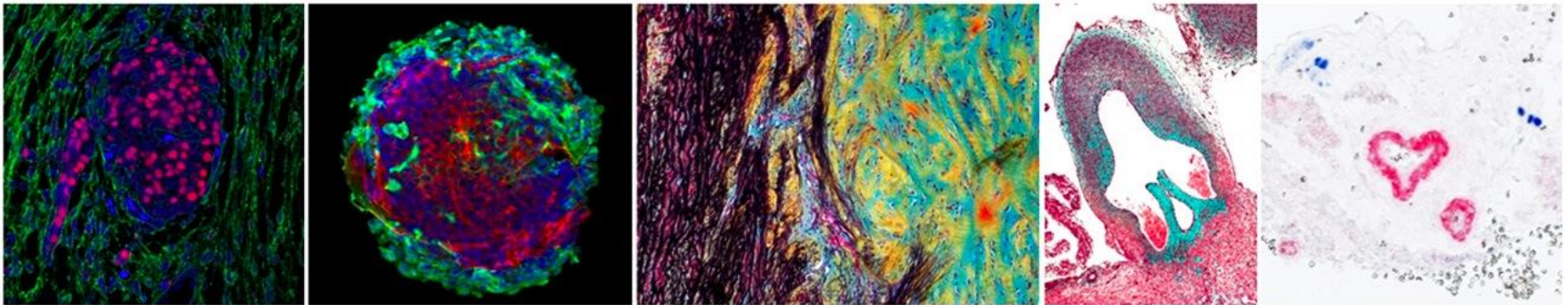
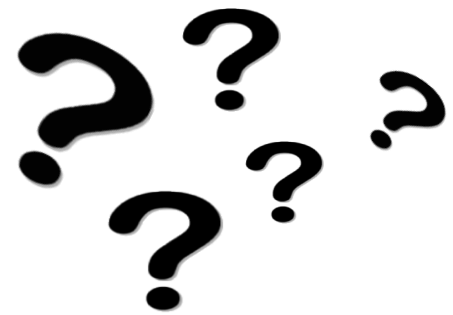


Polymer and processing methods

Dr Svenja Hinderer
Frauenklinik, UKT
und Zellsysteme, Fraunhofer IGB



Biomaterials



- ❖ Materials that directly interact with living organisms (cells, blood, tissue fluids) and which therefore have to meet certain requirements

➤ Requirements:

Biocompatibility

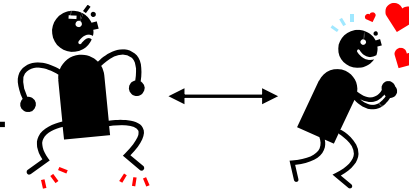
... is the tolerance between a biological and an engineered system

Biofunctionality

... is the ability of an engineered system to support or replace single or multiple functions of a biological system

Implant-Tissue Interaction

Any foreign body leads to a host response ...



Device Properties	Host Response
toxic	tissue necrosis
inert	loose fibrotic encapsulation of the device by surrounding tissue
bioactive	tissue forms close connection with the device
degradable	tissue replaces device

Routinely used Biomaterials

Material	Advantages	Disadvantages
Metals	High durability and tensile strength	Corrosion, may cause inflammation
Ceramics	Inert, commonly used as coating	Low elasticity, abrasion possible, expensive
Polymers	Adjustable properties, cheap	Low strength, sterilisation is difficult

Polymer

❖ As a mechanical or biomedical engineer , we should know:

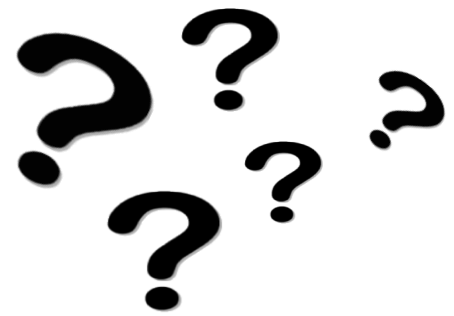
What is a polymer?

What are the applications?

What are the manufacturing techniques?

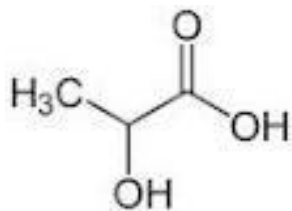


Polymer

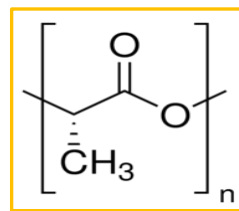


- ❖ Macromolecule or large molecule
- ❖ Greek: „poly“ = many „meros“ = parts

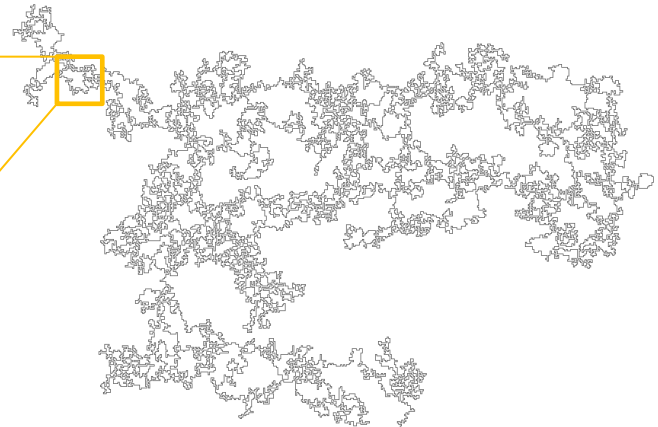
→ Long molecule consisting of many small units called monomers



Monomer



Polymer



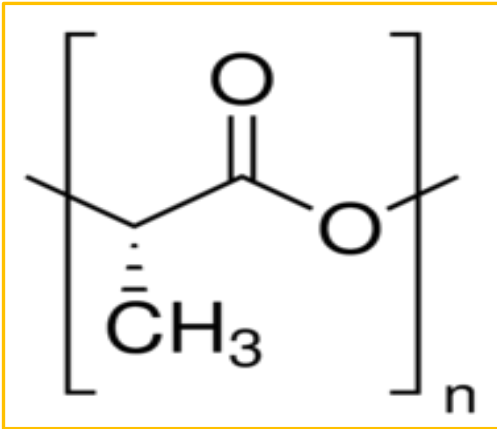
History of Polymers

❖ The Aztecs used natural rubber to produce elastic articles

1851	hard rubber (Goodyear)
1863	cellulose nitrate
1932	ring opening polymerization of PLA
1937	polystyrene
1938	nylon-66 fibers
1941	low-density polyethylene (LDPE)
1943	Silicones and polyurethanes
1957	High-density polyethylene (HDPE)
1965	Polysulfones

Defining polymers

repeating unit



Polymerisation degree
(number of monomers)

Repeating unit/ backbone:

Homochain polymers: -C-C-

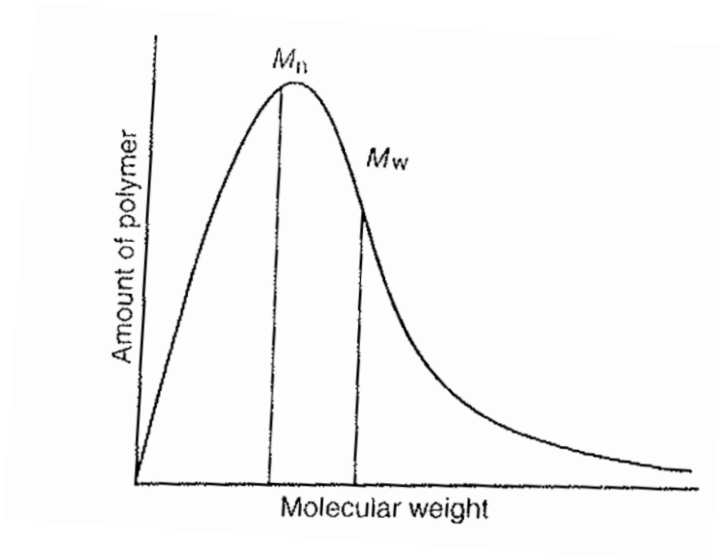
Heterochain polymers: -C-O- ; -C-S- ; -C-N-

Chemistry of a polymer depends on the monomer

Physics of a polymer depends on polymerisation degree, chain length,...

