Lecture 3:
Biodegradable Polymers

Learning outcomes

By the end of todays lecture you should be able to:

(i) discuss what ‘biodegradability’ means, and why it is important in the context of polymer chemistry;

(ii) list the different types of biodegradable polymers;

(iii) describe in detail what factors effect the degradation rates of polyesters.

Why are biodegradable polymers important?

In groups of 2-3, you have two minutes to come up with answers!

Environmental factors (avoidance of persistent plastics)

"Smart" applications
e.g. drug delivery devices agricultural mulches

And what is green and 'ungreen' about non-degradable polymers?

Green

Brown

What do we mean by a ‘biodegradable polymer’?

Lots of definitions!

e.g. European Union norm EN13432 defines a compostable material as:

‘ one possessing biodegradability (i.e. converted into carbon dioxide under microbial action’), disintegrability (i.e. fragmentation and loss of visibility in the final compost), and an absence of negative effects in the final compost (e.g. a low level of heavy metals).’

More important than definitions – what are the implications of polymer biodegradation?

- **Molecular weight decreases**
- **Crystallinity is destroyed**
- **Physical properties (e.g. mechanical strength) diminish**

A common misconception

In nearly all cases, biodegradable polymers will NOT degrade in landfill

Why?

Biodegradation is mediated by either microorganisms (i.e. bacteria, fungi) or by enzymes (*in vivo* degradation).

Such processes typically require water and oxygen i.e. aerobic conditions.

Deep inside landfills, the environment will be dry and anaerobic.

One major exception:
poly(hydroxyl alkanoates) - PHAs may degrade under anerobic conditions.

So what sorts of polymers are biodegradable?

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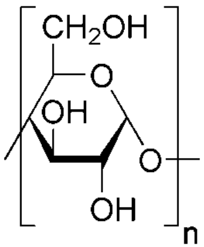
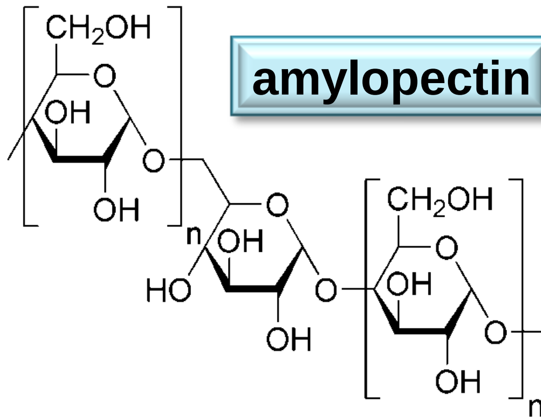
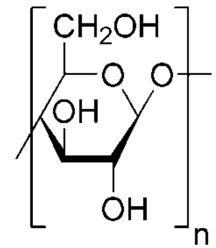
Type I:
Naturally occurring polymers

amylose





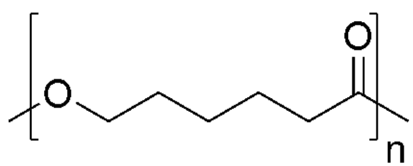
amylopectin



cellulose

Type II:
Polymers possessing a hydrolysable backbone

e.g. polyesters

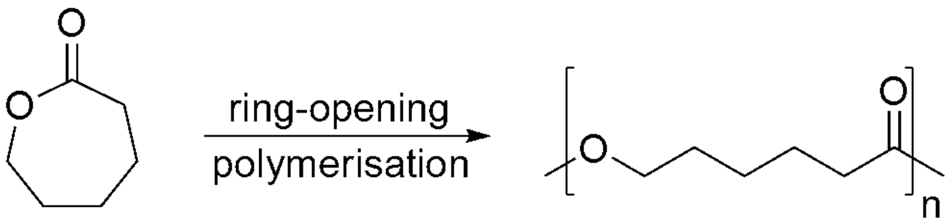


poly(caprolactone)

Type III:
Copolymers or blends of non-degradable polymers with type I or II polymers

