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# Biodegradable Polymers:
# Synthesis, Properties and Current Challenges

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# 1. Overview on Biodegradable Polymers

**Plastics World Production in 2016: 280 millions of tons**

More than 95 % derives from petrochemistry

**World Production of Biodegradable Polymers**

1990 → 500 t.

2002 → 254,000 t.

2017 → 882,000 t. ⇒ (~ 0.34 % of the market in 2017)

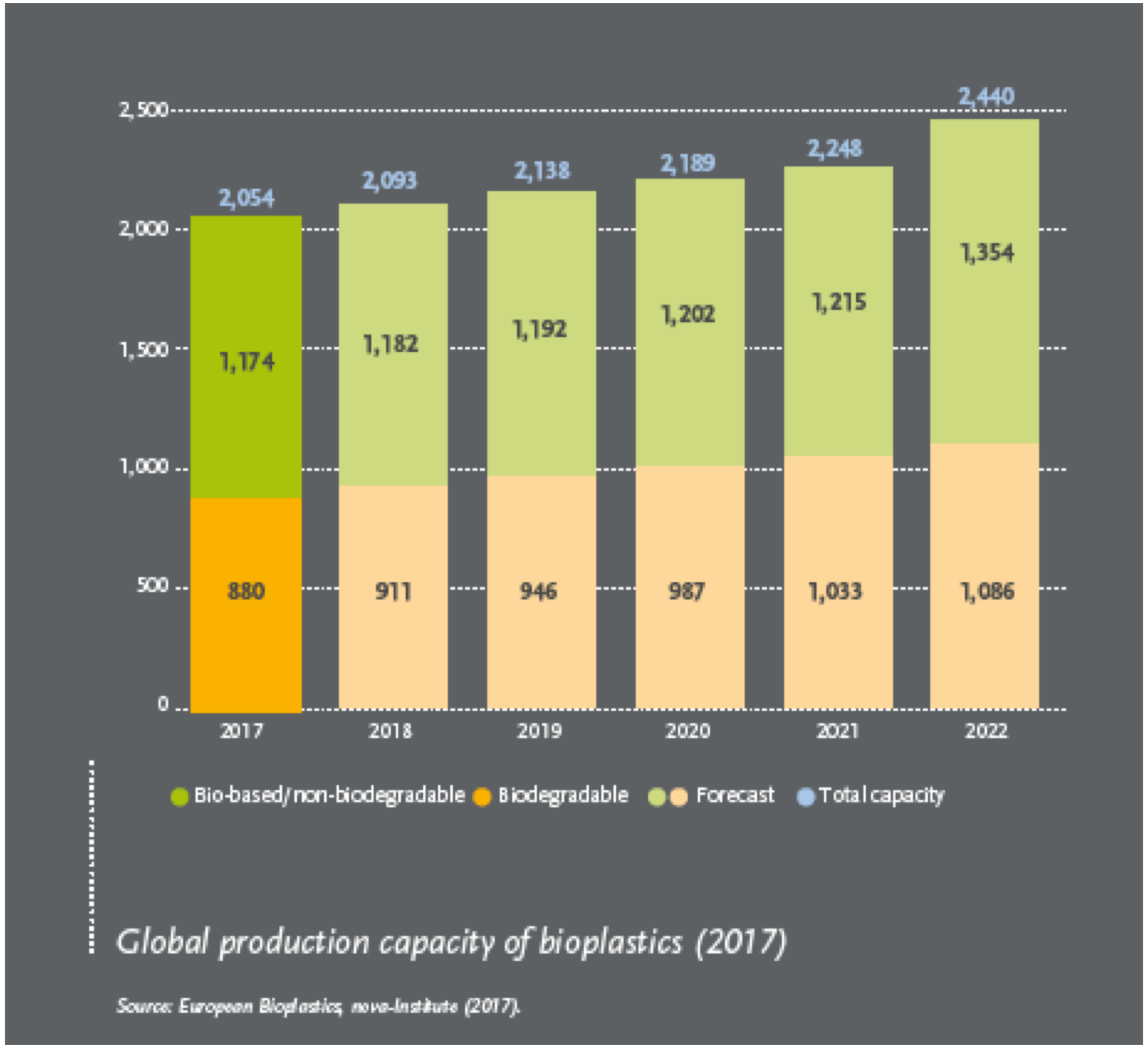
Source: ADEME (Agence De l'Environnement et de la Maîtrise de l'Energie)

**Context**: Expected decrease of petrochemical resources, waste production

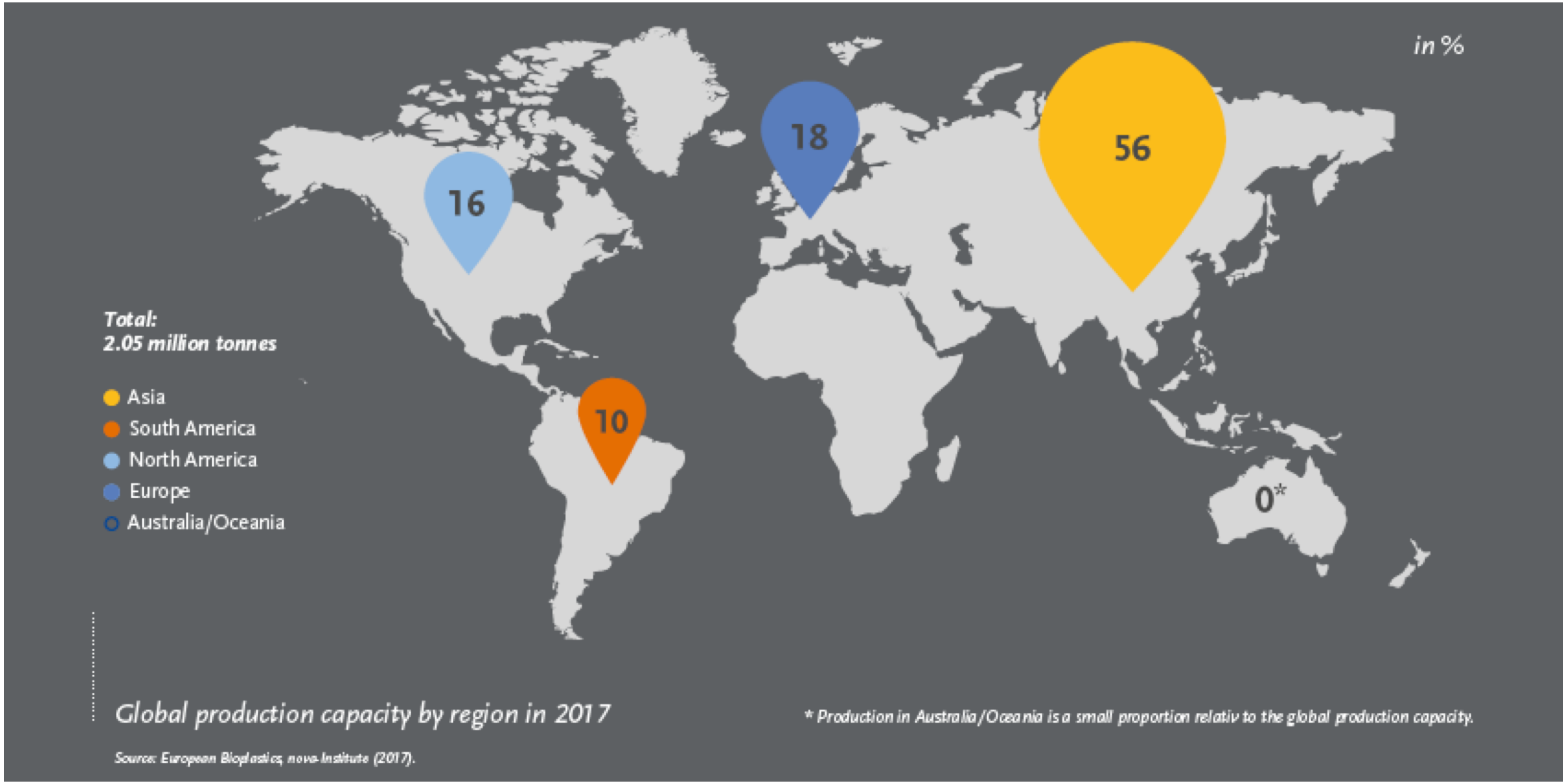
**Key Challenges: Development of *alternative* materials from renewable and natural resources** that exhibit the essential properties of « classical » plastics (polyolefins) and may even outperform them.