Defining polymers

The „size“ of a polymer is described by the molecular weight distribution:



M_n : number average

M_w : weight average

$$\text{Polydispersity} = M_w / M_n \geq 1$$



→ Impact on thermal and mechanical properties

Polymer structure

❖ Thermoplastics

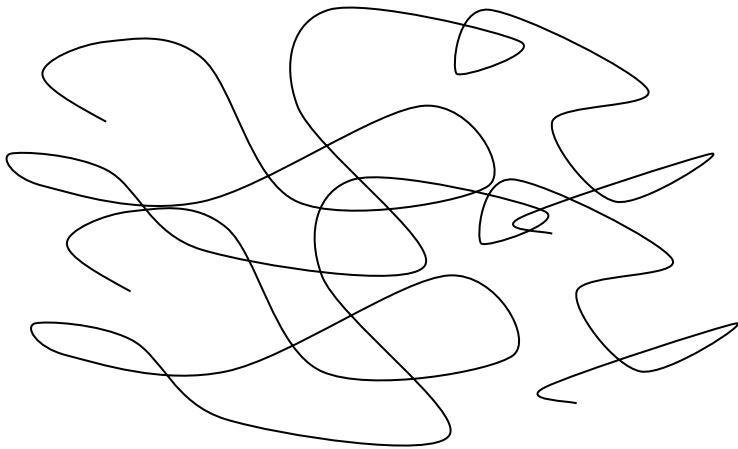
Heating and cooling several times

Reforming possible

Tough

Linear or branched chains

Examples: PE, PP, PEEK, PVC



❖ Thermosets

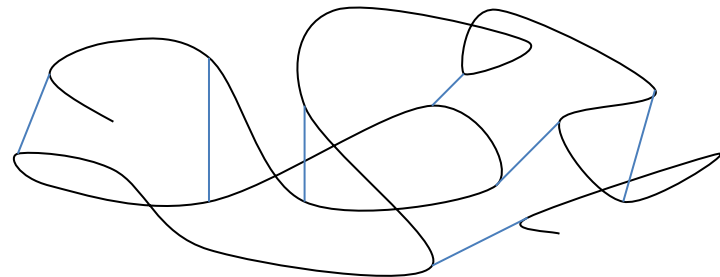
Degrades before melting

Not reforming

High stiffness

Cross-linked network

Examples: epoxy, bakelite



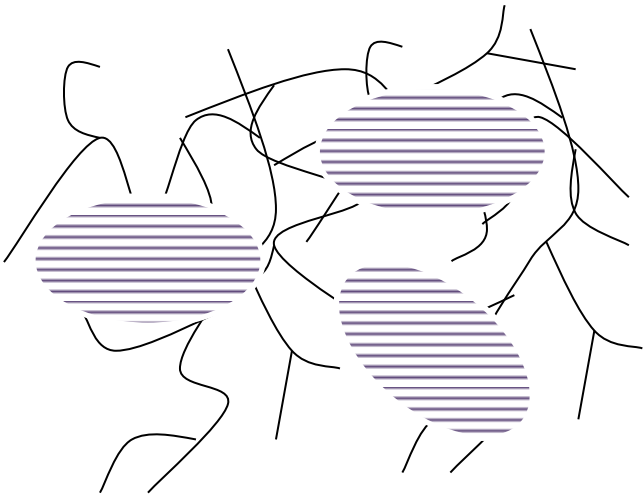
Polymer structure - Thermoplastics

❖ Semi-crystalline

melting point and T_g

opaque

well ordered

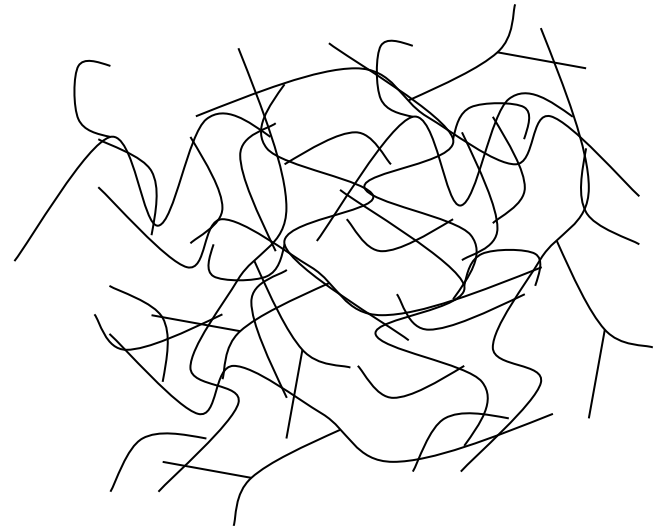


❖ Amorphous

only T_g

transparent

random



Additives

❖ Small molecules or reagents to adjust properties

Antistatic agents

→ prevent static charge build up

Coupling agents

→ improve bonding with fillers

Fillers

→ glass beads, short fibers

Flame retardants

→ reduce risk of combustion

Lubricants

→ improve forming

Pigments

→ adds color

Plasticizers

→ adds flexibility

Reinforcement

→ improve structural strength/stiffness

Stabilizers

→ Anti-oxidants, heat stabilizers

Polymer synthesis



Chain-Growth

&

Step-Growth

Double bonds $C=C$

Catalyst needed

3 Steps

Bifunctional monomers

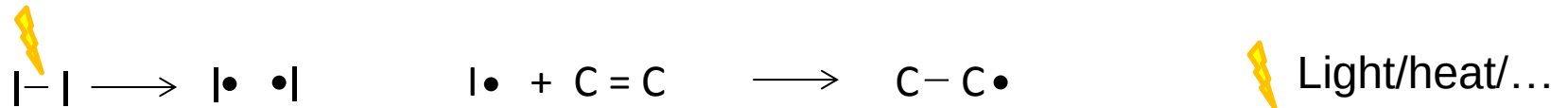
Condensation: Byproducts

Addition: No Byproducts

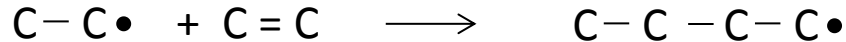
Polymer synthesis

❖ CHAIN-GROWTH

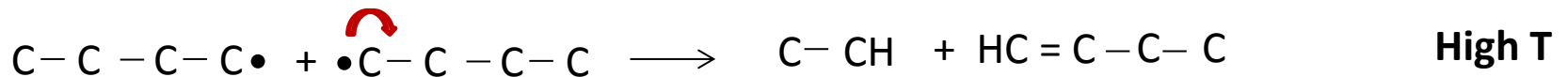
I) Initiation: free radical generation



II) Propagation: growth of the active chain



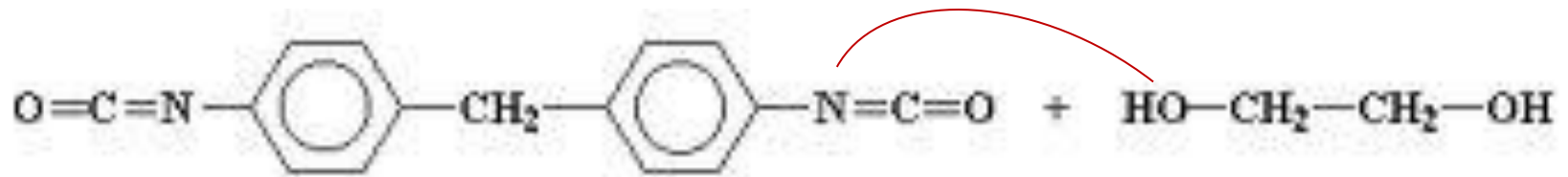
III) Termination: of the active chain to give the final polymer product



