CH3214
Moderne Aspekte und industrielle Anwendungen der Makromolekularen Chemie

7) Recycling of Polymeric Materials

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Learning objectives

- Understand why the current plastic industry is mostly unsustainable
- Know fundamental differences between the recycling of polymers produced by step growth and chain growth polymerization and be able to discuss
- Know about poly(ethylene terephthalate) (PET) and understand why it is a promising material for a more circular economy
- ...
- ...
- ...
- ...

Overview

- Plastics and recycling
- Recycling of step growth polymers
  - PET
  - Polyurethanes
- Recycling of chain growth polymers
  - Ceiling temperature
  - Examples from industry
  - Examples from research

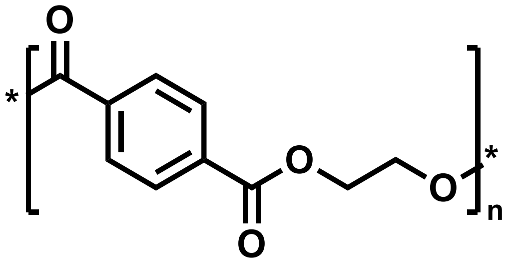
Polymer recycling

Bio-based & bio-attributed - 0.5%

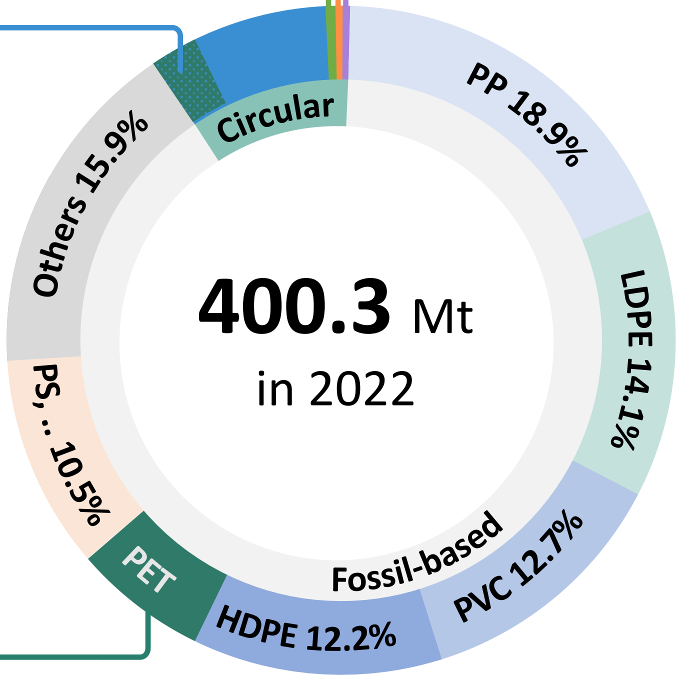
- Growing
- Mostly Polyesters and starch

Mechanically recycled - 8.9%

- rPET – 2.3 % (9 Mt)



PET - 6.2 %



Carbon captured <0.1%

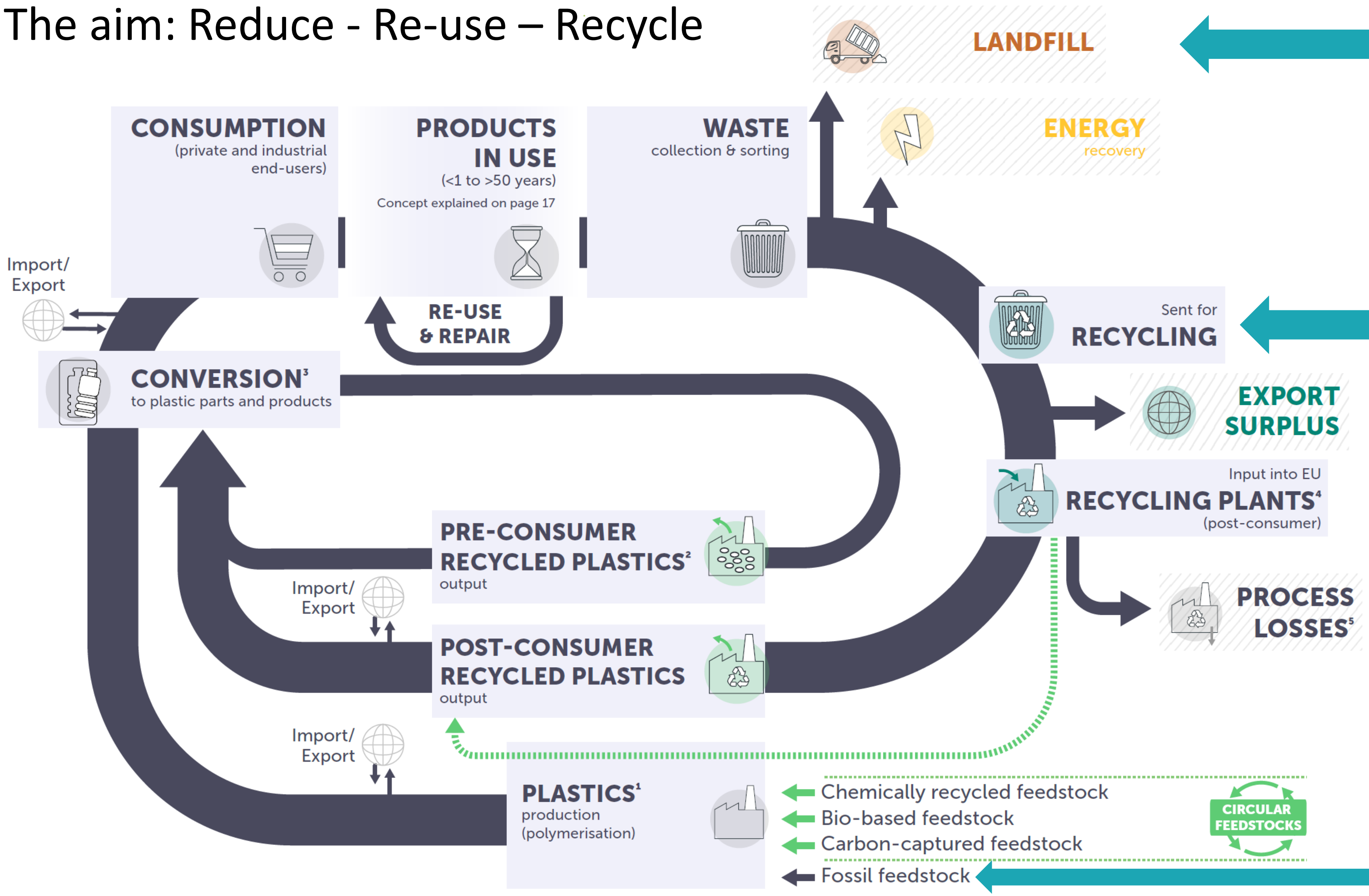
Chemically recycled <0.1%

- Growing
- Mostly PET
- Solvolysis
  - Glycolysis
  - Hydrolysis
  - Methanolysis

Plastics Europe: Plastics – the Facts 2023
Vollmer, Jenks, Roelands, White, van Harmelen, de Wild, van der Laan, Meirer, Keurentjes, Weckhuysen. *Angew. Chem. Int. Ed.* **2020**, *59*, 15402-15423.

