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Chemical modification of PHA – Hydrolysis and Alcoholysis

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Chemistry of Renewables and Polymer Chemistry

PHA Modifications - Approaches Discussion, Online, August 19, 2026

Why chemical modification of PHA?

What is most sucessfull biobased polymer on the market?

... PLA

What is the main technological difference between PLA and PHA?

- **For PLA, microorganisms supply only the monomer lactid acid; the polymerization has to be done conventionally**
- **For PHA, microorganisms supply the polymer**

Advantage PHA: **At least one industrial step less**

But: **Microorganisms produce the polymer as they seem fit**

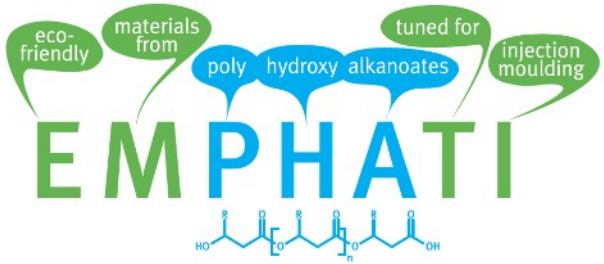
(and not fit for our applications)

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Why chemical modification of PHA?

Project: Tuneable PHA-based Biodegradable Binder Platform

(Emphati sub project)



- Biotechnological modification

  by changing microorganisms and / or the feed and the conditions of the fermentation

  (Group of Janneke Krooneman, Hanze, Groningen)
- **Our part: Chemical modification and analysis**
- (together with Wydo)

  about 50 % of 42k €, 12 months, master thesis +

  (M.Sc. Bahar Shokuienia)

Which reactions for chemical modification?

- **Hydrolysis**



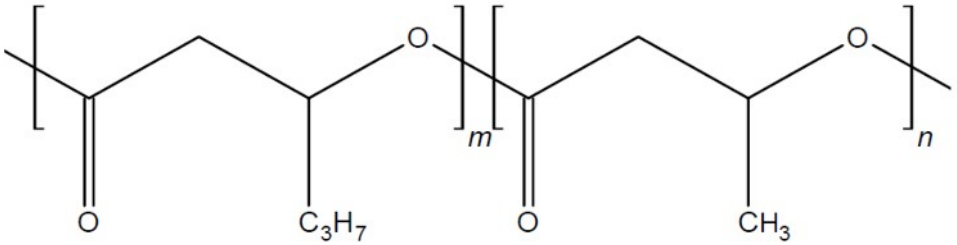
- **Alcoholysis**

  analogous reactions with alcohols

Both reactions lead to lower molecular weights and were analyzed by GPC, DSC, IR, LC-MS and NMR

Which starting materials for chemical modification?

- **PHBHHx**



contains ca. 11 % hexanoate

only ca. 25 % cristallinity and therefore reasonably soluble

mp 112 °C / 128 °C and Tg –2 °C , Mnz >= 120,000 g/mol

- **Crude biomass containing ca. 15 % weight PHA**

  from *cupriavidus necator (cells disrupted)*

Hydrolysis - Conditions

- **Hydrolysis**



Reaction conditions

Solvent: **4-methyl tetrahydropyrane**

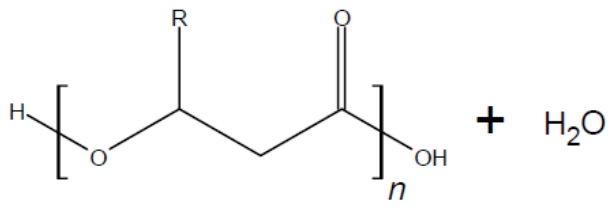
Catalyst: **p-toluene sulfonic acid (1 weight-%)**

Reaction time: 4 – 24 h

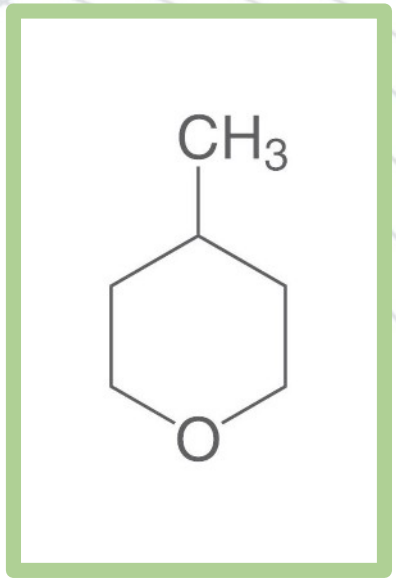
Water content: water / ester = 0.1 - 10 / 1 (molar)

Hydrolysis - Conditions

- **Hydrolysis**



sugar-based solvent
“green“ alternative to THF, MTBE
bp 108 °C
forms an azeotrope with water



Reaction conditions

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Catalyst: **p-toluene sulfonic acid (1 weight-%)**