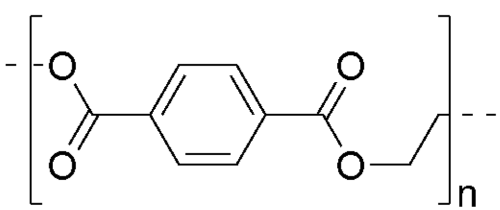
Type II: Polyesters

1973 - first report of a biodegradable polymer: poly(caprolactone)



degraded by numerous different enzymes

However, not all polyesters are biodegradable, e.g. poly(ethylene terephthlate)



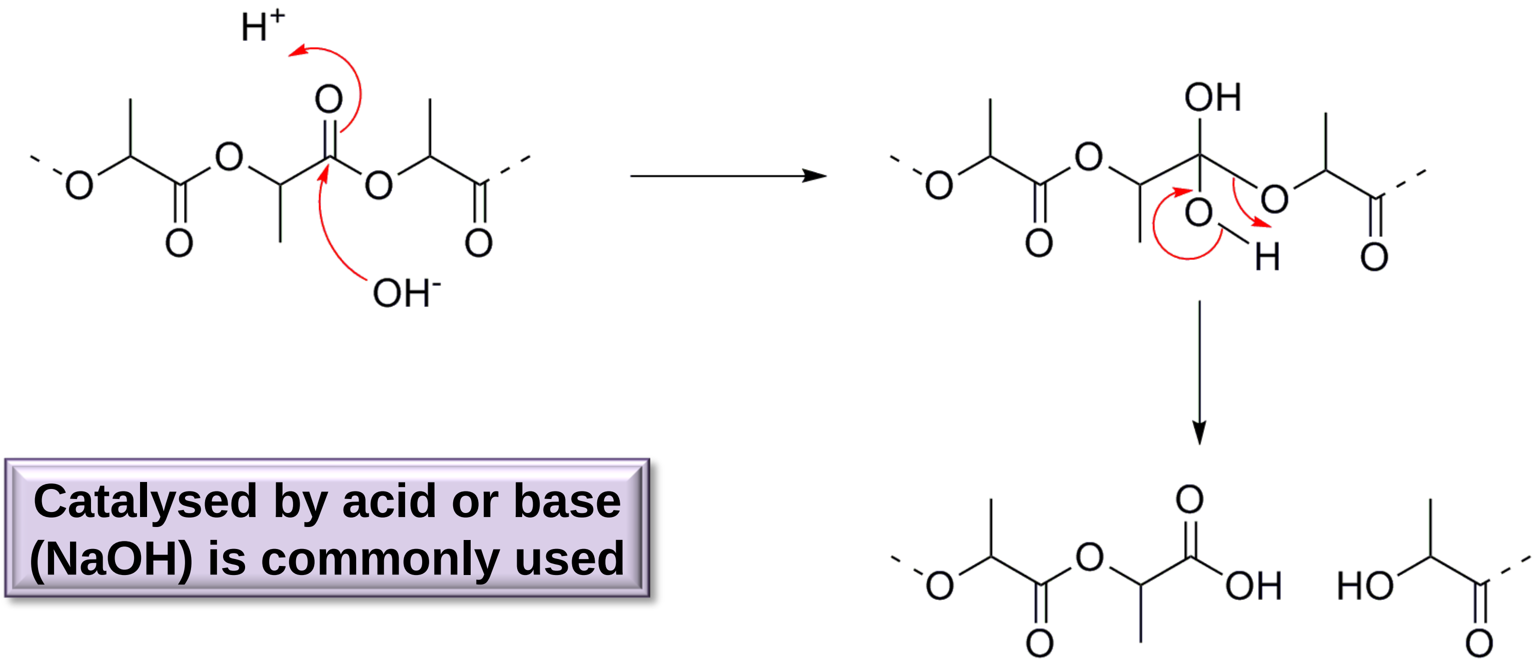
non-biodegradable

poly(ethylene terephthlate), PET

In order to access the active site of enzymes, aliphatic polyesters must be flexible

Type II: Poly(lactide)

Despite claims to the contrary, PLA is probably not biodegradable. However, it may be readily degraded chemically:



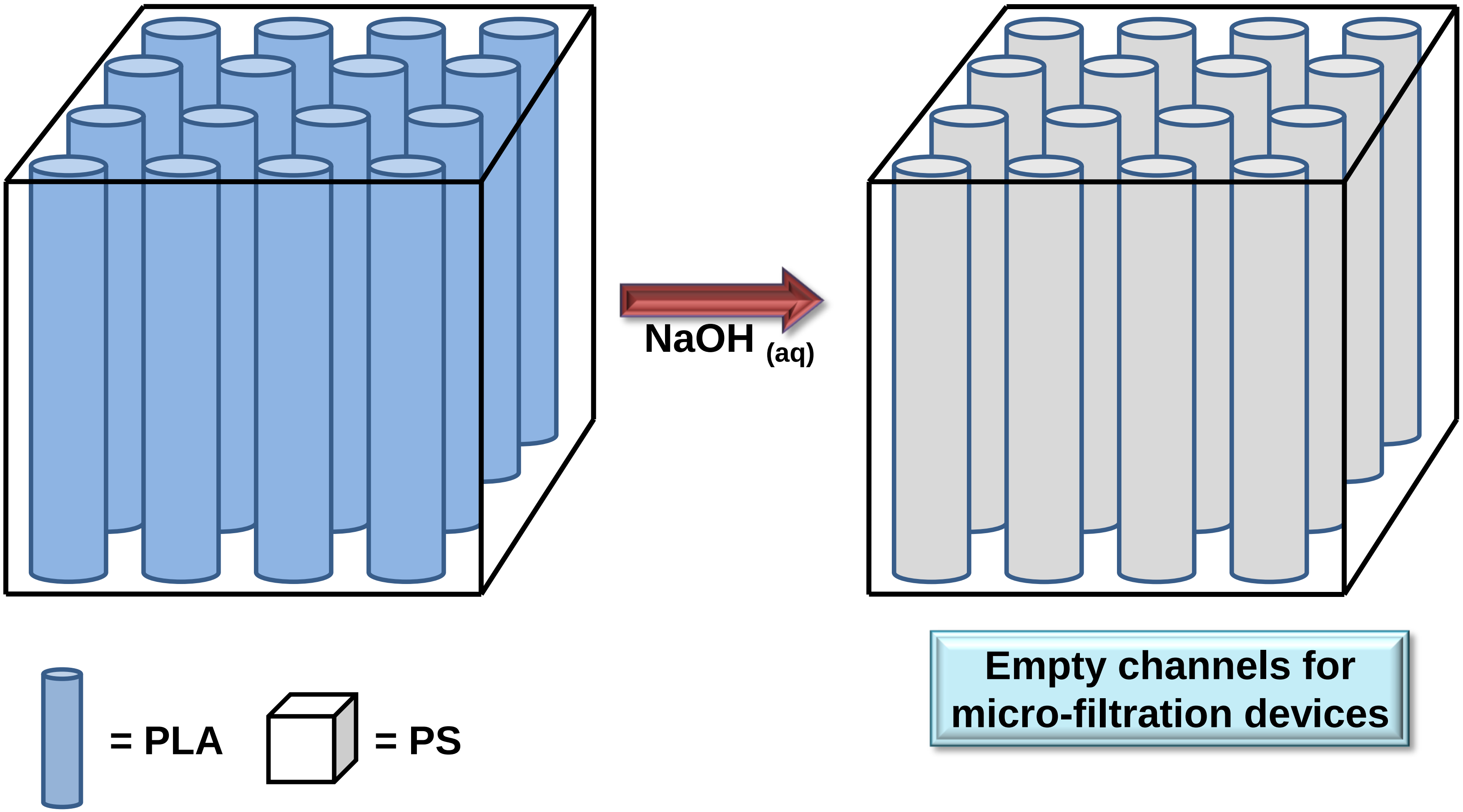
Catalysed by acid or base (NaOH) is commonly used

Ultimate product = lactic acid (degrades in vivo to CO_2 + H_2O)

The resistance of PLA to attack from bacteria and fungi is an advantage for food packaging applications

Application of the chemical degradation of PLA

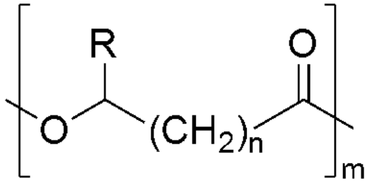
Columnar block copolymer of poly(lactic acid) – poly(styrene)



Empty channels for micro-filtration devices

Poly(hydroxyl alkanoates) - PHAs

General structure



R = C_1 – C_{13} alkyl group (all *R* stereochemistry)
n = 1 – 4
m = 100 – 30,000

PHAs are the manufactured by bacteria for energy storage (just as plants manufacture starch).