⇒ Thus, the tremendous interest for biodegradable polymers from renewable resources over the last 15 years

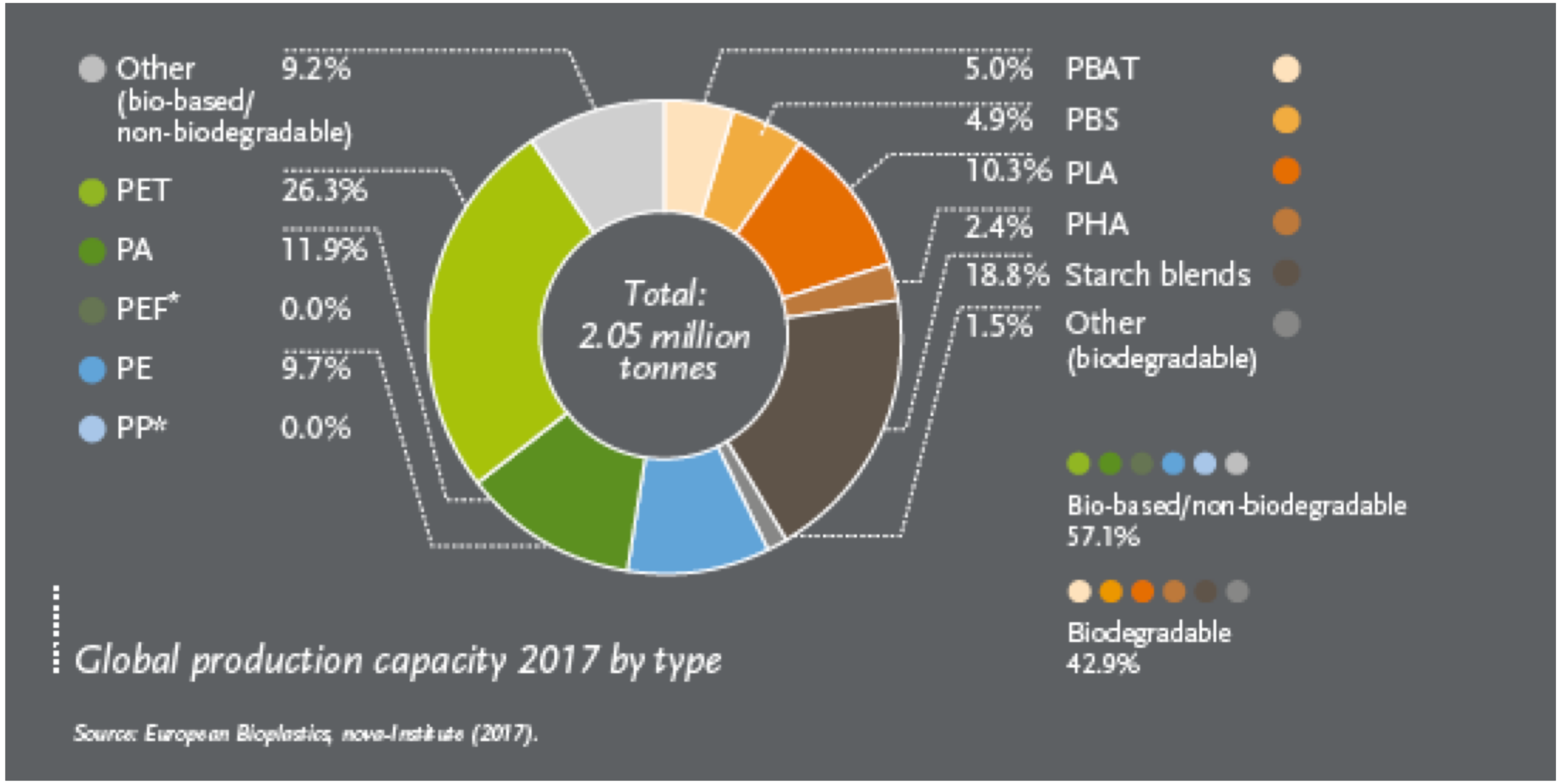
# Global Production of Bioplastics



# Bioplastics production: region by region



# Bioplastics by type of polymers




**In 2017, only 43% of produced bioplastics are biodegradable**

# Biodegradable Material: Definition

A material is said to be biodegradable when it may undergo

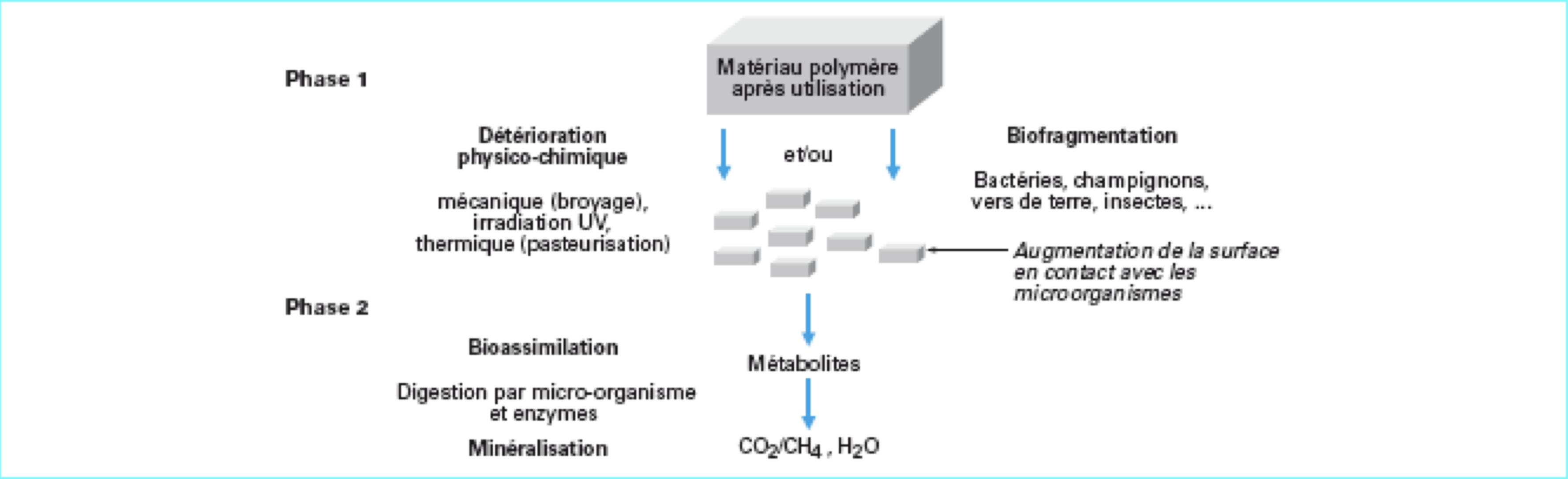
a decomposition process yielding the formation of $CO_2$, $CH_4$

and $H_2O$ and other non-toxic inorganic compounds.

