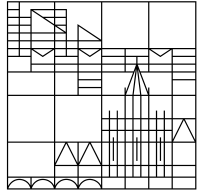


Coffee Lectures: Polymers at OST

Universität
Konstanz



Polymers
for the Future



OST COFFEE LECTURES 2024



Closed-loop recyclable polyethylene-like materials

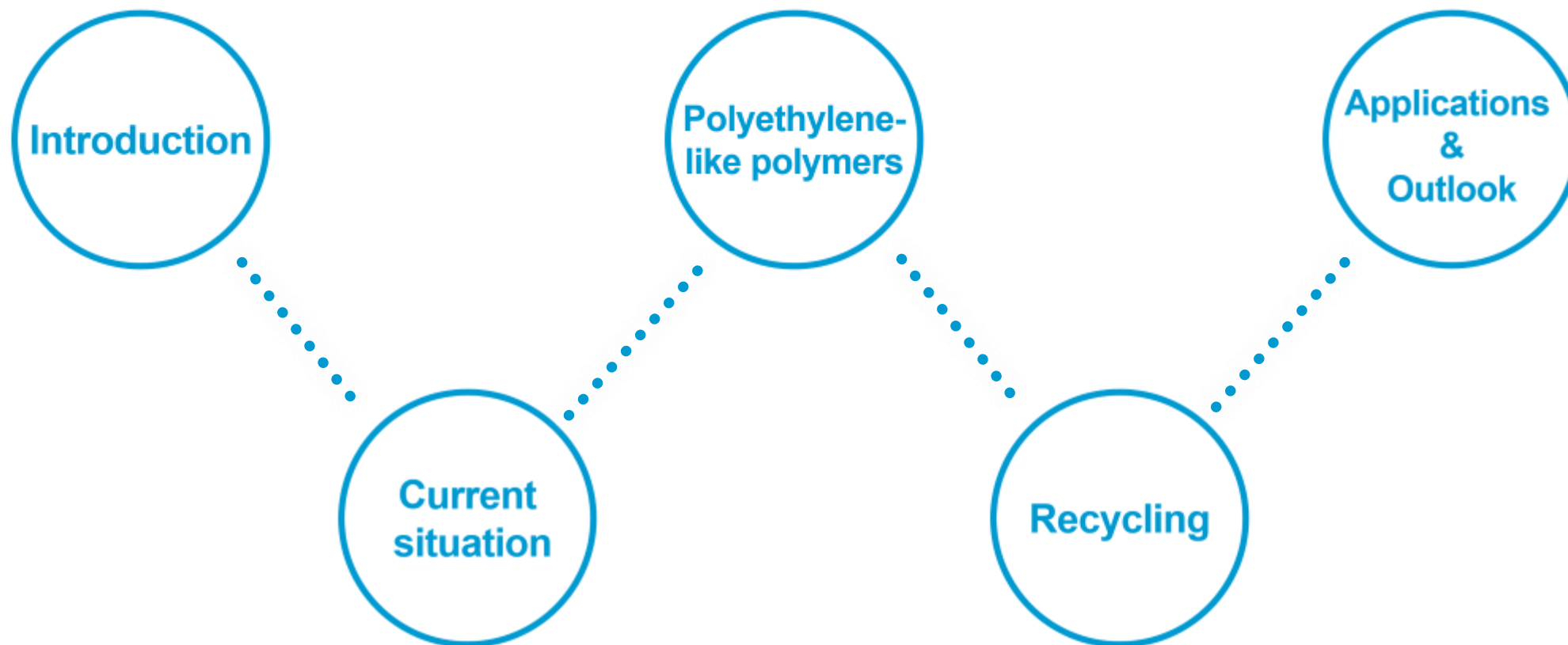


Dario Rothauer, 09.04.2024

Ostschweizer Fachhochschule (OST)



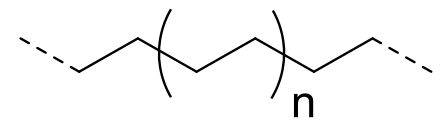
Overview



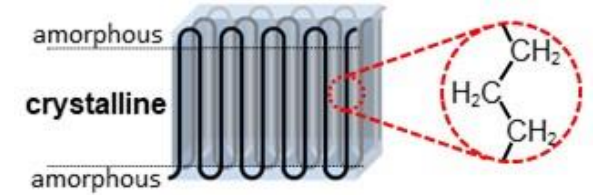


**Current
situation**

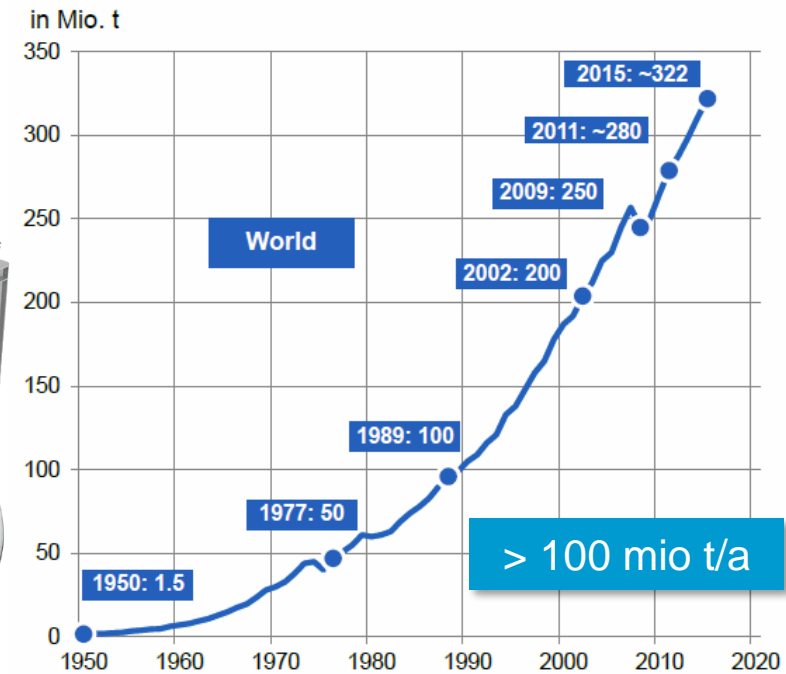
Polyethylene – Assets...



Chemically resistant hydrocarbon backbone

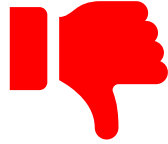


- most important synthetic polymer
- low **price**
- excellent material **properties**
 - mechanical strength and ductility
 - processability
 - low weight
 - Impact and chemical resistance
- various **applications**
- different **types and grades**
 - HDPE
 - LLDPE
 - LDPE
 - UHMWPE
 - waxes
 - oligomers, ...

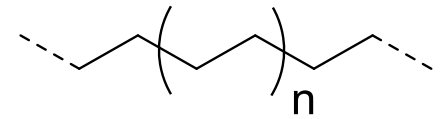
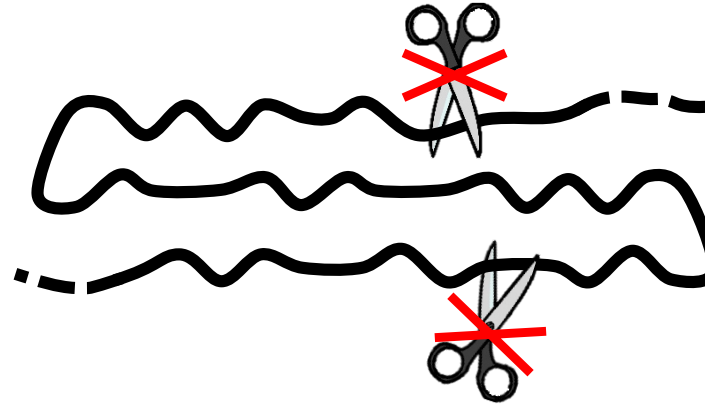


Source: Stahl-Zentrum/International Iron and Steel Institute (IISI), PlasticsEurope Market Research Group (PEMRG) / Consultic Marketing & Industrieberatung GmbH

Polyethylene – ... and drawbacks



- persistent in nature: hydrocarbon chains
- **no break points**
- very **apolar** and **hydrophobic**
- **reasons:** traditional polymerization catalysts very sensitive
→ do not allow for introduction of polar groups



Chemically **resistant**
hydrocarbon backbone

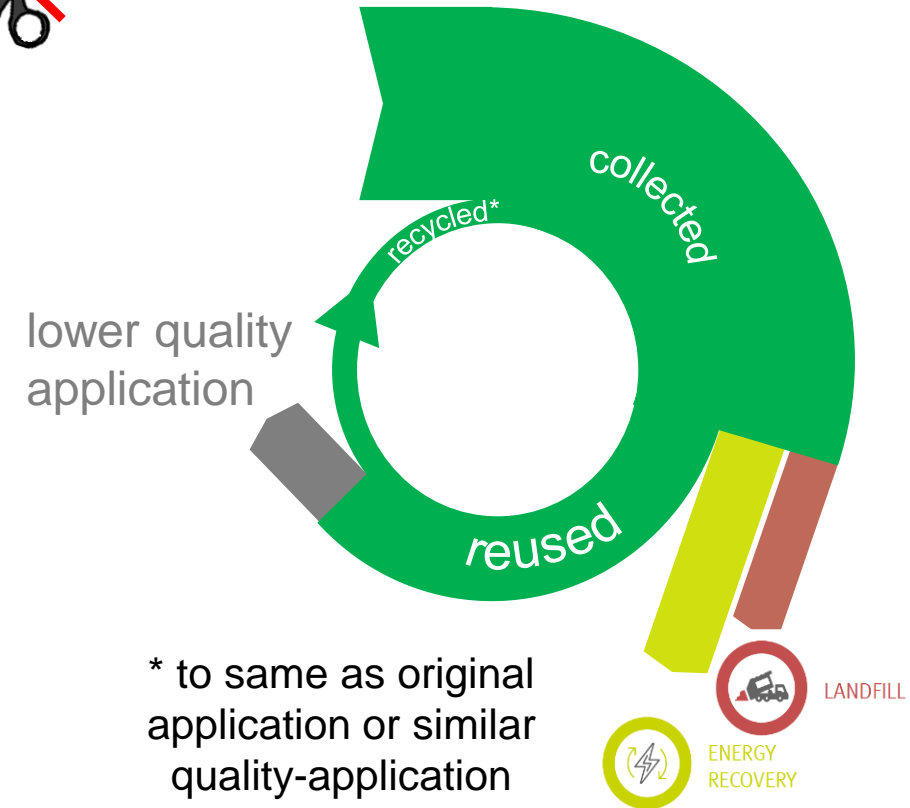


<https://www.peta.de/mediadb/cache/990x/Ente-Vermuellung-Plastikring-c-PETA-USA.jpg>
(accessed 01.10.2019).



<https://www.ukri.org/news/ukri-invests-20m-to-tackle-plastic-waste-in-developing-countries/>