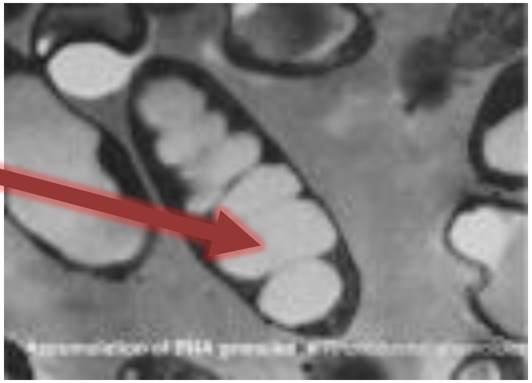
R = Me: poly(3-hydroxybutyrate) – P3HB
R = Et: poly(3-hydroxyvalerate) – P3HV

A very large number of PHAs are known (as well as copolymers), and their properties, applications, and degradation kinetics vary widely.

Properties	P3HB	P3HV	P4HB
Glass transition temperature, Tg (°C)	+4	-7	-50
Melting point, Tm (°C)	177	150	60
Tensile strength (MPa)	40	25	104
Elongation at break (%)	6	20	1000

PHAs are produced by a wide range of microorganisms, including *Pseudomonas, Bacillus, Rhodobacter,* cyanobacteria and marine algae, using a range of carbon sources.

Accumulation of PHA in rhodobacter sphaeroides



In order to be successfully used industrially, a cost-effective method for the extraction of PHAs from bacteria needs to be developed. P&G have commercialised a PHA called Novax at $2.20 / kg, but even this is not competitive.

One reason is the relatively low %-content of the bacteria stored as PHAs.

However, an alternative approach may be more promising...

Transgenics – a new type of chemical plant

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Monsanto, and now Metabolix have transferred the PHA synthase gene from bacteria into a variety of plants, such as switchgrass (perennial, grows in poor soil conditions).

Following harvesting and drying up to 90% of the dry mass = PHAs.

Degradation of PHAs

PHAs degrade via a variety of mechanisms:

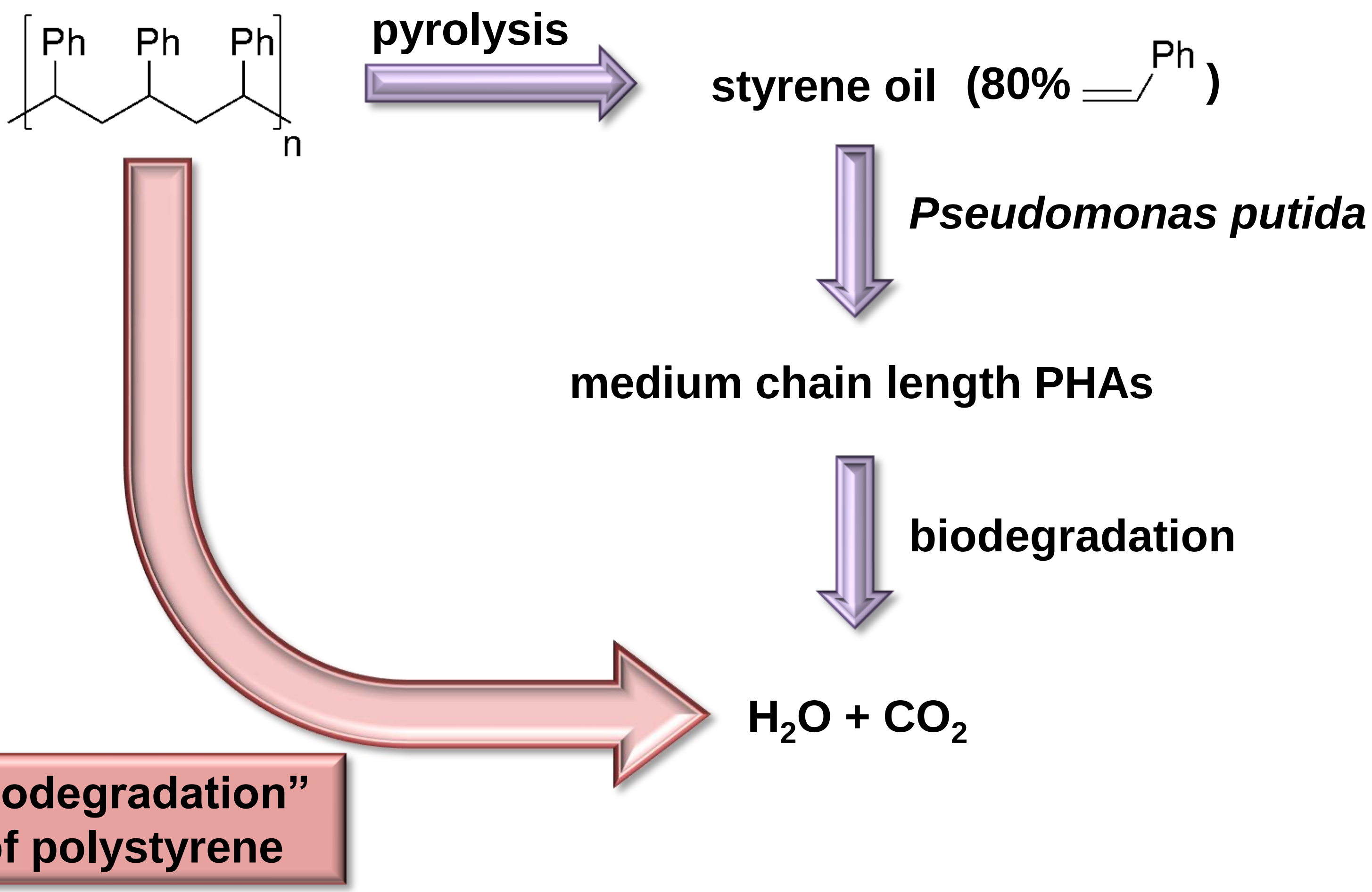
in bacteria: enzymatic hydrolysis

in animals or in the environment: enzymatic or chemical hydrolysis

Degradation follows typical rules seen earlier,

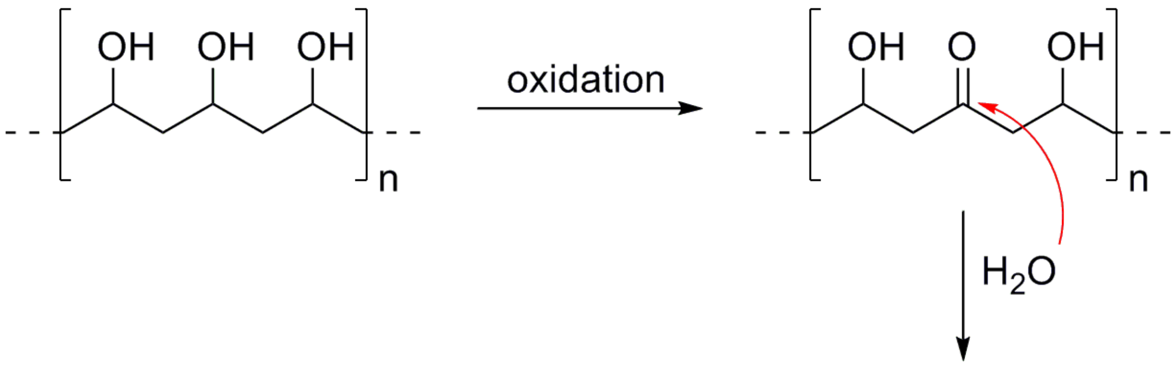
i.e. slowest for highest Tm, most crystalline, longer chain length etc