**Biodegradability** is one of the most important parameters to characterize the environment impact of organic products. It is directly related to the rate of decomposition under natural biological conditions

**Example:** A dead tree leave is 100% biodegraded within a few weeks. In constrast, it would take 450 years to fully degrade a « PE-made leave » under identical conditions.

# biodegradation




**Phase 1:** polymer breaking, biofragmentation
**Phase 2:** bioassimilation, mineralisation

**Important factors impacting biodegradation**

– Degree of polymerisation : a low molecular weight polymer favors biodegradation.
– Hydrophilic or hydrophobic character of the material
– The crystallinity of the polymer: the higher it is, the slower biodegradation is.
– Thickness of the material

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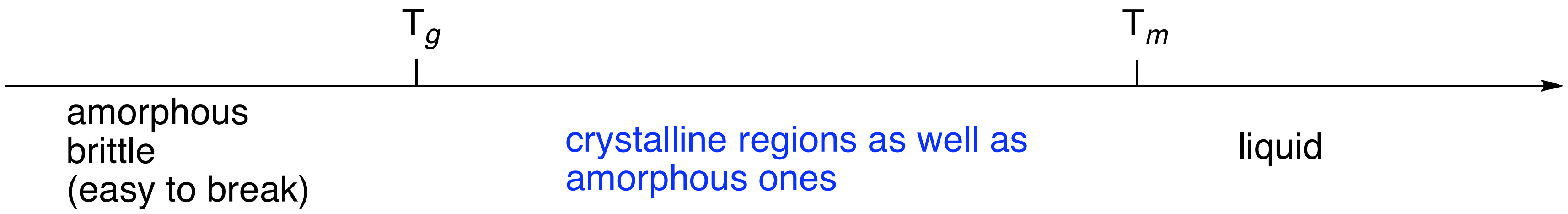
# Thermoplastic properties

**Definition:** a thermoplastic material is characterized by elastic and flexible properties above a glass transition temperature ($T_g$). Above a higher temperature **($T_m$)**, it melts.




**Crystallinity** → Strength

**Amorphous character** → Flexibility

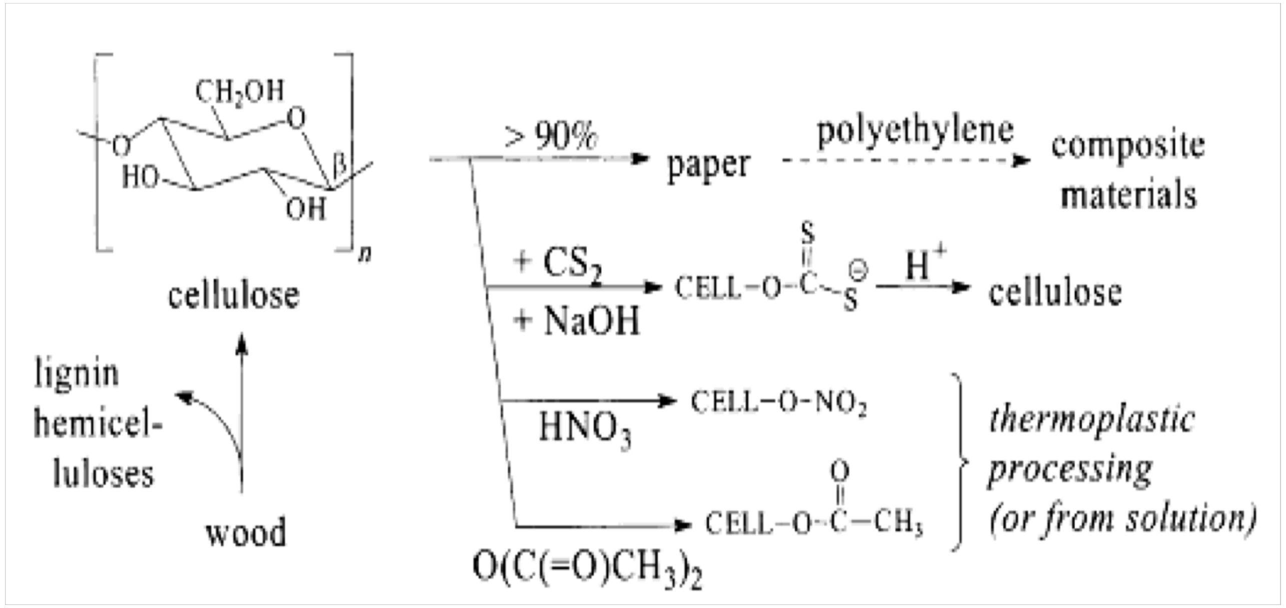
**Ideal thermoplastic**: low $T_g$ and high $T_m$ (large Tg-Tm region)

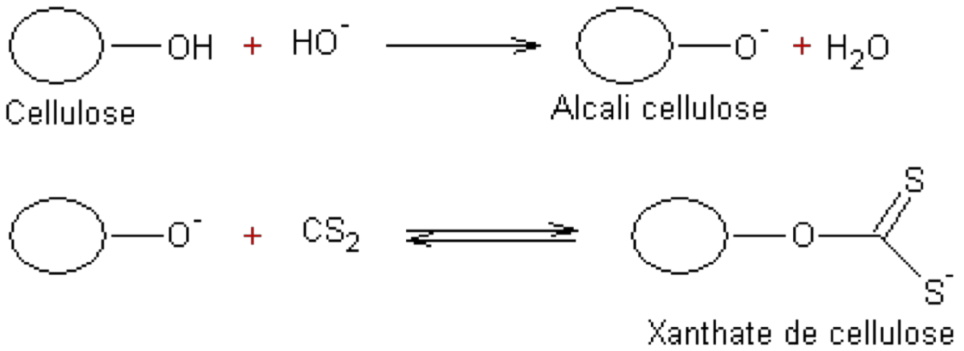
Example: polyethylene (PE): Tg = - 127 °C; Tm = 130 °C

