates)

Synthesis of PHA's





Via intracellular enzymatic polymerization reaction…

→ After polymerization, the polymer is **extracted** and processed

Poly(hydroxyalkanoates): properties

- PHA's show excellent properties and processability
  - Easy processing with range of properties
  - Range of modulus possible
  - Heat and moisture resistance
  - Dimensional stability
  - Resistance to grease and oils

- Industrially produced by Procter & Gamble, Monsanto, Metabolix, …

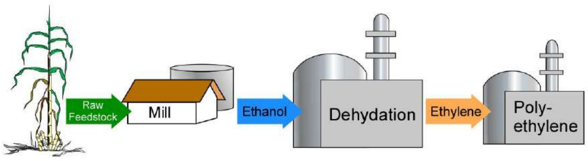
Poly(hydroxyalkanoates): applications

- Packaging
  - Caps & closures
  - Foam
  - Bags
- Electronics
- Compost bags
- Fibers
- Agricultural and horticultural
- Consumer goods

But … price should decrease to be competitive with polymers from fossile feed stock

Polyethylene

- Can be made from renewable resources



$$\text{“}CH_2O\text{”} \xrightarrow{\text{fermentation}} CH_3CH_2OH + CO_2 \xrightarrow[\text{dehydration}]{\text{catalytic}} CH_2{=}CH_2 + H_2O \longrightarrow \text{Polyethylene}$$

- **Not bio-degradable**
- Same properties, processing and performance as PE made from natural gas or oil feedstocks – because the PE molecules are the same

Polyethylene

Braskem start
« Green Ethylene plant »
in Triunfo, Brazilië
Sept. 2010

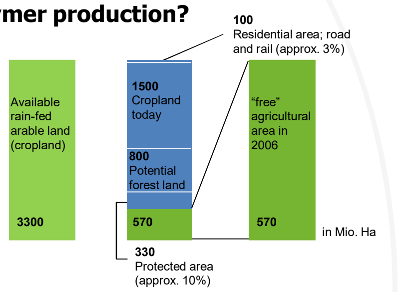
↓

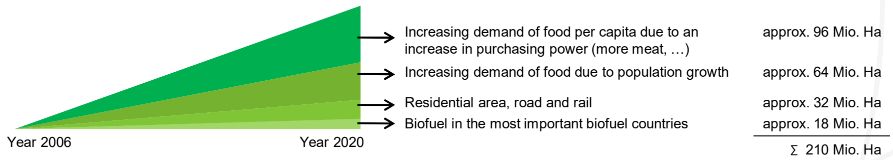
200,000 ton/year PE

Bio-polymers: impact on world food market

Is it rational to use cropland for bio-polymer production?

→'Free' potential agricultural area in 2006 and the global demand for agricultural land in 2020





In 2020, still 360 millions hectares are expected to remain "free" for other agricultural uses (mostly in Russia, Kazakhstan, Africa and South America)

NB : In E.U., about 8 millions hectares are "free" and could be used for bioenergy… and biomaterials !!!

Bioplastics Magazine (04/2009)

Bio-polymers: impact on world food market

Is it rational to use cropland for bio-polymer production?

"Recently the impact of bioplastics has been about 250 times lower than the impact of biofuels, hence lower than 0,1%. Therefore, the impact of bioplastics on the world food market is negligible. Additionally, producing biofuels or bioplastics means in most cases also producing high value protein-rich by-products that can be used as animal feed."

Bioplastics Magazine (04/2009)

Bio-polymers, the future?

Biodegradable and/or biobased polymers will never fully resolve the world's energy/resources and plastic waste problems…

… But, **smartly** used, they contribute increasingly to some major issues having an impact on all of us.