Polymer synthesis

❖ STEP-GROWTH

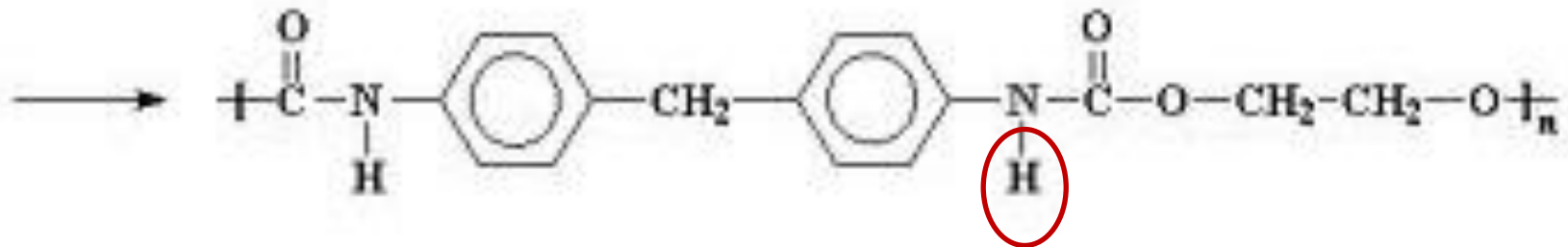
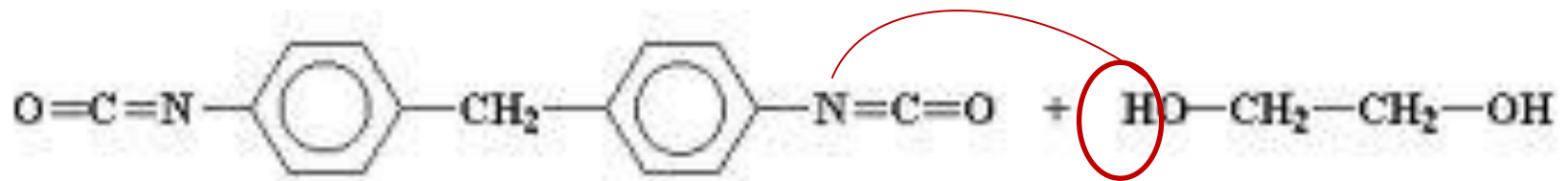
Polyaddition