Circular economy/ Cradle to Cradle

The aim: Reduce - Re-use – Recycle

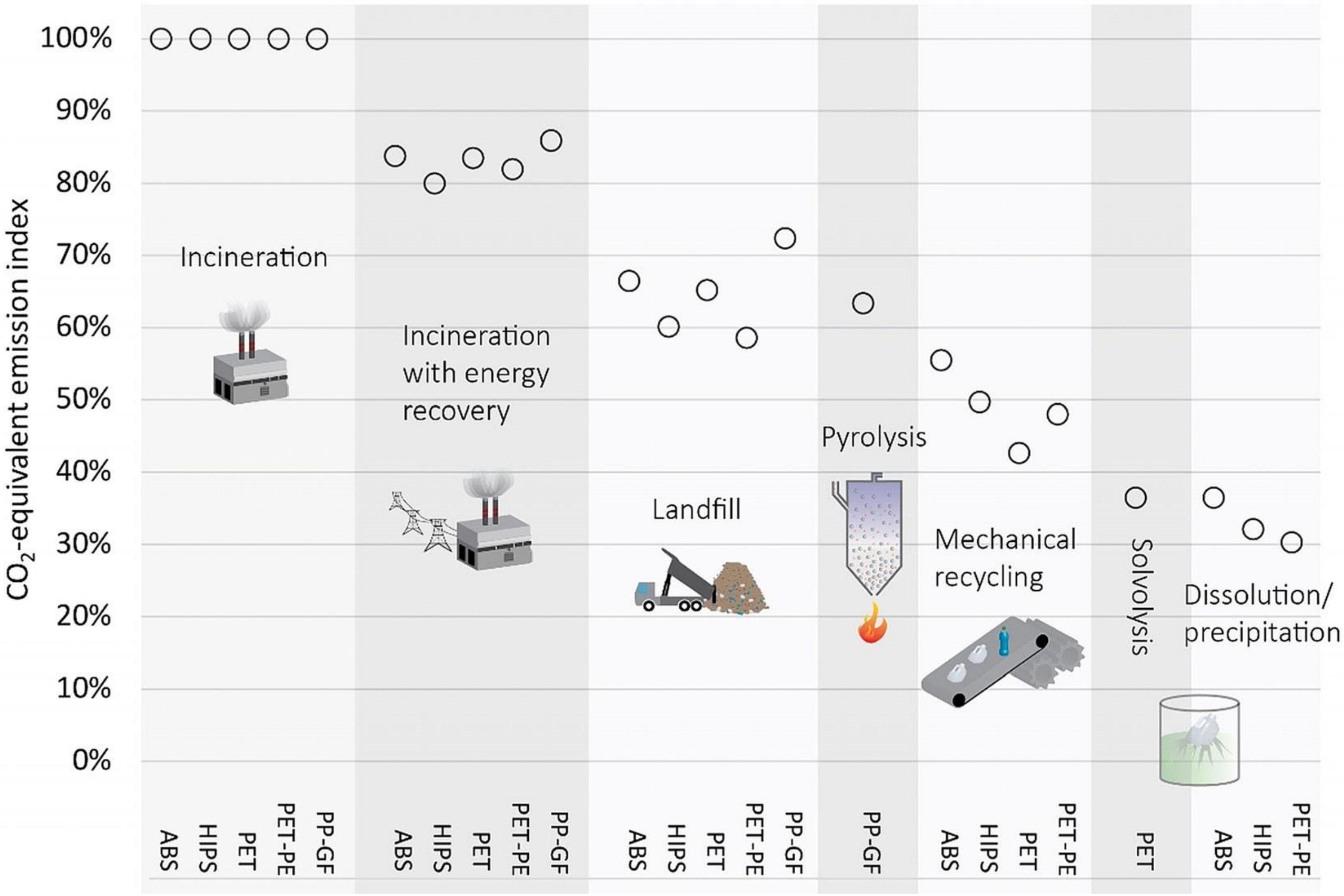


~80%

Most processes reduce polymer quality = downcycling

~90%

CO_2 footprint of polymer recycling



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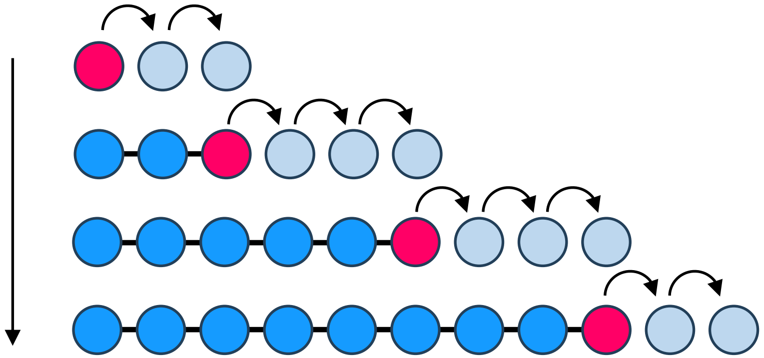
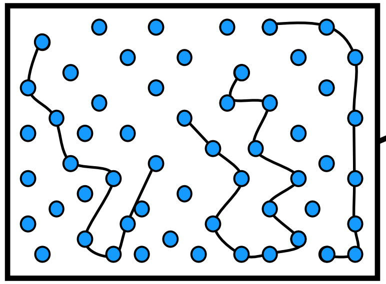
Recap: Polymerization types

