Renewable polyether polyols via the hydrogenation of polyesters

Bernhard M. Stadler Sandra Hinze, Sergey Tin and Johannes G. de Vries

Plastic soup

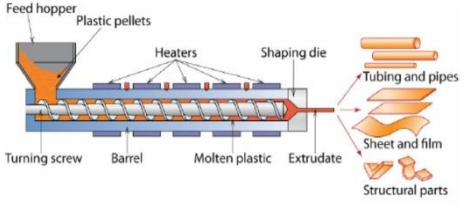
Picture: D. Cressy, *The Plastic Ocean*, Nature, **2016**, *536*, 263-265.

What to do with all the plastic

- Thus far 8.3 billion metric tons of plastic have been produced since the 1950's.
- Only about 9% of all plastic is recycled.
- About 12% is incinerated
- The remaining 80% went into landfills or is floating around.
- It is clear that recycling plastic could be a great solution.
- How can we do that?

Polymer recycling - Overview

Mechanical recycling

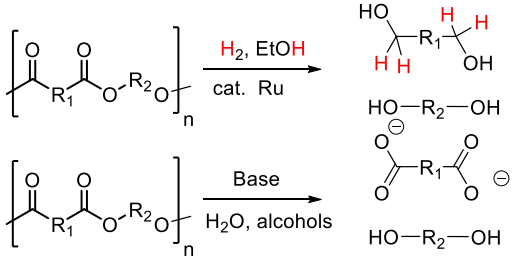


- Relative easy to implement
- Applicable to a wide range of thermoplastic polymers
- Reduced mechanical properties
- Usage of the products in food contact applications is prohibited

Cracking

- Resulting product can be directly used in existing processes
- PE, PS, PP preferred
- Energy input for the monomer synthesis + polymerization needs to be spent again

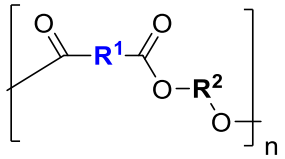
Depolymerization



- Typically very pure products
- Complementary to cracking, as polyesters, polycarbonates and polyamides can be used
- Polymers need to be soluble or melt below catalyst decomposition T; Hydrolysis ➔ Lots of salt
- Obtained products may not be cost competitive to virgin monomers

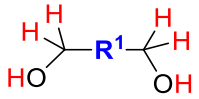
Review: B. Vander Beke, *ChemSusChem* **2014**, *7*, 1579-1593

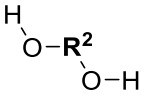
Polyesterhydrogenation – Recent examples

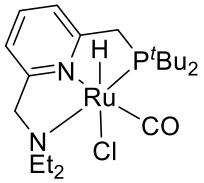


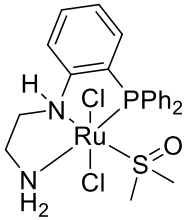
H_2

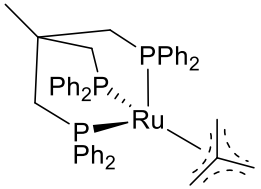
Catalyst, Additive











Robertson, *Chem. Commun.*
2014, *50*, 4884-4887.