Polymer synthesis

❖ STEP-GROWTH

Polyaddition

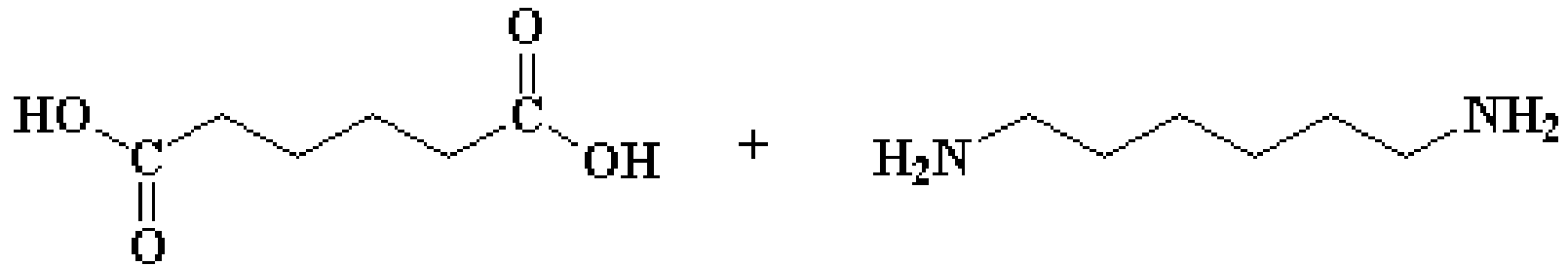


Polyurethane

Polymer synthesis

❖ STEP-GROWTH

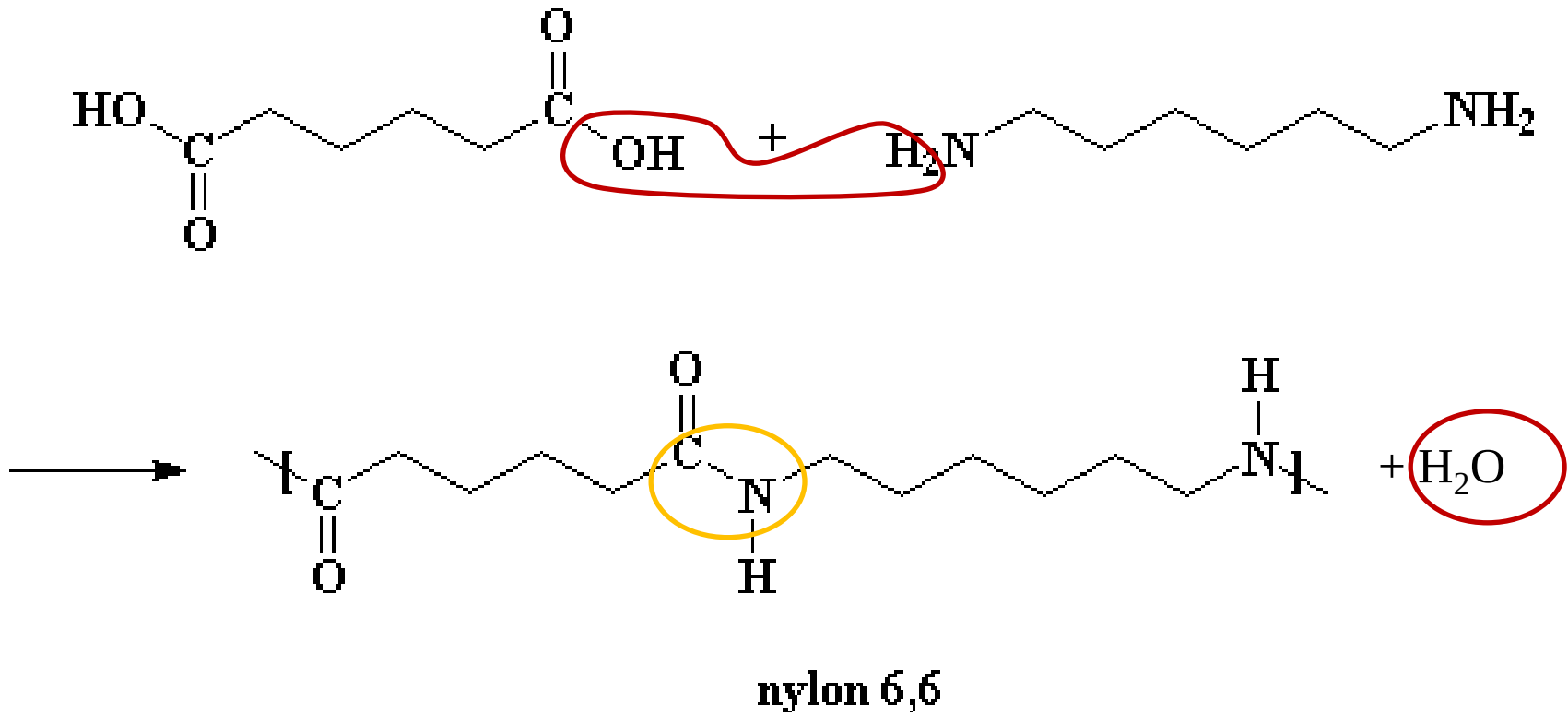
Polycondensation



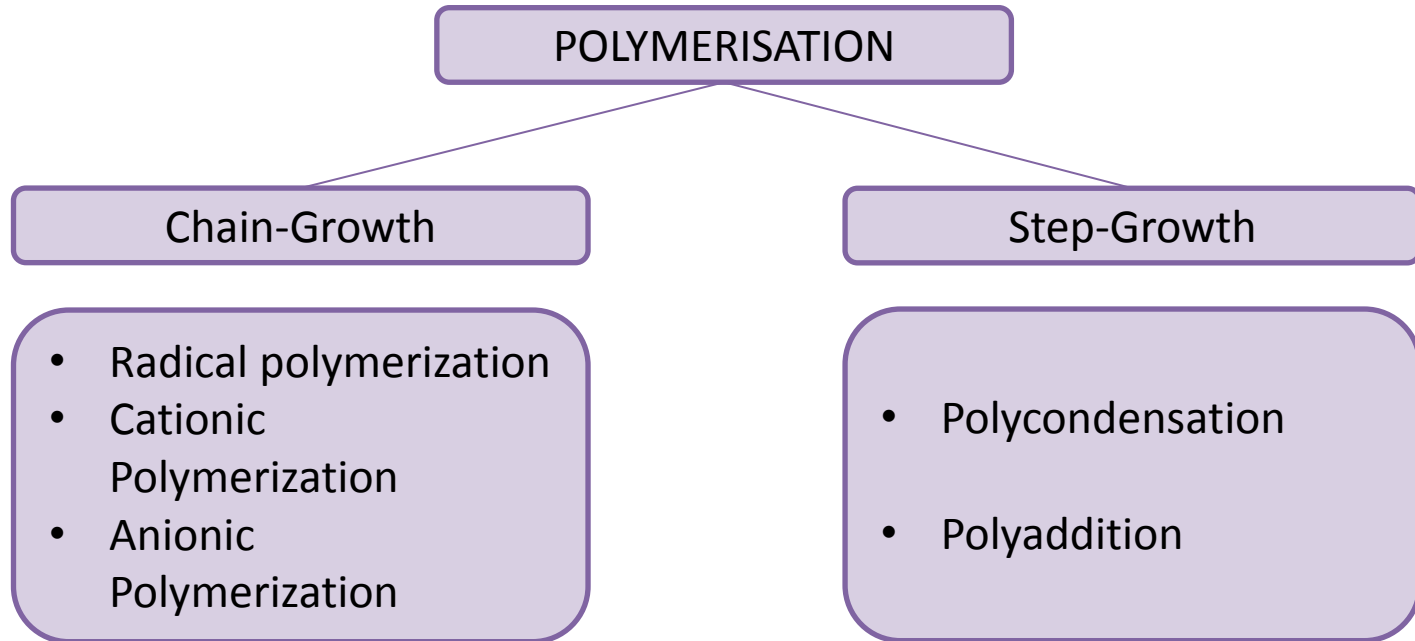
Polymer synthesis

❖ STEP-GROWTH

Polycondensation



Polymer synthesis



Thermodynamics

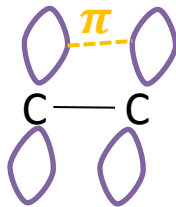
❖ GIBBS Energy

$$\Delta G = \Delta H - T\Delta S$$

Reaction, when **ΔG = negative**

Polymerization: Entropy (S) decreases [disorder decreases]

❖ ENERGY



π opens, because it has more energy
→ Free energy as soon as it is opened

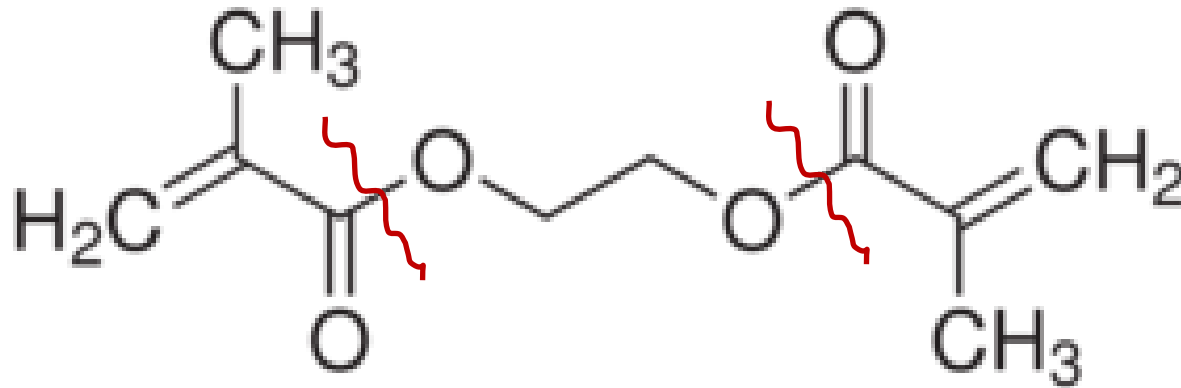
How does a polymer degrade?

Polymer degradation

Hydrolytic



Enzymatic



Mechanisms of degradation

❖ **Surface erosion:**

Rate at which water penetrates into polymer is slower than rate of water-solubility

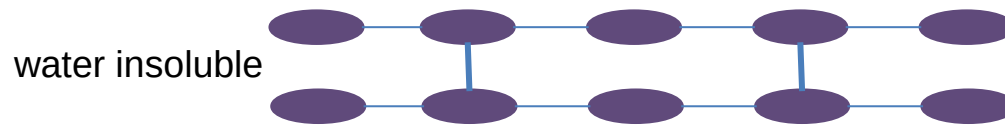
Matrix becomes thinner with time, but maintains structural integrity

❖ **Bulk erosion:**

Rate of water penetration into solid exceeds rate at which polymer is transformed into water soluble material

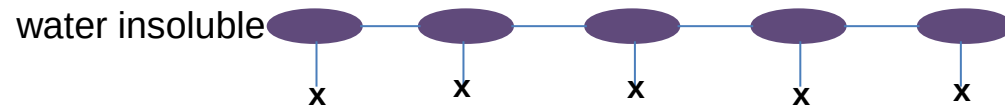
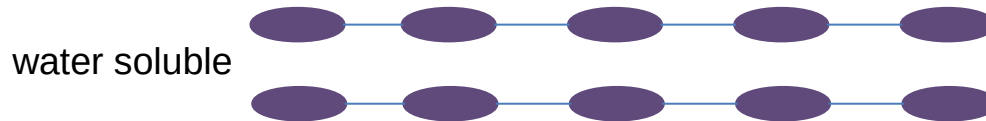
Uptake of water followed by an erosion process throughout the *bulk* of the material

Hydrolytic degradation



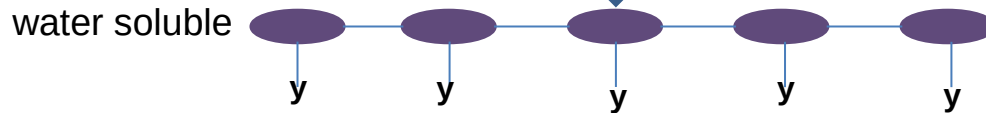
Mechanism I

Cross-link degradation



Mechanism II

Side chain degradation



Mechanism III

Backbone degradation



Polymer used in medicine

❖ POLYVINYL CHLORIDE (PVC)

- Rigid amorphous polymer
- High melt viscosity
- Difficult to process
- Plasticisers used

Uses:

Storage bag (solution)
Blood bags,
Surgical packaging
Catheters



<http://www.gera-ident.de>



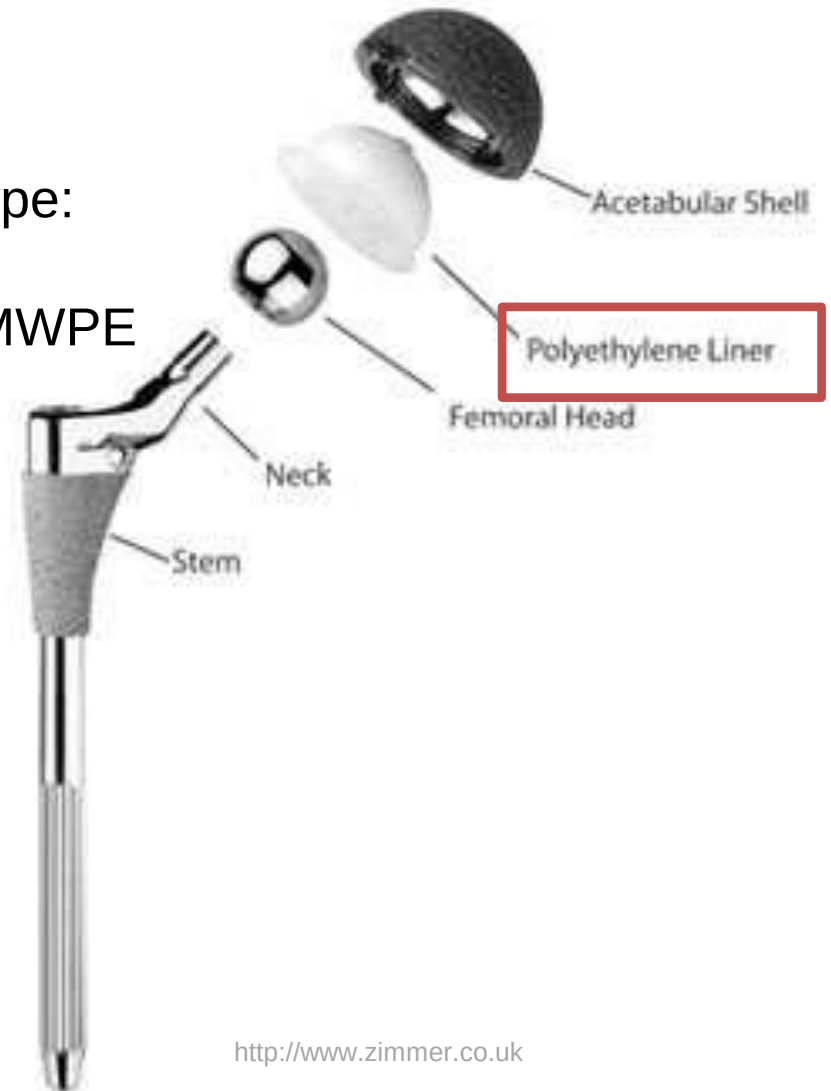
<http://german.alibaba.com/product-gs/>

Polymer used in medicine

❖ POLYETHYLENE (PE)

- Application depends on the PE type:

HDPE, LDPE, LLDPE, VLDPE, UHMWPE



Polymer used in medicine

❖ POLYPROPYLENE (PP)

- Physical properties similar to PE

Uses:

Finger joint prosthesis

Syringes

Membranes

Sutures

Vascular grafts



<http://www.ad-surgical.com/medical-polypropylene/>



<http://museumvictoria.com.au>

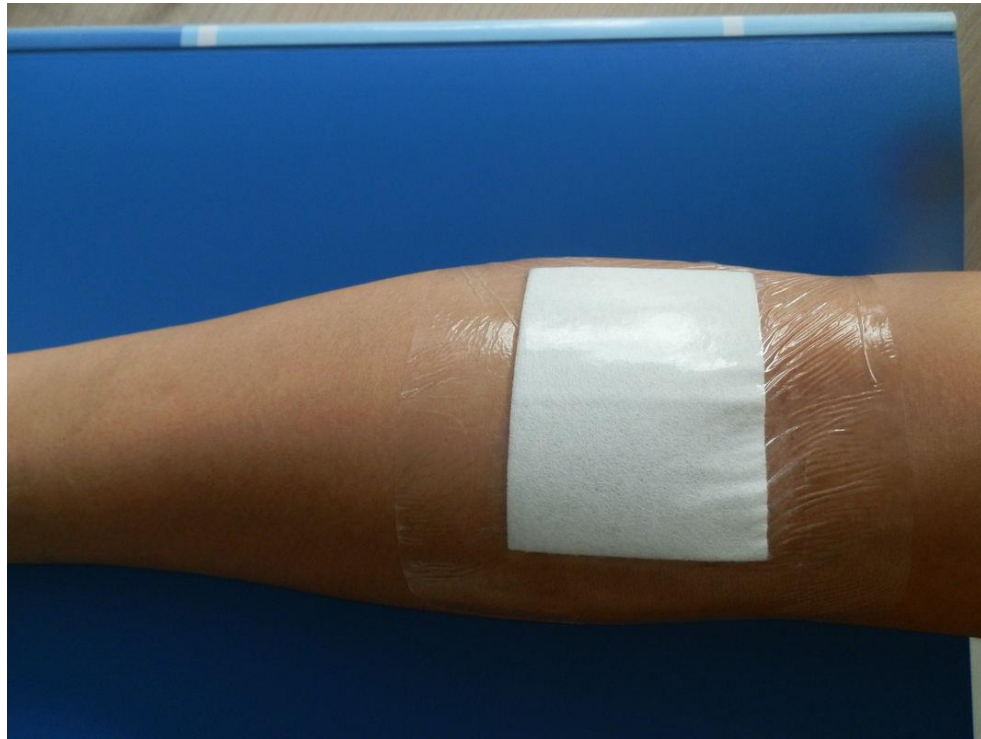
Polymer used in medicine

❖ POLYURETHANE (PU)

It exhibits the elasticity of rubber combined with the toughness and durability of metals

Uses:

Wound dressing



<http://www.medical-adhesivetape.com>

Polymer used in medicine

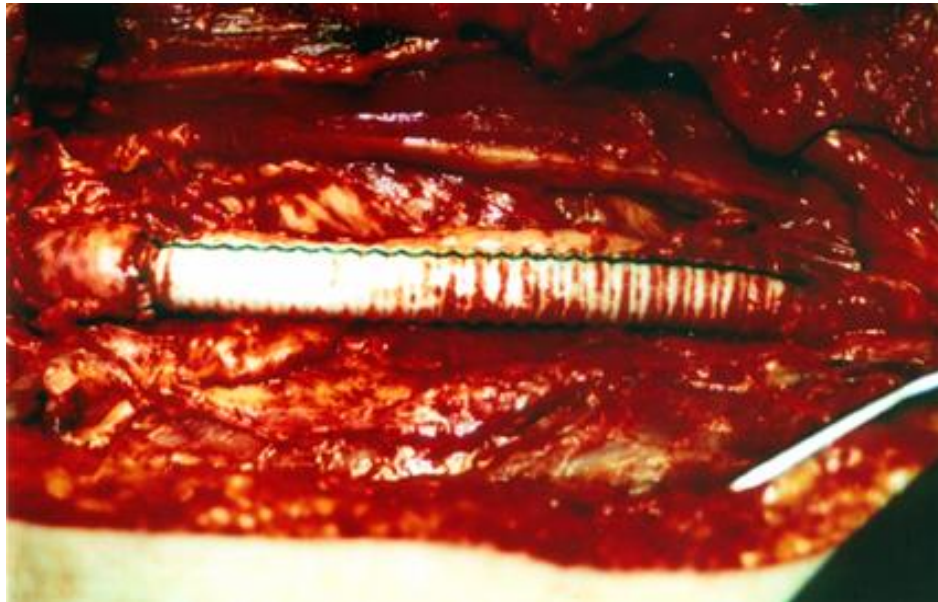
❖ POLYESTERS

- PET: Polyethyleneterephtalate (**Dacron™**)
- Rigid aromatic rings in a polymeric backbone
- High melting point, and high tensile strength
- Hydrophobic

Uses:

Vascular grafts

Sutures



Polymer used in medicine

❖ POLYSTYRENE (PS)

- Pure polystyrene – hard but brittle
- ABS: Acrylonitrile-Butadiene-Styrene copolymers

Uses:

Blood Dialysis
Diagnostic Kits



<http://www.kawasumiamerica.com>

Polymer used in medicine

❖ POLYMETHYLMETHACRYLATE (PMMA)

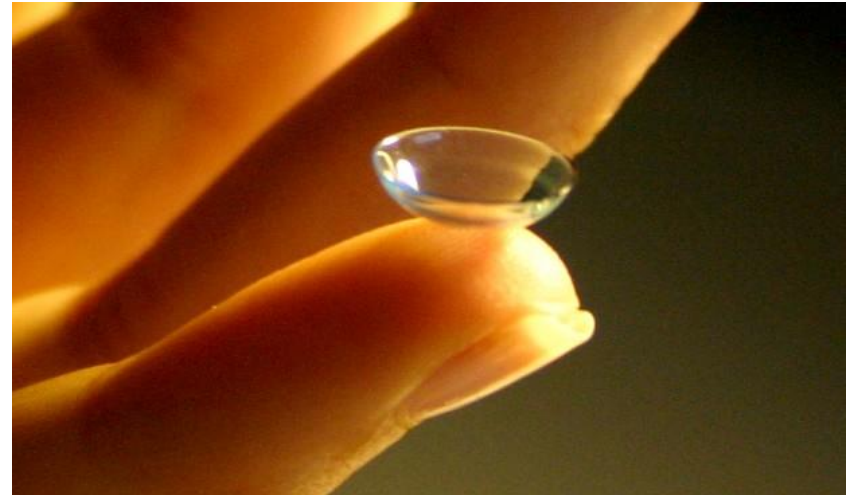
- Light transparent (92%)
- Easily machined, molded, surface coated