Chain Growth polymerization

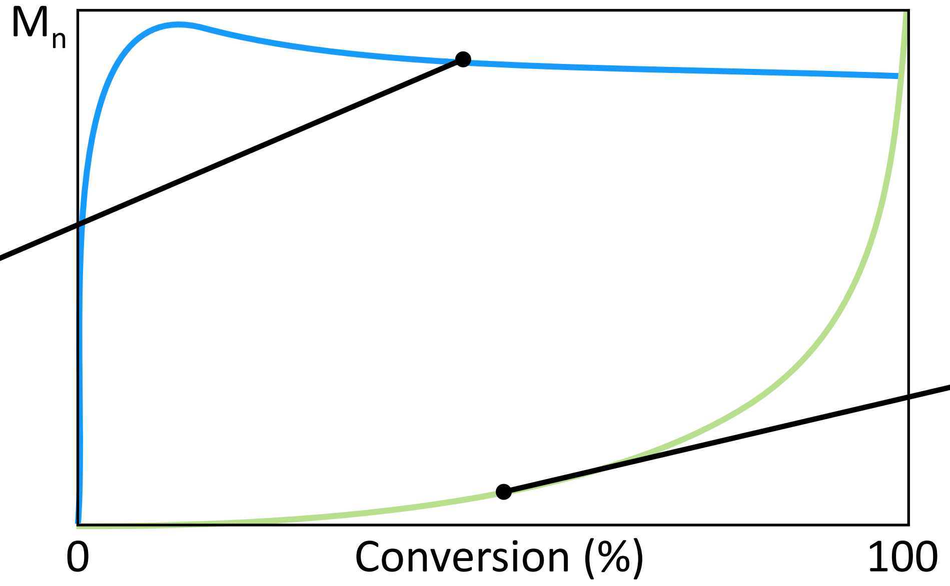
- Sequential addition to an **active centre**



- High activation energy
- High MM early in the process

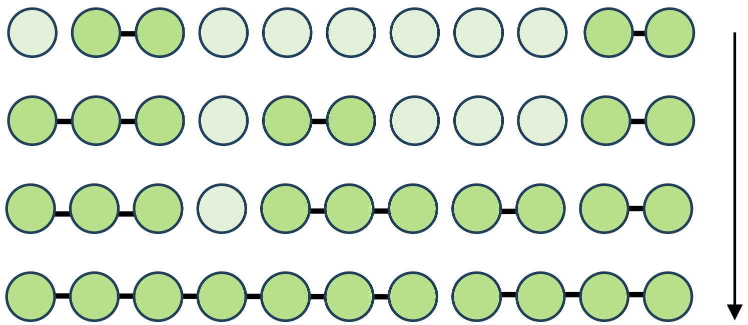


50% Conversion

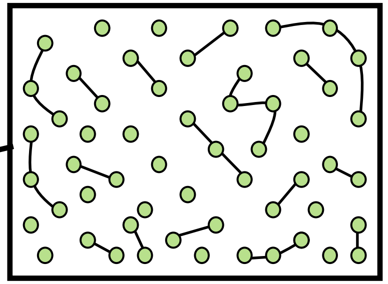


Step Growth polymerization

- **All monomers are active** at the same time
  - Random formation of bonds



- Every step has same energy
- High MM only at high conv.



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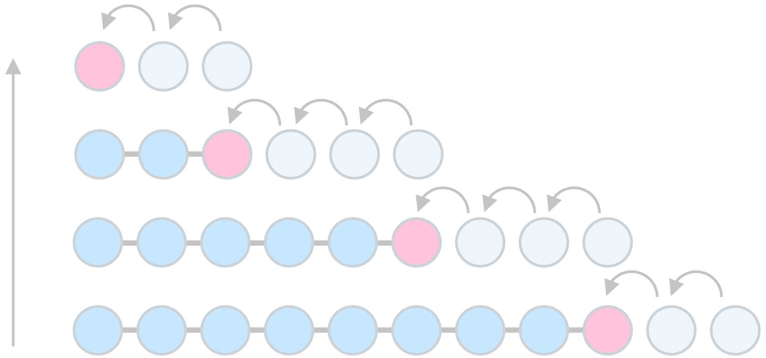

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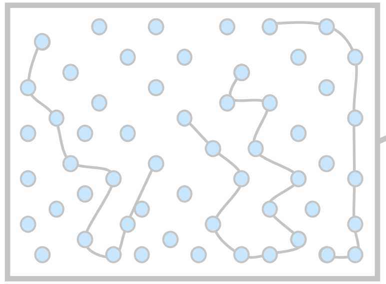

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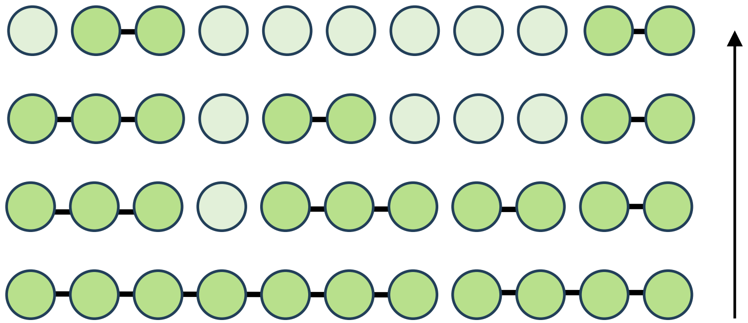

