**Structure**

Extremely interesting BPs (very high Tm ~ 220-230°C)
Excellent thermic and mechanical properties

**Limitations:** no straightforward synthetic pathways available
(Expensive material)

**Applications:** biomedical devices

*Ikada et al. Macromolecules* 1987
Through polymerization catalysis of lactide with a well-defined catalyst

Possibility of a controlled polymerization process affording polymers with well-defined chain length and stereoregularity

**Current Approach:** Ring-opening polymerization of lactides catalyzed by a well-defined metal complex M-OR

1) M-OR Catalyst
2) Hydrolysis

Dimers of lactic acid

Poly(lactic acid)
General Mechanism for the Ring-opening Polymerization of Lactides by Metal Alkoxides Complexes

M = oxophilic and electropositive
(Mg, Ca, Al, Y, Ti, Zr, Zn,)

Important features of the catalyst:
- Lewis acidity of M
- Nucleophilicity de RO⁻
- Nature of the ligand L

Living polymerization (in the ideal case)
Positive Aspect:

Living Polymerization (control of the polymer chain length)

Negative Aspect:

No discrimination between the two lactide enantiomers

No stereoregularity in the prepared PLA
Stereoselective Polymerization of *rac*-lactide:
Access to stereoregular PLAs

Properties: New material, extremely high melting point ($T_m$ up to 190 °C)
And highly resistant

- Importance of the use of a well-defined and single-site catalyst

Chain-end Stereocontrol mechanism

The last inserted lactide unit stereocontrols the insertion of the subsequent unit.

Transtesterification
Hydrolysis

Isotactic Stereoblock PLA
Extremely interesting BPs (very high T<sub>m</sub> ~230°C)
Excellent mechanical properties

Commercial Poly(lactic acid)
T<sub>m</sub> = 162 °C

**Isotactic Stereoblock Poly(lactic acid)** (T<sub>m</sub> ~ 190 °C)

Inter-molecular Chain interactions

\[
\begin{align*}
R & R R R R R R \cdots S S S S S S S S S S \\
S & S S S S S S S S S S R R R R R R R R R R \\
S & S S S S S S S S S S R R R R R R R R R R R R \\
S & S S S S S S S S S S R R R R R R R R R R R R
\end{align*}
\]

Intra-molecular Chain interactions

\[
\begin{align*}
S & S S S S S S S S S S S S S S S S \\
R & R R R R R R R R R R R R R R R R
\end{align*}
\]

The «Stereocomplex Character» improves its thermal properties
**Principle:** In an enantioselective polymerization, one enantiomer of a racemic monomer mixture is preferentially polymerized to give an optically active polymer (with a specific chain stereochemistry).

**Major advantage:** - Obtention of a polymer with a controlled stereochemistry

50% conversion
The use of enantiomerically pure Al Complexes: Enantioselective Polymerization of Lactides

- **Interest:** Access to stereoregular PLA polymers

![Diagram of Al complexes and lactide polymerization](image)

At 50% conversion, ee (unreacted monomer) = 80% ee

\[ k_D/k_L = 20 \]

Formation of new materials via the formation of enantiomeric poly(L-LA) and poly(D-LA) block polymers


Due to chain transfer during the polymerization process

**Isotactic Stereoblock Poly(lactide)**

Properties: New material, extremely high melting point ($T_m = 187 \degree C$) And highly resistant
**Metal-site Stereocontrol Mechanism**

L*\(^{(R)}\)Al = "chiral pocket" that induces stereocontrol
Importance of the Metal Catalyst

**Activity:** Mg, Ca, Y > Zn, Sn > Al > Ti, Zr

**Stereoregularity:** Al > Zn, Sn, Y > Ti, Zr > Mg, Ca

**Toxicity:** Sn whereas Zn, Ca, Mg are biocompatible

**Cost:** Y is an expensive metal

Lactide Monomer

High purity required for high activity (it costs!!!)
**Latest Developments: Organocatalytic Polymerization of Lactides**

**Interest:**
- use of metal-free catalysts (because of toxicity problems)
- no need to remove metal traces prior to polymer processing (costly)

**Approach:**
- use of very nucleophilic organic species to ring-open lactide
- the ring-opened species ring-opens another lactide unit and so on....

