

Biodegradation (part 2)

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Biopolymers
CHEM-E2155

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Schedule

Day	Subject of lecture	Discussion part
08 January	Introduction to the course	
15 January	Biopolymers overview	Reading 1
22 January	Biopolymers for packaging	Reading 2
29 January	Discussion day	Reading 3 & Assignment 1
05 February	Biodegradation 1	Reading 4
12 February	Biodegradation 2	Reading 5
26 February	Discussion day	Reading 6 & Assignment 2
04 March	Chitin, alginates and others	Reading 7
12 March	Proteins	Reading 8
19 March	Discussion day	Reading 9 & Assignment 3
25 March	TBD	Reading 10

Content

- Definitions
- Biodegradation and composting
- Test Methods
- Photodegradation and Oxo-degradable Plastics

- Degradation of Polymers
 - Synthetic polymers
 - Modified natural polymers
 - Bio-based polymers
- Factors and mechanisms of Biodegradation
- Polymers as biomaterials



Learning Outcomes

After today's course you

- can distinguish different factors affecting biodegradability
- know the requirements of biomaterials

Degradation of polymers

Polymers

ASTM D1566 **polymer**: “a macromolecular material formed by the chemical combination of monomers having either the same or different chemical composition”

Synthetic
Polymers

Natural
Polymers

Bio-based
Polymers

Definition

Polymer degradation:

- a change in the properties of the polymer or of a polymer-based product
- caused by one or more environmental factors
- often due to a change in the chemical and/or physical structure of the polymer chain

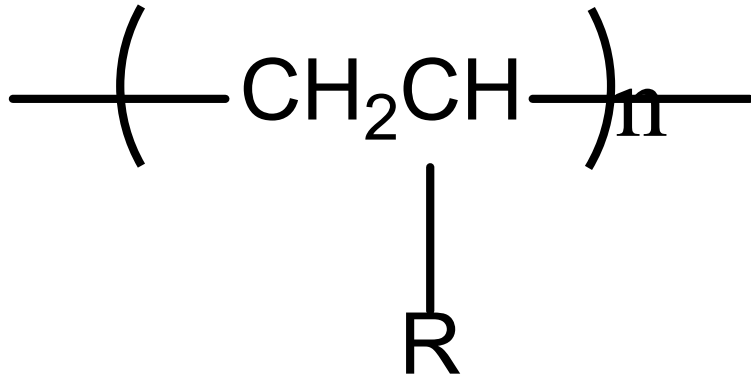
The susceptibility of a polymer to degradation depends on **its structure**.

Synthetic polymers

Rule of thumb concerning the polymer structure:

- A higher hydrophilic/hydrophobic ratio **increase** biodegradation.
- Presence of carbon chain polymers **reduce** biodegradation.
- Chain branching **reduce** biodegradation.
- Presence of condensation polymers **increase** biodegradation.
- Crystallinity **reduce** biodegradation.

Carbon chain backbone polymers



The functional groups and the molecular weight of the polymers control their properties varying in:

- **hydrophobicity,**
- **solubility characteristics,**
- **glass-transition temperature,**
- **crystallinity.**

where R: H (polyethylene), -CH₃ (polypropylene), carboxyl (poly(acrylic acid)), chlorine (poly(vinyl chloride)), phenyl (polystyrene) hydroxyl (poly(vinyl alcohol)), ester (poly(vinyl acetate)), nitrile (polyacrylonitrile), vinyl (polybutadiene), etc.

Carbon chain backbone polymers

Compound	MW	# Branchs	Growth test *
Dodecane	170	0	4
2,6,11-trimethyldodecane	212	3	0
Hexadecane	226	0	4
2,6,11,15-hexadecane	282	4	0
Tetracosane	338	0	4
Squalene	422	6	0
Dotriacontane	450	0	4
Hexatriacontane	506	0	0
Tetracontane	562	0	0
Tetratetracontane	618	0	0

**ASTM tests G21-70 and G22-76. Higher numbers correlate with the susceptibility of the plastic to biodegradation.*

Fungal and bacterial growth tests indicated that PE and other high molecular weight carbon chain polymers did not support growth.

Branching of hydrocarbon chains limits biodegradation and the MW cut-off for linear molecules appears to be in the 500 Da range

Low MW Pyrolysis Products of HDPE and LDPE

Pyrolysis T, °C	MW	Growth rating*
Control (HDPE)	123,000	0
400	16,000	1
450	8,000	1
500	3,200	3
535	1,000	3
Control (LDPE)	56,000	0
400	19,000	1
450	12,000	1
500	2,100	2
535	1,000	3

*ASTM tests G21-70 and G22-76. Higher numbers are considered to correlate with the susceptibility of the plastic to biodegradation.

Increase in degradation with lower MW:

- Transportation of polymer across cell walls is more likely
- Mechanism of biodegradation: Random or chain-end cleavage prior to entering the cell.
- Chain-end *exo*-biodegradation by β -oxidation

Individual oxidation steps are enzyme-catalyzed with a final hydrolysis to a two-carbon diminished chain and acetic acid, which is then presumably biodegraded.

Such a mechanism would explain the occurrence of slower biodegradation at higher MW, where there would be fewer chain ends.

The terminal groups found in oxidized and photodegraded polyethylene are oxygen-containing and these should expedite biodegradation via a β -oxidation mechanism.

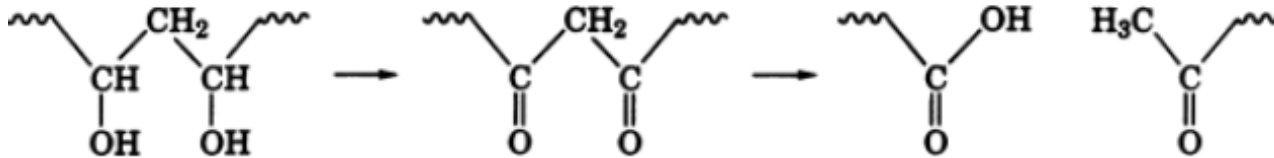
Poly(vinyl alcohol)

Probably **only** carbon chain polymer to be fully biodegradable.

Biodegradation: a random chain cleavage of 1,3-diketones formed by an enzyme-catalyzed oxidation of the secondary alcohol functional groups in the polymer backbone (observed as a reduction in aqueous viscosity of the polymer in the presence of soil bacteria).