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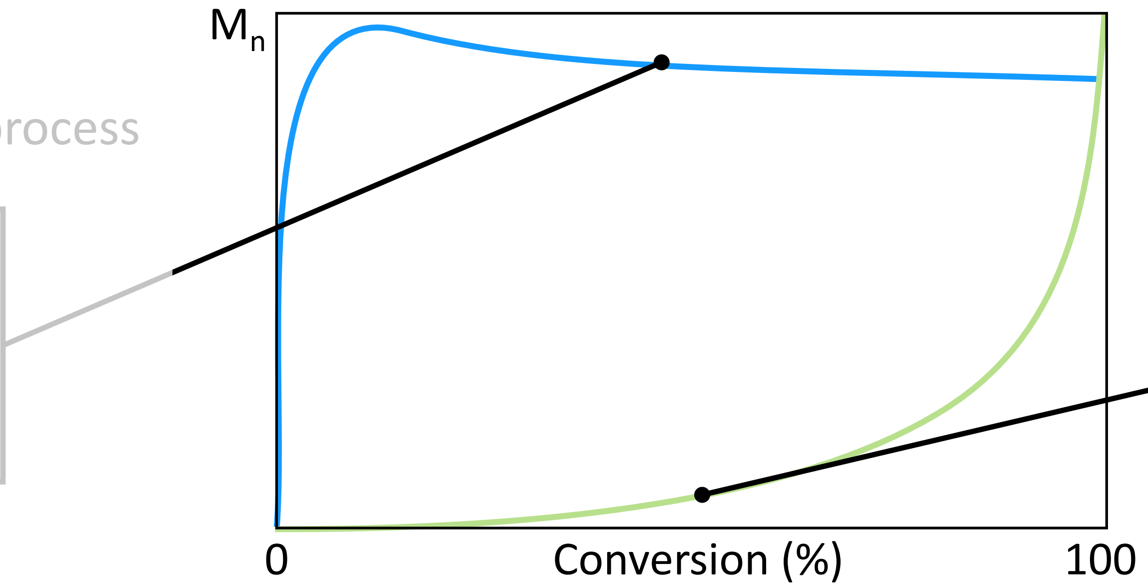
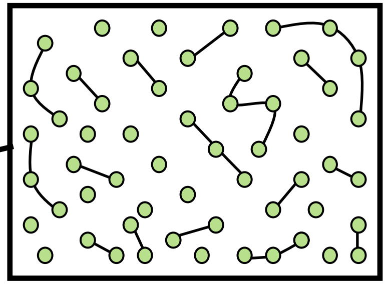
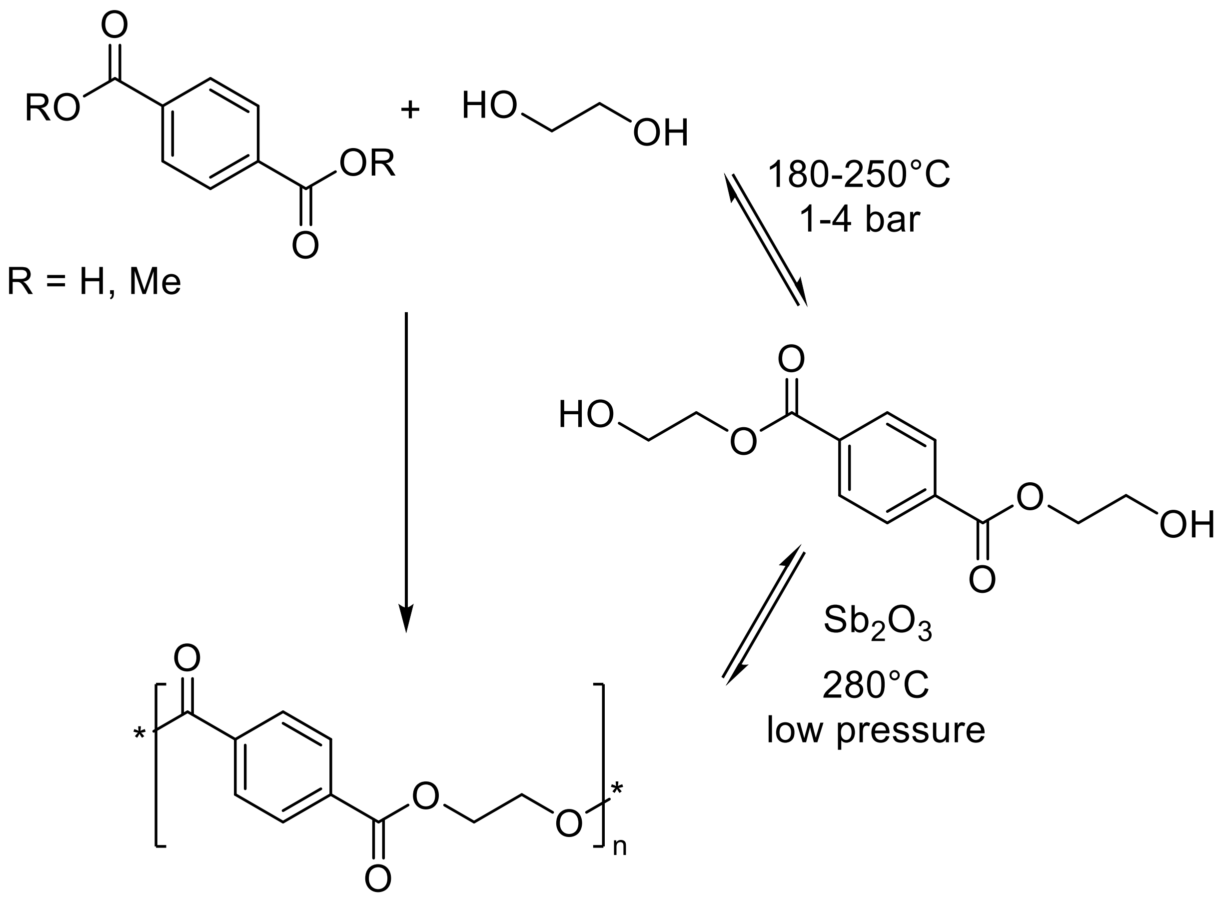


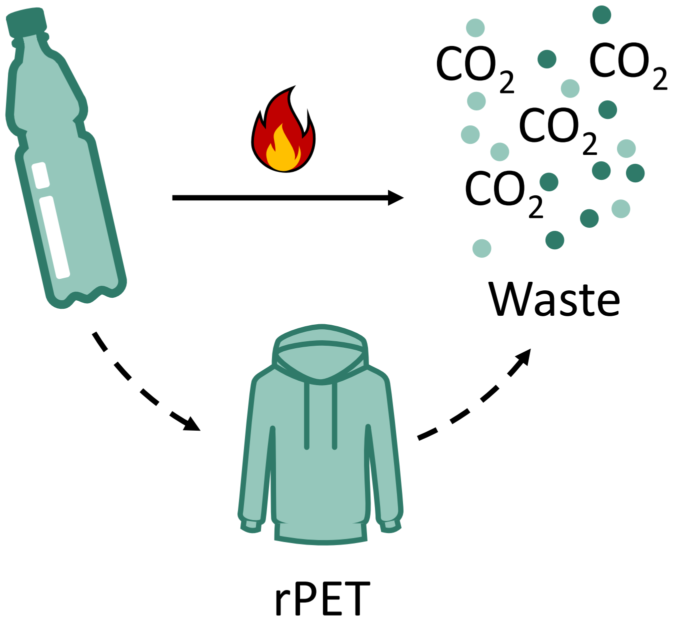


50% Conversion

Example: polyethylene terephthalate (PET)