**Most efficient Nucleophiles to date:**

- dimethylamino-pyridine (DMAP)
- N-heterocyclic carbenes (highly nucleophilic)
Metal-free Lactide Polymerization: Organocatalysis

Mechanism

« ROH »
Access to unprecedented Cyclic PLA materials

Cyclic PLAs are more thermally stable linear PLAs

**Scheme 2.** Proposed mechanism for NHC-mediated zwitterionic polymerization of lactide.
Organocatalysis: ROP of lactide thanks to supramolecular recognition


Use of a thiourea-amine
Bifunctional catalyst such as 1

*Scheme 2.* Polymerization of Lactide by 1
## Overview of Agro-resources based Polyesters

<table>
<thead>
<tr>
<th>Agro-resources based polyesters:</th>
<th>Trade Name</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Poly(lactic acid) (PLA)</em></td>
<td>Natureworks</td>
<td>Cargill (USA)</td>
</tr>
<tr>
<td></td>
<td>Lacty</td>
<td>Shimadzu (Japan)</td>
</tr>
<tr>
<td></td>
<td>Lacea</td>
<td>Mitsui Chemicals (Japan)</td>
</tr>
<tr>
<td></td>
<td>Heplon</td>
<td>Chronopon (USA)</td>
</tr>
<tr>
<td></td>
<td>CPLA</td>
<td>Dainippon Ink Chem. (Japan)</td>
</tr>
<tr>
<td></td>
<td>PLA</td>
<td>Galactic/Total (Belgium)</td>
</tr>
<tr>
<td></td>
<td>Eco Plastic</td>
<td>Toyota (Japan)</td>
</tr>
<tr>
<td></td>
<td>Treofan</td>
<td>Treofan (Netherland)</td>
</tr>
<tr>
<td></td>
<td>PDLA</td>
<td>Puren (Netherland)</td>
</tr>
<tr>
<td></td>
<td>Ecoloju</td>
<td>Mitsubishi (Japan)</td>
</tr>
<tr>
<td></td>
<td>Biomer L</td>
<td>Biomer (Germany)</td>
</tr>
<tr>
<td><em>Polyhydroxyalkanoate (PHA)</em></td>
<td>Biopol</td>
<td>Monsanto (USA)*</td>
</tr>
<tr>
<td></td>
<td>Mirel</td>
<td>Metabolix/ADM (USA)</td>
</tr>
<tr>
<td></td>
<td>Biocyte</td>
<td>PHB Industrial (Brazil)</td>
</tr>
<tr>
<td></td>
<td>Biomer P</td>
<td>Biomer (Germany)</td>
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<tr>
<td></td>
<td>Enamat</td>
<td>Tianan (China)</td>
</tr>
<tr>
<td></td>
<td>Nodax</td>
<td>Procter &amp; Gamble (USA)*</td>
</tr>
</tbody>
</table>

From: P. Bordes et al. / Progress in Polymer Science 34 (2009) 125–155
PHAs are naturally produced by micro-organisms from various carbon sources (typically from the sugar family)

- Some micro-organisms may accumulate PHA
  From 30% to 80 % of cellular dry weight

- Depending on the carbon source, different monomers and thus Polymers may be obtained.

- Polyhydrobutyrate (PHB) is the main polymer of this family

![Polyhydrobutyrate (PHB) and Polyhydroxyvalerate (PHV)](images)

(Biopol, Monsanto, 20% HV)

**Major problem:** the extraction and recovery steps are expensive
- First observed in bacteria by Lemoigne et al. in the 1920s

Optically active macromolecules (PHBs) used as a «carbon reserves» by bacteria

Figure 2. Transmission electron micrograph of ultrathin section of *Azotobacter chroococcum* cell treated with phenylacetic acid. From
Biosynthesis of PHB

Implicated enzymes:

1. ketothiolase: dimerizes acetyl-CoA
2. reductase: hydrogenation to (R)-3-hydroxy-butyryl-CoA
3. Synthase (or polymerase): polymerisation: access to PHB
Two thiol groups within the polymerase enzyme are believed to be involved in the initiation and propagation polymerisation process.
**Polyhydroxybutyrate: PHB**

**PHB** is a highly crystalline biodegradable and biocompatible polymer (T_g = 5 °C, T_m = 153°C)

<table>
<thead>
<tr>
<th></th>
<th>PLA Dow-Cargill (NatureWorks)</th>
<th>PHBV Monsanto (Biopol D400G – HV = 7 mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>Melting point (°C)_a</td>
<td>152</td>
<td>153</td>
</tr>
<tr>
<td>Glass transition (°C)_a</td>
<td>58</td>
<td>5</td>
</tr>
<tr>
<td>Crystallinity (in %)</td>
<td>0–1</td>
<td>51</td>
</tr>
<tr>
<td>Modulus (MPa) (NFT 51-035)</td>
<td>2050</td>
<td>900</td>
</tr>
<tr>
<td>Elongation at break (%) (NFT 51-035)</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>Tensile stress at break or max. (MPa) (NFT 51-035)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Biodegradation (mineralization in %)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Water permeability WVTR at 25°C (g/m²/day)</td>
<td>172</td>
<td>21</td>
</tr>
<tr>
<td>Surface tension (γ) (mN/m)</td>
<td>50</td>
<td>–</td>
</tr>
<tr>
<td>γ_d (dispersive component)</td>
<td>37</td>
<td>–</td>
</tr>
<tr>
<td>γ_p (polar component)</td>
<td>13</td>
<td>–</td>
</tr>
</tbody>
</table>