lower quality
application



* to same as original
application or similar
quality-application

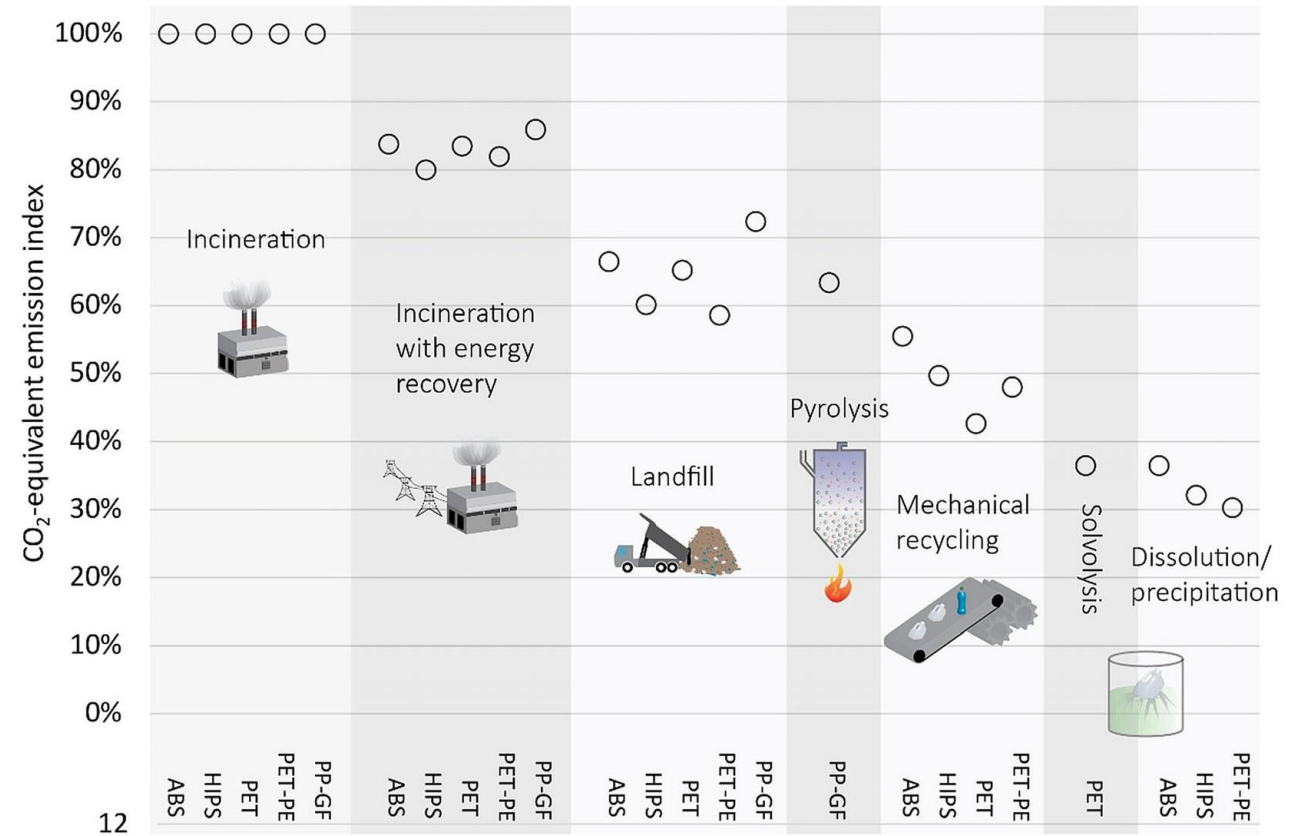
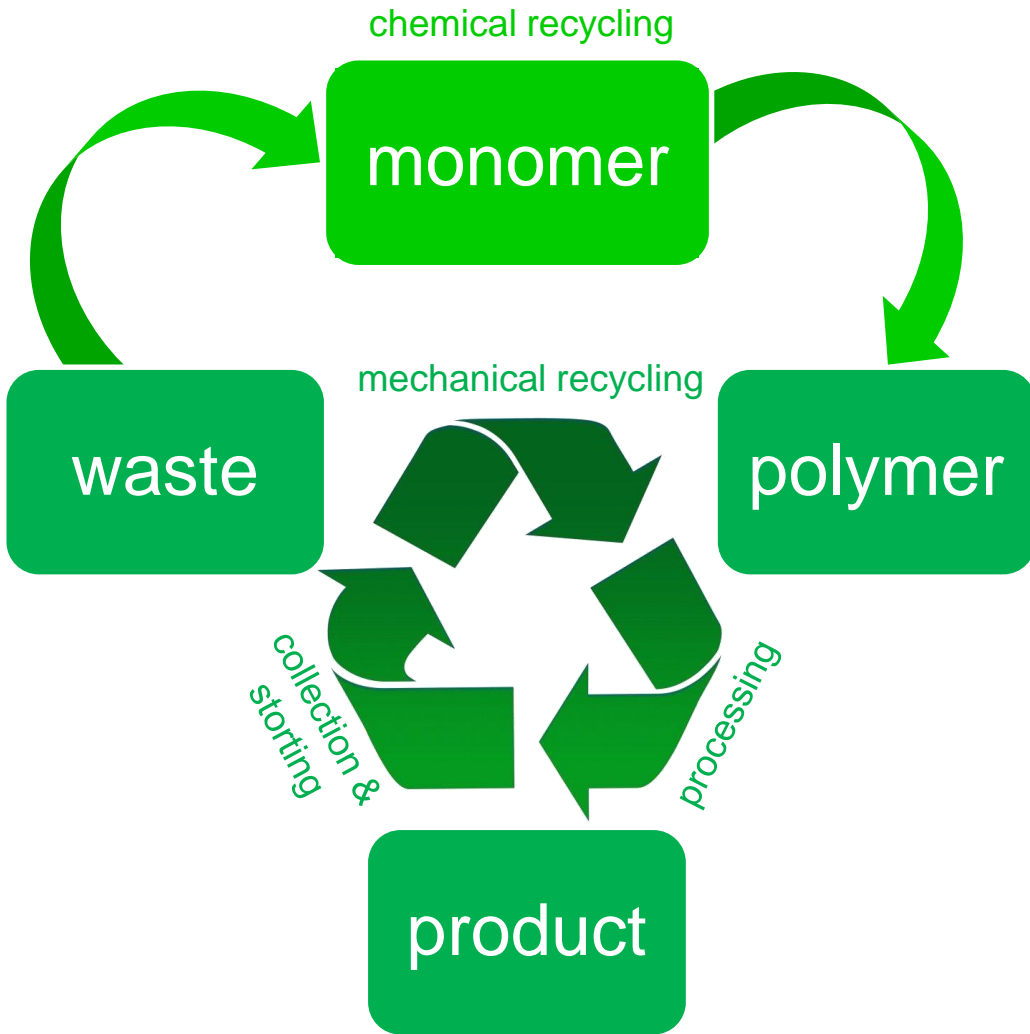


LANDFILL

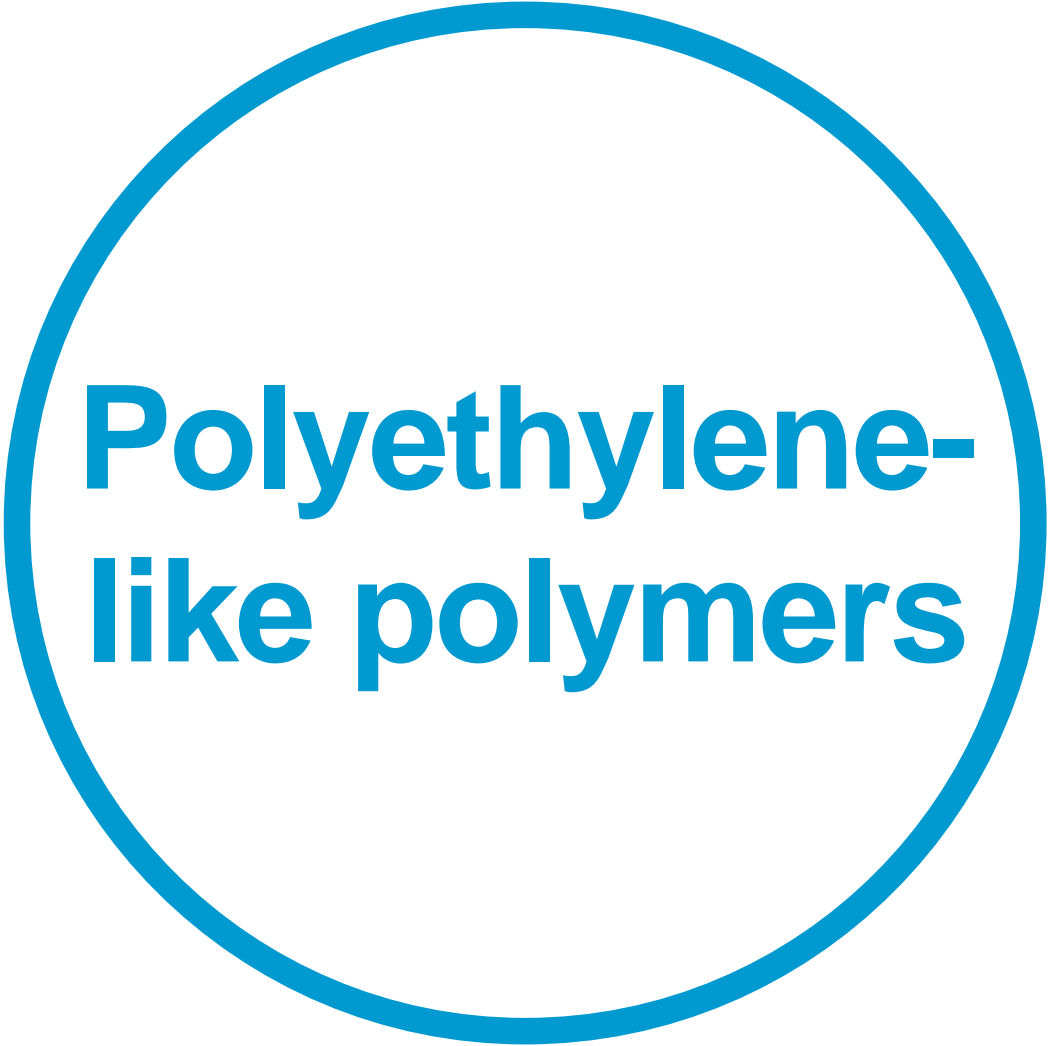
ENERGY
RECOVERY

Adapted from 'Plastics – The facts 2020', Plastics Europe

Polyethylene – Waste management



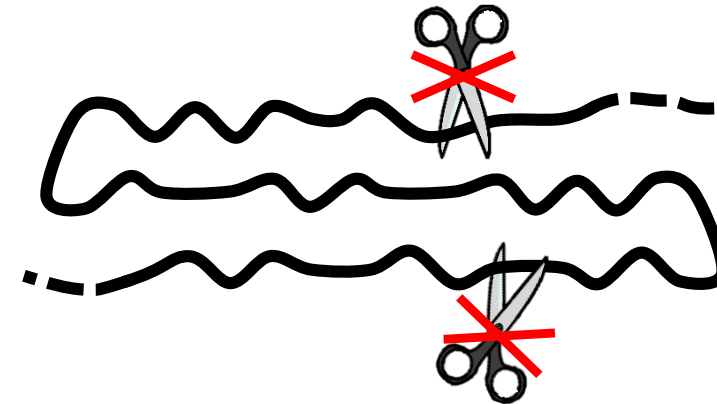
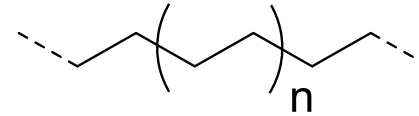
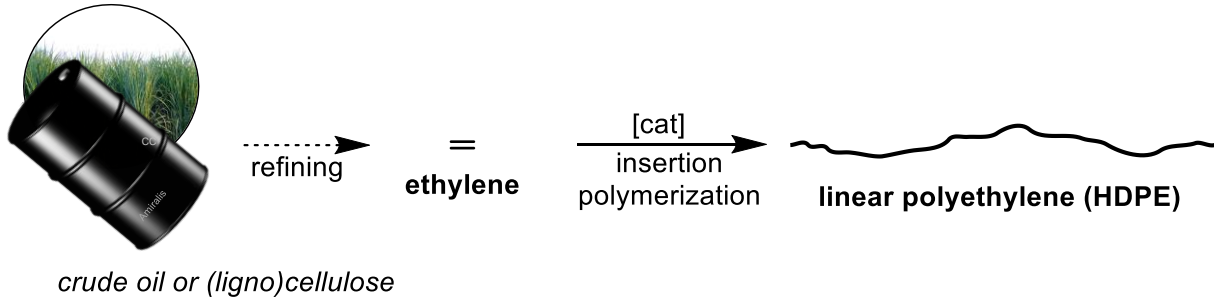
B. Weckhuysen et al. *Angew. Chem. Int. Ed.* 2020, 59, 15402–15423.



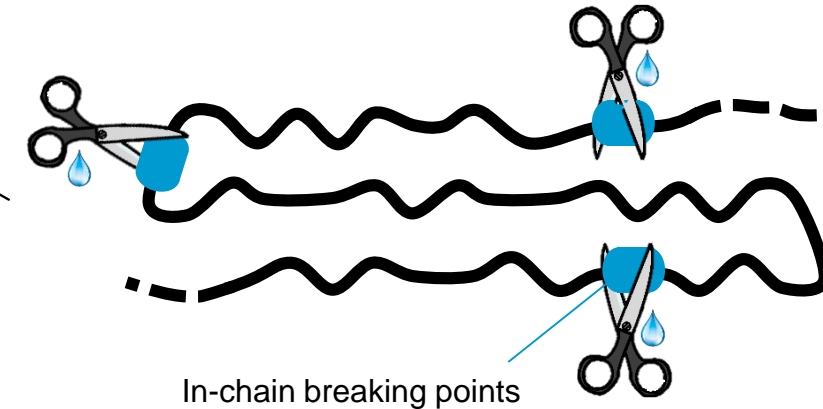
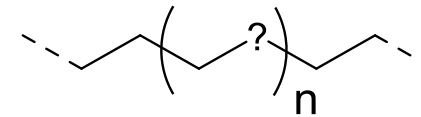
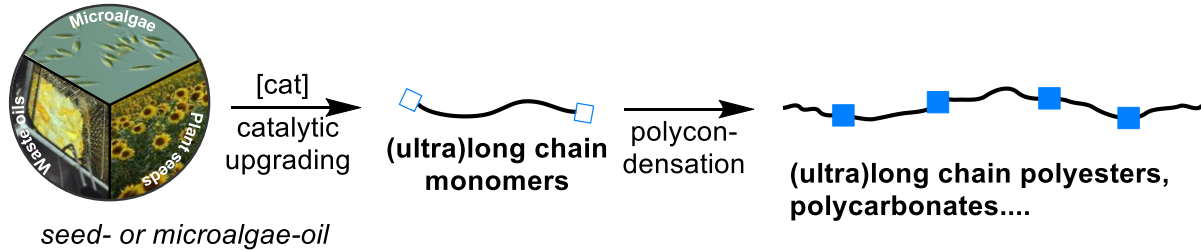
**Polyethylene-
like polymers**