T=120°C, $p(H_2)$=54 bar, *t*=48 h
Substrat/Cat: 20-50
Additive: KO^{t}Bu

Substrates: Polylactide, Polycarbonate

M. L. Clarke, *Chem. Eur. J.*
2015, *21*, 10851-10860.

T=120°C, $p(H_2)$=54 bar, *t*=48 h
Substrat/Cat: 50
Additive: KO^{t}Bu

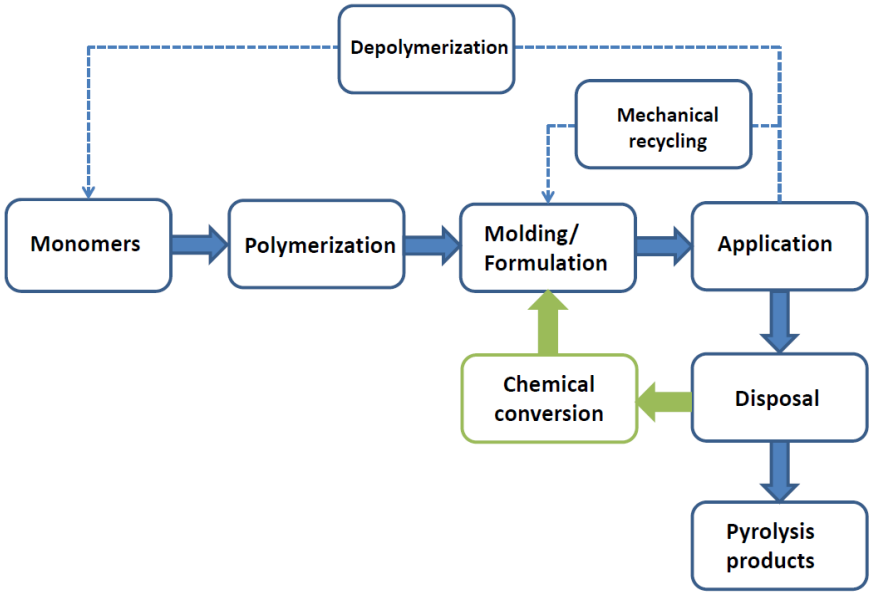
Substrates: PET

Klankermayer, *Sci. Adv.*
2018, *4*, eaat9669.

T=140°C, $p(H_2)$=90 bar, *t*=16 h
Substrat/Cat: 100-200
Additive: $HN(Tf)_2$

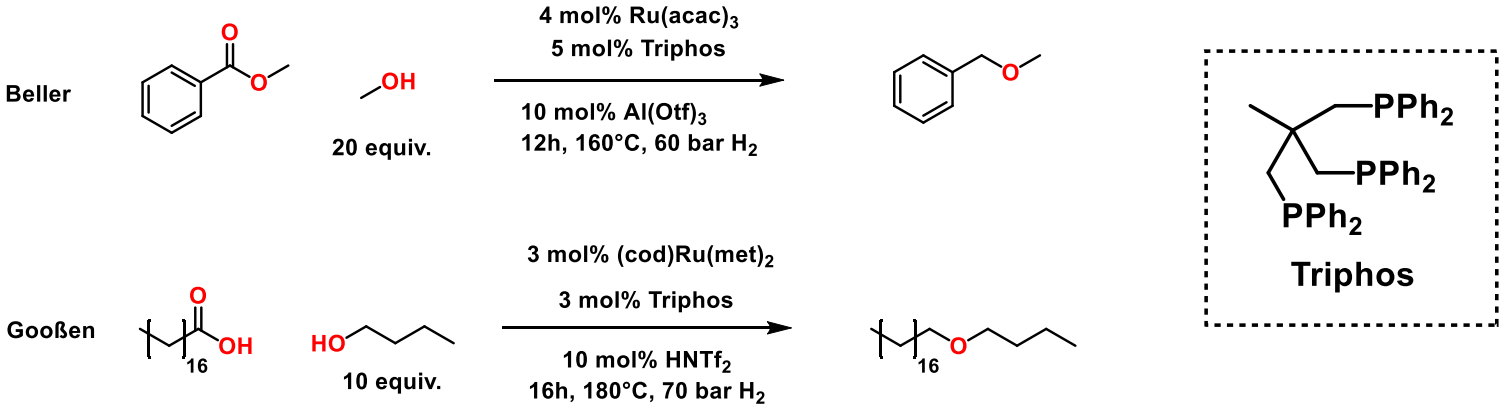
Substrates: PET, Polylactide, Polycarbonates, Aliphatic Polyesters