An interesting appliction of PHAs

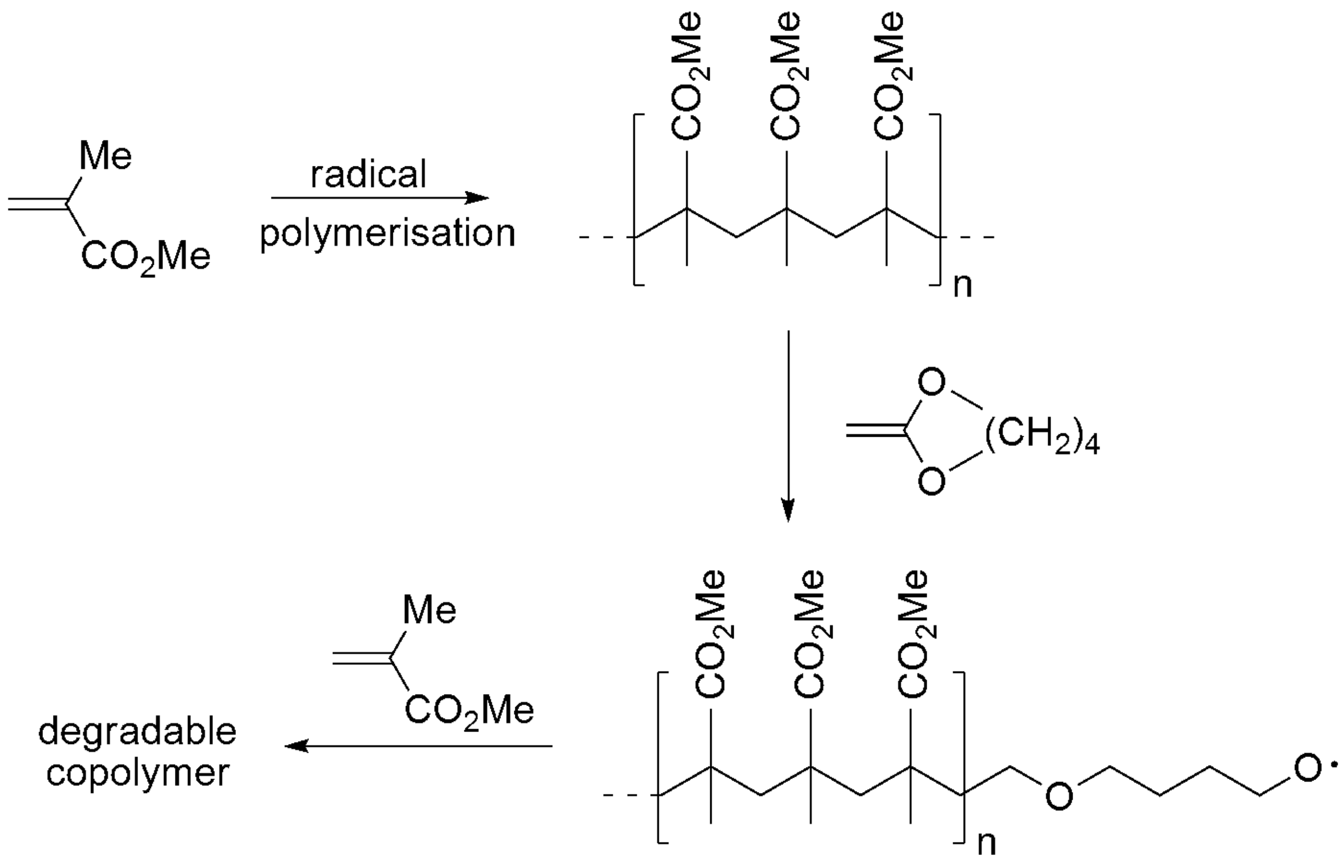


Type- III: Non-degradables

The only major all carbon backbone polymer which is biodegradable is poly(vinyl alcohol), PVA:



However, degradability may be 'built-in' to acrylics, e.g:



Conclusions

Biodegradation is a function of:

- **molecular weight**
- **morphology (crystallinity)**
- **polymer structure (e.g. hydrolysable backbone)**

Most biodegration is enzymatic hydrolysis or oxidation.

Landfill is still a problem!