Introducing in-chain breaking points for hydrolysis

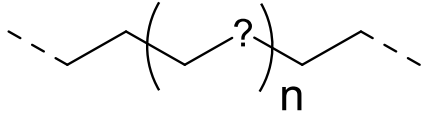
Polyethylene



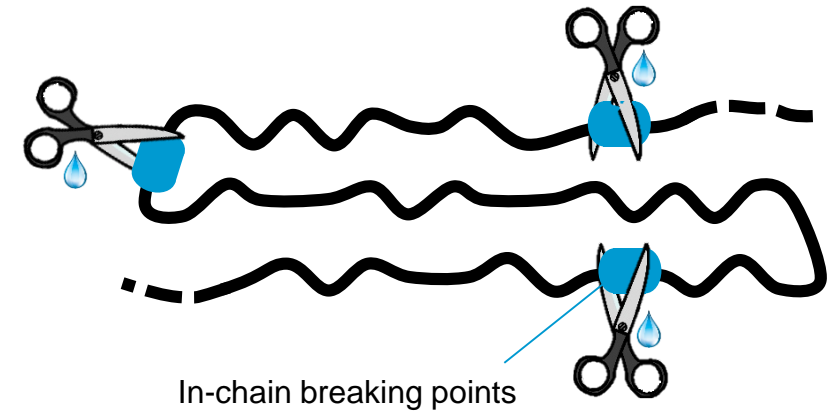
Polyethylene-like polymers



In-chain breaking points for hydrolysis



Polyethylene-like polymers



GDCh
Zuschriften
Angewandte Chemie
www.angewandte.org

Renewable Polymers Hot Paper

Zitierweise: *Angew. Chem. Int. Ed.* **2023**, *62*, e202213438
Internationale Ausgabe: doi.org/10.1002/anie.202213438
Deutsche Ausgabe: doi.org/10.1002/ange.202213438

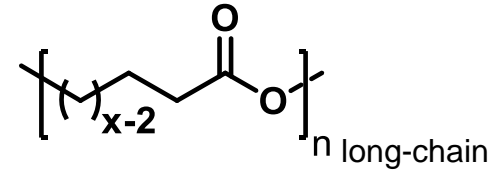
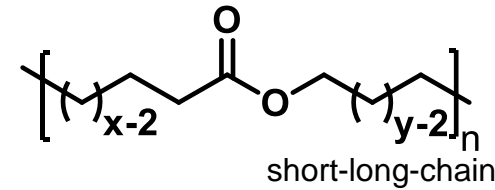
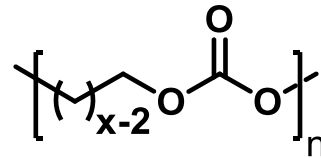
Biodegradable High-Density Polyethylene-like Material

Marcel Eck*, Simon Timm Schwab*, Taylor Frederick Nelson, Katrin Wurst, Steffen Ibert, David Schleheck, Christoph Link, Glauco Battaglini, and Stefan Mecking*

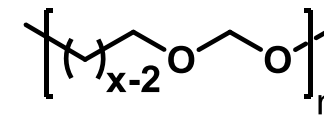
Abstract: We report a novel polyester material generated from readily available biobased 1,18-octadecanedicarboxylic acid and ethylene glycol possesses a polyethylene-like solid-state structure and also tensile properties similar to high density polyethylene (HDPE). most prominent and relevant example is high density polyethylene (HDPE) in which the linear hydrocarbon chains pack to crystalline domains by van der Waals interactions. However, crystallinity, even in the presence of cleavable bonds, in general hinders biodegradation of plastics due to

PE-X.X polyesters

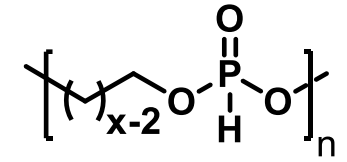
PC-X polycarbonates



PA-X polyacetals



PPh-X poly-H-phosphonates



degradability

Article

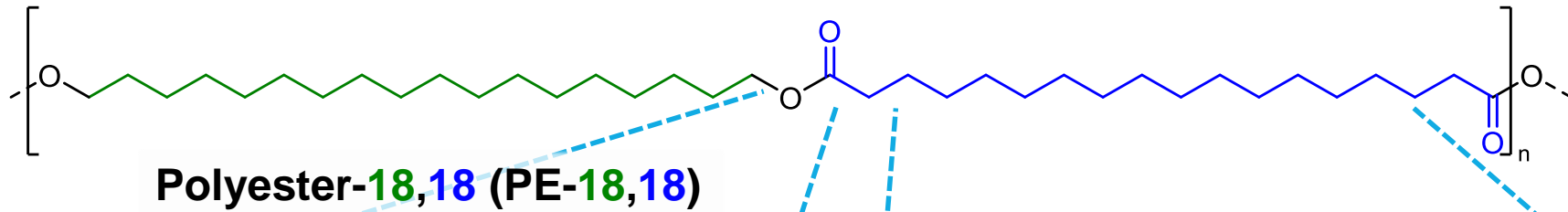
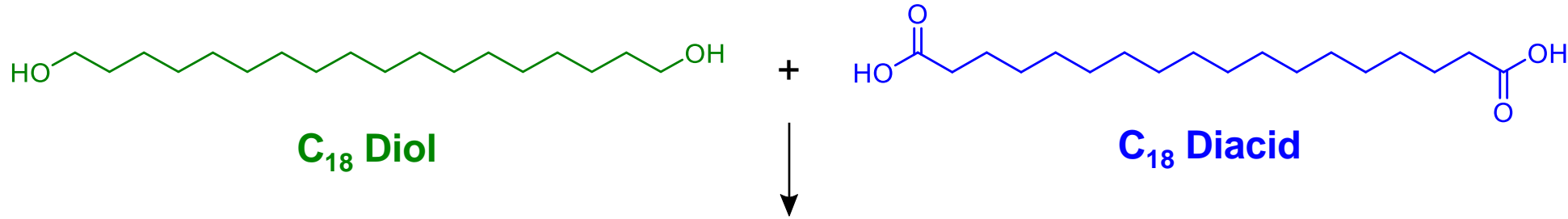
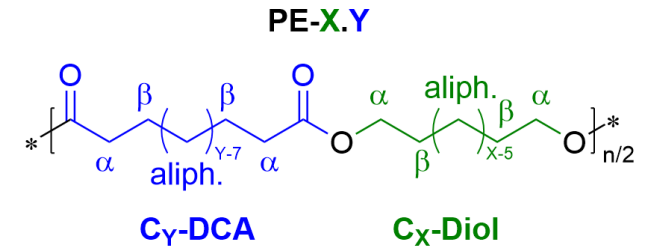
Closed-loop recycling of polyethylene-like materials

<https://doi.org/10.1038/s41586-020-03149-9> Manuel Häubler^{1,2}, Marcel Eck^{1,2}, Dario Rothauer³ & Stefan Mecking^{1,2}

Received: 24 May 2020
Accepted: 21 December 2020
Published online: 17 February 2021
Check for updates

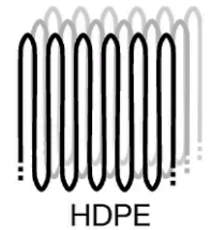
Plastics are key components of almost any technology today. Although their production consumes substantial feedstock resources, plastics are largely disposed of after their service life. In terms of a circular economy^{1–6}, reuse of post-consumer sorted polymers ('mechanical recycling') is hampered by deterioration of materials performance^{7,8}. Chemical recycling^{9,10} via depolymerization to monomer offers an alternative that retains high-performance

Side-Note: Nomenclature of the Polyesters

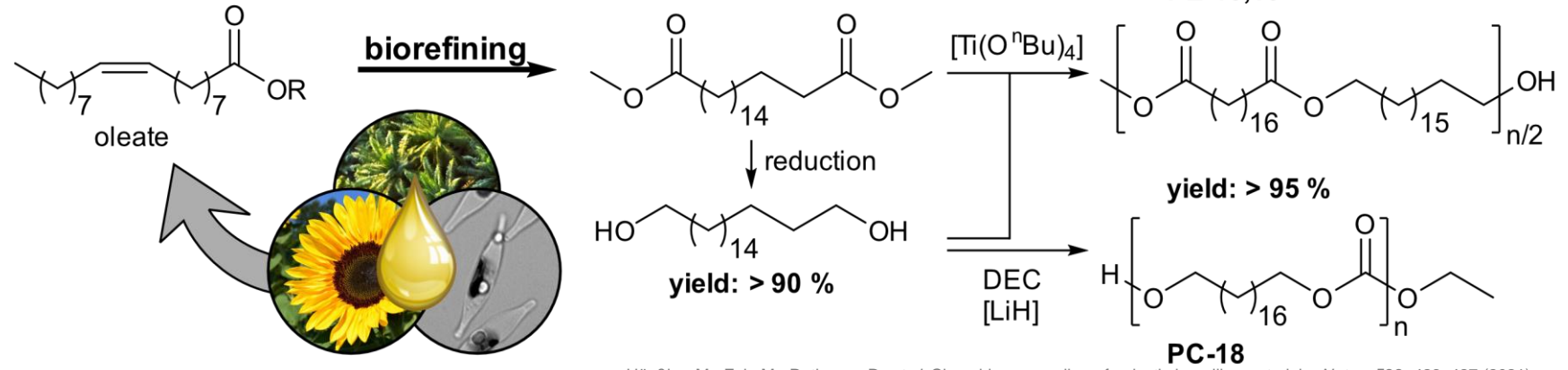


Predetermined "breaking points" enable non-persistency

Long aliphatic repeat units facilitate HDPE-like crystallization

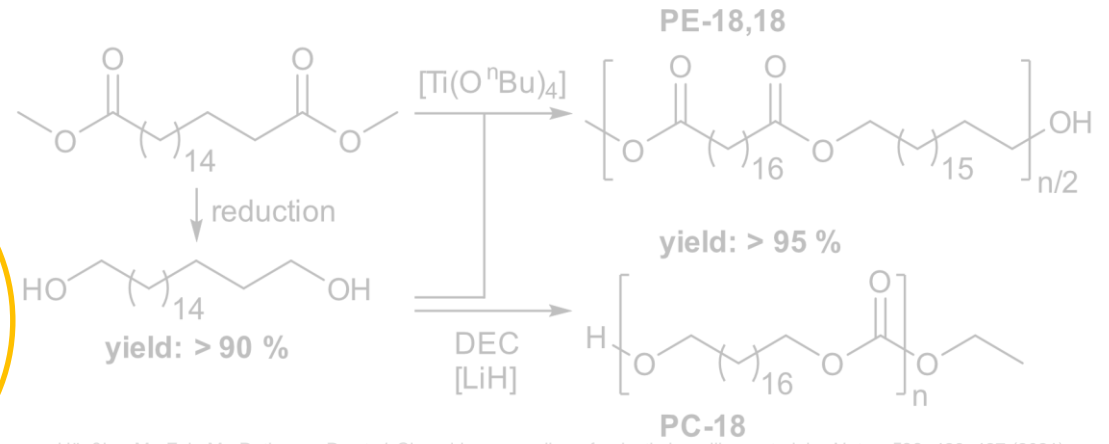
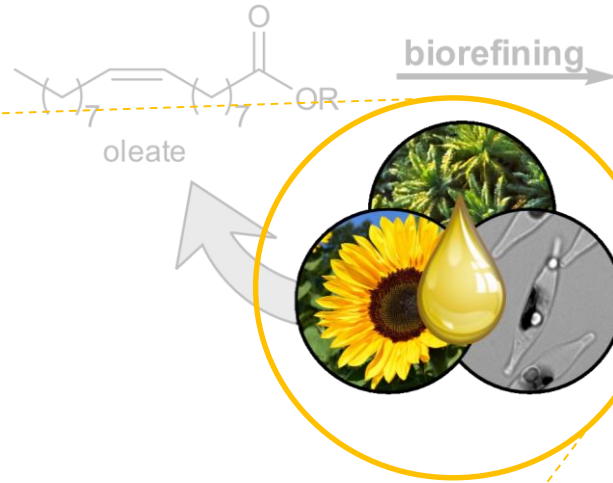
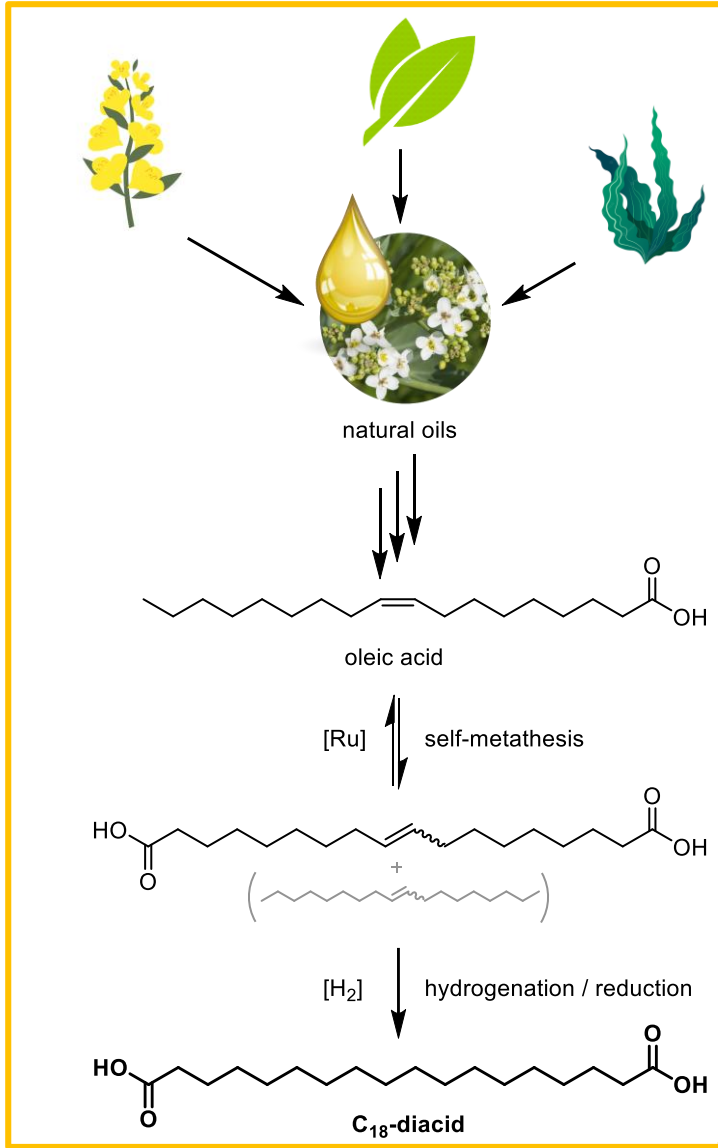