Reaction time: 4 – 24 h

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Hydrolysis – Results depending on water content and/or reaction time

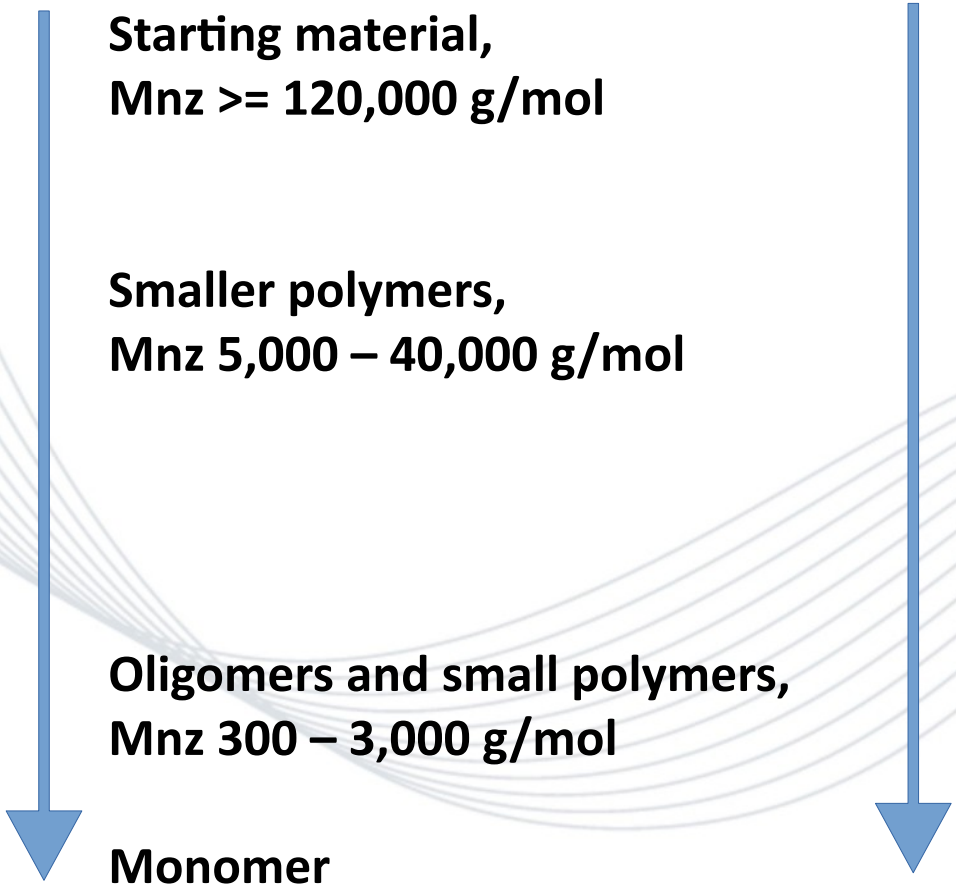
Starting material,
Mnz >= 120,000 g/mol

Smaller polymers,
Mnz 5,000 – 40,000 g/mol

Oligomers and small polymers,
Mnz 300 – 3,000 g/mol

Monomer

Hydrolysis – Results depending on water content and/or reaction time



Starting material,
Mnz >= 120,000 g/mol

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Oligomers and small polymers,