PLA (after extrusion): Tg ≈ 55 °C, Tm = 50 – 80 °C

# The Use of Naturally-Occurring Polymers

## 1) Cellulose-derived Biodegradable Polymers (BPs)

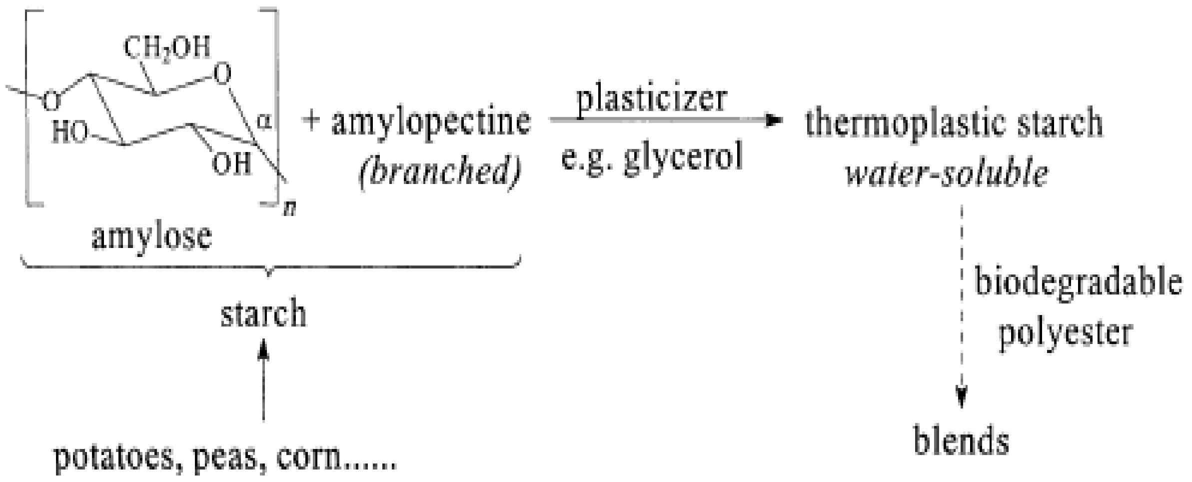


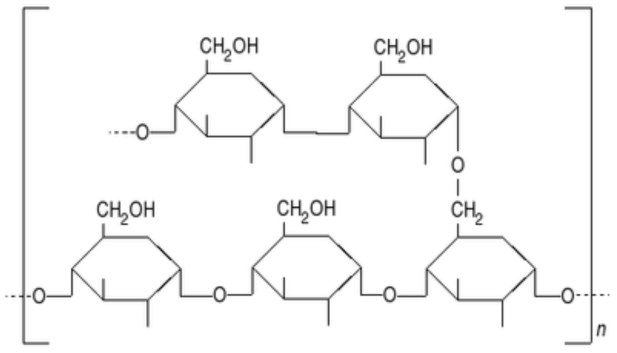




**Applications:** - paper, cellophane (cellulose sheets), viscose (cellulose fibers)

**Limitations:** - overall environmental impact similar to that of PE
- additional synthetic steps consume fossil resources
- limited biodegradability

# 2) Starch-derived Biodegradable Polymers (BPs)



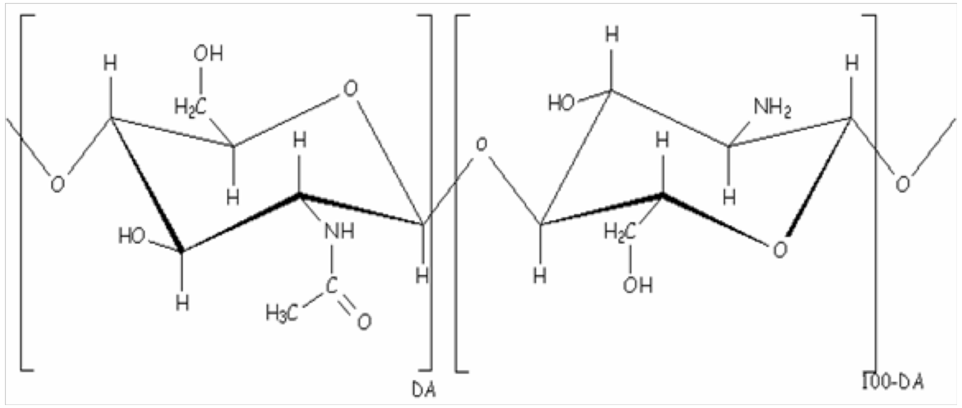

Amylopectine

**Products of current interest:** Starch foam, biodegradable polyesters/starch blends.

**Blends with biodegradable polyesters are completely compostable**
**(see the material under the tradename Mater-Bi produced by Novamont)**
**http://www.materbi.com/ing/html/index_home.html**

**Limitations:** - necessity to isolate from biomass
- limited processability

# Chitosan

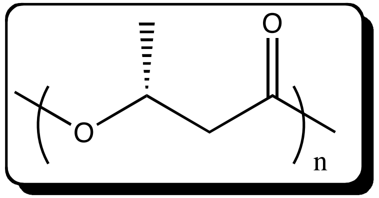



**Natural Polysaccharide:**
- Excellent mechanical properties (crystallinity)
- Biodegradability and biocompatibility

- Important application in the biomedical area (implants)
- Excellent biocompatibility (better than synthetic biodegradable materials)

**Drawbacks:**
- Insoluble at physiological pH
- Moderate processability

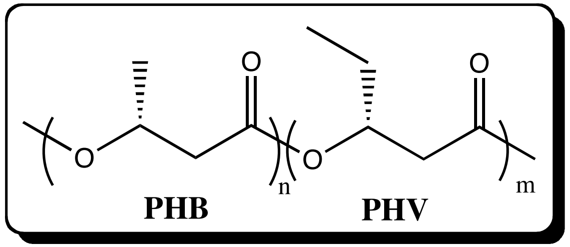
# Microbially Synthesized Polyesters




Poly(3-hydroxybutyrate (**PHB**)

(stereoregular isotactic polymer)

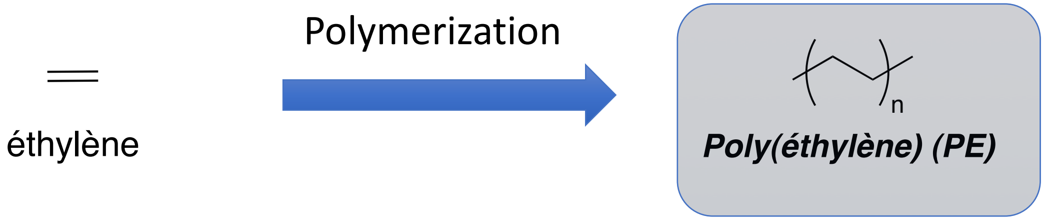
PHB and PHVB
may be produced by various bacteria
by fermentation of carbohydrates
under controlled nutrition conditions




**PHVB versus PHB:**
-better thermoplastic processability and mechanical stability

# Non-biodegradable Polymers from renewable feed stocks

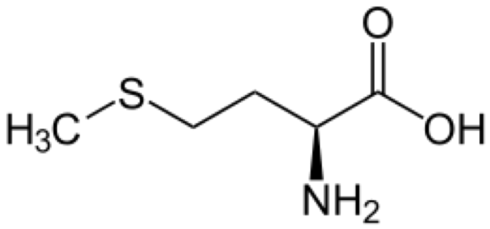
## Bio-PE




Numerous applications

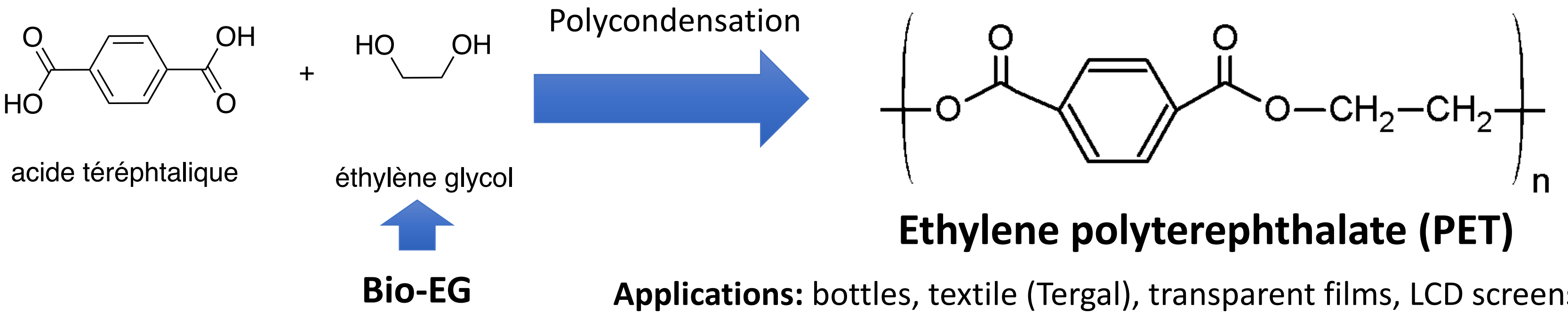
**Production of Bio-ethylene (200,000 t in 2017):**