The Dilemma

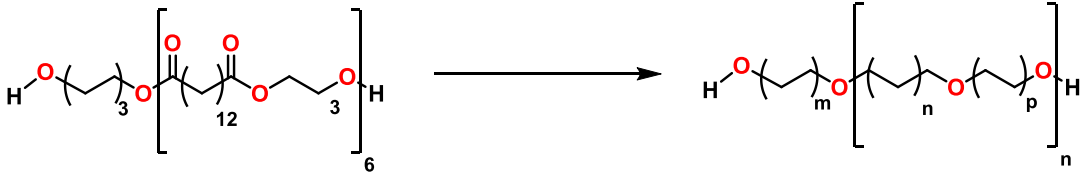


- Depolymerisation to monomers by hydrogenation or hydrolysis needs to compete with low feed-stock prices
- Chemical conversion of polymers could turn plastic waste into a source for new materials

Reductive etherification



What about polyesters?



Industrially used oligomer

Potentially new oligomer

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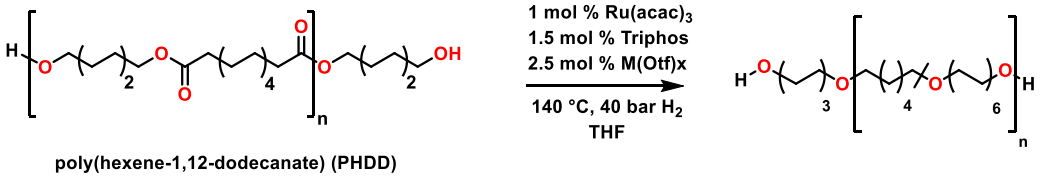
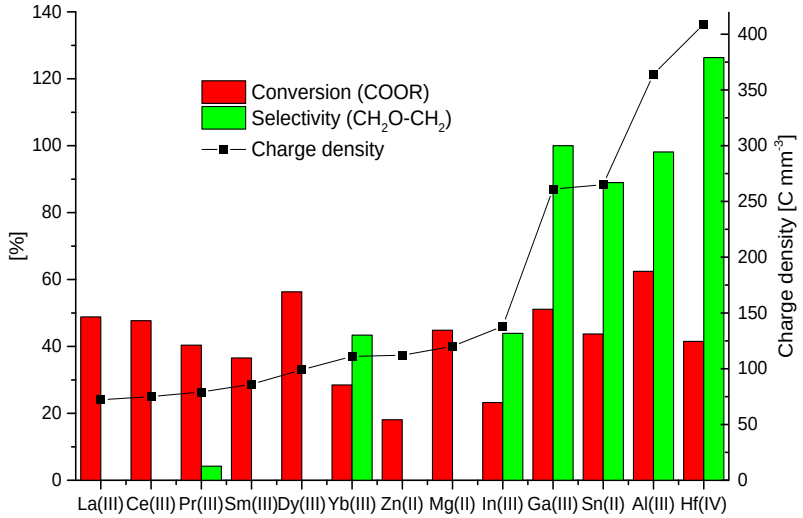
Hydrogenation of polyesters to polyethers



poly(hexene-1,12-dodecanate) (PHDD)



- Selectivity for ether formation increases with charge density of LA
- Hafnium triflate interestingly increase selectivity over 120% which is due to catalytic THF ring- opening. Conversion of THF to *n*-dibutyl ether at high T and p(H2) has been observed in the presence of Hf (T. J. Marks, *J. Am. Chem. Soc.* **2014**, 136, 104-107.)