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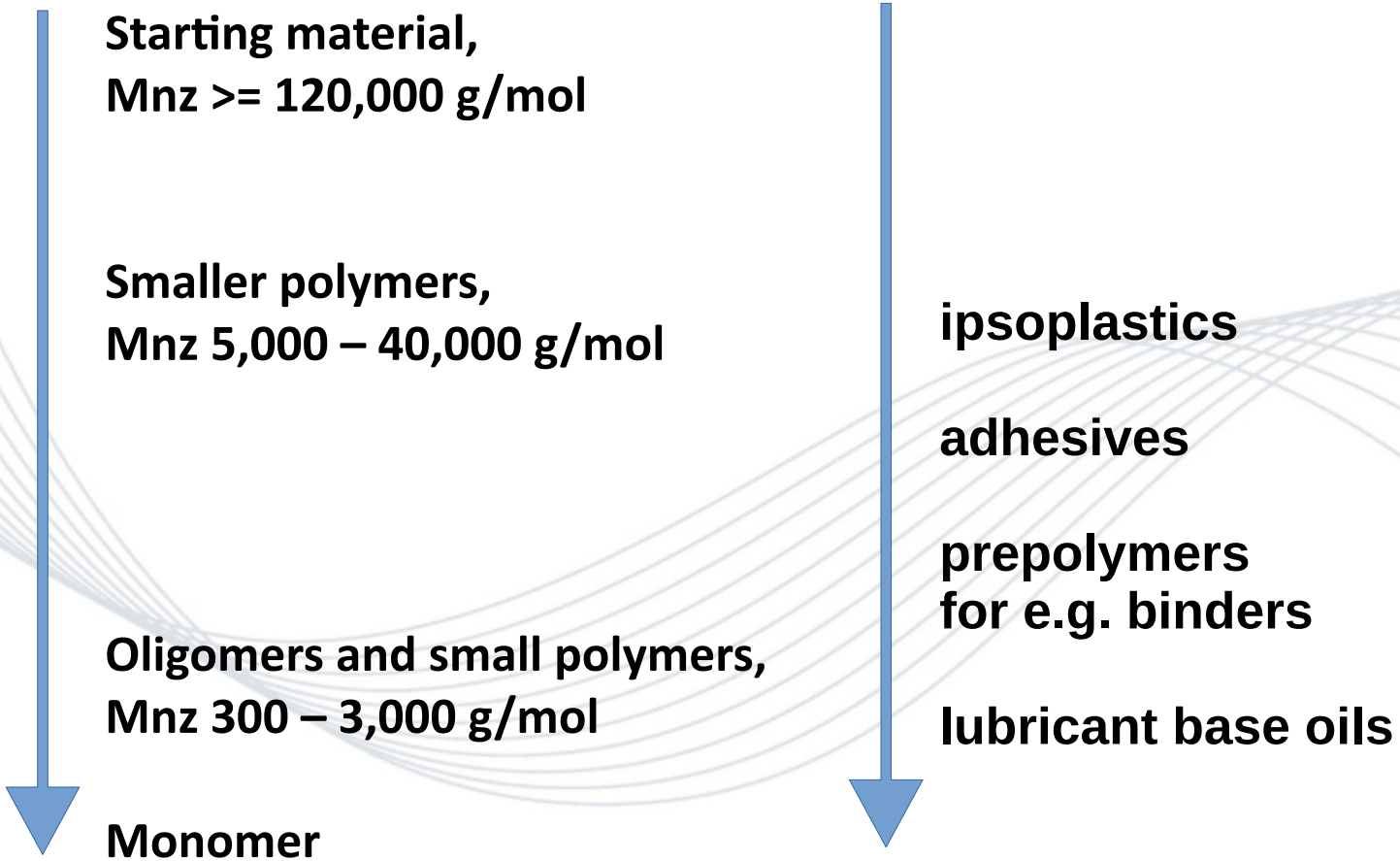
Monomer

mp and Tg
decrease

crystallinity
decreases

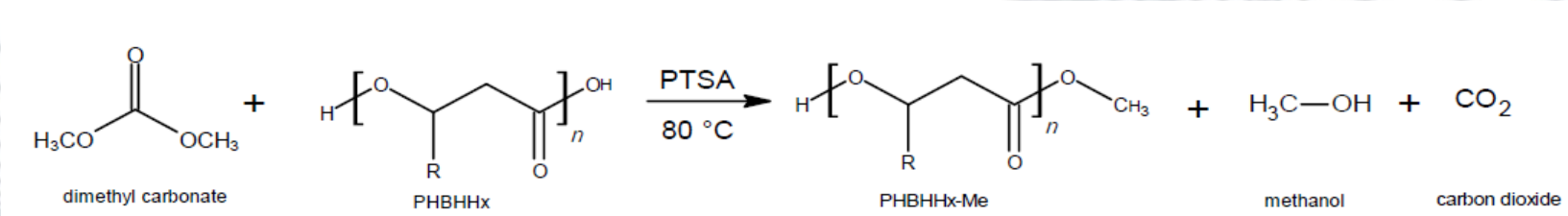
solubilty
increases

Hydrolysis – Results depending on water content and/or reaction time



Alcoholysis - Conditions

- **Methanolysis** in an analogous way with methanol instead of water possible but serious drawbacks (solubility, equibilibrium)
- **Reaction with dimethyl carbonate**



Reaction conditions

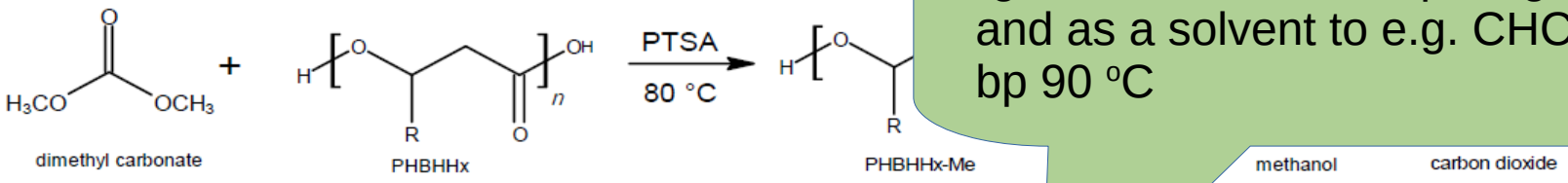
Solvent and reagent: **Dimethyl carbonate**