Synthetic approach



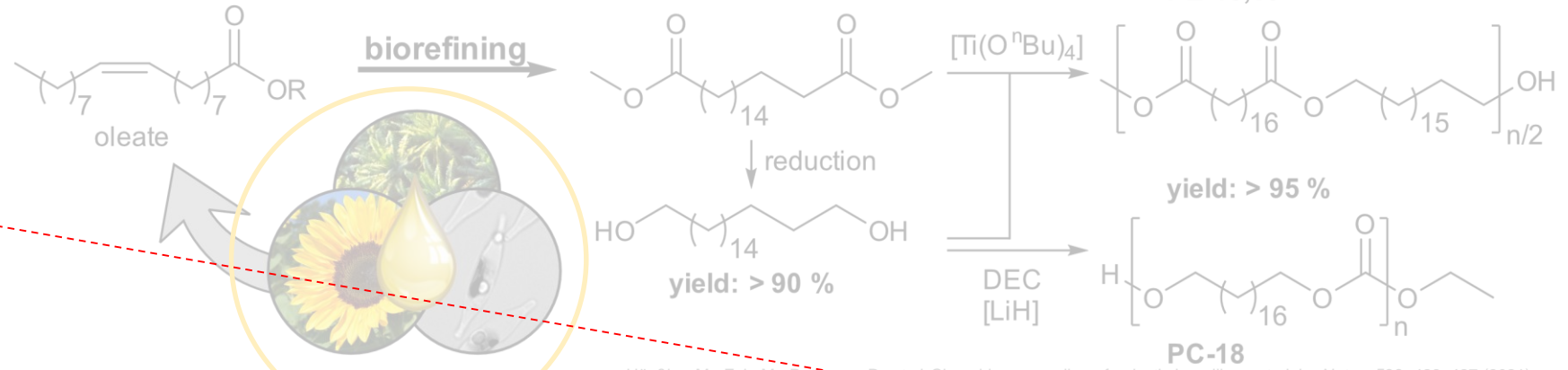
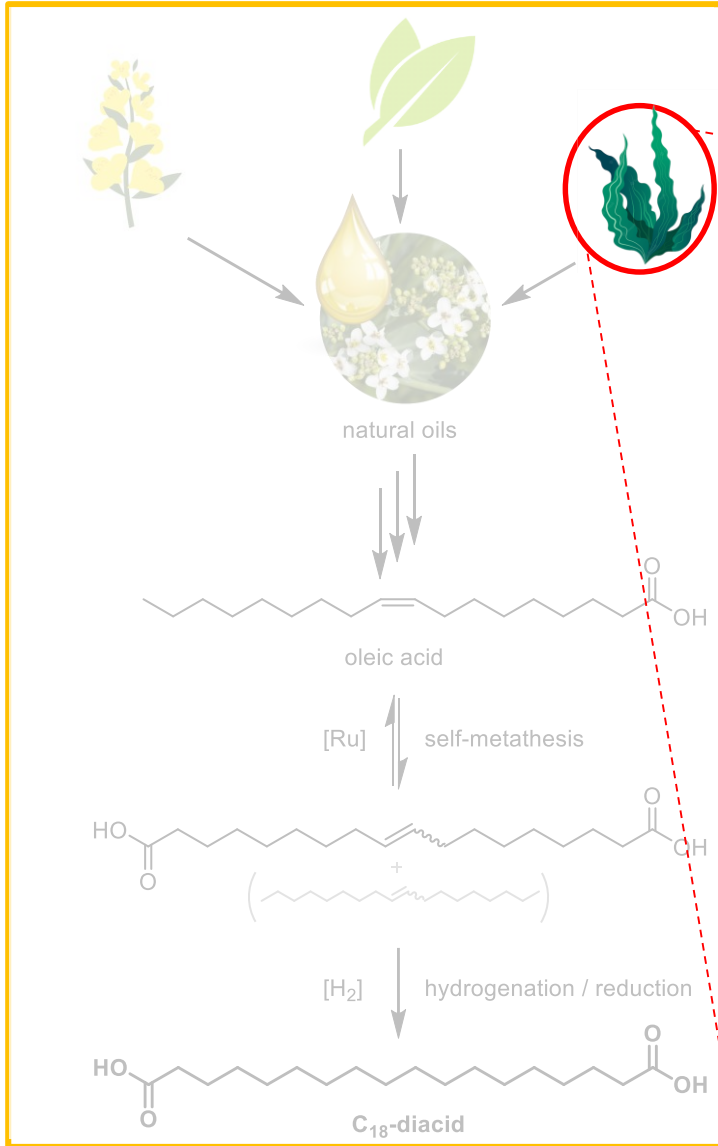
Häußler, M., Eck, M., Rothauer, D. *et al.* Closed-loop recycling of polyethylene-like materials. *Nature* **590**, 423–427 (2021).

Synthetic approach

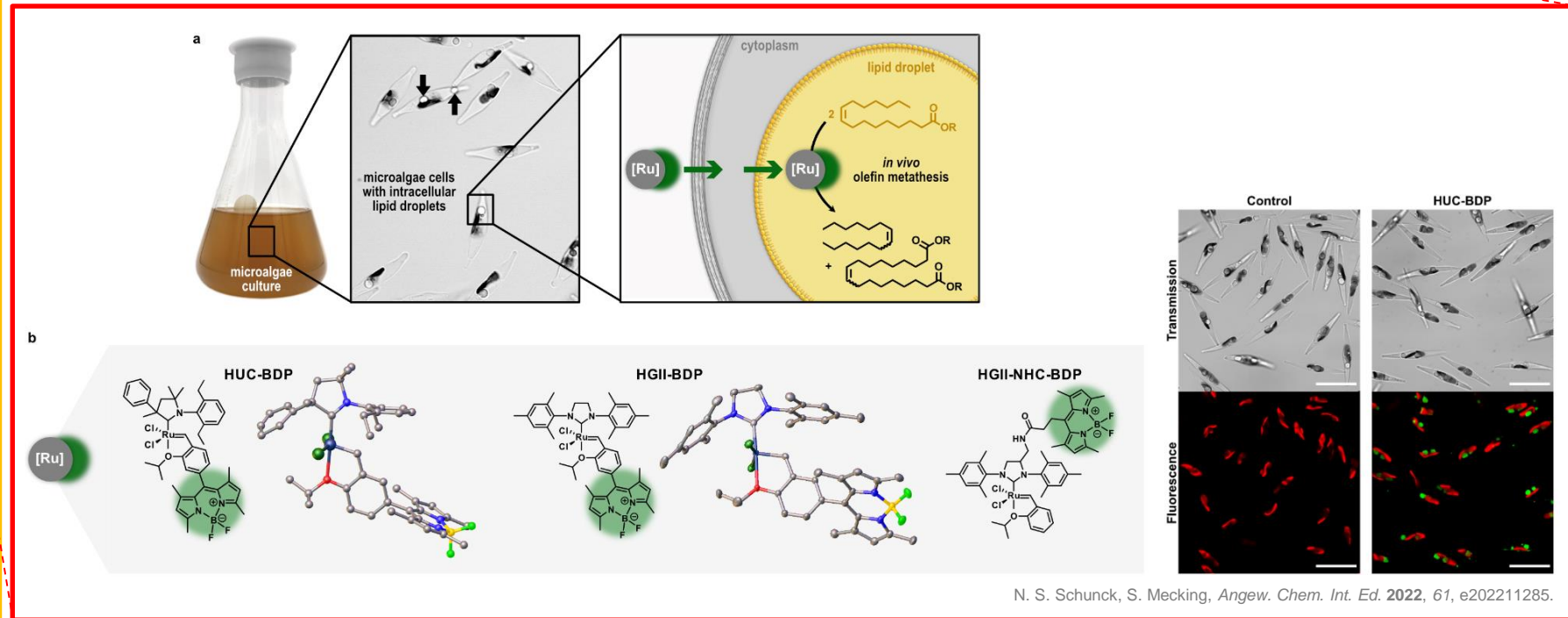


Häußler, M., Eck, M., Rothauer, D. *et al.* Closed-loop recycling of polyethylene-like materials. *Nature* 590, 423–427 (2021).

Synthetic approach

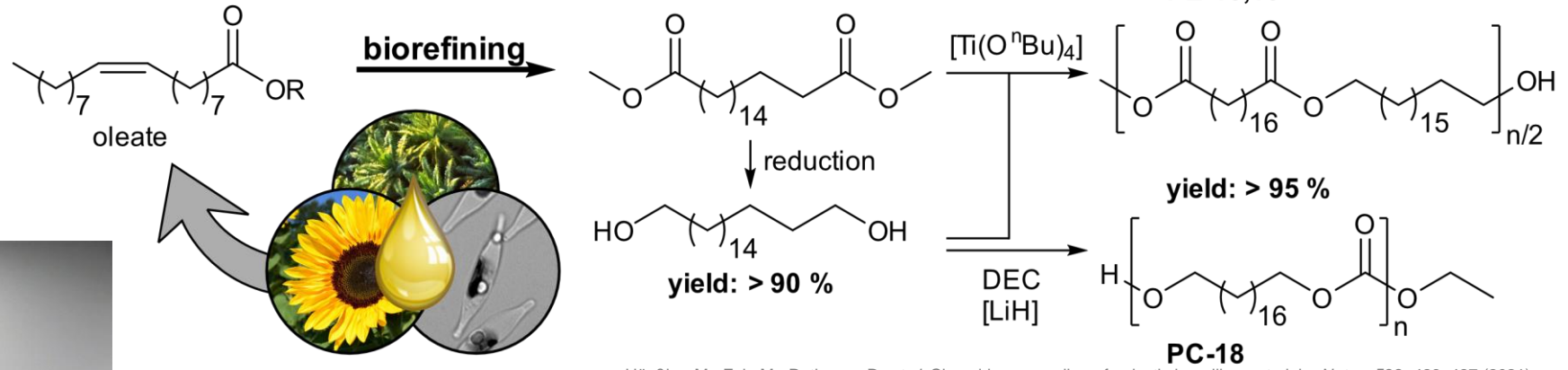


Häußler, M., Eck, M., Röthlisberger, D. et al. Closed-loop recycling of polyethylene-like materials. *Nature* 590, 423–427 (2021).

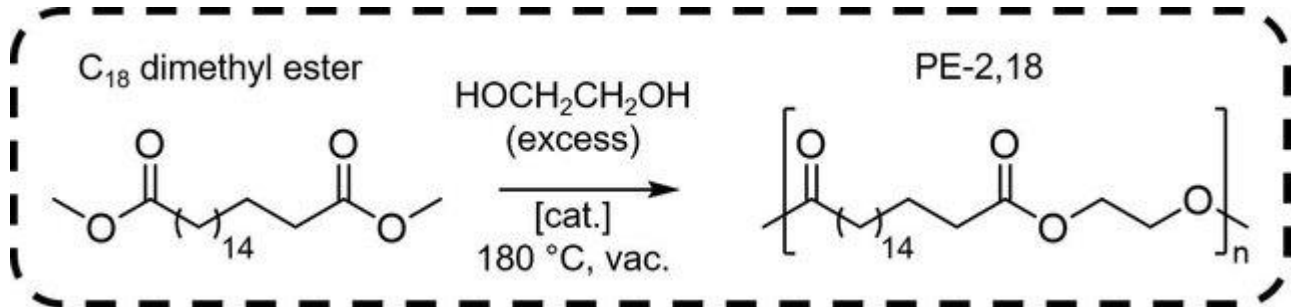
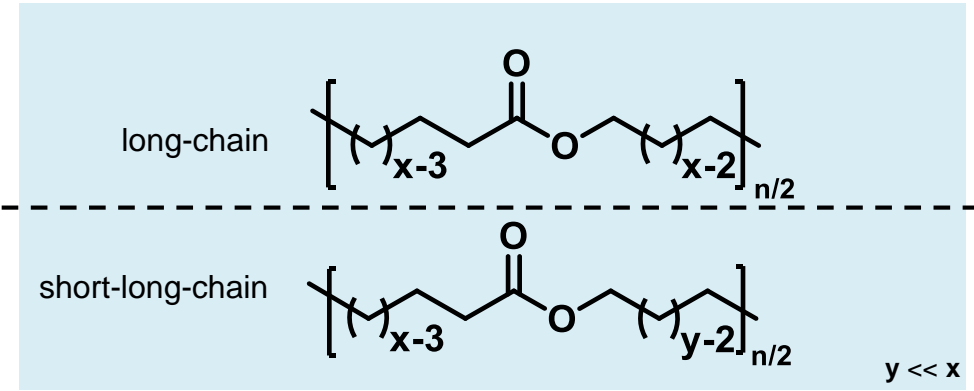
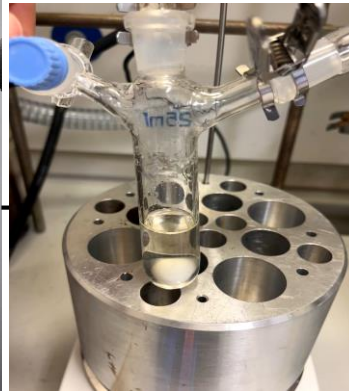


N. S. Schunck, S. Mecking, *Angew. Chem. Int. Ed.* 2022, 61, e202211285.

Synthetic approach



Häußler, M., Eck, M., Rothauer, D. et al. Closed-loop recycling of polyethylene-like materials. *Nature* 590, 423–427 (2021).