Uses:

Blood pumps

Contact lenses

Dentures & bone cements



<http://www.kontaktlinse-ol.de/>

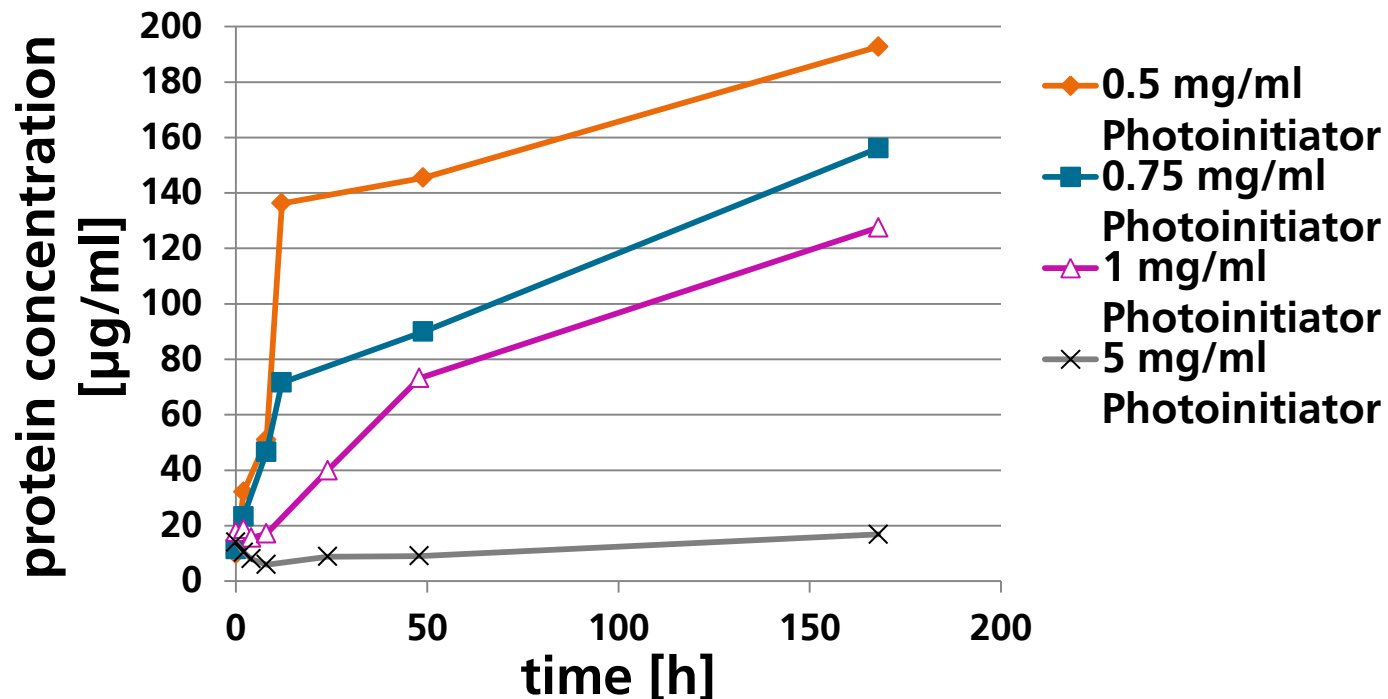
Polymer used in medicine

❖ POLYETHYLENE GLYCOL (PEG)

- PEG of high Mw is called polyethylene oxide (PEO)
- PEG has been FDA approved for medical and food applications
- It facilitates cell infiltration and tissue in-growth
- Prevents „fouling“ on surfaces
- Used as drug delivery system

Uses:

Drug delivery
Coating



Polymer used in medicine

❖ POLYAMIDE (PA)

- Nylon - first commercial polymer
- Amide group – highly polar
- Strong bonds
- High melting temperature
- High modulus & strength

Uses:

Surgical sutures



Polymer used in medicine

❖ POLYDIMETHYL SILOXANES (PDMS)

- Poor mechanical strength
- Si-O backbone instead of C backbone
- Flexibility

Uses:

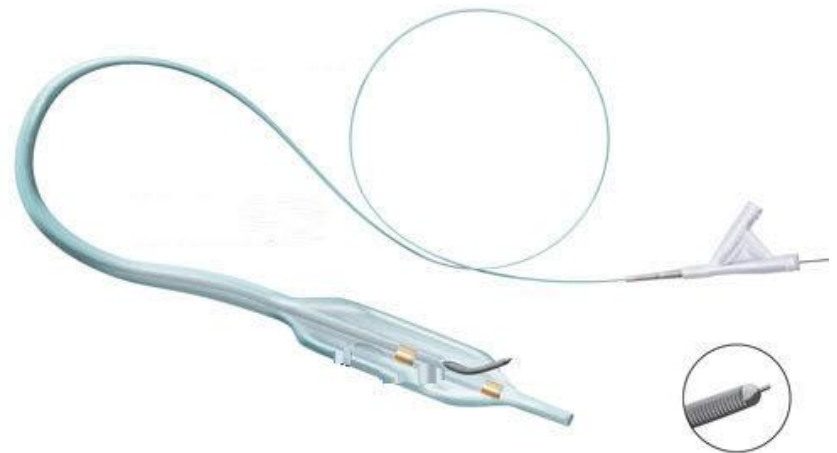
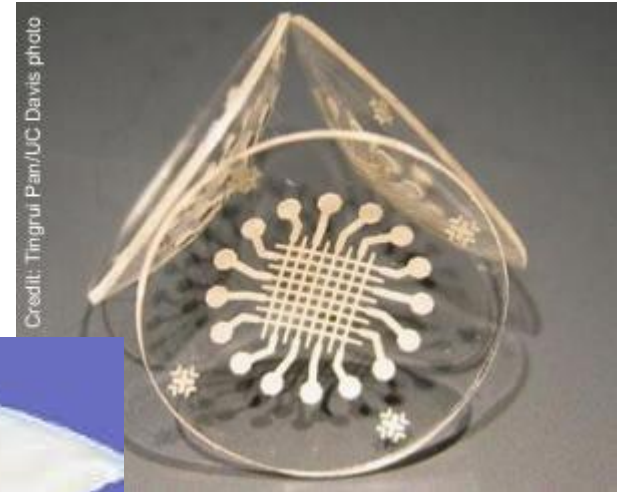
Finger joints

Heart valves

Breast implants

Ear/nose/chin reconstruction

Catheters



Polymer used in medicine

❖ FLUOROCARBON POLYMERS

- Multiple strong carbon–fluorine bonds
- PTFE: polytetrafluoroethylene (Teflon)
- Linear, Highly crystalline (>94%)

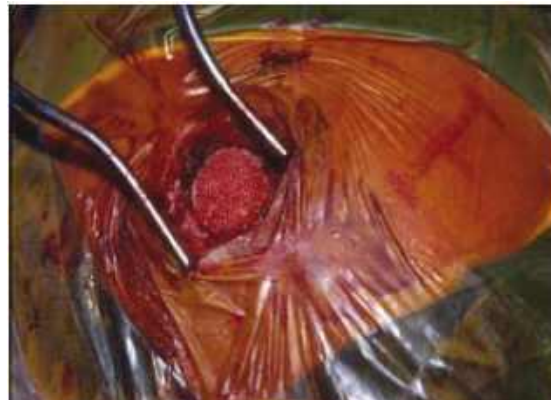
Uses:
vascular grafts



Polymer used in medicine

❖ POLY- ϵ -CAPROLACTONE

- Semicrystalline polymer: degraded hydrolysis
- High solubility and low melting point make it an attractive biomaterial
- Degrades at a slow pace (Useful for >1 year applications)



Uses:

Osteointegration studies

Scaffold for Tissue engineering

Polymer used in medicine

❖ POLYGLYCOLIC ACID (PGA)

- Highly crystalline
- Minimal tissue reaction - Degradation to non-toxic monomers upon exposure to water
- Absorbed by hydrolysis within 60-90 days

Uses:
Sutures



Polymer used in medicine

❖ POLY-LACTIDE ACID (PLA)