- Dehydration of ethanol (from glucose fermentation)
- Biosynthesis from methionine (amino acid)




***L*-méthionine**
(one of the eight amino-acids essential to mankind)

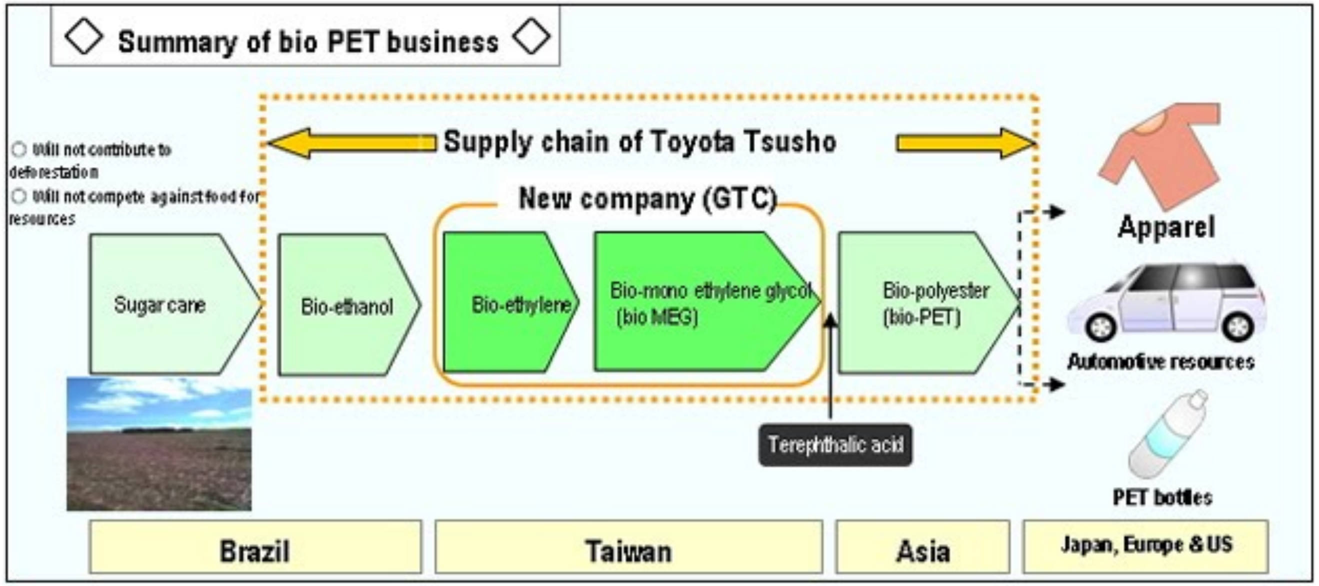
# Bio-PET




**Ethylene polyterephthalate (PET)**

**Applications:** bottles, textile (Tergal), transparent films, LCD screens
**Production:** 26% of all bioplastics

- **Use of Bio-ethylene glycol (bio-EG):** from bio-ethylene




Toyota Tsusho control all production chain from ethanol to PET
and supply Bio-PET as sustainable material in the world.

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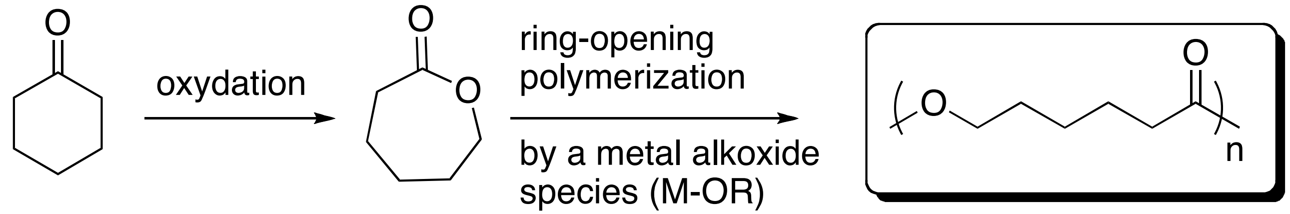
# Biodegradable Polymers derived from non-renewable resources

## Aliphatic Polyesters

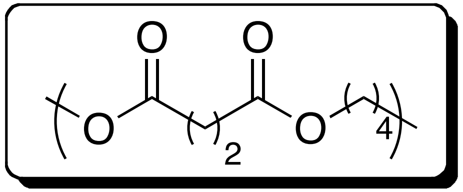



petrochemical origin

**ε-caprolactone** (production of 33000 t. in 2006)

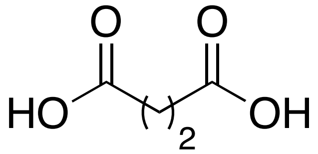
**poly(ε-caprolactone)**

Used in blending with starch
Easy to process (low melting point)

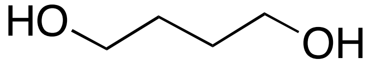


**polybutylenesuccinate (PBS)**

Excellent mechanical properties
**Applications:** films, packaging
**Production:** 100,000 t in 2017

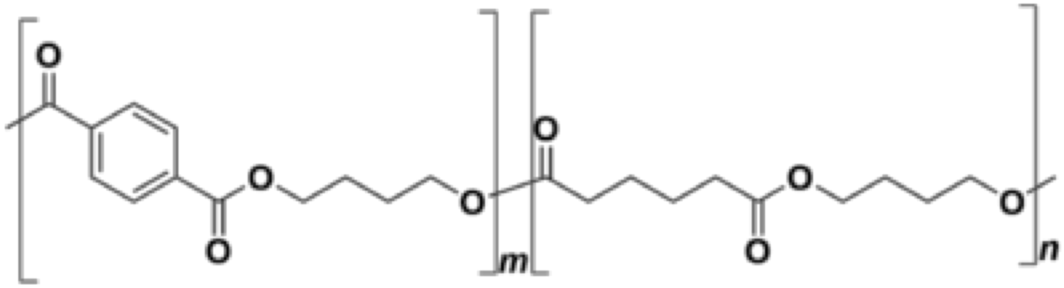


succinic acid

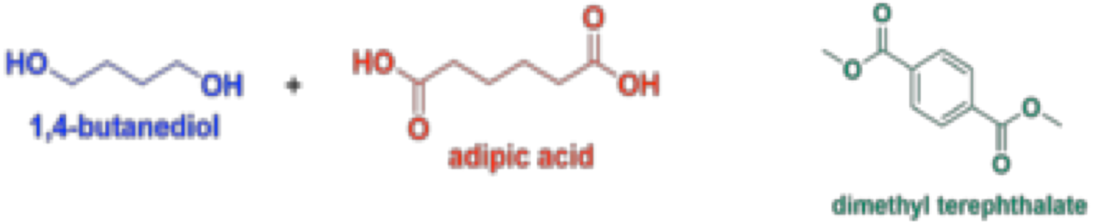


1,4-butanediol

**Polybutylene adipate terephthalate (PBAT):**
Biodegradable co-polymeric material



Monomers:



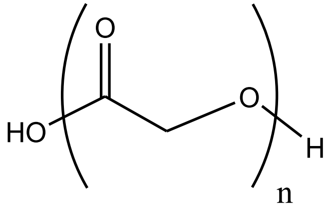

**Polybutylene adipate terephthalate (PBAT)**: a co-polymer as an alternative to low-density PE

Flexible, rigid and biodegradable material

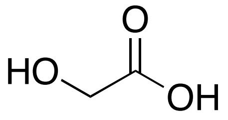
**Applications:** packaging, coatings
**Production in 2017:** 100,000 t (5% of all bioplastics)

# Biodegradable Polymers derived from renewable resources

## - Poly(glycolic acid) (PGA)



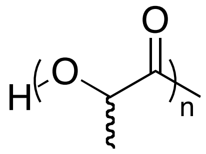

Poly(glycolic acid)



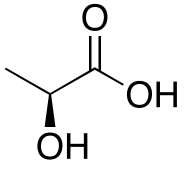

glycolic acid

- Bio-synthesis from glucose
- Extracted from corn or sugar beets

## - Poly(lactic acid) (PLA)




poly(lactic) acid (PLA)




(*L*)-lactic acid

- Bio-synthesis from glucose
- Extracted from corn or sugar beets

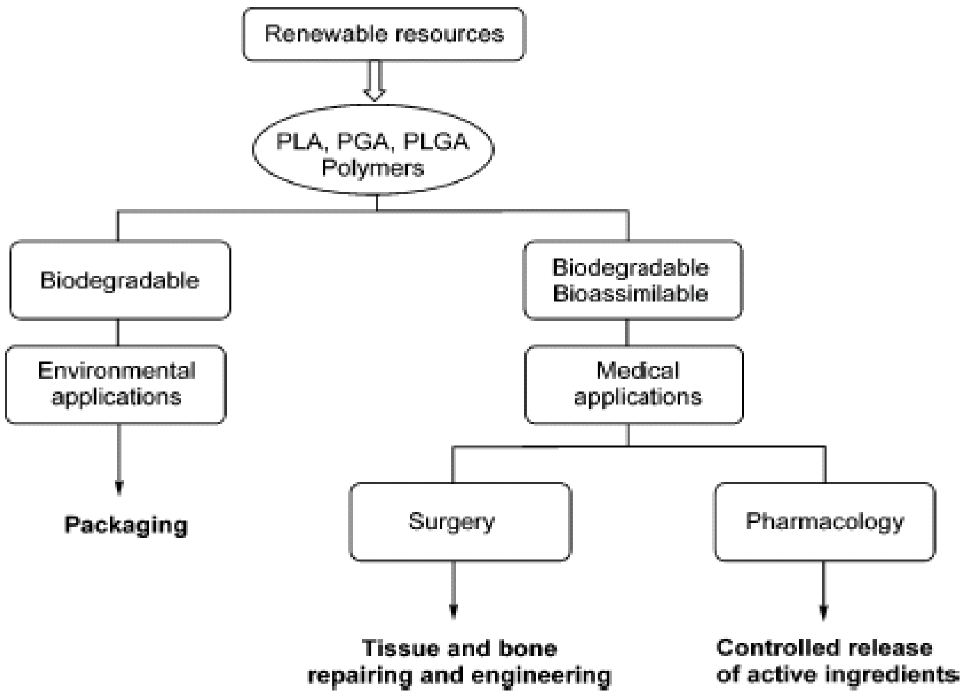



**Figure 2.** Practical applications of the biodegradable polymers based on lactic and glycolic acids.

# Present Limitations of these polymers

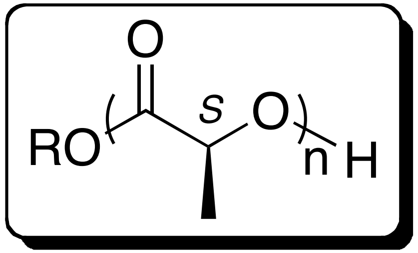
Their mechanical and thermal properties are not yet good enough to replace polyolefins (« classical » plastics)

# The case of Poly(lactic acid)

**Industrial Production:** 200,000 t. in 2017 (from lactic acid)

First and most important BP from renewable raw resources to be produced on an industrial scale