Pseudomonas species (*): soil bacterium responsible for the degradation over a degree of polymerization range of 500–2000

Proposed oxidative endo mechanism:

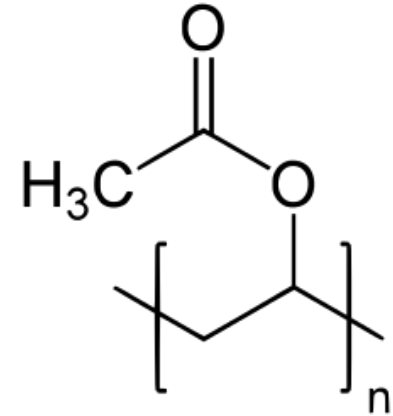


(*) Also *Flavobacterium*, *Acinetobacter* and many others, as well as fungi, molds, and yeasts

Poly(vinyl acetate)

Carboxylate derivatives of poly(vinyl alcohol) are **biodegradable** and function in detergents as cobuilders

Poly(vinyl acetate) hydrolyzes to poly(vinyl alcohol) and then biodegrade.



Heteroatom Chain Backbone Polymers

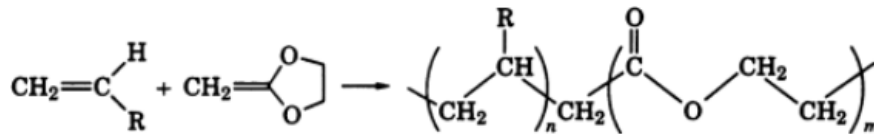
Polyesters, polyamides, polyethers, polyacetals, and other condensation polymers

- Their linkages are quite frequently found in nature
 - ↳ They are more likely to biodegrade than hydrocarbon-based polymers.
- Low melting, low MW aliphatic polyesters can be readily biodegradable.
- Polycaprolactone (PCL): one of a few commercially available synthetic polymers that is biodegradable.
- As the aliphatic polyesters become more hydrophobic (acid or alcohol chain length extension): biodegradation rate is slower.

Heteroatom Chain Backbone Polymers

Polyesters, polyamides, polyethers, polyacetals, and other condensation polymers

- **Amorphous regions** of polyesters are more readily biodegradable
- Free-radical route to polyesters was used to introduce weak linkages into the backbones of hydrocarbon polymers and render them susceptible to biodegradability
- Copolymerization of ketene acetals with vinyl monomers incorporates an ester linkage into the polymer backbone by rearrangement of the ketene acetal radical. The ester is a potential site for biological attack.



Poly(lactic acid)

- Medical field: sutures and other biomaterials.

Polyamides

- Stereochemistry of the groups close to the amide linkages and the hydrophilic nature **control biodegradability**
- Polyesteramides are difficult to hydrolyze chemically yet can be biodegraded rapidly at ambient conditions in the right environment.
- Polymers of nylon-6 are considered non-biodegradable, oligomers and low molecular weight polymers of less than 157 (11 kDa) can biodegrade.

Poly(ethylene glycol)

- Anaerobically degrades slowly (up to 2000 Da biodegrade).
- The biodegradation of poly(alkylene glycols) is hindered by their lack of water solubility, and only the low oligomers of poly(propylene glycol) are biodegradable.
- Polyether carboxylates have been evaluated as biodegradable detergent polymers

Modified Natural Polymers

Blends with other natural and synthetic polymers, **grafting** of another polymeric composition, and **chemical modification** to introduce functional groups by oxidation, chemical reaction (esterification or etherification), etc.

Blending of polyethylene with starch and compatibilizers.

Biodegradation studies of starch blends have not been conclusive (bio-disintegration would be a better term to describe these polymers).

Modified Natural Polymers

Simple chemical reactions on natural polymers are widely known to produce commercial polymers such as *hydroxyethylcellulose*, *hydroxypropylcellulose*, *carboxymethyl cellulose*, *cellulose acetates* and *propionates*. **Their biodegradability is not as well established.**

Carboxymethyl cellulose: has been claimed to be biodegradable below a degree of substitution of about 2, which is similar to that of cellulose acetate.

Modified Natural Polymers

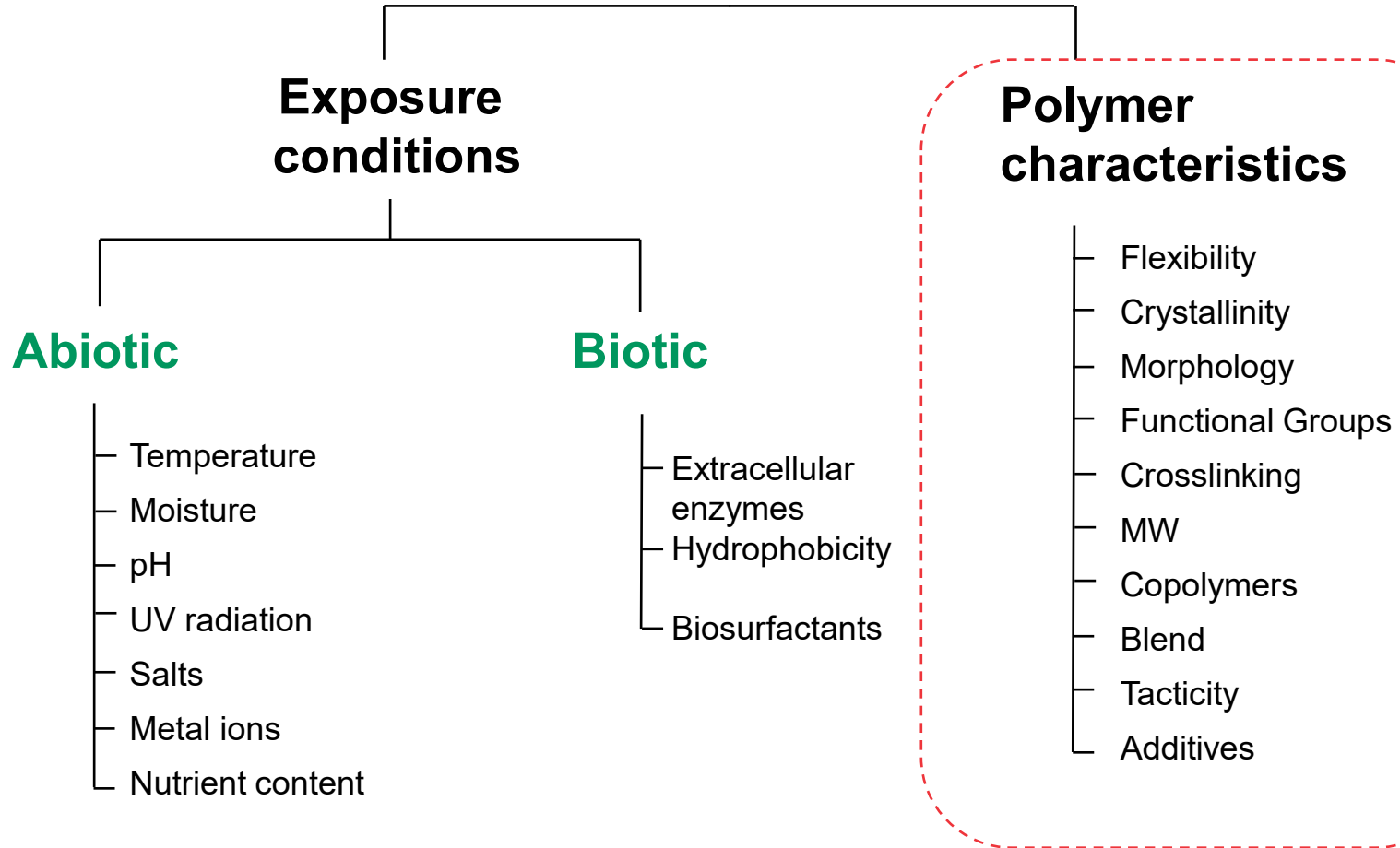
Carboxylated natural polymers have been known for many years, with the introduction of carboxymethyl cellulose. This product has wide use in detergents and household cleaning formulations, although **it is of questionable biodegradability at the level of substitution on cellulose required for performance.**