- Hydrophobic polymer
- Undergoes less hydrolysis than PGA

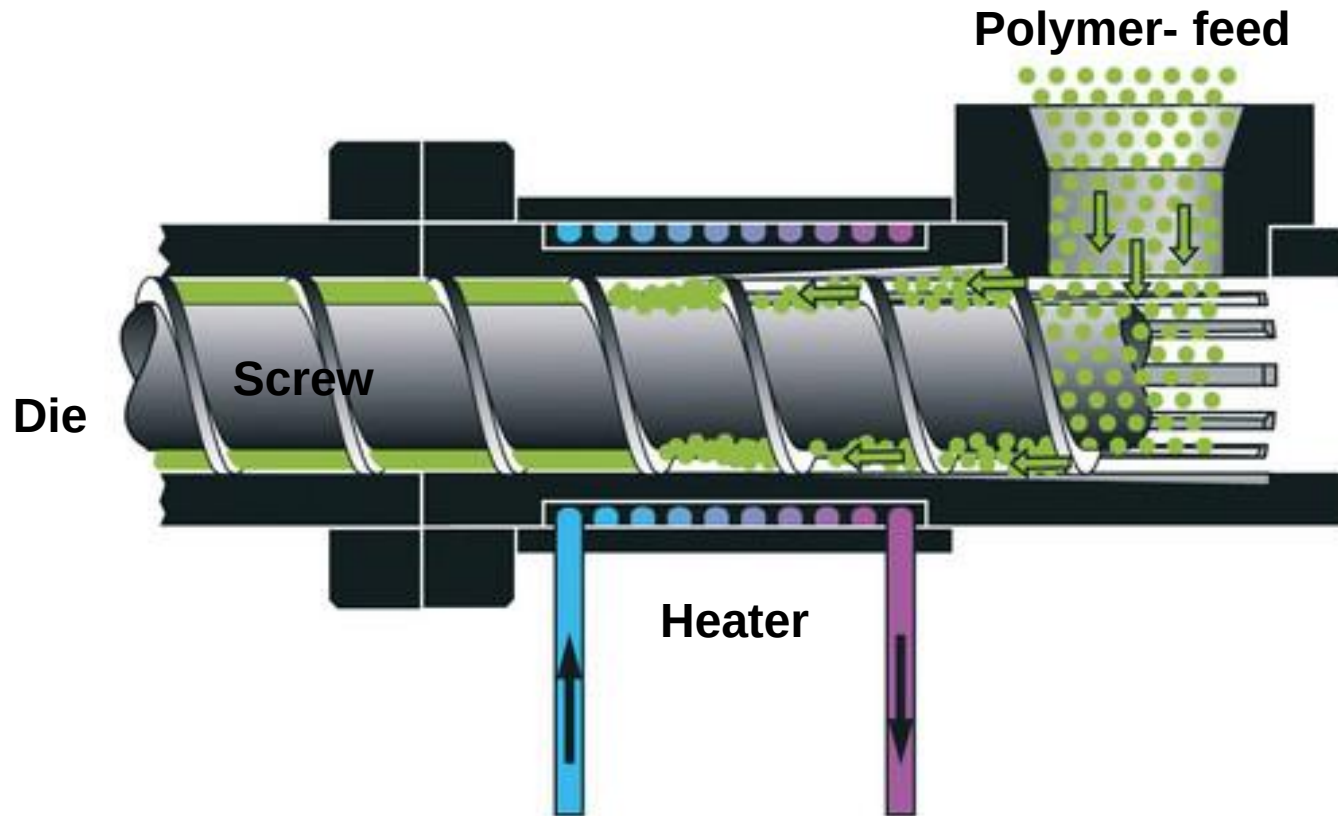
Uses:

Choice of application based on crystallinity



Polymer processing

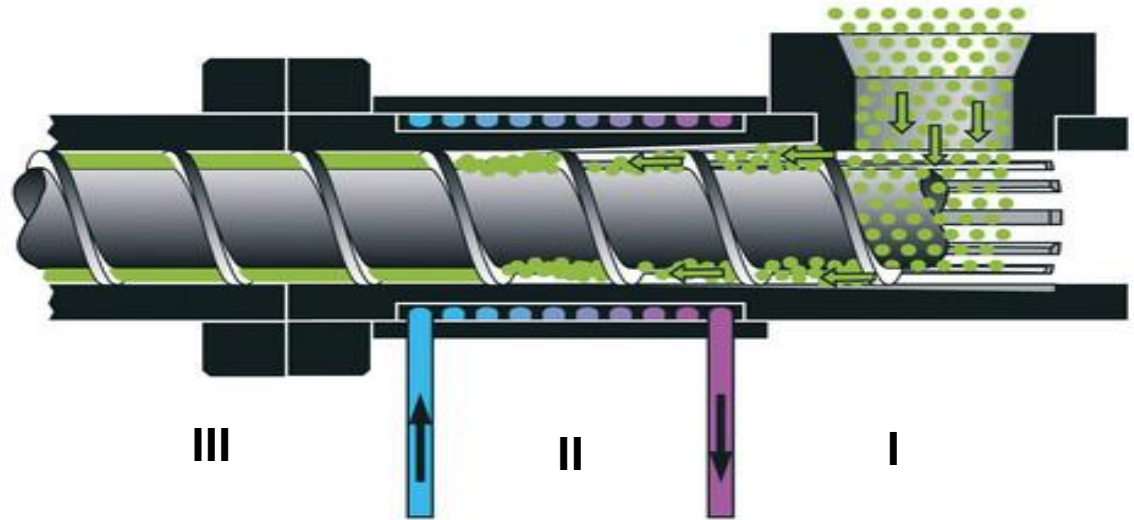
❖ EXTRUSION



Shape of die defines the shape of extrusion product

Polymer processing

❖ EXTRUSION



I) Feed Zone:

Preheats the plastic

It has a constant screw depth

II) Compression Zone:

Screw depth gradually decreases so that plastic is compacted

This squeezes trapped air pockets back to the feed zone

III) Metering Zone:

Screw depth is constant, but much less than feed zone

Melt is homogenised so that there is a constant rate of material with uniform temperature and pressure supplied to the die

Polymer processing

❖ INJECTION MOULDING

- An extruder type screw in a heated barrel rotates
- The melt is injected into a mould (hydraulic system for opening and closing)
- Most common processing method

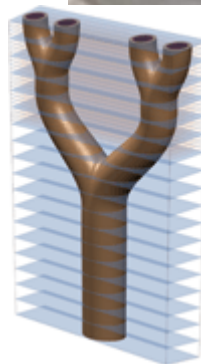
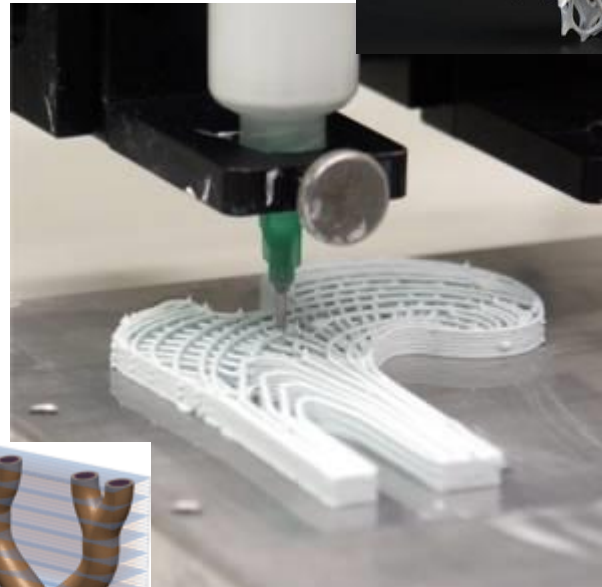