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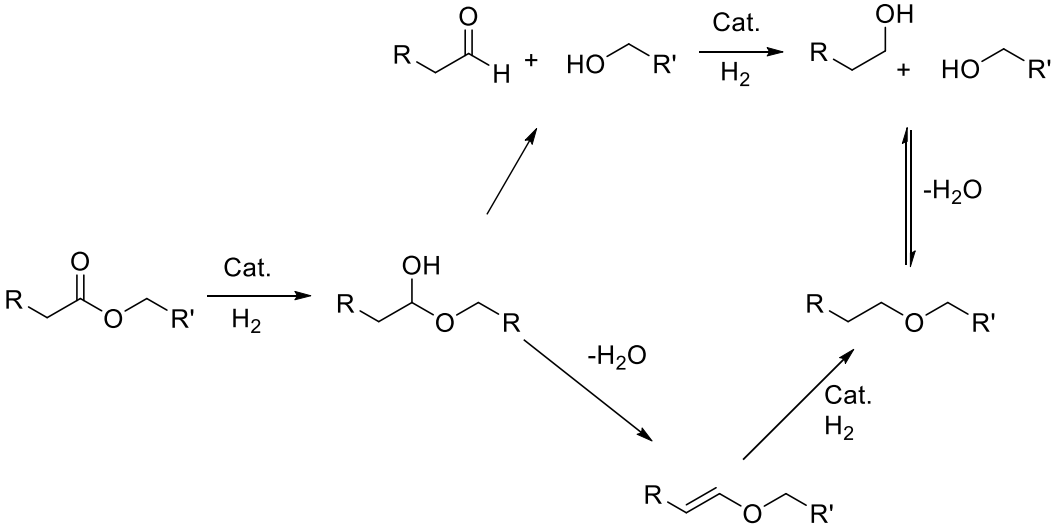
How does this reaction work?

Two mechanistic proposals



Mechanistic proposals: M. Beller, *Angew. Chem. Int. Ed.* **2015,** *54*, 5196-5200 Gooßen, *ChemSusChem* **2016**, *9*, 1442-1448

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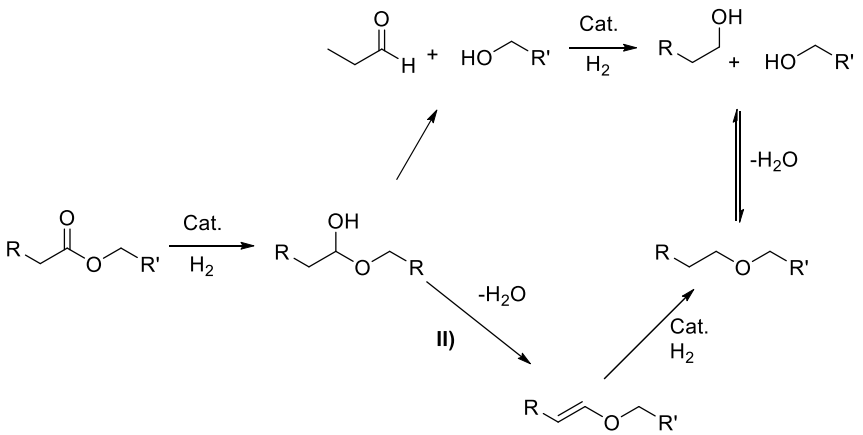
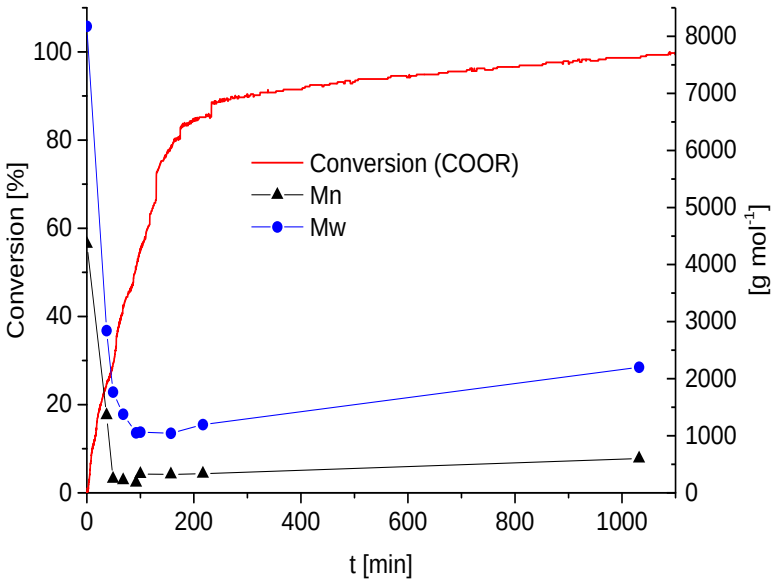
Monitoring of the Mw over time

- In the first mechanism the chain is broken and MW should drop.
- In the second mechanism the M_W of the polymer should remain the same.