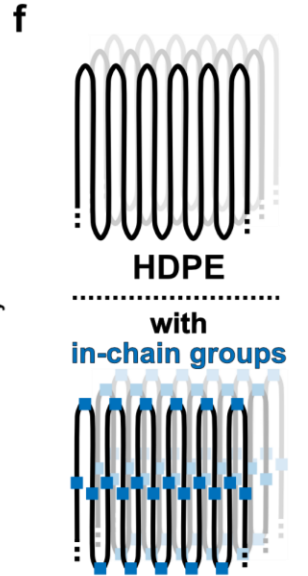
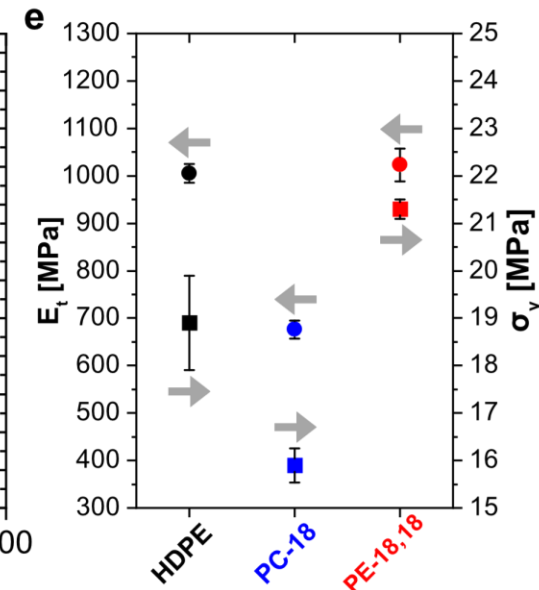
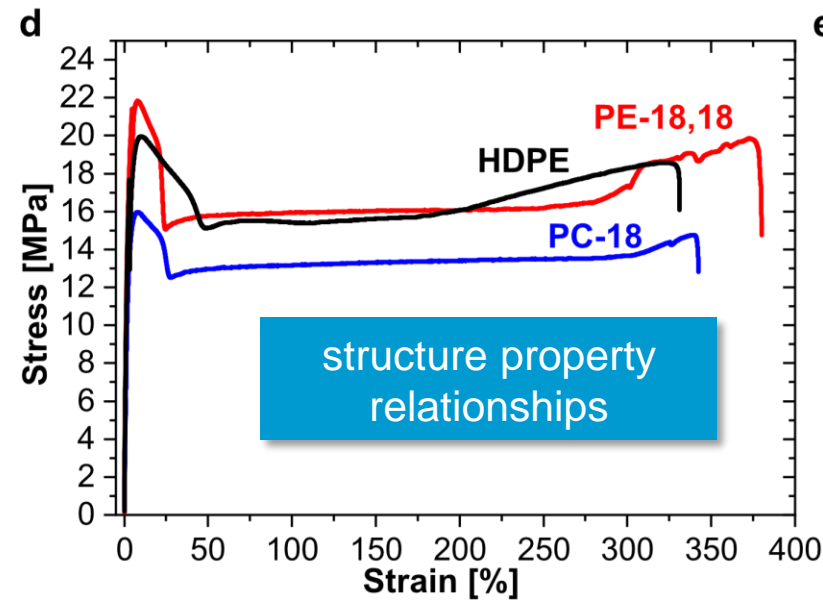
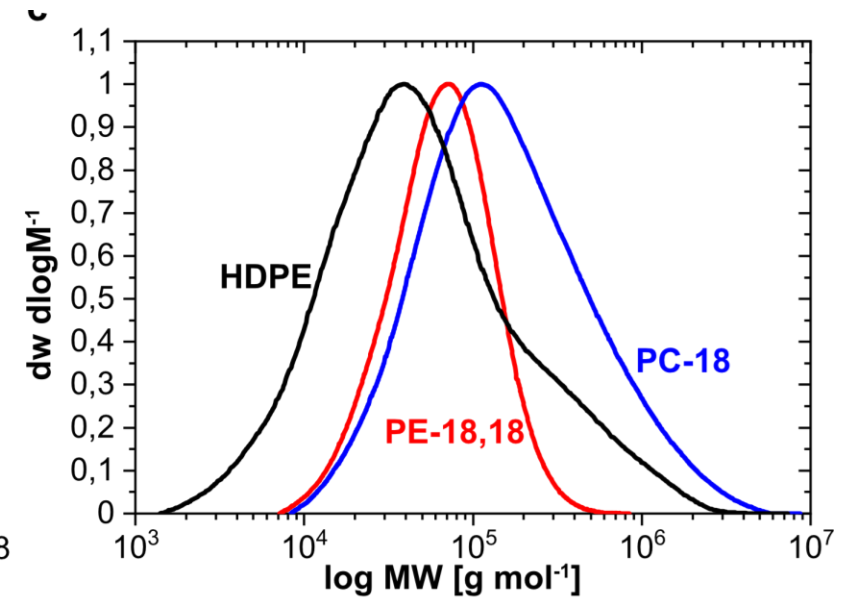
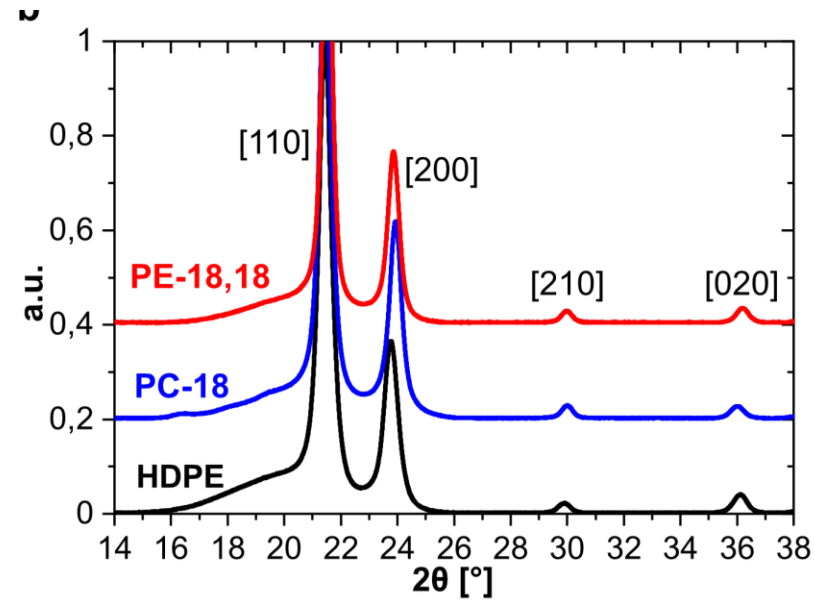
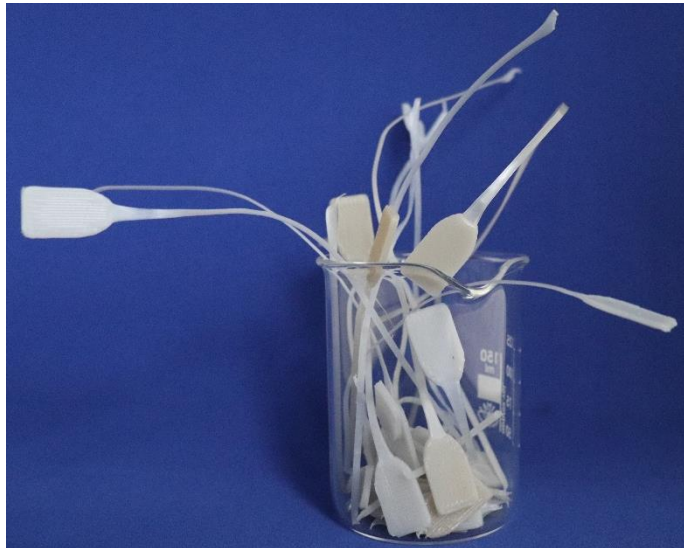


Eck, M. et al. Biodegradable High-Density Polyethylene-like Material. *Angewandte Chemie International Edition* vol. 62 (2022).



uncomplicated synthesis
(also on larger scales)

Properties



Small scale processing equipment



compounder

Xplore MC-5



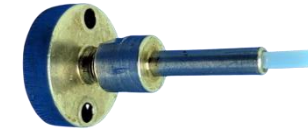
cast film line

Xplore CFL-35



Strand Pelletizer

Collin Teach Line SP



filament extruder

(custom)



3D-Printer

Prusa i3 MK3



compounder

Xplore MC-15

continuous feeding unit



conditioning unit

fiber line

Xplore FL

winding unit



injection moulder

Xplore IM-5.5



filament maker

3devo Precision 350



3D-Printer

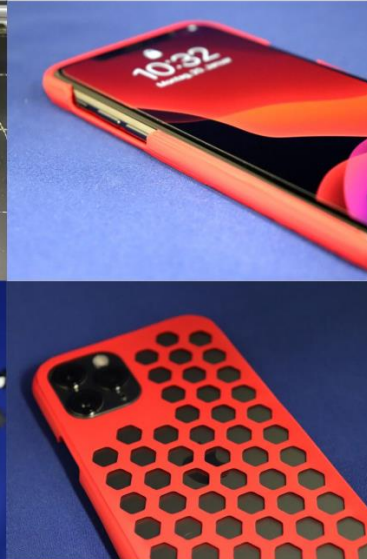
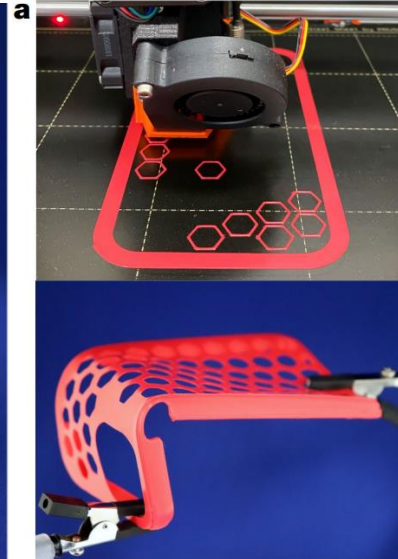
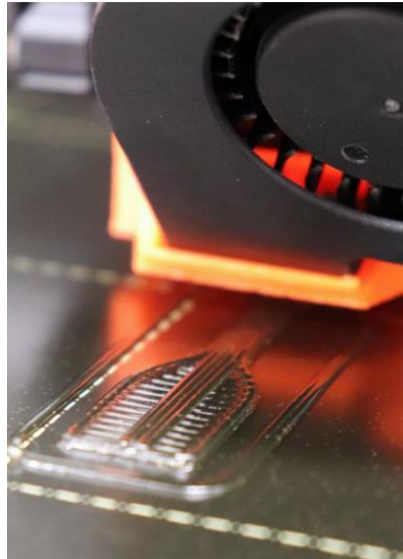
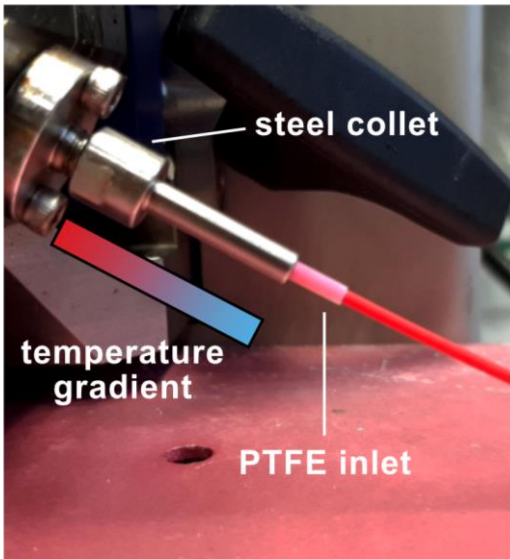
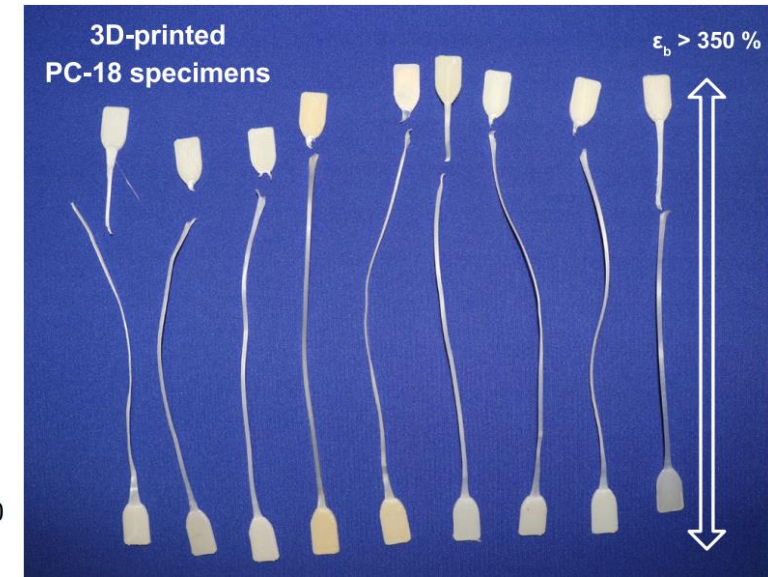
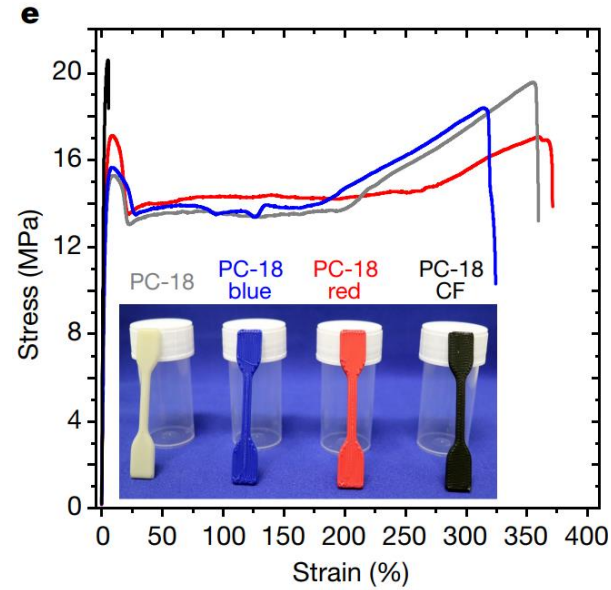
Ultimaker 2+