Polymer processing

❖ RAPID PROTOTYPING

Layer by layer production of constructs

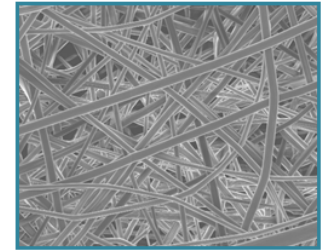
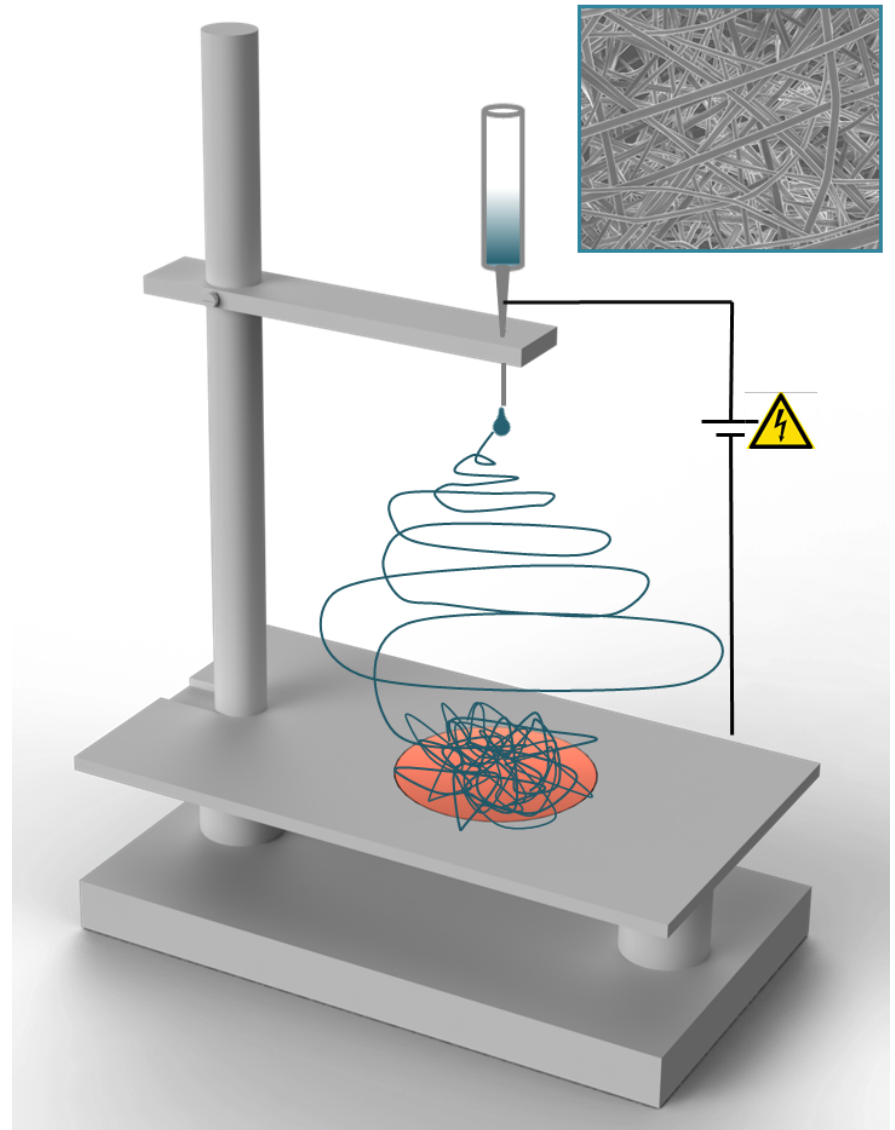
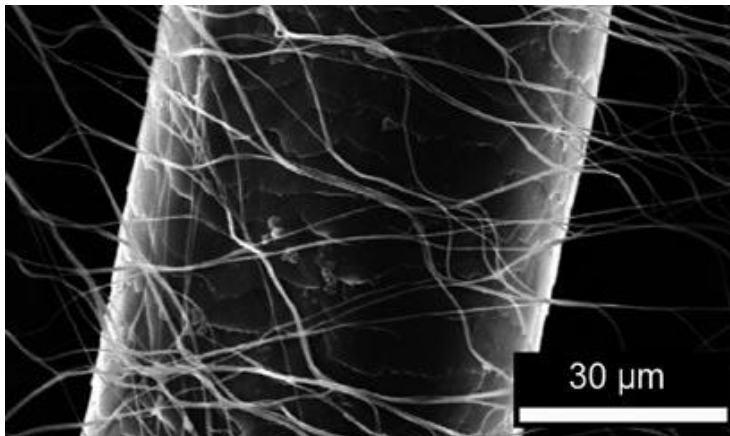
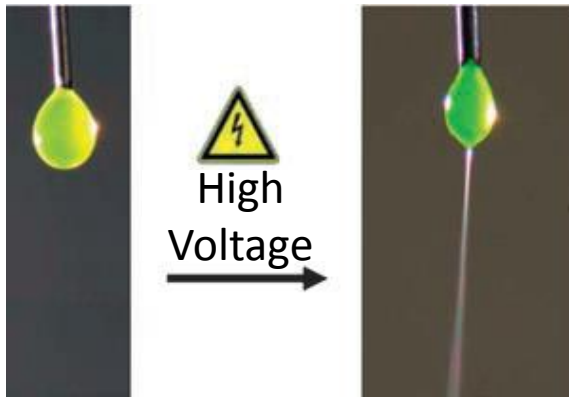
- 3D printing
- Melting
- Stereolithographie
- Laser sintering



http://www.bayreuth.de/images/wirtschaft/rapid_prototypingkl ein.jpg

Polymer processing

❖ ELECTROSPINNING



Polymer processing

❖ FOAMING

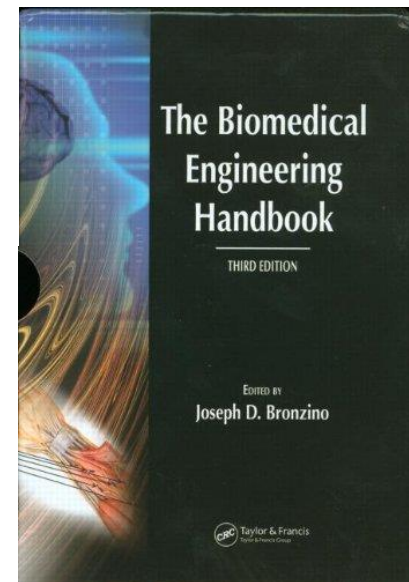
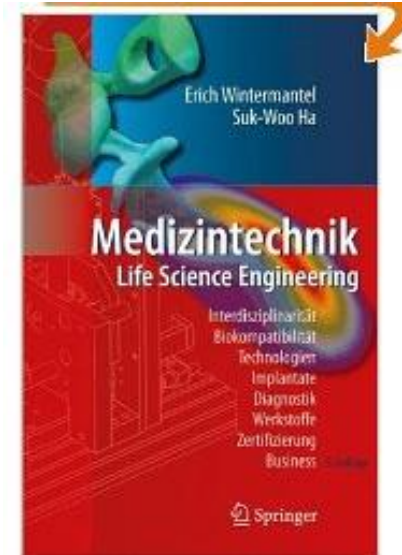
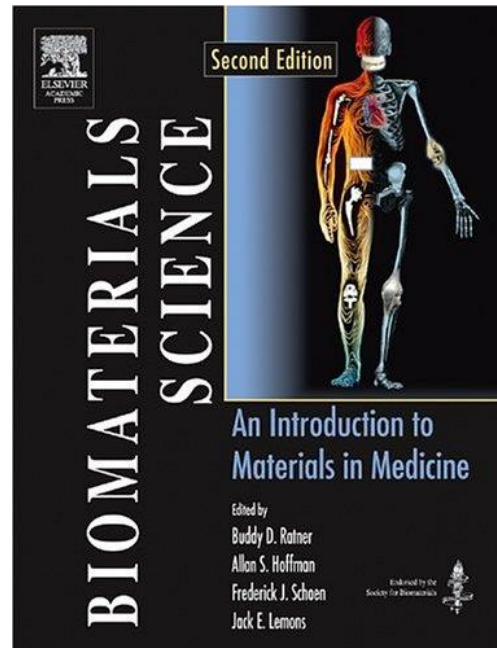
❖ GELLATION

❖ PHASE INVERSION

❖ SALT LEACHING

❖ KNITTING/ WOVEN STRUCTURES

Literatur und Quellen



Thank you for your attention!