Nevertheless, carboxylated polysaccharides are a desirable choice for many applications, and the balance of biodegradation with performance that is achievable has been recognized as an attractive possible goal met in this case with a high probability of success.

Three approaches have been employed: **esterification, oxidation, or Michael addition of the hydroxyl groups to unsaturated carboxylic acids such as maleic and acrylic**, with some attempts to react specifically at the primary or secondary sites.

Factors and mechanisms of biodegradation

Factors affecting biodegradation



Factors affecting biodegradation

Polymer characteristics:

- Polymer structure and chain flexibility
- Copolymer composition
- Molecular weight and MW distribution
- Melting and glass transition T
- Hydrophilicity / Hydrophobicity
- Crystallinity
- Surface area (size and shape)

Factors affecting biodegradation

Polymer characteristics

Steps in Hydrolytic Degradation

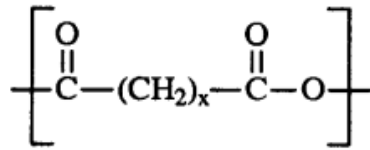
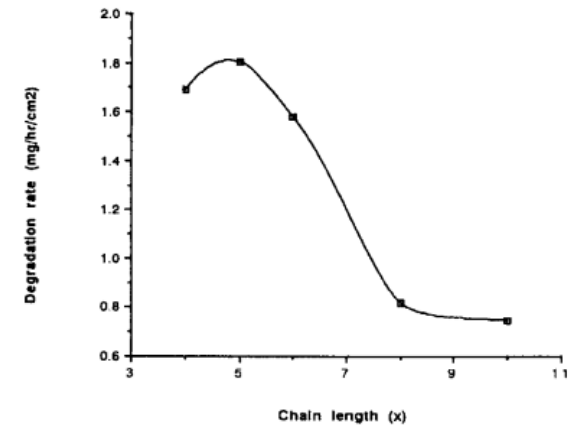
- Water diffusion into the polymer
- Decrease in MW
- Change in physical properties
- Mass loss
- Formation of oligomers and monomers

Backbone structure and side groups

- C-C backbones are normally stable
- Hetero-chain polymers, especially those having O or N in their backbones, are more susceptible to hydrolysis and biodegradation
- Aliphatic chains are more flexible than aromatic structures and thus more susceptible to hydrolysis and biodegradation
- Bulky side groups limit chain flexibility

Case: Aliphatic polyanhydride

Crystallinity & Monomer solubility



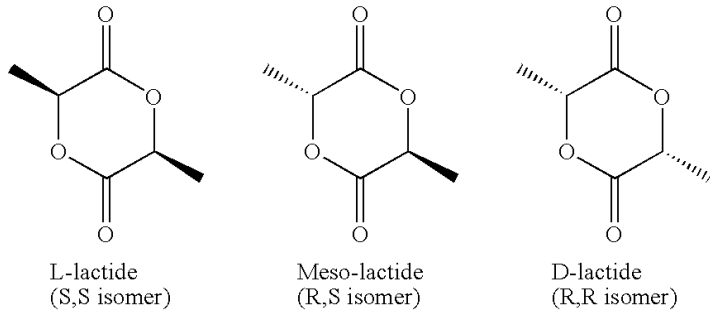
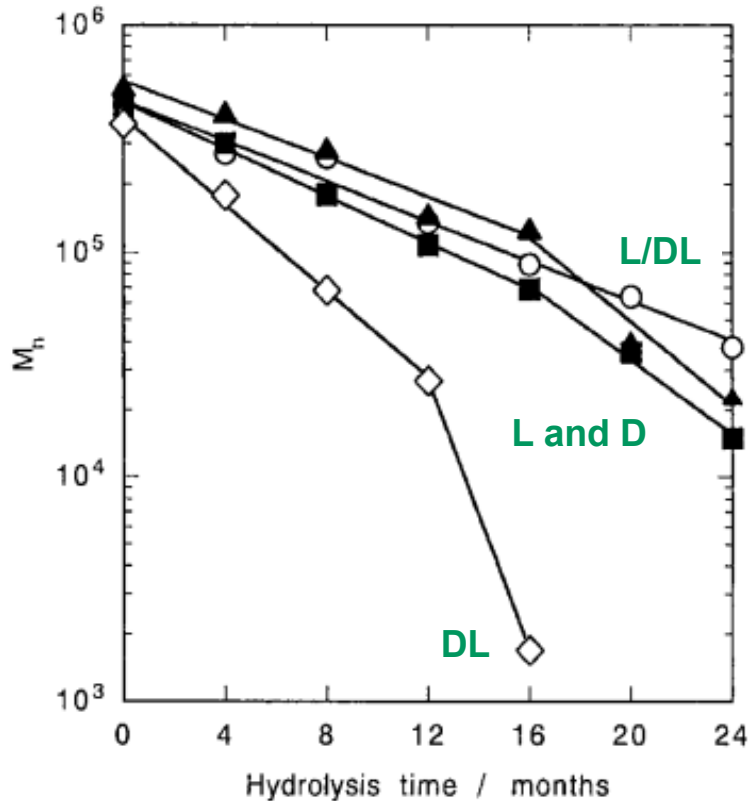
	Monomer chain length (x)	Polymer M_w ($\times 10^{-3}$) g/mol	DSC analysis		Monomer solubility (mg/ml)
			Tmax ($^{\circ}\text{C}$)	ΔH (J / g)	
Adipic acid (PAA)	4	6	79	110	14.4
Pimelic acid (PPA)	5	22	72	110	50.0
Suberic acid (PSU)	6	23	78	111	1.6
Azelaic acid (PAZ)	7	37	72	118	2.4
Sebacic acid (PSA)	8	466	89	132	1.0
Dodecanedioic acid (PDD)	10	353	95	86	<0.1
Dodecanedicarboxylic acid (PDX)	12	24	94	134	<0.01