- Semi-crystalline polymer
- Used for packaging, bottles, textiles, …

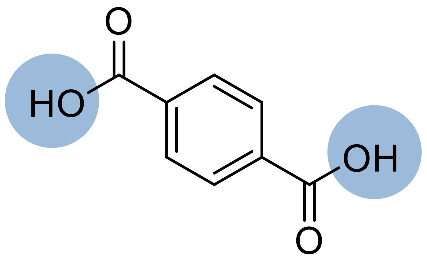




- Mechanical recycling faces problems:
  - Shorter chains
  - Impurities

$$n\,A{-}A + n\,B{-}B \xrightarrow{\text{(cat)}} \left[A{-}A{-}B{-}B\right]_n$$

For PET autocatalysed



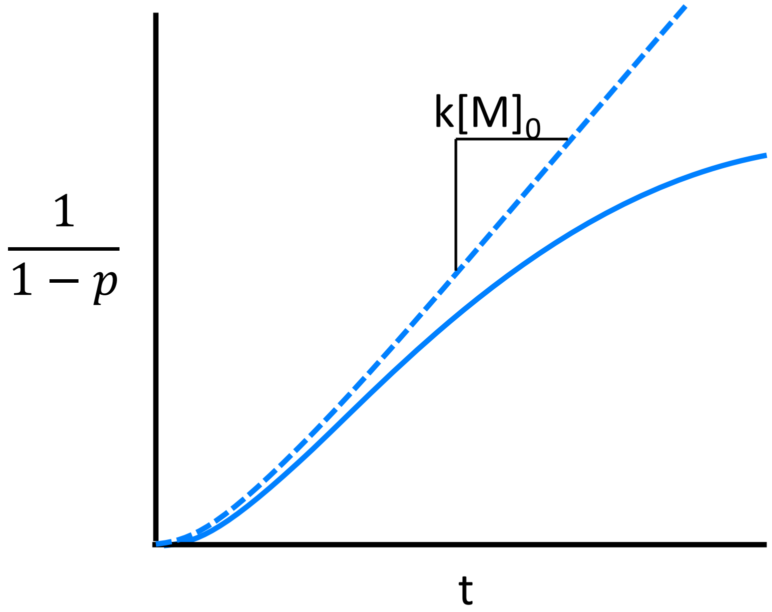
$$\frac{-d[AA]}{dt} = \frac{-d[BB]}{dt} = \frac{-d[M]}{dt} = k[AA][BB] = k[M]^2$$

Integration gives us: $$\frac{1}{[M]_t} - \frac{1}{[M]_0} = kt$$

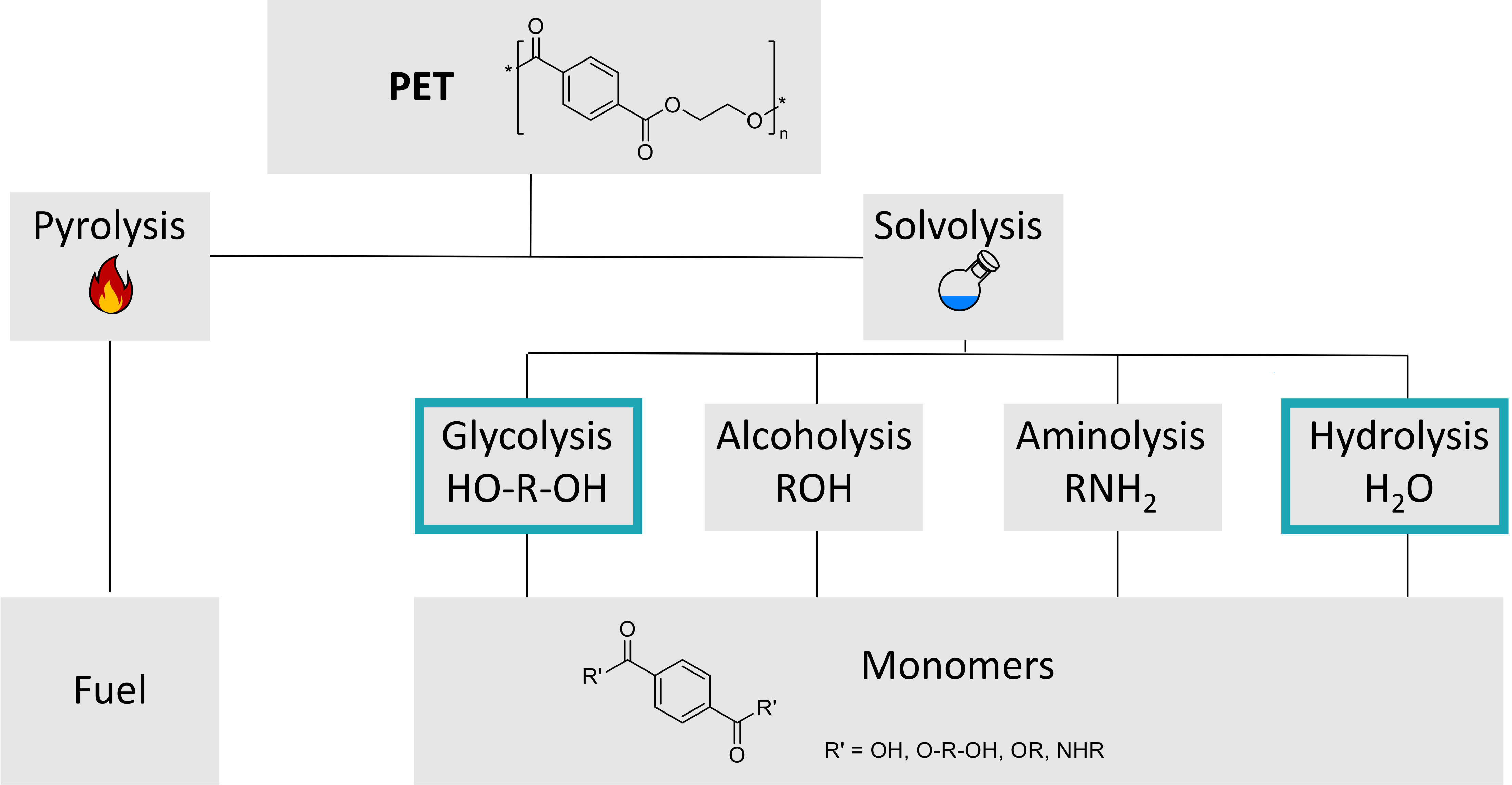
$$\bar{P}_n = \frac{1}{1-p} = \frac{[M]_0}{[M]_t}$$