Processing

Easily processible

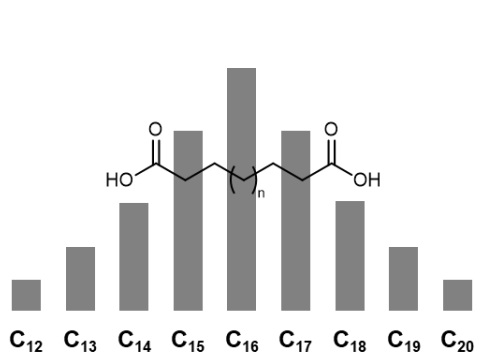
- injection-Moulding
- filament production
- 3D-printing
- compatible with colorants, carbon fibers

Filament diameters:
1.75 mm \pm 0.02 mm
(around 1 %)

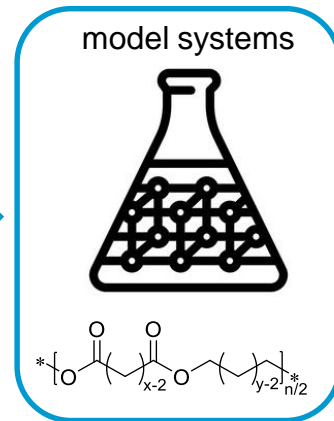


Häußler, M., Eck, M., Rothauer, D. *et al.* Closed-loop recycling of polyethylene-like materials. *Nature* 590, 423–427 (2021).

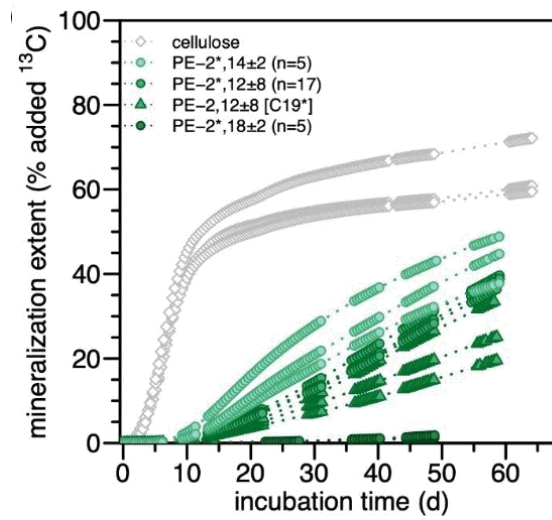
New materials – from waste



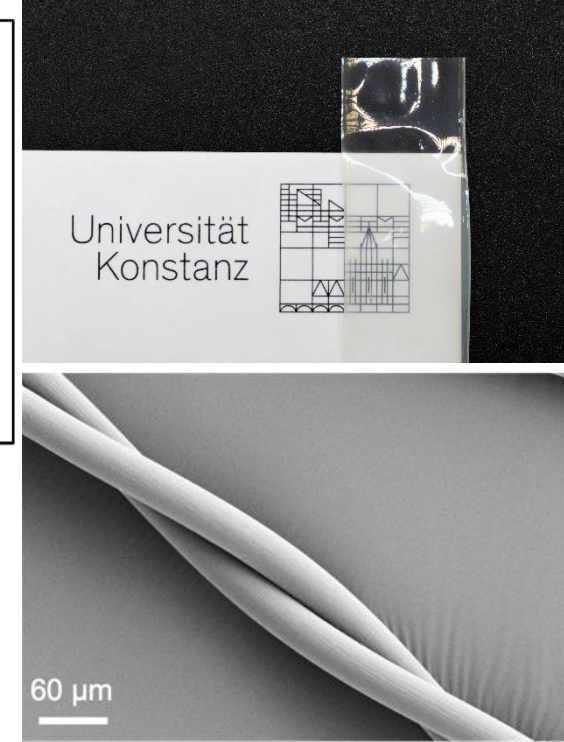
polymerization



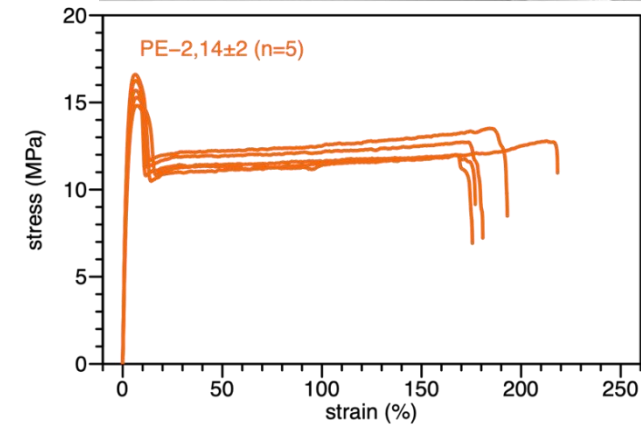
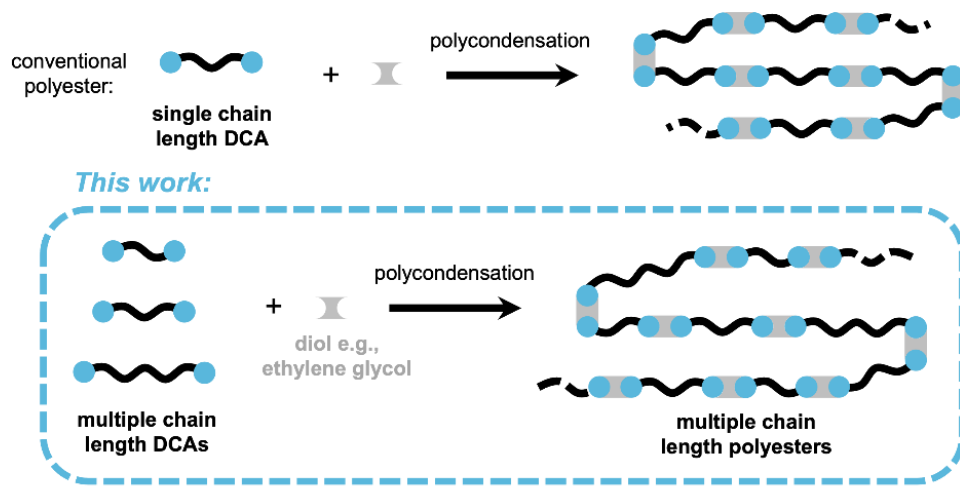
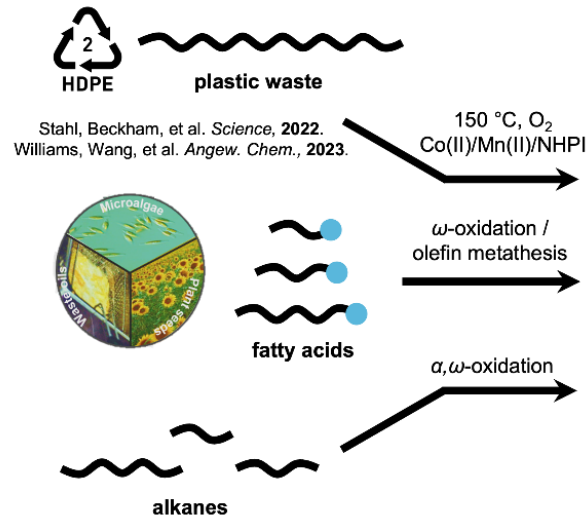
New generation of polyesters



degrade in soil



Recycling of HPDE



good mechanics

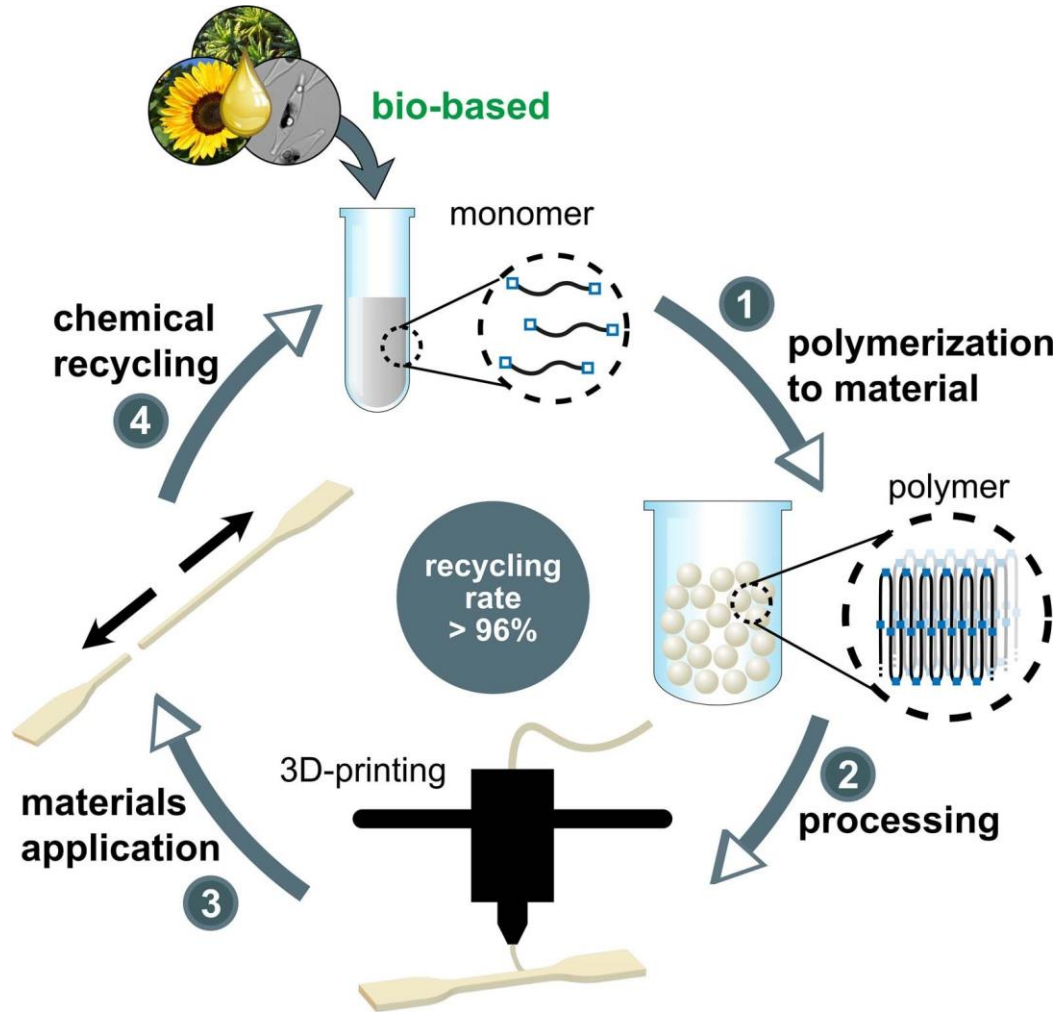
Nelson, T. F.; Rothauer, D.; Sander, M.; Mecking, S.: Degradable and Recyclable Polyesters from Multiple Chain Length Bio- and Waste-Sourceable Monomers. *Angewandte Chemie International Edition*, 62 (2023).