The degradation rate of aliphatic polyanhydride decreases as the monomer chain length increases

Stereostructure

Hydrolysis rate of the amorphous phase: DL > D & L > L/DL

The ratio of the two stereo-isomers L(+) and D (-) in PLA determines the morphology of the polymer



PLLA & PDLA

- optically active
- isotactic sequences
- semi-crystalline

PDLLA

- optically inactive
- both isotactic and atactic sequences
- amorphous

Copolymer composition

Case: Aliphatic-aromatic copolyanhydride

CPP = 1,3-bis(p-carboxyphenoxy)propane

SA = Sebacic acid

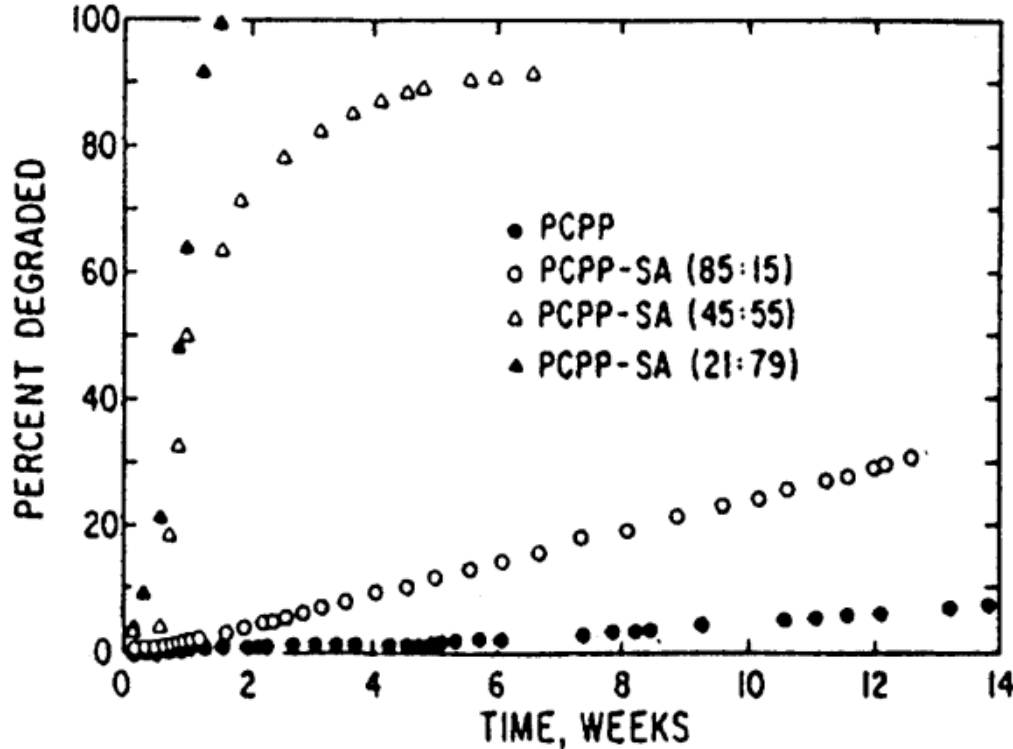
Polymeeri	T _m °C	T _g °C	ΔH Cal / g	Crystallinity %
Poly(SA), 100 %	86	60	37	66
Poly(CPP-SA) 4:96	76	42	25	47
Poly(CPP-SA) 13:87	75	47	21	40
Poly(CPP-SA) 22:78	66	47	15	30
Poly(CPP-SA) 31:69	66	40	5	11
Poly(CPP-SA) 41:59	178	4	2	4
Poly(CPP-SA) 46:54	185	2	3	6
Poly(CPP-SA) 60:40	200	0	6	14
Poly(CPP-SA) 80:20	205	15	8	18
Poly(CPP), 100 %	240	96	27	

In general, **co-monomers increase irregularity of polymer chains**, which usually reduce crystallinity and improve **accessibility to water and microbes**.

Aromatic structures on the other hand **increase rigidity** of polymer chains, thus **reducing degradability**.

Molar ratio

Case of aliphatic-aromatic copolyanhydride



Aliphatic blocks
degrade **faster** than
aromatic blocks

- Difference in the solubility of degrading monomers may induce porous areas on the surface of polymer.
- The solubility of monomers is dependent on polymer structure and pH.

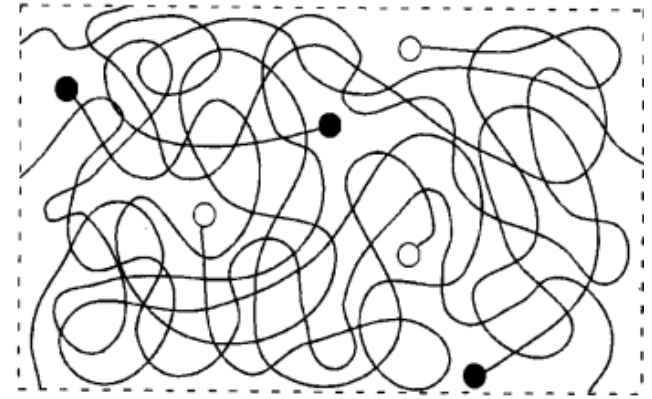
Hydrophilicity - Hydrophobicity

- Hydrophilic polymers are more susceptible to hydrolytic degradation
- Hydrophilic polymers that contain hydrolysable bonds degrade homogeneously (bulk degradation)
- Hydrophobic polymers that contain hydrolysable bonds degrade heterogeneously (surface erosion)

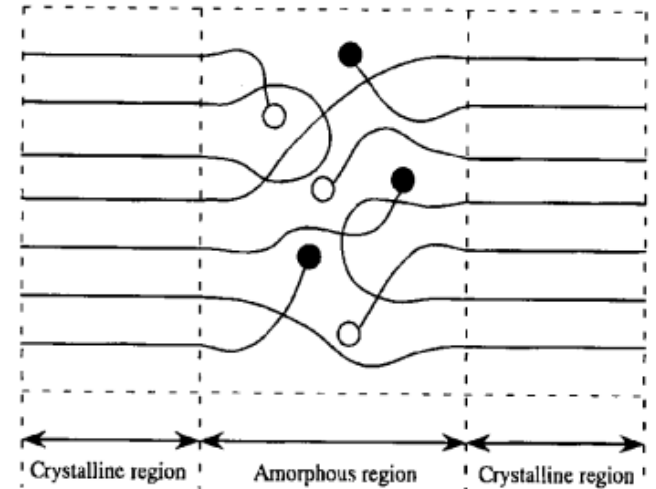
Crystallinity

The degradation of semi-crystalline polymers occurs in two stages:

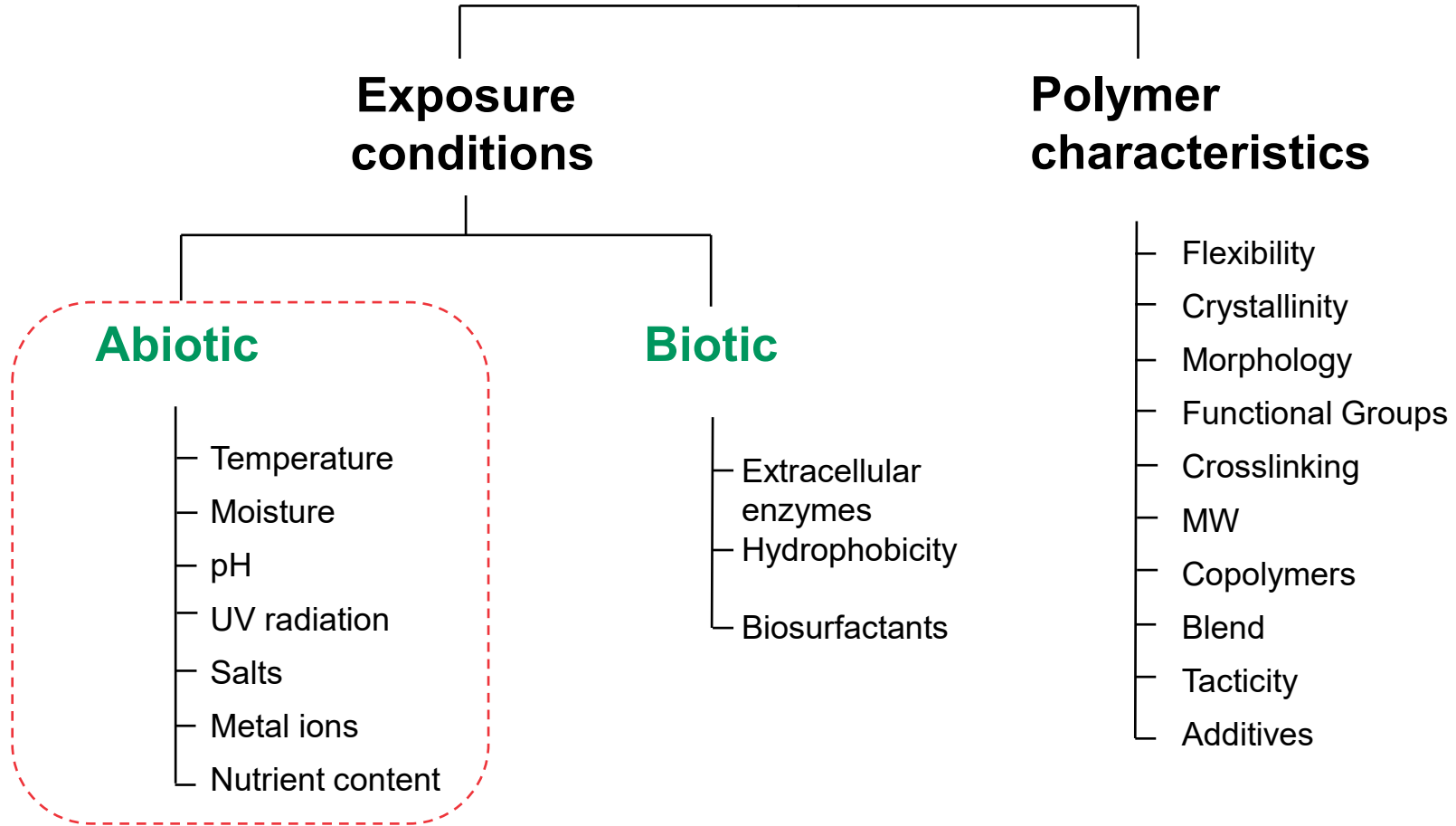
- (1) **Water diffusion** into the amorphous regions of the polymer and random chain scission → increase in crystallinity
- (2) As **hydrolysis** advances, crystalline areas are attacked and eventually removed → decrease in crystallinity



Crystallized PLLA film

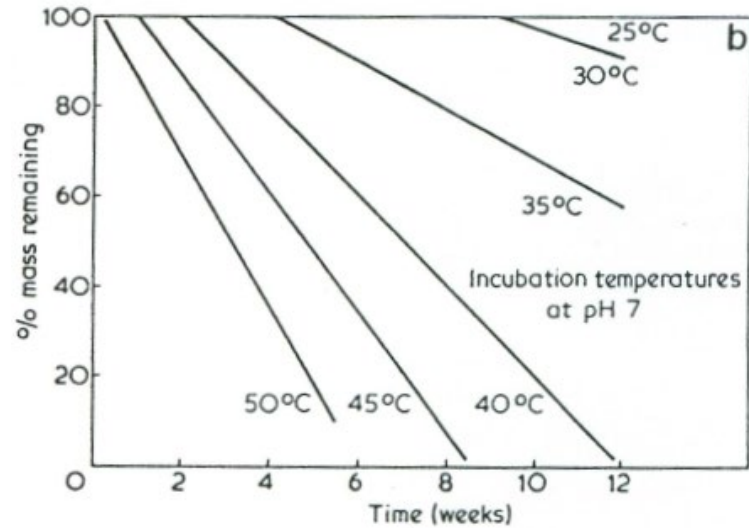
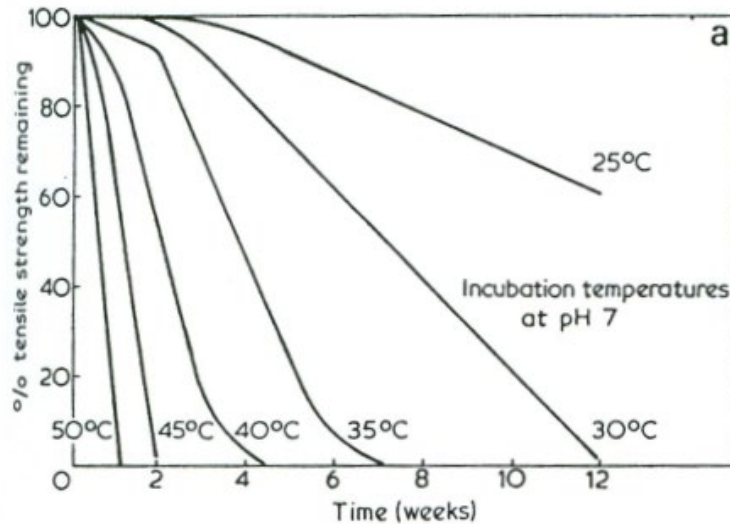