**Structure of commonly commercialized PLA:** Highly Isotactic

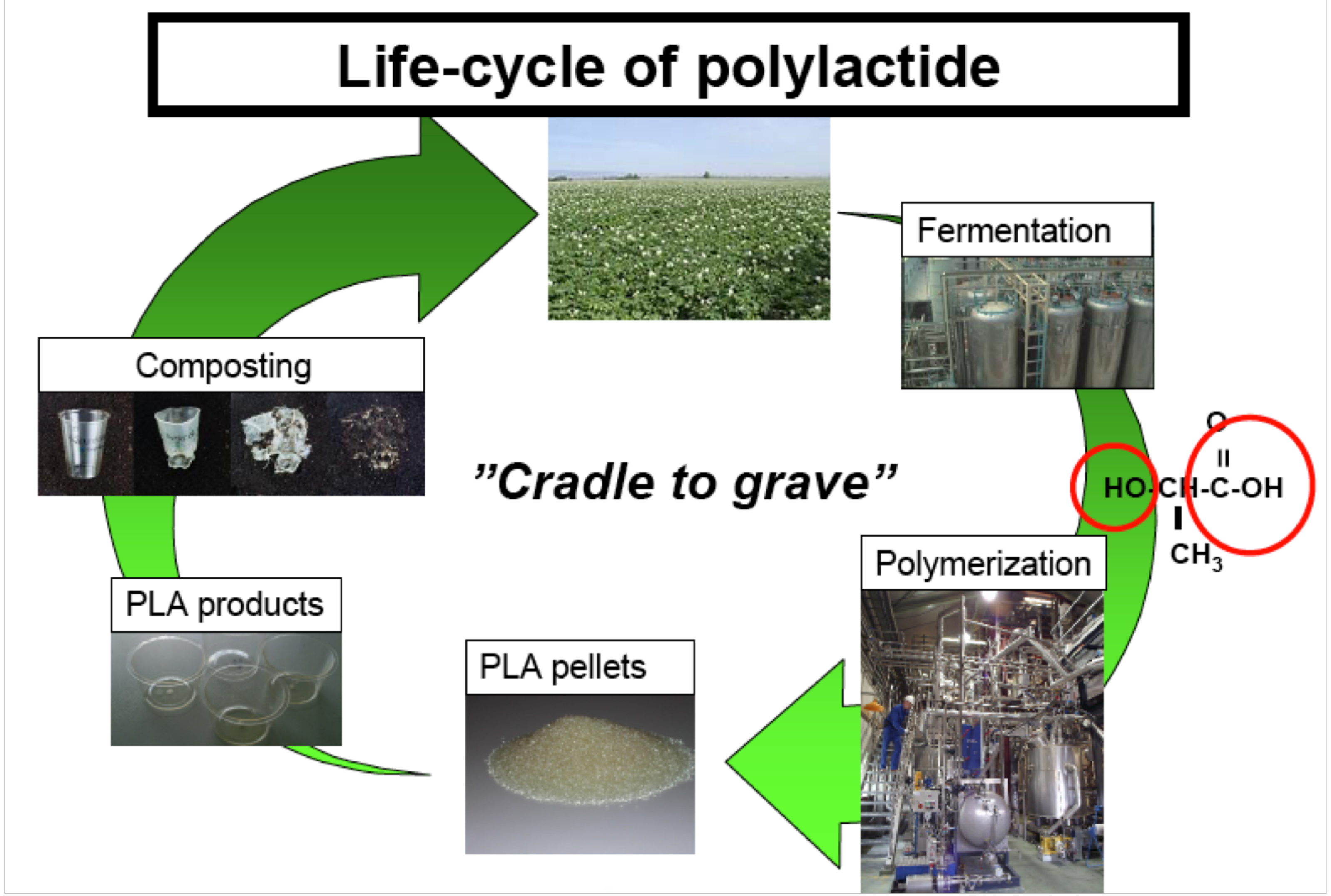



Poly (L-lactic) acid

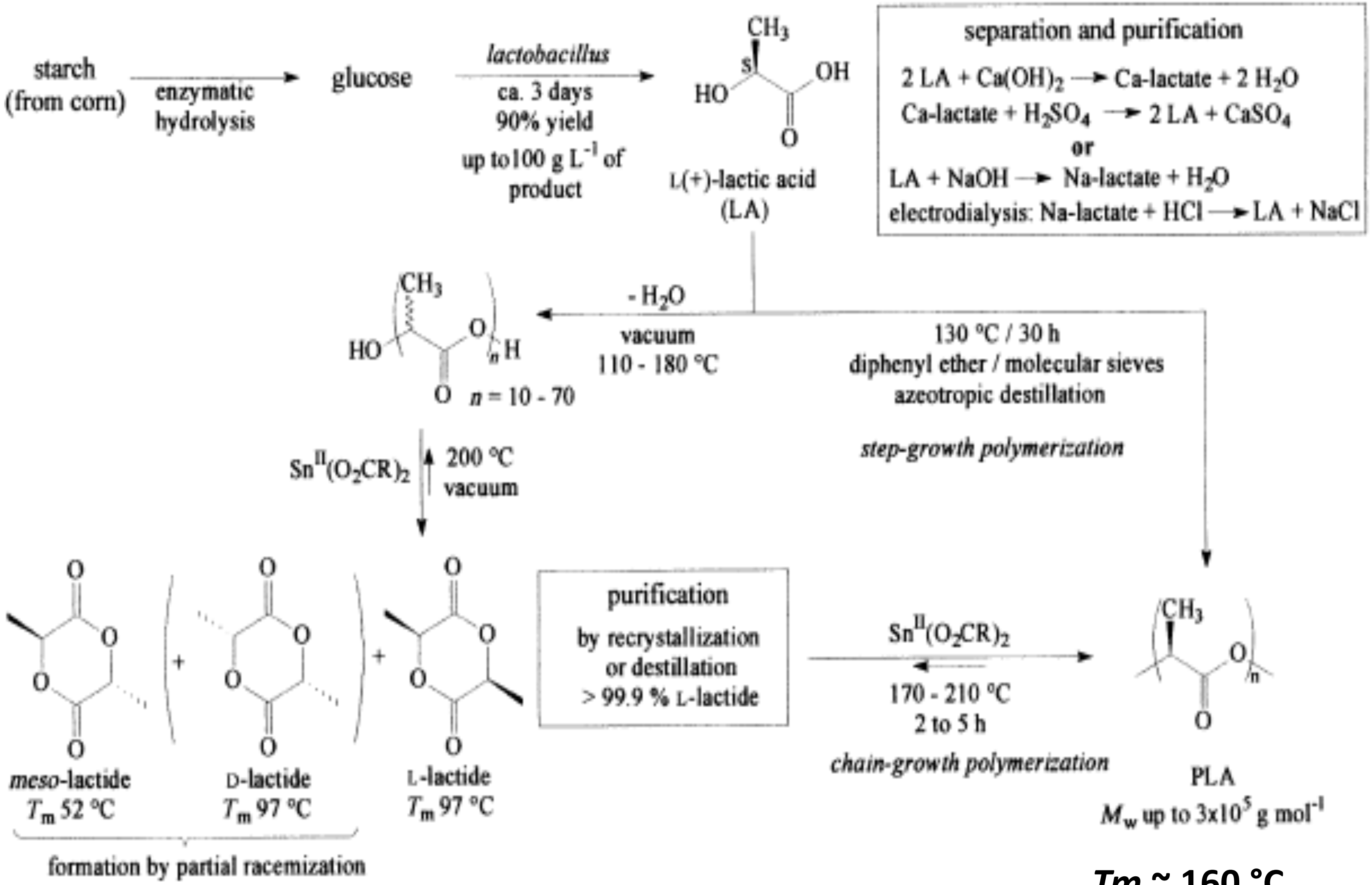
$T_g$ = 50 to 55 °C
$T_m$ = 162 °C

The stereoregularity of the PLA greatly improves its thermal and mechanical properties

**Current Applications (other than medical):** packaging, food containers, clothes


Life-cycle of polylactide
Fermentation
HO-CH-C-OH
O
CH3
Polymerization
PLA pellets
PLA products
Composting
"Cradle to grave"

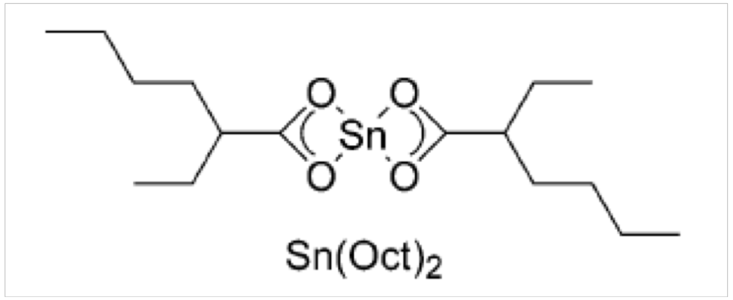
# Industrial production of PLA




Synthesis of poly(lactic acid) (PLA).