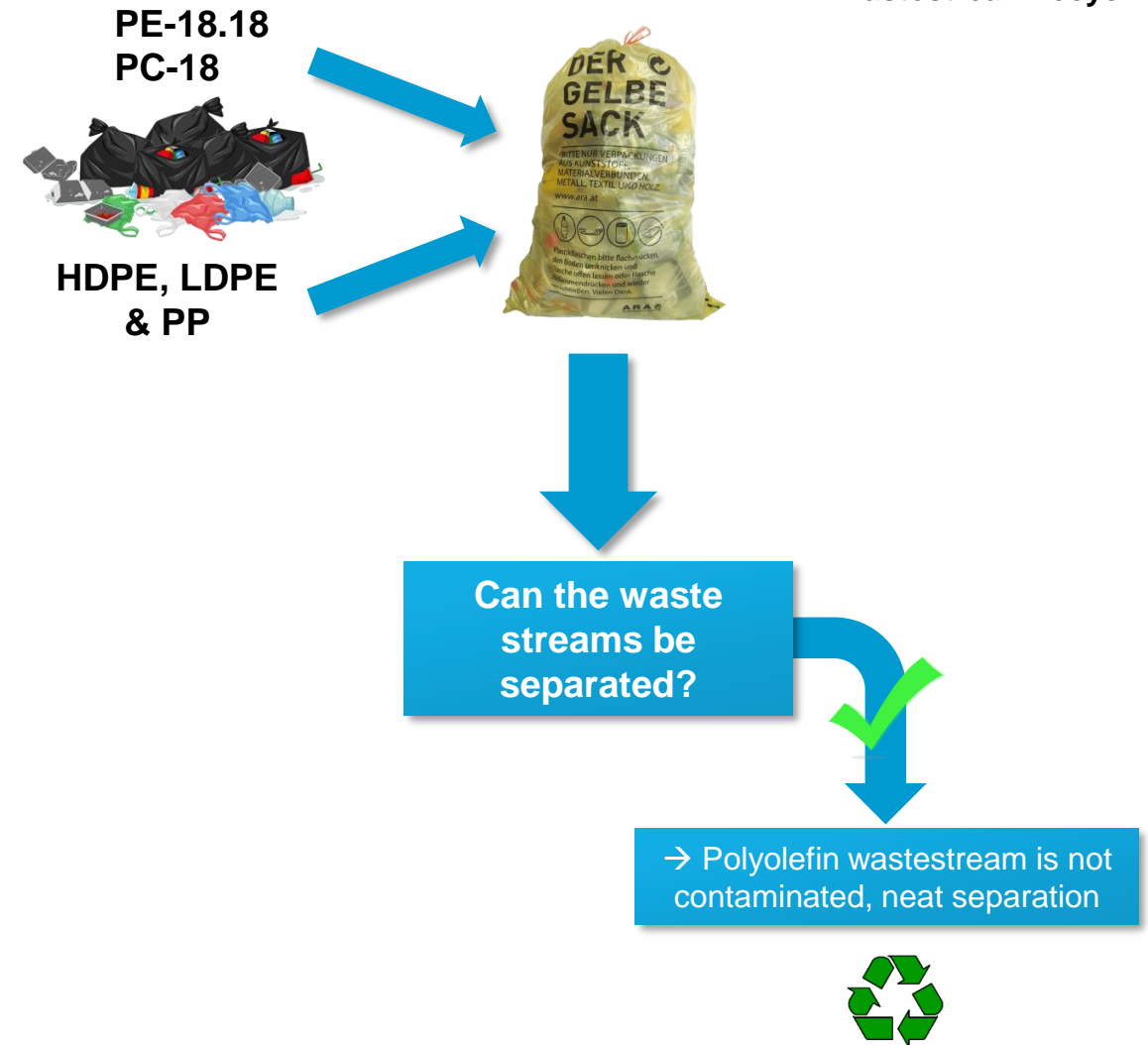
Recycling

Recycling concept

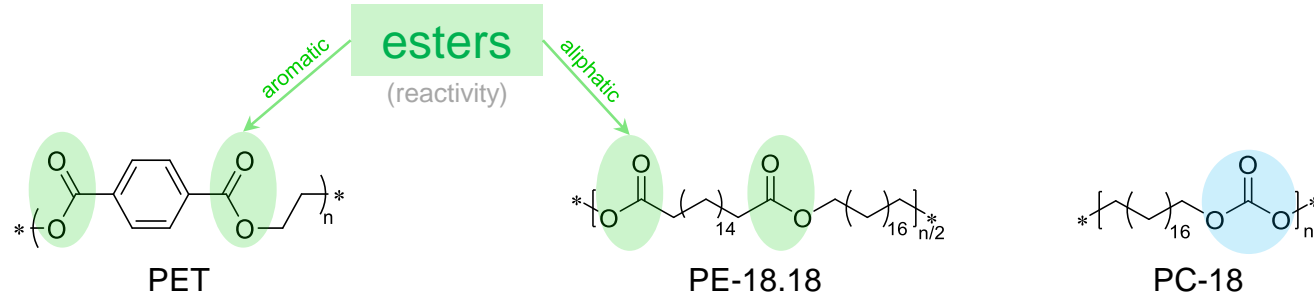
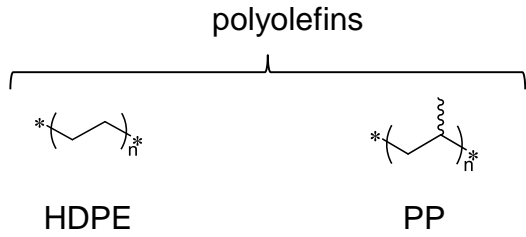
closed-loop recycling



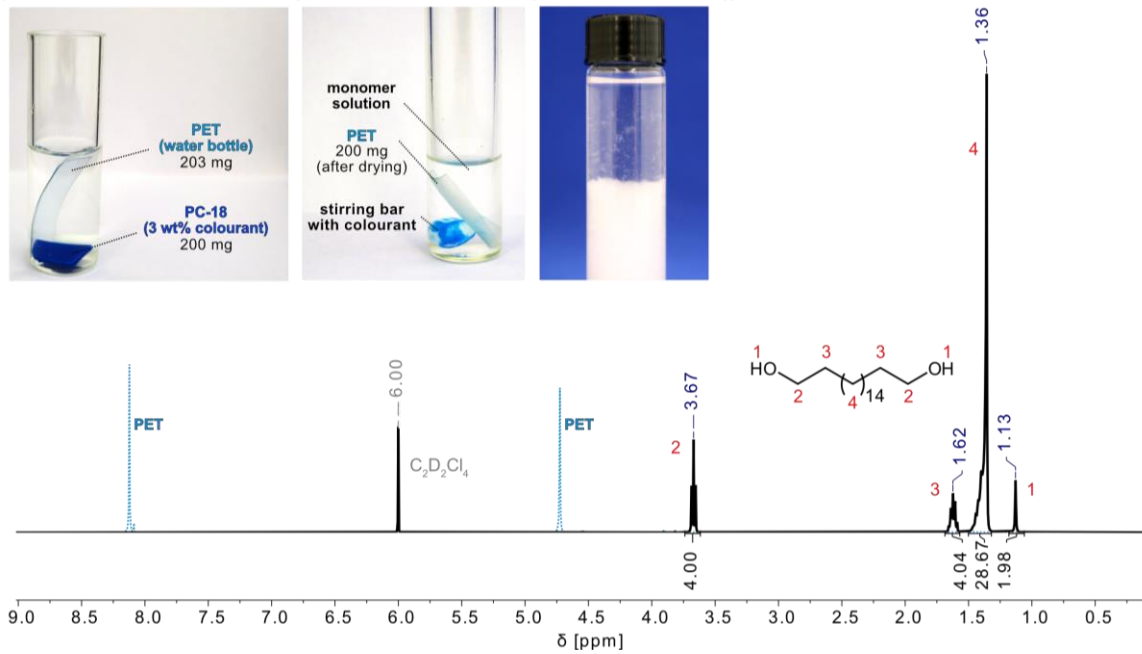
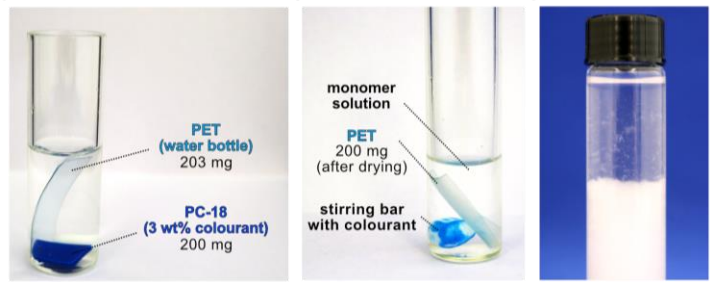
wastestream recycling



Recycling and waste stream separation



Häußler, M., Eck, M., Rothauer, D. *et al.* Closed-loop recycling of polyethylene-like materials. *Nature* 590, 423–427 (2021).



1

20.0 g
3D-printed
PC-18
specimens

2

17.91 g
long-chain diol
monomer

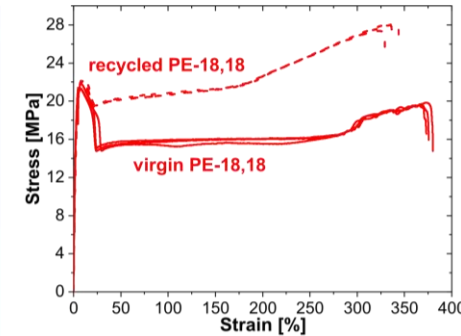
98 mol%
recovery

purity (GC): < 99%

3

19.25 g
PC-18

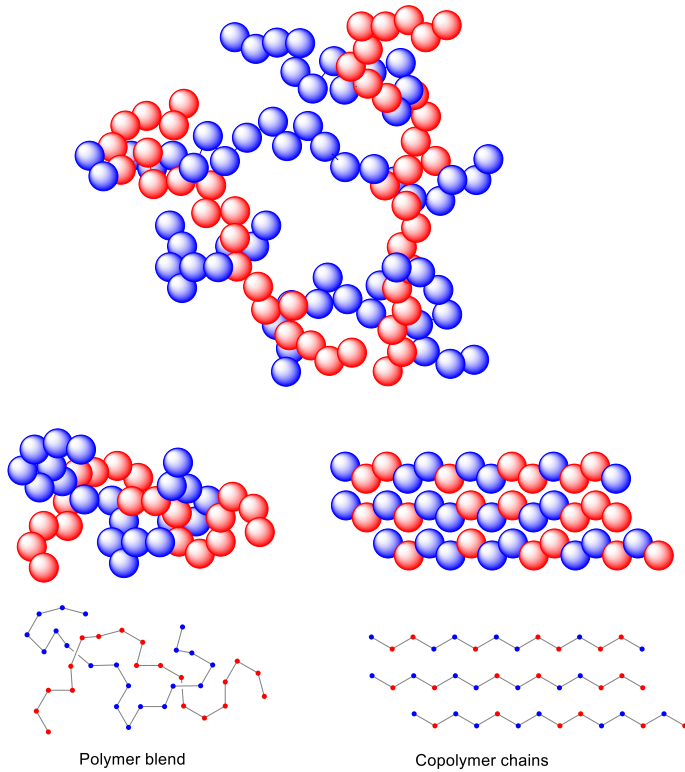
96%
polymer-to-polymer
recovery



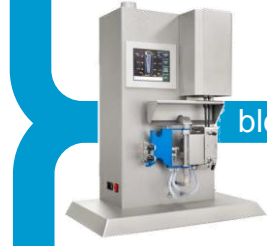
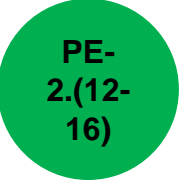
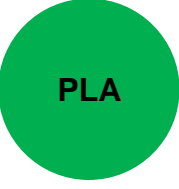
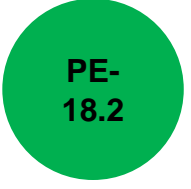
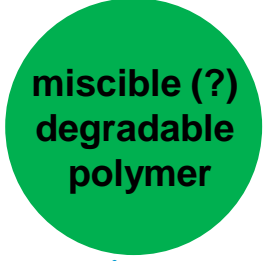
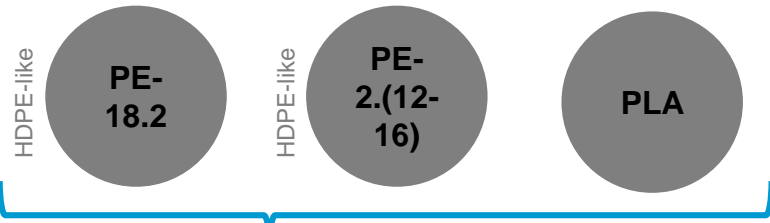


**Applications
&
Outlook**

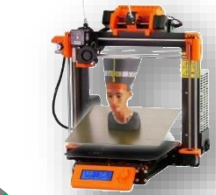
Outlook: Blending



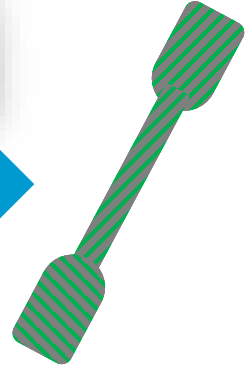
Blend: physical mixture of multiple polymers



blending



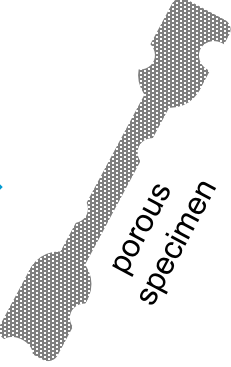
processing



separation



removed depolymerizable component



Blends:

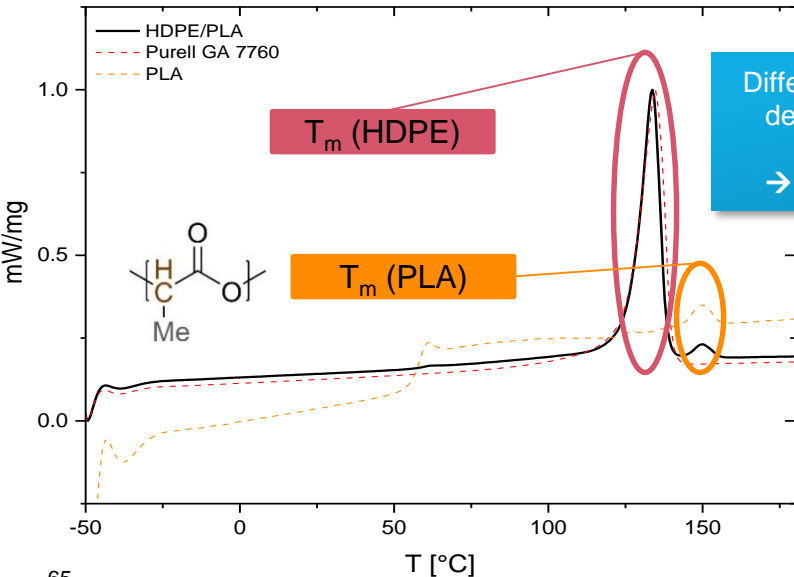
- Alter properties
- Optimize material
- Compatibilize with new materials („mediator“)