Catalyst: **p-toluene sulfonic acid (1 weight-%)**

Reaction time: **4 – 24 h**

Alcoholysis - Conditions

- **Methanolysis** in an analogous way with methanol instead of water possible but serious drawbacks (solubility, equibilibrium)
- **Reaction with dimethyl carbonate**



DMC from methanol and CO
"green" alternative to phosgene and as a solvent to e.g. $CHCl_3$
bp 90 °C

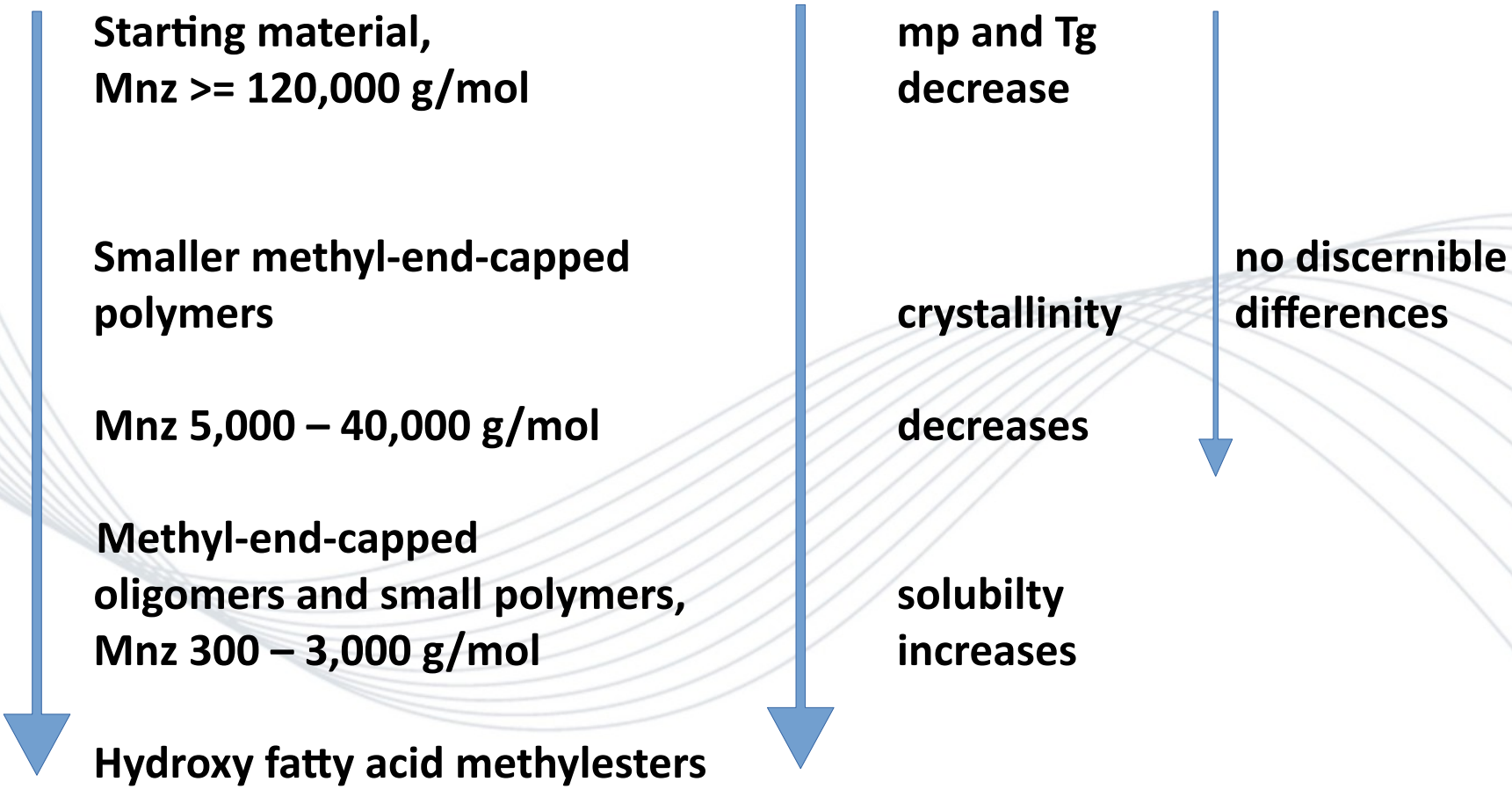
Reaction conditions

Solvent and reagent: **Dimethyl carbonate**

Catalyst: **p-toluene sulfonic acid (1 weight-%)**

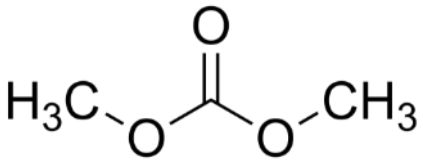
Reaction time: **4 – 24 h**

Methanolysis – Results depending on reaction time



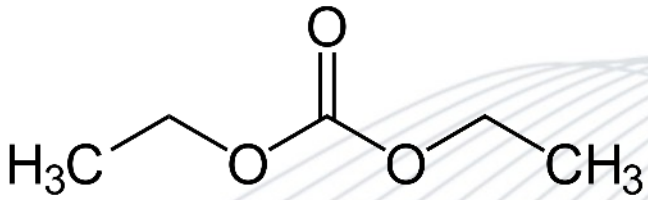
Alcoholysis – Other carbonic acid esters