Factors affecting biodegradation



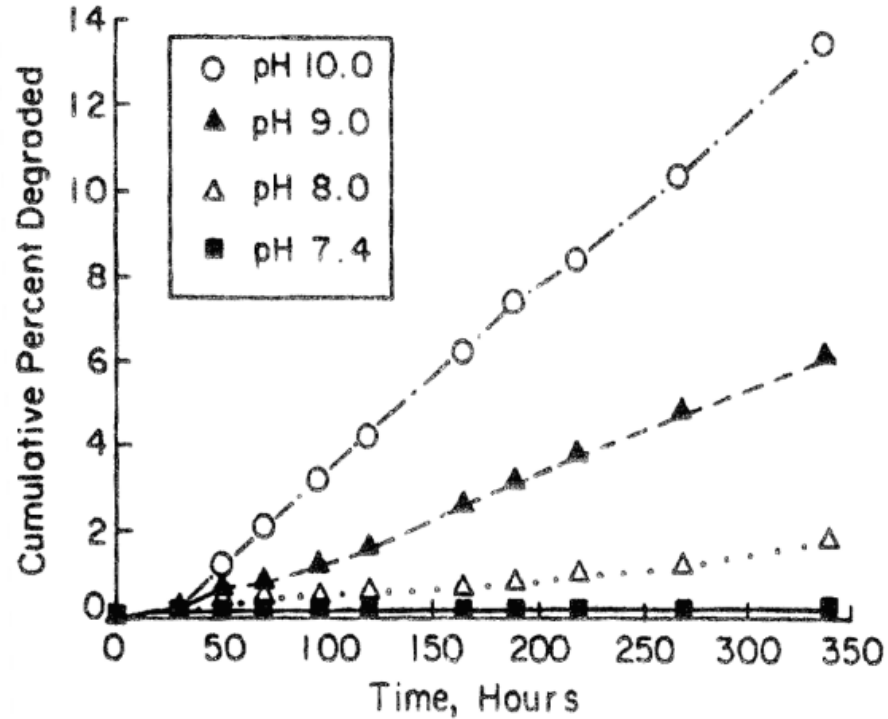
Temperature

Rate of hydrolytic degradation increases as $T > T_g$
Case of PGA filaments ($T_g = 36\text{ }^\circ\text{C}$)



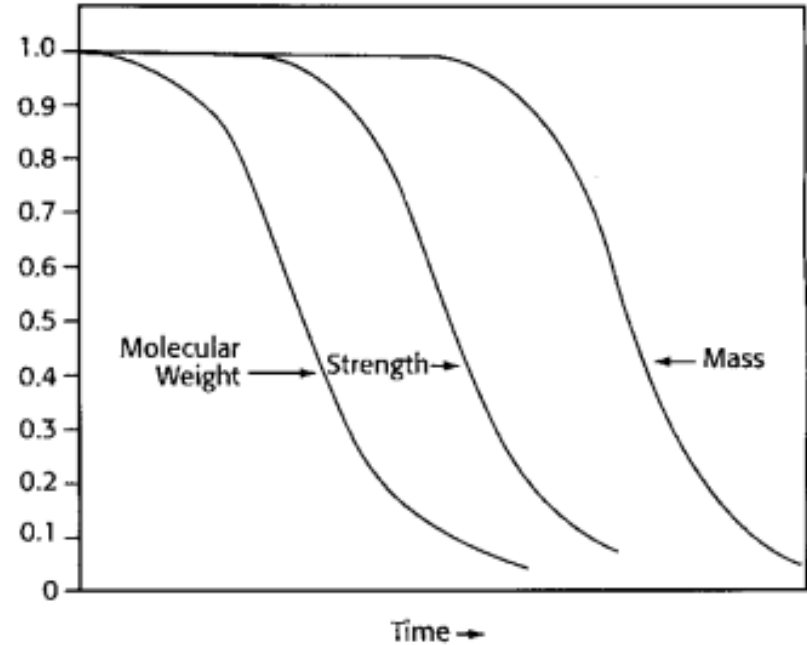
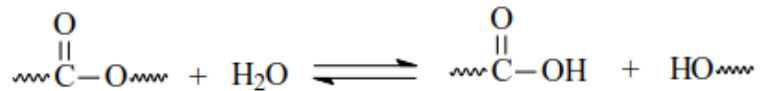
pH

Rate of hydrolytic degradation increases as $T > T_g$
Case of PGA filaments ($T_g = 36\text{ }^\circ\text{C}$)



Steps of hydrolytic degradation

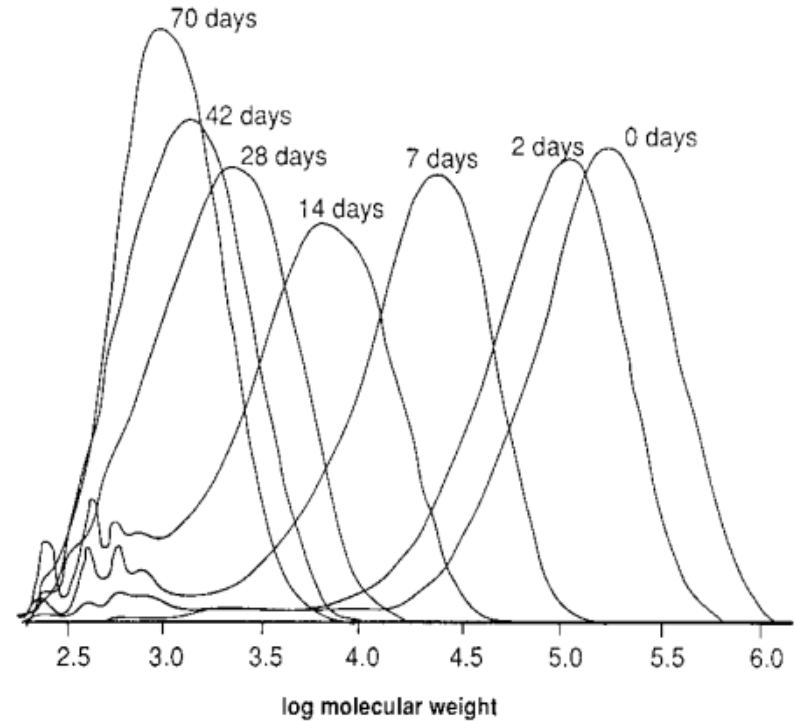
- Water diffusion into the polymer
- Decrease in MW
- Change in physical properties
- Mass loss
- Formation of oligomers and monomers