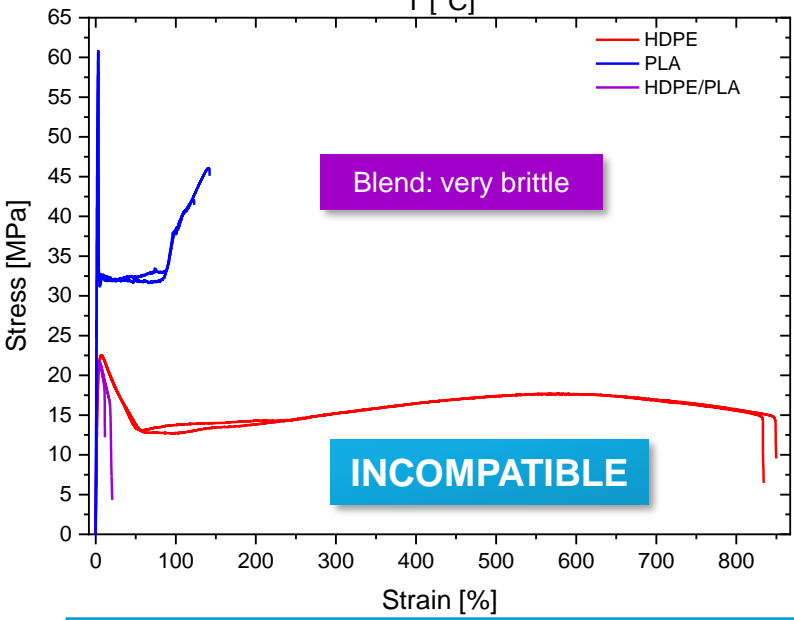
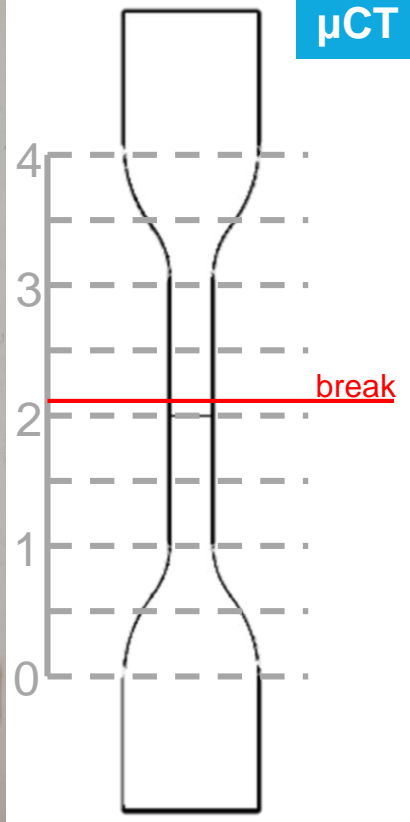
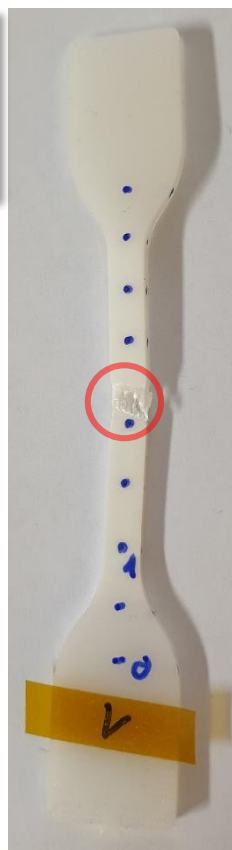
Blending – Reference blend: HDPE/PLA (80/20 wt%)

Exact composition:
 – 74 % HDPE
 – 26 % PLA
 (by ¹H NMR)

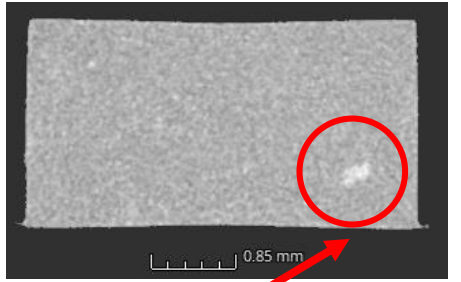
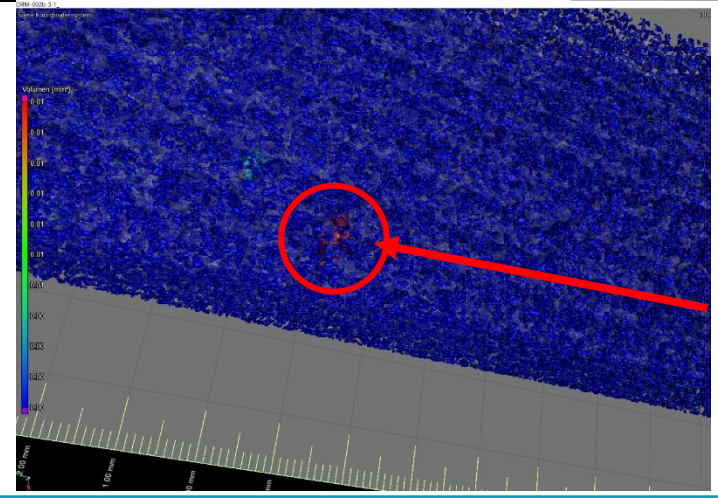
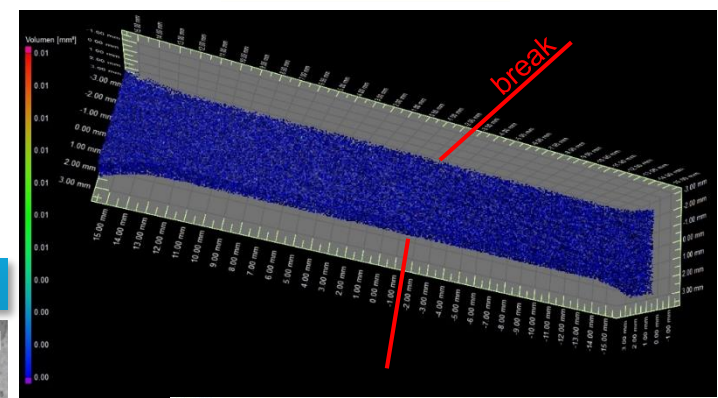
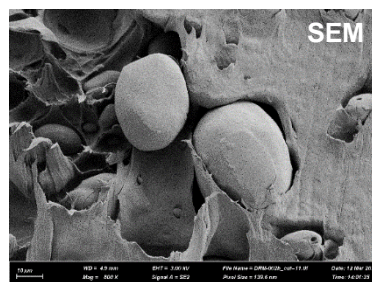
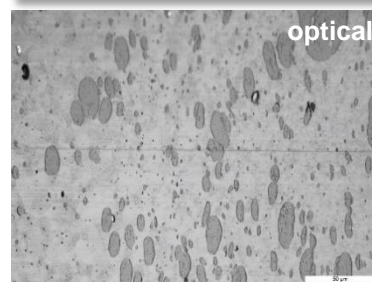
μCT



Different melting endotherms detectable for the blends!
 → No co-crystallization.



Visible phase separation

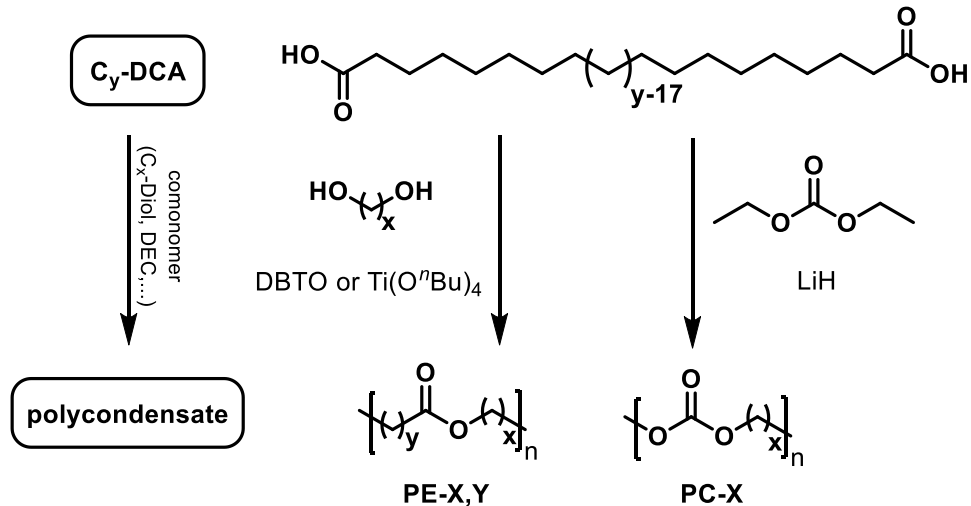


large PLA phase

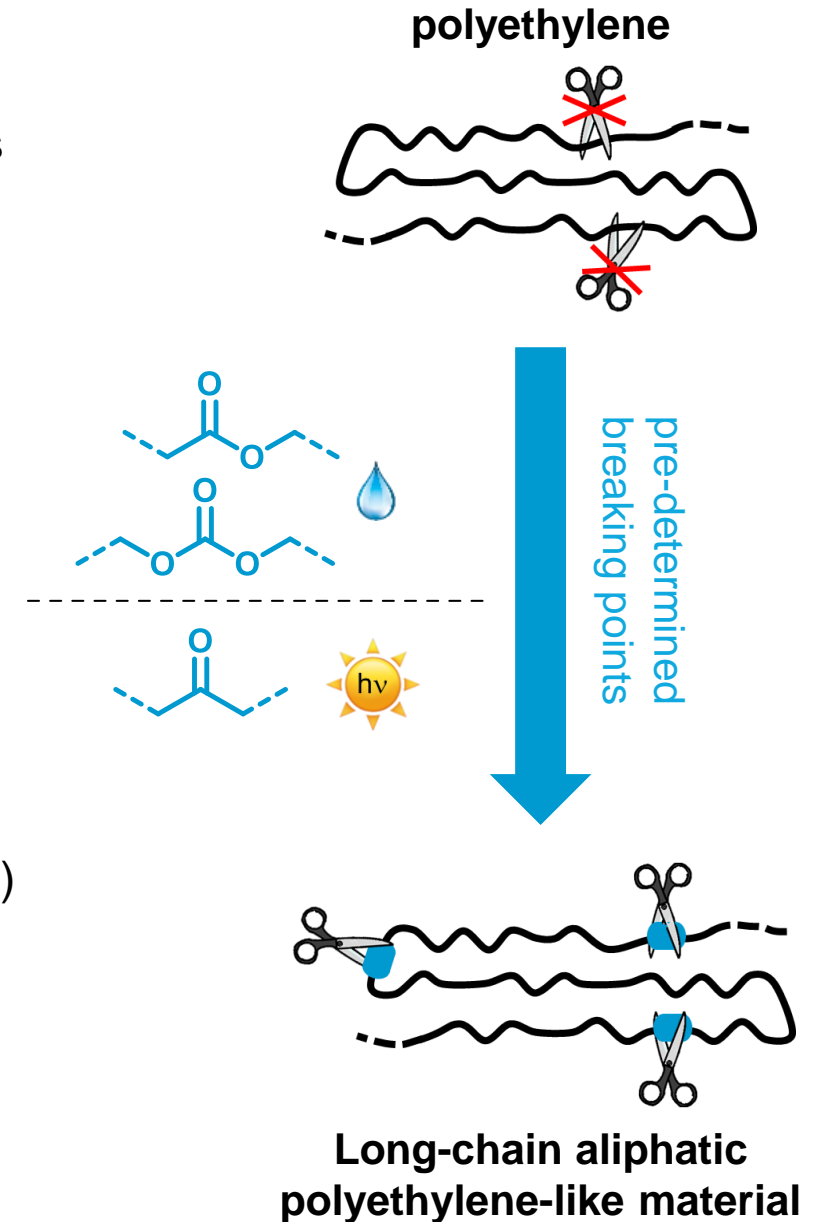
maXerial

Summary

- PE: persistent in nature: hydrocarbon chains → Introduce breaking points
- Scalable, robust syntheses from renewable feedstocks (HDPE waste)



- PE-like properties (structure, mechanics, high molecular weights possible)
- processible, blendable, 3D-printable
- closed-loop chemically recyclable (recovery through monomer)
- separable from waste stream
- degradable

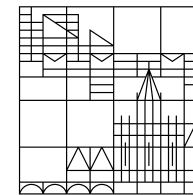


**Coffee Lectures:
Polymers at
OST**

Thank you!

**Closed-loop recyclable
polyethylene-like materials**

Universität
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Polymers
for the Future



OST COFFEE LECTURES 2024



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Dario Rothauer, 09.04.2024

Ostschweizer Fachhochschule (OST)