- In principle the reaction can be applied to any other carbonic acid ester but only **very few are industrially available**:



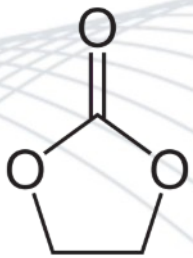
Dimethyl carbonate

methyl-end-capped products



Diethyl carbonate

ethyl-end-capped products

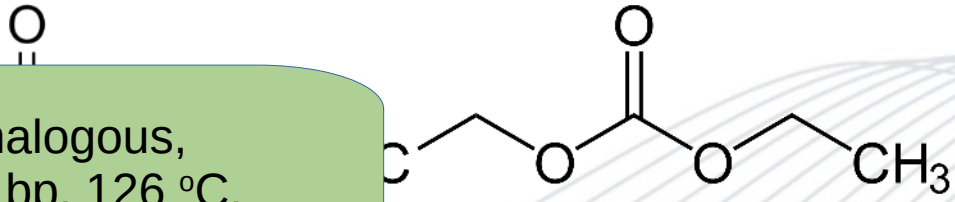


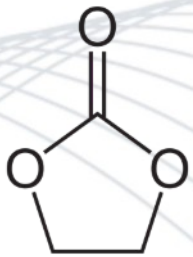
Ethylen carbonate

hydroxyethyl-end-capped products

Alcoholysis – Other carbonic acid esters

- In principle the reaction can be applied to any other carbonic acid ester but only **very few are industrially available**:





Completely analogous, slightly higher bp. 126 °C, differences for applications?

Dimethyl carbon

methyl-end-capped products

Diethyl carbonate

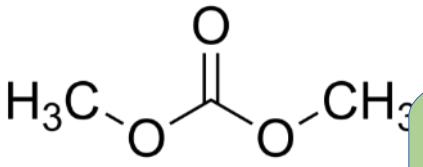
ethyl-end-capped products

Ethylen carbonate

hydroxyethyl-end-capped products

Alcoholysis – the bigger picture

- In principle the reaction can be applied to any other carbonic acid ester but only **very few are industrially available**:



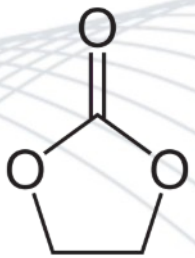
Dimethyl carbonate

methyl-end-capped products



Low melting solid, mp. 36 °C,
tedious work-up
only down to about 6000 g/mol
but two hydroxyl ends (diols)