➔ A tandem sequence of hydrogenation to diols and etherification is observed

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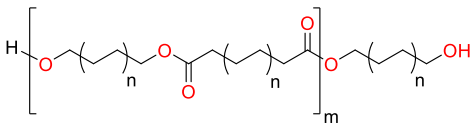
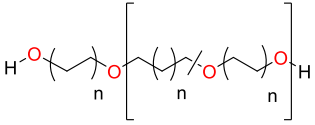
Scope and limitations of industrial samples

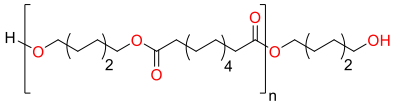


3 mol % Ru(acac)3
4 mol % Triphos
7.5 mol % Al(OTf3)

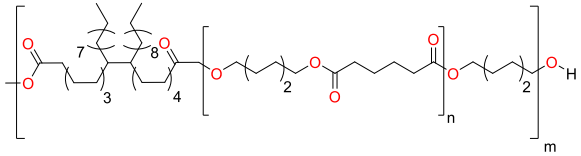
140 °C, 40 bar H2
THF



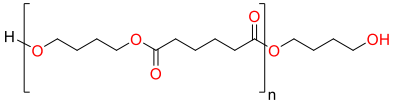
X: Conversion of COOR
Y: yield of -CH2O- groups



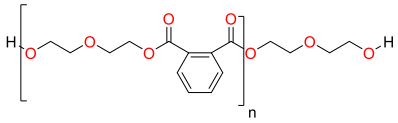
poly(hexene-1,12-dodecanate) (PHDD)
X:99% Y:80% Mn(NMR):614 g/mol Mn(GPC): 600 g/mol



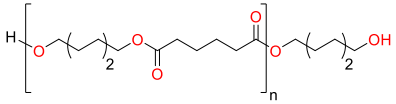
poly(hexene-1,6-adipate-co-distereate) C36-co-PHA
X:99% Y:80% Mn(NMR):1000 g/mol Mn(GPC): 1500 g/mol



poly(butyl-1,4-adipate) PBA
X:99% Y:90% Mn(NMR):563 g/mol Mn(GPC): 700 g/mol



poly[(2-(ethoxy)ethyl)-phthalate] PEGP
X:50% Y:n.d mixture of polyether and polyester



poly(hexene-1,6-adipate) PHA
X:96% Y:90% Mn(NMR):892 g/mol Mn(GPC): 900 g/mol

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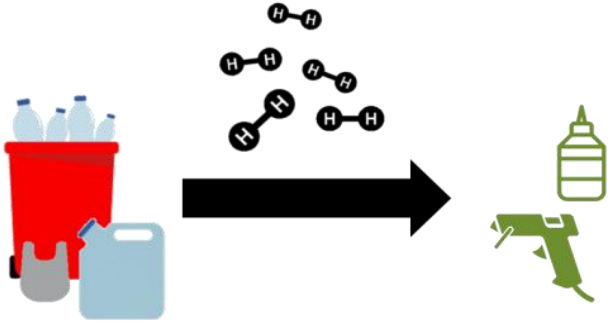
Are the polyethers useful? Yes they are.

- The formed polyether polyols have exactly the right size for use in adhesives.
- Preliminary experiments in which one of the polyether polyols was reacted with 2,4-toluenediisocyanate showed formation of a transparent film with a leather like haptic.



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