Carothers equation

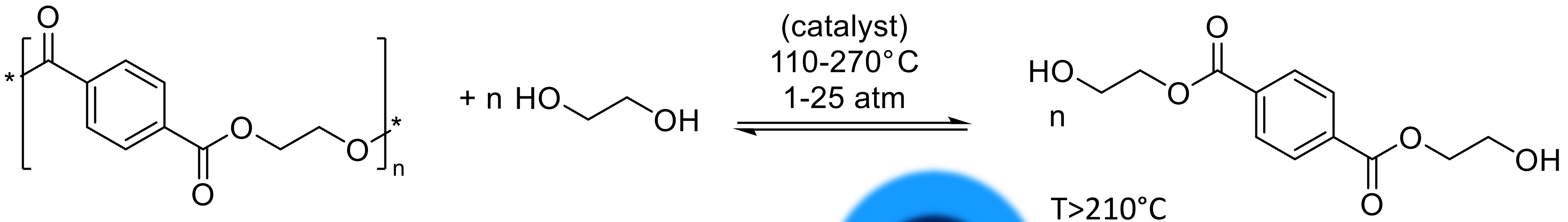
$$\frac{1}{1-p} = k[M]_0 t + 1$$



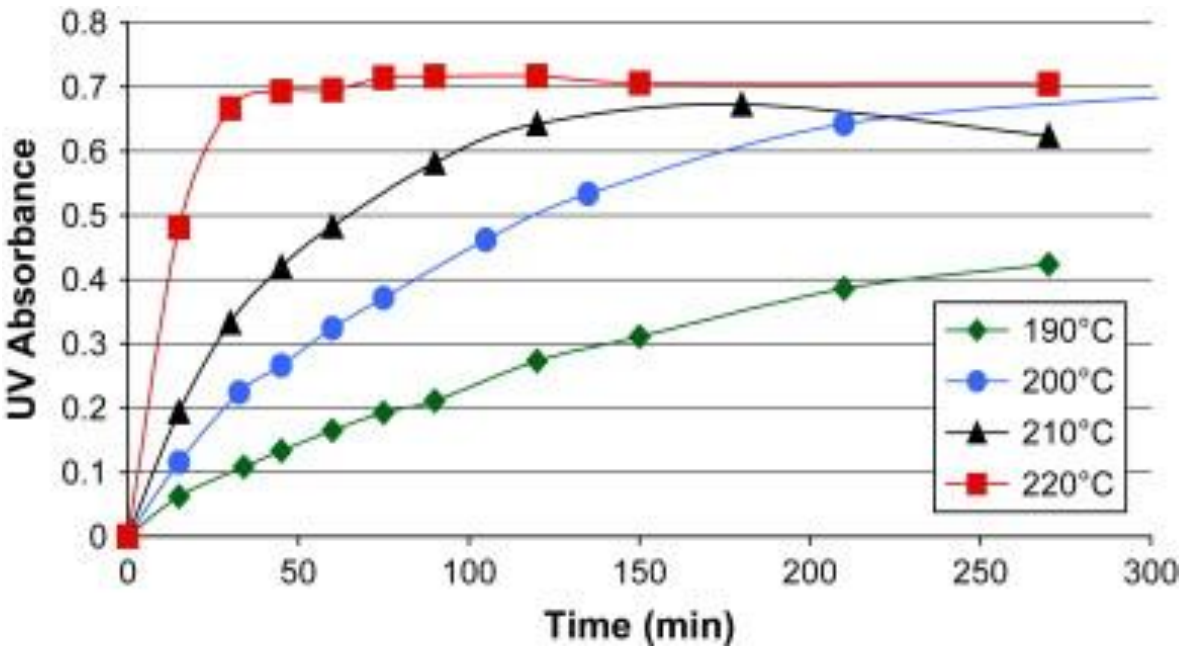
Chemical Degradation/Recycling of PET

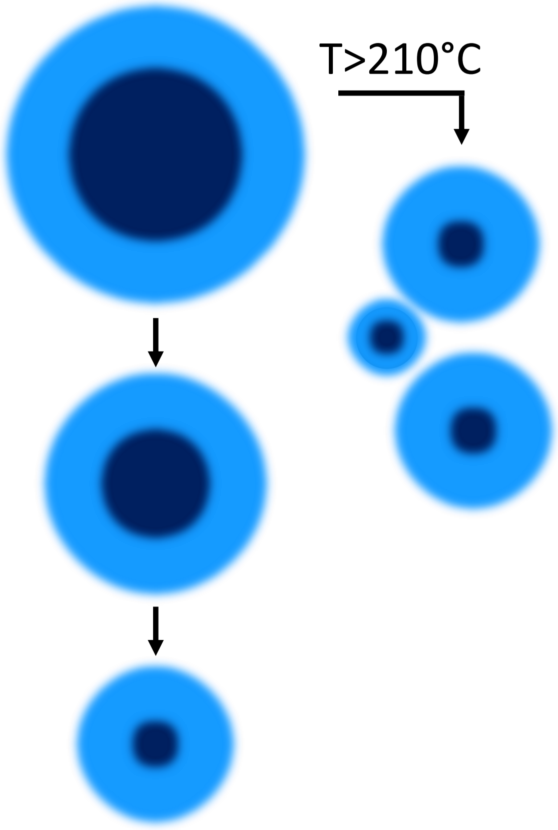


Glycolysis on example of EG



Uncatalysed reaction

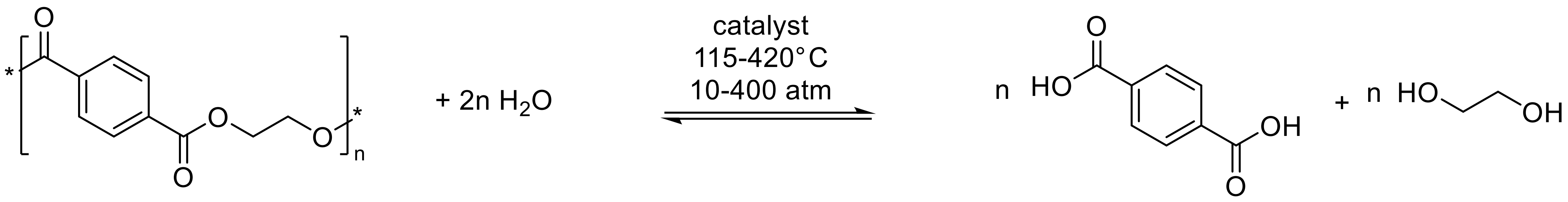




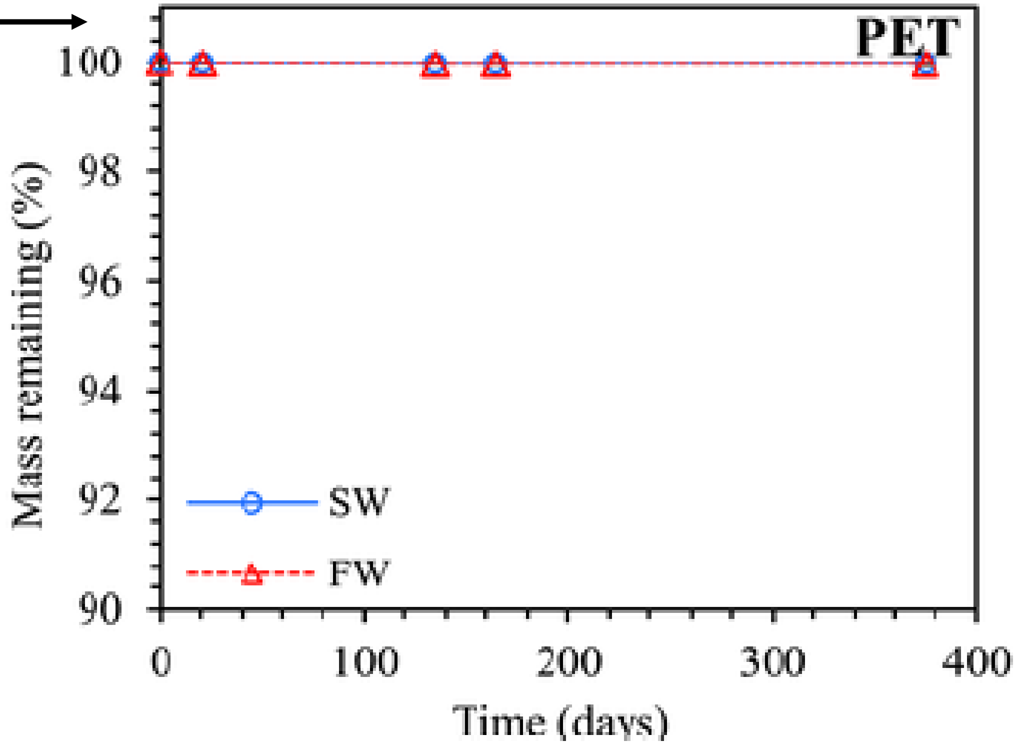
Surface erosion

- 210°C is above T_g and below T_m
- Likely activation by increased rate of transesterification
- Different for catalysed system

Hydrolysis of PET



- Uncatalyzed extremely slow kinetics



- Catalysis by
  - Acid (e.g. H_2SO_4)
  - Base (e.g. NaOH)