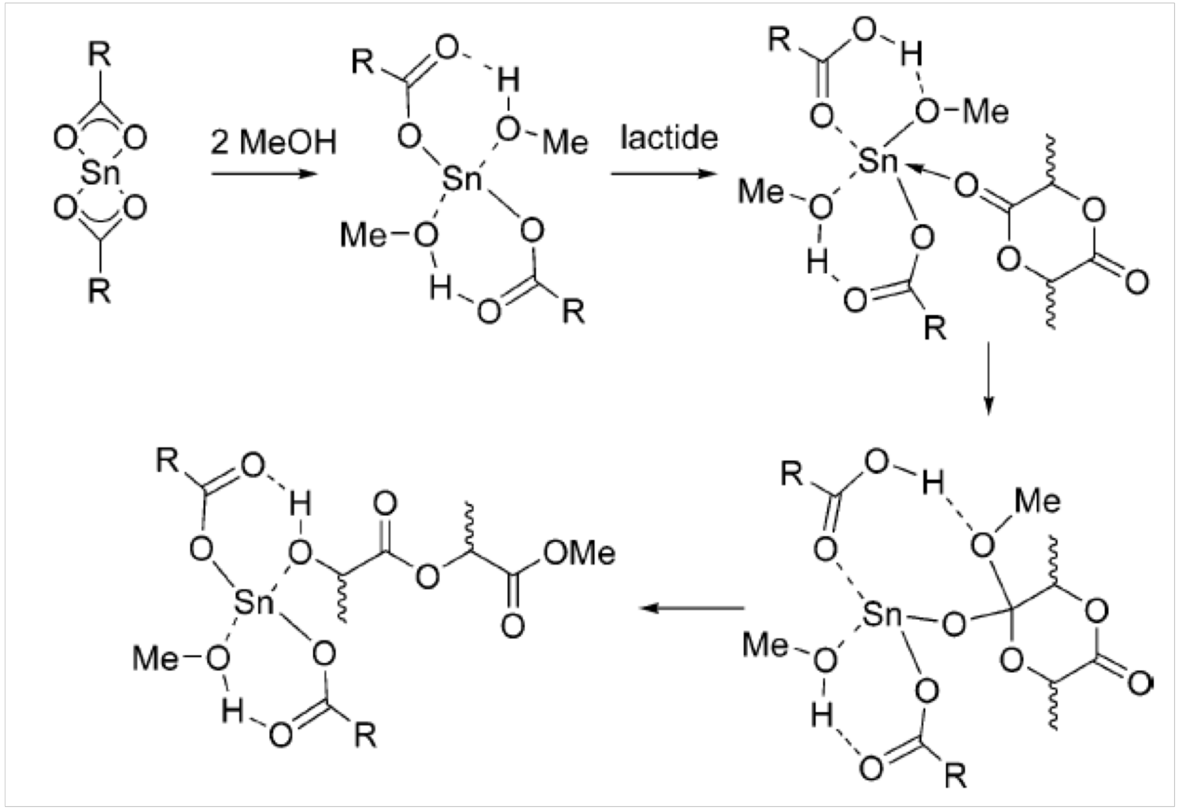
***Tm* ~ 160 °C**

# $Sn(Oct)_2$ as ROP initiator of lactide




Industrially used for the production
Of PLA

**Mechanism:**



# Biodegradation of PLA

**Via Chemical hydrolysis and subsequent enzymatic chain cleavage**

**First stage: 2 weeks hydrolysis at 60 °C**

→ **PLA degrades to water-soluble compounds**
**And lactid acid**

**Second stage: Enzymatic chain cleavage (several months)**

→ **Rapid metabolisation of these products into $CO_2$,**
**$H_2O$ and biomass by a variety of microorganisms**

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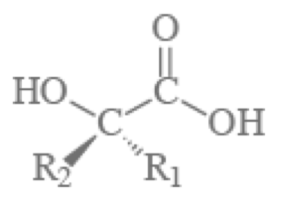
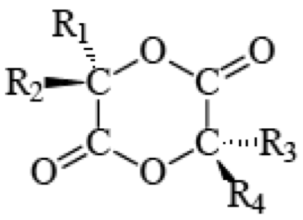
# Stereochemistry of lactic acid and lactide




| | | |
|---|---|---|
| D(*R*)-lactic acid | $R_1$: H<br>$R_2$: $CH_3$ | D-lactic acid + L-lactic acid (*rac*-lactic acid) |
| L(*S*)-lactic acid | $R_2$: H<br>$R_1$: $CH_3$ | |



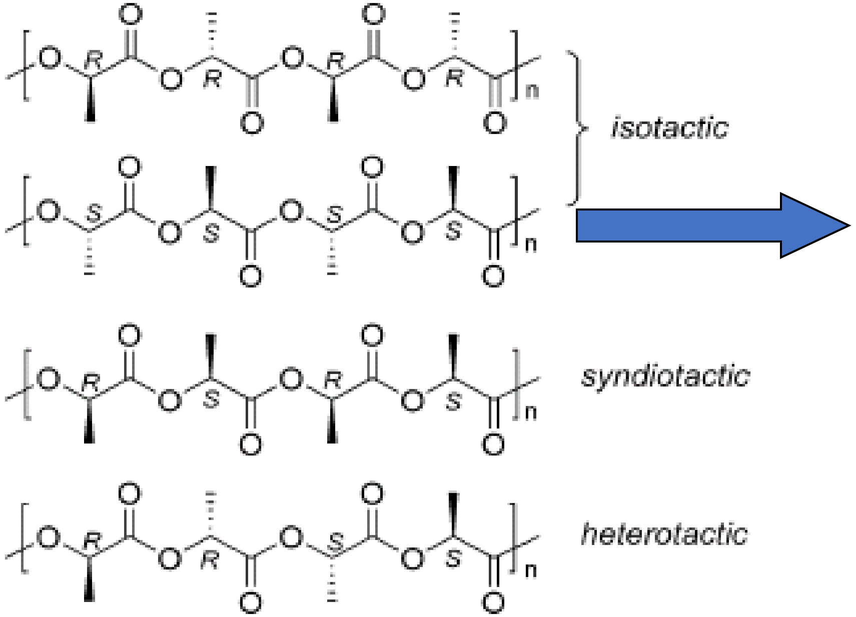

| | | |
|---|---|---|
| D,D(*R*,*R*)-lactide | $R_1$, $R_3$: H<br>$R_2$, $R_4$: $CH_3$ | D,D-lactide + L,L-lactide (*rac*-lactide) |
| L,L(*S*,*S*)-lactide | $R_2$, $R_4$: H<br>$R_1$, $R_3$: $CH_3$ | |
| D,L(*R*,*S*)-lactide (*meso*-lactide) | $R_1$, $R_4$: H<br>$R_2$, $R_3$: $CH_3$ | |

***L = Levorotatory***
***D = Dextrorotatory***

# Research on PLA:
# Improvement of its **properties**
# And access to new materials

**Better Control of the Chain length and of the Stereoregularity**

- ➡ Improve mechanical and thermal properties
- ➡ Access to potentially interesting new BPs




**Tm ~ 150 to 230 °C**

**The only PLA commercially available**

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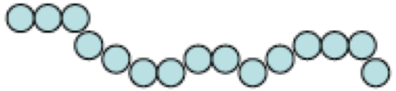
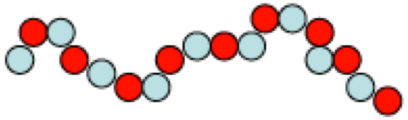
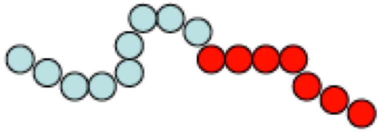
# Some examples on effects from the repeating units in polylactide

| | | $T_g$ | $T_m$ |
|---|---|---|---|
|  | Poly(L,L-lactide) | 53-64 °C | 145-186 °C |
|  | Poly(*meso*-lactide) | 40-50 °C | - |
|  | Poly(D,L-lactide) | 45-55 °C | - |
|  | Poly(L-lactide-*b*-D-lactide) | 53-64 °C | 145-186 °C |
|  | Poly(L-lactide) / Poly(D-lactide) stereocomplexes | 65-75 °C | 220-230 °C |