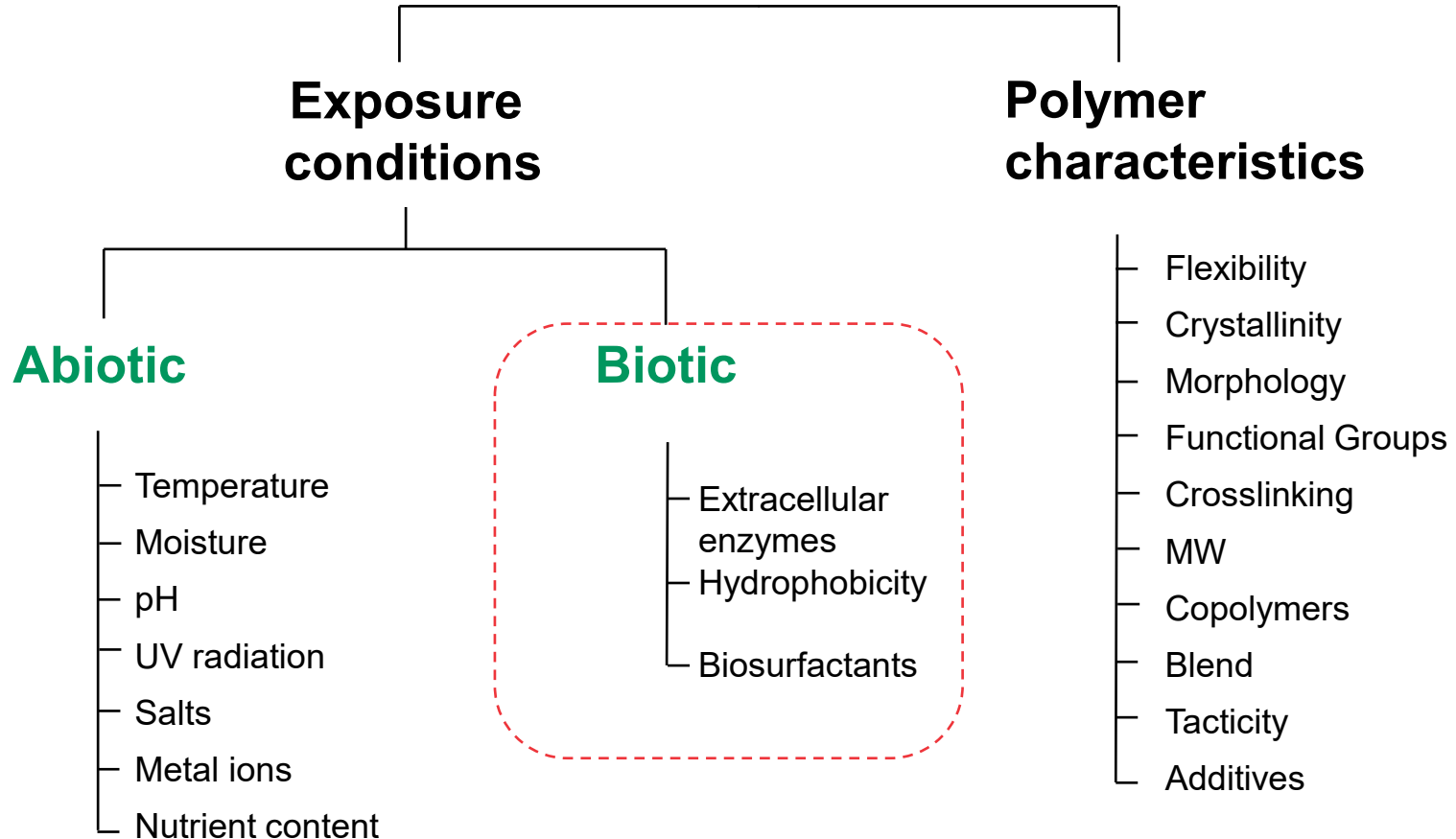
Hydrolytic degradation *in vitro*

Analysis of the polymer:

- Visual evaluation (SEM)
- Mass (weighing)
 - Mass loss
 - Water absorption
- Molecular weight (SEC)
- Mechanical properties
- Crystallinity changes (DSC)
- Hydrophobicity (contact angle)
- Structure (NMR, FTIR)

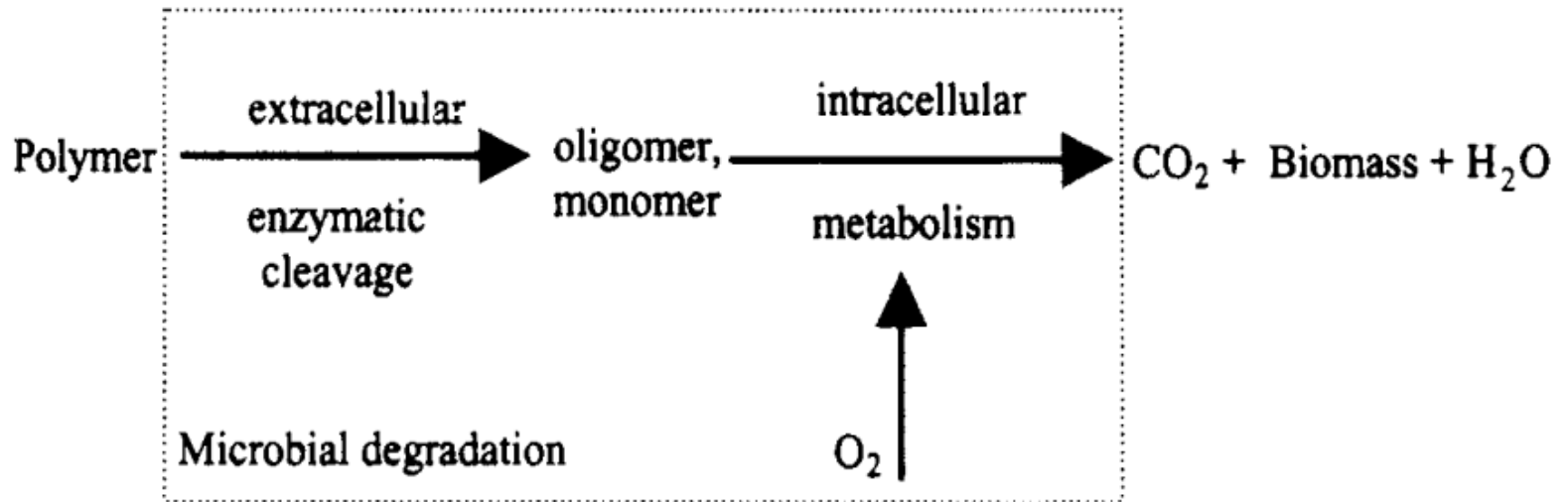


Factors affecting biodegradation



Enzymatic degradation mechanisms

- Extracellular degradation
- Intracellular degradation



Activity of enzymes and principle of function

The conformational structure of the polypeptide is sensitive to changes in:

- temperature,
- pH,
- Osmotic concentration (osmolarity).