- Process is greener but more expensive compared to glycolysis

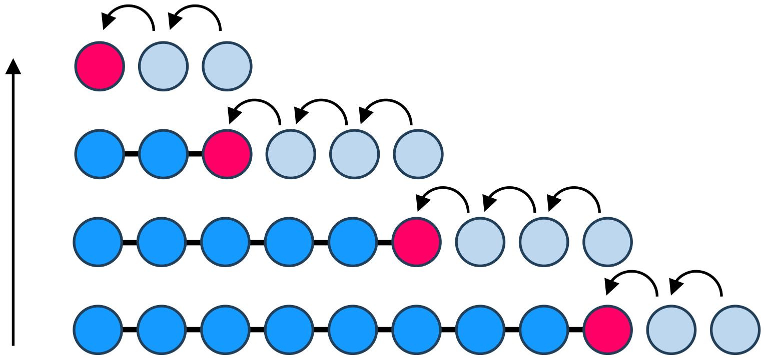
Bagheri, Laforsch, Greiner, Agarwal, *Global Challenges* **2017**, *1*, 1700048.

FW: Fresh water; SW: Sea water
25°C, no light, no biology

(De-)Polymerization kinetics

Chain Growth polymerization

- Sequential addition to an **active centre**



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Step Growth polymerization

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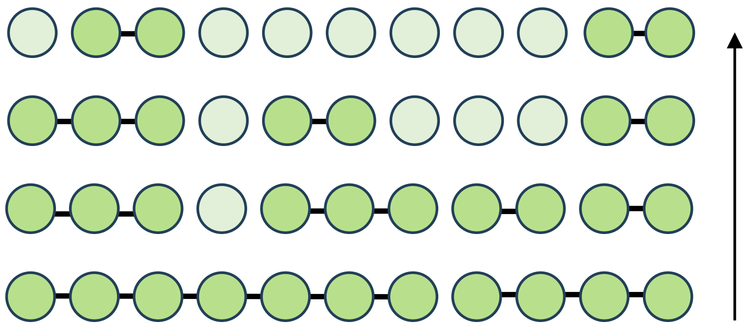

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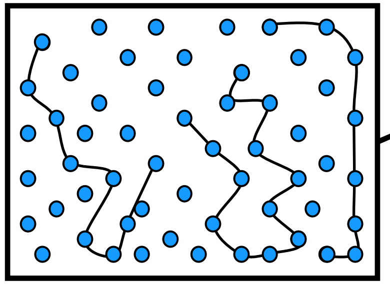