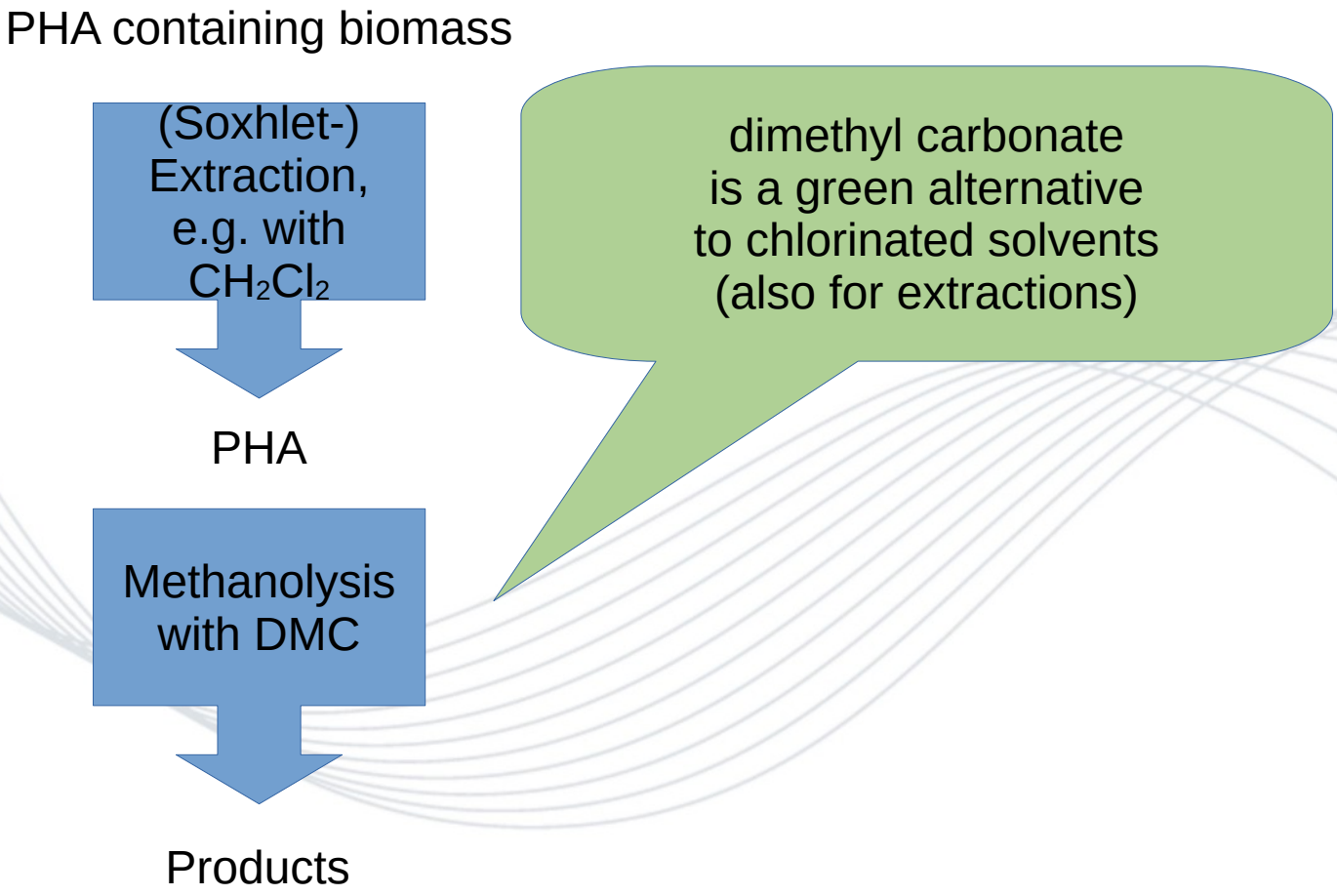
ethyl-end-capped products



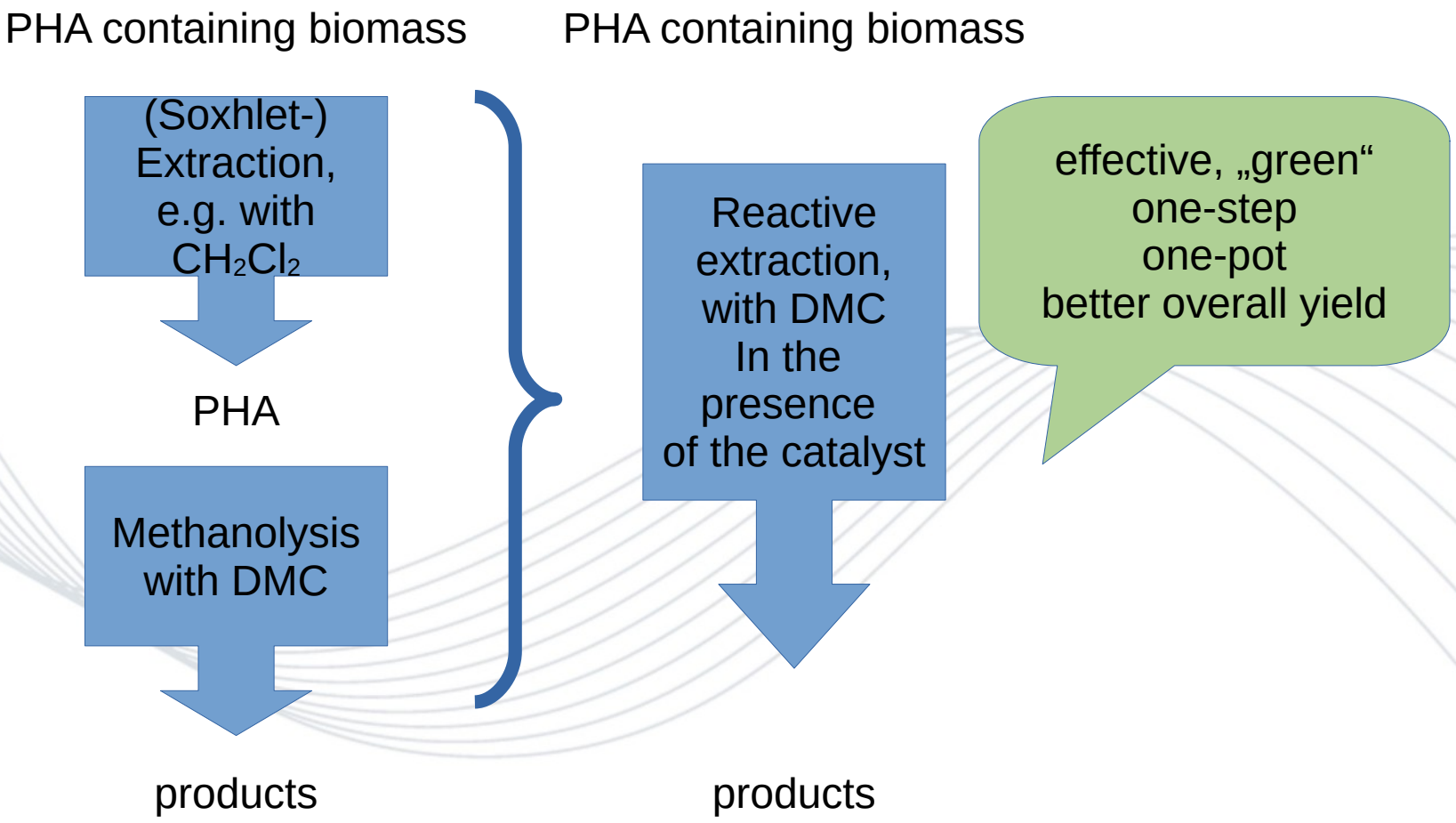
Ethylen carbonate

hydroxyethyl-end-capped products

Alcoholysis – the bigger picture



Reactive extraction with DMC



What has not worked - reesterifaction

- **The plan**

  Reesterification of a 7000 g/mol PHA prepolymer with maleic acid anhydride (MSA)

  by azetropic water removal with 4-methyl tetrahydropyrane

  to obtain a crosslinkable paint binder like in :

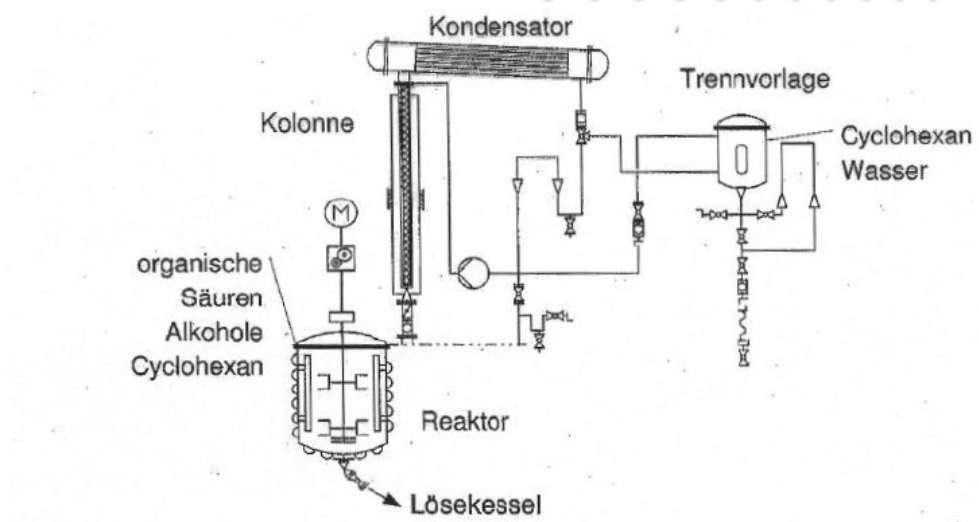


Abb. 11 Schema einer Anlage zur Herstellung von Polykondensationsharzen

What has not worked - reesterifaction

- **The plan**

  Reesterification of a 7000 g/mol PHA prepolymer with

  maleic acid anhydride (MSA)

  by azetropic water removal with 4-methyl tetrahydropyrane

  to obtain a crosslinkable paint binder

- **It didn't work, because:**

  Under these conditions the PHA prepolymer splits off water

  in a concurrent reaction

Next steps

- **Identify the „right“ lower molecular products for new applications**
- **Scale-up reactive extraction**
- **Make reesterification work,**

  maybe better starting from methyl-end-capped intermediates

  (but avoid „non-green“ techniques)
- **Combine with other biopolymers well-known in paint-binders (colophony, shellac)** ♥
- and in the longer run ….

Why is PLA so successfull?

There are different types of PLA with vastly different properties for different applications on the market, because we can controll the lactic acid and PLA stereochemistry.