Optimal activity is also dependent on such cofactors as:

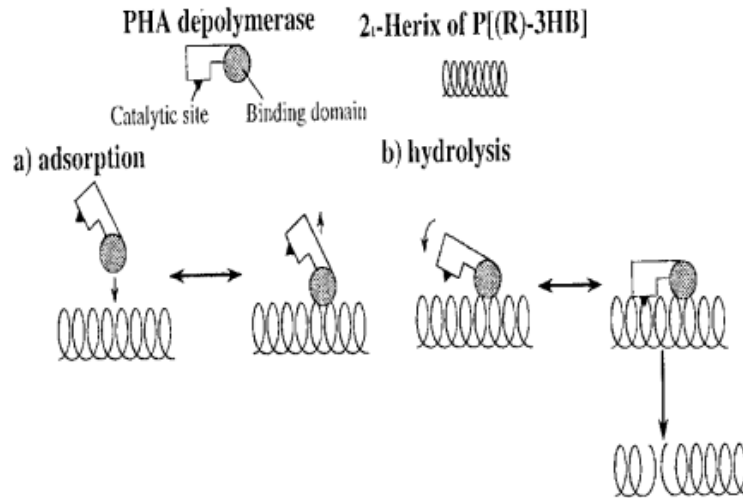
- Inorganic metal ions (Fe^{2+} , Zn^{2+} , etc.)
- Organic molecules (= coenzymes; NAD, FAD, ATP), which function as intermediate carriers of electrons or chemical groups that are transferred in the overall enzymatic reaction

Activity of enzymes and principle of function

- Enzymes lower the activation energy of the reactions and thereby increase the reaction rates
- Catalyze only single type of reactions without side reactions or by-products
- Function in dilute aqueous solution under moderate conditions of temperature and pH

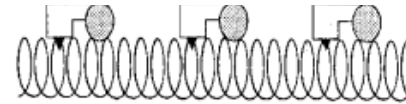
Mechanisms of heterogeneous enzymatic reactions

Adsorption – Chain scission



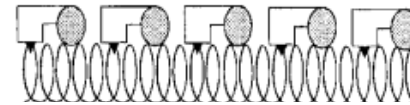
Concentration of the enzyme

Low concentration



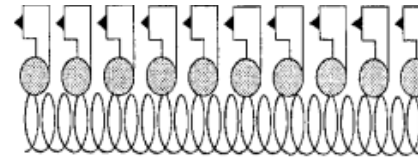
$$K[E] \ll 1$$

Optimum concentration



$$K[E] = 1$$

High concentration



$$K[E] \gg 1$$

Typical enzymes related to biodegradation of different main chain polymer structures

Main chain structure	Polymer	Corresponding enzyme responsible to the primary degradation
-C-C- C-C linkage	polyethylene natural rubber	Oxidoreductase peroxidase oxidase lignin peroxidase dehydrogenase
-C=C- C=C linkage	polyisoprene lignin	
$\begin{array}{c} \text{-C-C-C-} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$ β -Hydroxy group	poly(vinyl alcohol)	dehydrogenase oxidase peroxidase
-C-O-C- Ether linkage	poly(ethylene glycol) poly(propylene glycol)	Hydrolase PHA depolymerase lipase, esterase protease
$\begin{array}{c} \text{-C-O-} \\ \\ \text{O} \end{array}$ Ester linkage	polyesters PHA, PCL PLLA	
$\begin{array}{c} \text{-O-C-O-} \\ \\ \text{O} \end{array}$ Carbonate linkage	polycarbonate	
$\begin{array}{c} \text{-C-N-} \\ \quad \\ \text{O} \quad \text{H} \end{array}$ Amide linkage	protein polylysine poly(glutamic acid) poly(aspartic acid)	
$\begin{array}{c} \text{-N-C-O-} \\ \quad \\ \text{H} \quad \text{O} \end{array}$ Urethane linkage	polyurethane	

Polymers as biomaterials

- requirements in medical applications

Biomaterial

"Synthetic material used to replace part of a living system, or to function in intimate contact with living system"

" A material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body"

" A substance which is used to direct the course of any therapeutic or diagnostic procedure in medicine"

Synthetic biomaterials:

- Metals
- Alloys and ceramics
- Polymers
- Composites

Joint replacements, bone plates and screws, dental root implants, pacer and suture wires, orthopedic implants, sutures, blood vessels, implantable ocular lenses, heart valves, surgical packaging, cannulaes etc.



Lumbar disc prosthesis PRODISC® L

Biocompatibility (ISO 10993), *in vitro* tests

- **Sensitization and irritation** (ISO 10993-10):
contact with skin or mucosal membrane (Guineapig or rabbit)
- **Toxicity** (10993-11):
needed for implants or devices with longer contact (24 hours to 3 months),
mouse is the most common test animal
- **Implantation** (10993-6):
needed for implants and external communication devices with long contact,
reference material with known tissue reactions needed,
testing period should cover the degradation process of the material,
minimum 3 parallel animals, 10 parallel samples

Requirements for long-term implantable devices:

non-toxic, non-immunogenic, non-thrombogenic, non-carcinogenic, non-irritant

Summary questions

- Which polymer characteristics can affect their biodegradability?
- Which exposure condition factors can affect the biodegradability of polymers?
- What is the definition of biomaterial?

Next Reading 6

Title: Disposable Paper-based Food Packaging
Report by Profundo

Read until page 41 before lecture on February 26:

- Executive summary
- Chapters 1-3

Reading 5 discussion

Title: US Patent: Polymer compositions
US 4121025, 17.10.1978

Discussion items:

- What does the invention describe?
- How much “metal complex” is described as optimum by the inventor?
- Which concrete metal complexes and which polymers are described?
- What information can be extracted from the “Examples”?

Instructions:

Write your names and summary of your discussion in e.g., PowerPoint. Save the text as image file (.jpg) and upload it to the Padlet page:

https://padlet.com/michaelhummel/CHEME2155_2024