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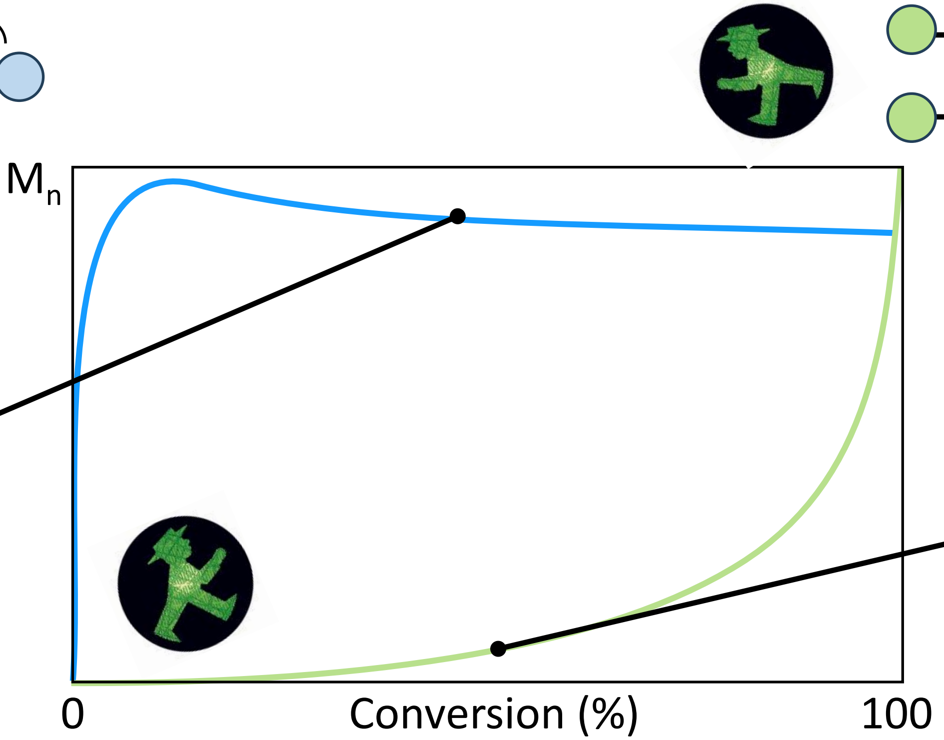
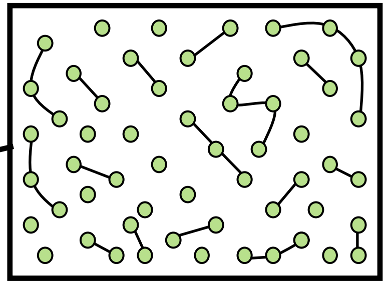
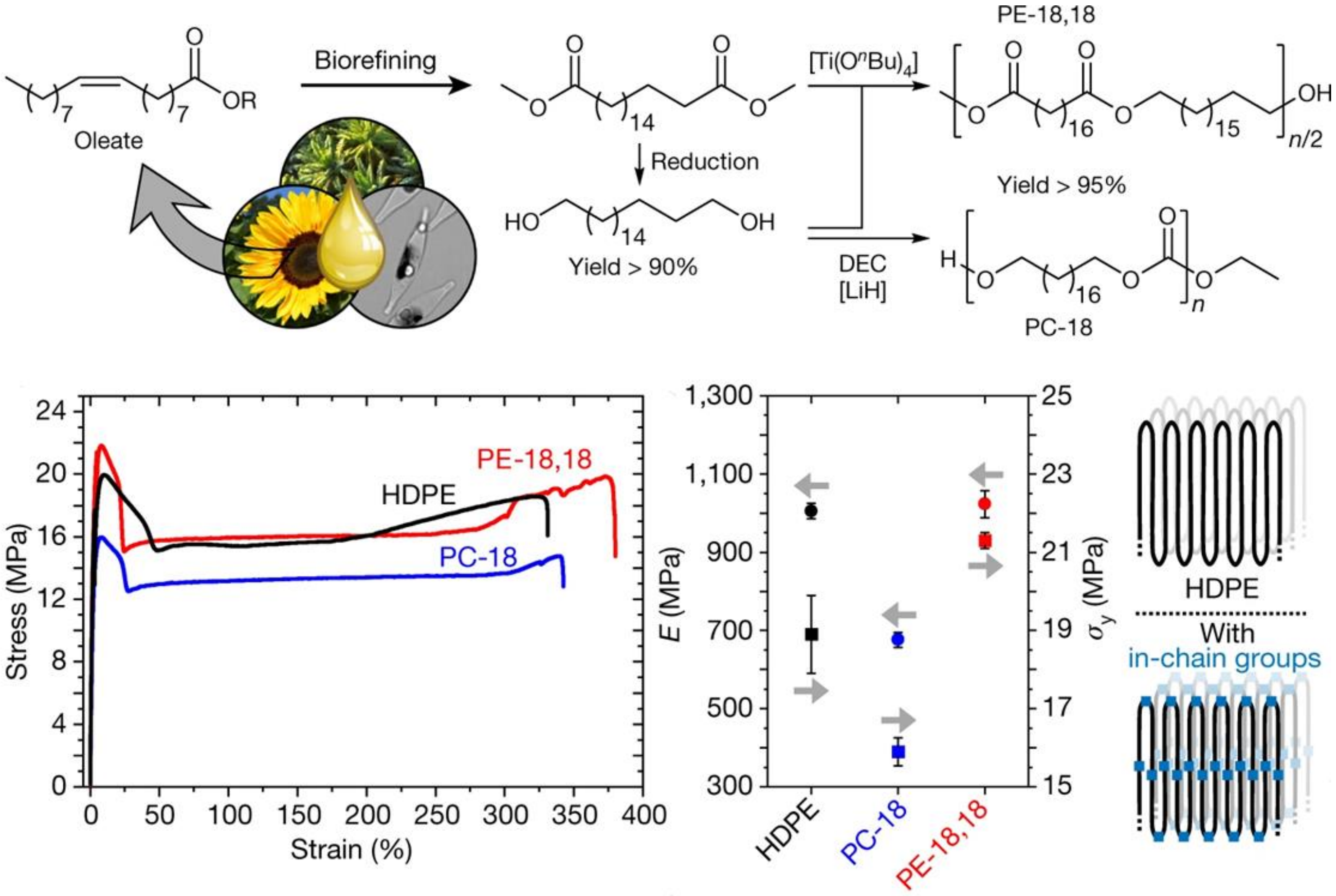
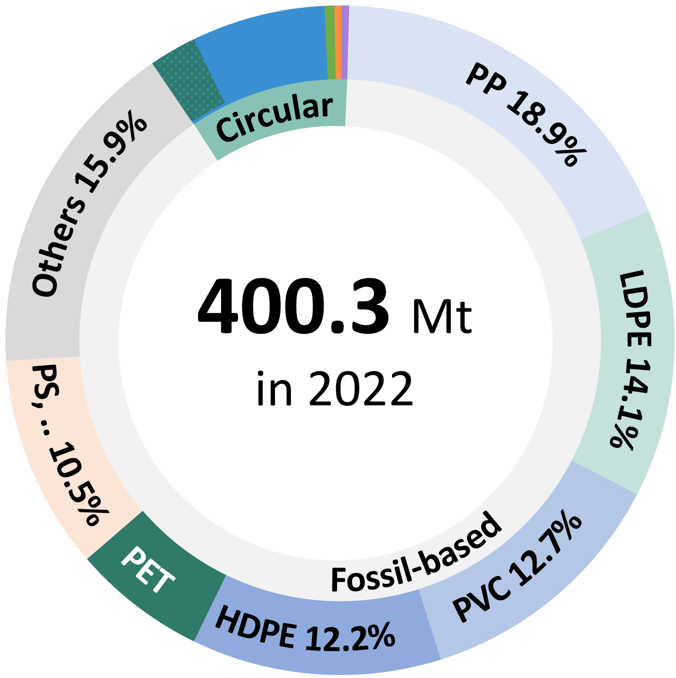




50% Conversion

- There are examples for replacing PE/PP by polyester based materials!





Seminarfragen

1) Welche biobasierte Alternative gibt es zu PET? Nennen Sie Vor- und Nachteile

2) Welche Bio-abbaubaren Polymere sind zurzeit in industrieller Verwendung? Nennen sie je ein Anwendungsbeispiel und die Halbwertszeit in der Umwelt

Alternativ: Verschiedene Vortragsthemen:

„Abbaubare Polyester in der Umwelt“

„Recycling of PE and PP“

…