Nature gives us both enantiomers and we produce the polymer via a dimer with controllable stereochemistry

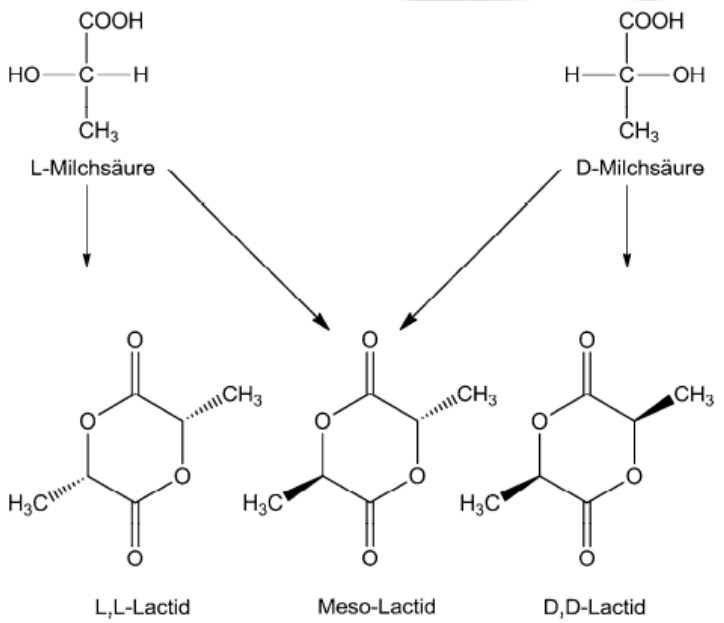
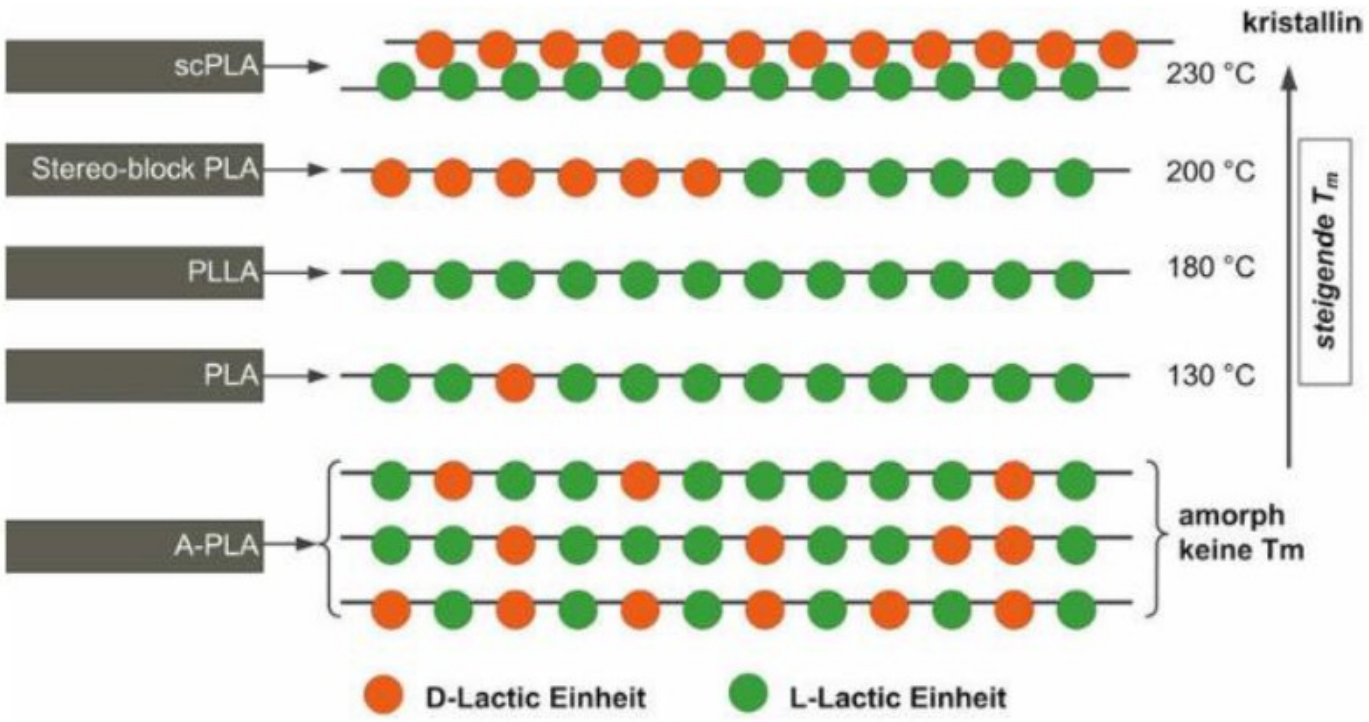


Bild 242 Bildung der drei Stereoisomere L,L-Lactic, Meso-Lactid und D,D-Lactid aus L-Milchsäure und D-Milchsäure.

PLA stereoisomers



Future steps

- Identify the „right“ lower molecular products for new applications
- Scale-up reactive extraction
- Make reesterification work,
  maybe better starting from methyl-end-capped intermediates
  (but avoid „non-green“ techniques)
- Combine with other biopolymers well-known in paint-binders (colophony, shellac) ♥
- controll the PHA stereochemistry by biotechnological or chemical means

Thanks

- Interreg Emphati (Frank Köster)



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