TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

MŠMT
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

KNT/PPO (EN) subject

Contacts

- Pavel Holec
    - KNT – building B, 3. floor, room 04006
    - pavel.holec@tul.cz
    - lecturer, instructor

Literature

- MATYJASZEWSKI: *Polymer Science*, 2013.
- AKAY: *Introduction to Polymer Science and Technology*, 2012.
- CARRAHER: *Polymer Chemistry*, 2006.
- CARRAHER: *Giant Molecules, Essentials Materials for Everyday Living and Problem Solving*, 2003.
- DAVIS: *Polymer Chemistry*, 2003.
- BARNES: *Polymer Physics and Engineering*, 2001.
- MARK: Polymer Data Handbook, 1999.

- POLYMER DATABASE: https://polymerdatabase.com/polymers

Subject content

- lectures
  - a total of 11 hours
  - access to all presentations on E-Learning
  - optional (but you'll lose the tea)
- lab exercise
  - 6 laboratory days, 11 exercises (usually in pairs)
  - compulsory participation in all exercises
    - pregnant women MUST NOT work or be in chemical laboratories
      - rather admit it than endanger the embryo/fetus/child
      - the teacher swears that it can be resolved humanely without giving the person more trouble
  - mandatory submission and recognition of all protocols
- compulsory student presentation on the given topic
- exam
  - oral

Grade evaluation of the subject

- laboratory protocols ... L
  - arithmetic mean of grades from all protocols
  - if 3 or more are rated insufficient, you cannot take the exam
- presentation of students ... P
  - evaluation of informational and formal correctness and substance
- oral exam
  - the default grade corresponds to the arithmetic mean of L and P
  - can be improved or worsened (usually by 1 degree)

Laboratory protocols

- everyone submits for himself
- submit the protocol electronically
    - it must be recognized no later than 2 weeks after the work has been completed
    - I recommend sending within 1 week so that repairs can be made
- the arithmetic average of the marks from the reports is included in the overall assessment

How to draw up a laboratory protocol

- *a formal text with specific rules that must be practiced*

1. header
   - author, subject, exercise number, exercise date, etc.
2. introduction/theoretical part
   - on what principle do the used methods, chemical reactions, etc. work?
3. chemicals and equipment used / methods
   - it is enough in points (in the case of chemicals, also state the purity)
4. workflow
   - how exactly you worked (can be in points) - according to the procedure, it should be possible to repeat the attempt without any additional information
5. results
   - what data you receaved
6. discussion
   - what follows from the measured data (can be connected to the previous point in the Results and Discussions chapter or similar)
7. conclusion
   - Briefly state what happened and how it turned out, usually in the following order:
     - What did you do?
     - How did you do it?
     - What did you measure?
     - What follows from this?
     - How did it all turn out?
     - Other information (where measurement errors may have occurred, how to improve the attempt, etc.)
8. list of sources (if any)

Formal pages of science work

1. serif font (not necessary but preferred)
2. captions of images and graphs <u>below</u> the object
3. table labels <u>above</u> the object
4. single-letter words (except a) should not stand alone at the end of a line (solve with fixed spacing ctrl + shift + spacebar)
5. uniform format for dividing paragraphs (either indentation of the first line or spaces between paragraphs - better not to combine)

Student presentation

- each for himself
- electronically annotated with a projector (not self-supporting - see next slide)
- lecture length (depending on the number of students) about 10 min
- content as agreed or assigned
- they take place at the end of the semester (or by agreement) as part of laboratory exercises

How to make a presentation

- be aware that this is a commented presentation
  - helps the viewer to orient himself in the presentation of the presenter (i.e. the presenter is indispensable for a full understanding of the presentation)
  - on the contrary, a self-supporting lecture should be comprehensible without further explanation, so the lecturer is dispensable (they are actually picture scripts)
- text only sparingly
  - write important points (not sentences) – the lecturer describes it in sentences
- use pictures and graphs
  - the meaning of the presentation lies in the fact that the viewer sees what is being talked about (without visualization, the presentation loses its meaning)
- visibly number the pages
  - for questions from the audience, the committee, etc., it makes it much easier to find your way around (it omits the awkward: "On that picture with the hedgehog... no, on the previous one. Even before that. Still... it‘s too much. Go back...")
- use a legible font (both font and color) and an appropriate background
- at the end of the presentation, thank the audience for their attention
- use formal language
- avoid colloquialisms (committees usually don't like it)
  - jokes, humorous, touching, cute or lascivious images can only be used in two cases:
    - you know you can get away with it (uncommon)
    - or you're lecturing for someone lower in the hierarchy, so they can't directly punish you for it (but it can be pushed through their manager, so it probably happens to everyone)
- rehearse the presentation in advance (see next slide)
- communicate with the audience during the presentation (do not look at the presentation and do not read it from the screen)

Content of the presentation (general)

1. opening shot
   - title of the lecture, name of the author, etc.
2. content
   - often not necessary (especially for short presentations)
3. motivation to solve the given topic
   - common with BP or DP (you make up why you're doing the topic scientifically, even though everyone knows it's just because it's compulsory)
4. information content of the presentation
   - only now are you getting the really essential information
5. discussion
   - you explain what the supplied information actually means and what could result from it
6. conclusion
   - you briefly summarize what was involved, what you found out, what follows from it and any additional information
7. thanks for your attention
8. backup images (see additional images)

Presentation exercise

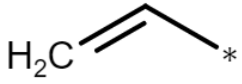
- methodology
  1. prepare water/tea/wine/beer
  2. choose viewers (e.g. favorite picture in the room, cat, cactus, monitor)
  3. start the presentation (I recommend the presenter format, where you can see the current slide, the next slide, notes and the time since the presentation started)
  4. to present the entire presentation from start to finish to a selected unhappy viewer and measure the length of the presentation
  5. repeat point 4. as many times until you stop saying during the lecture: eh..., hmm..., ooooh..., actually..., actually..., as if..., as if... etc. and until the duration of the lecture corresponds to the assignment
- reasons to exercise
  - remembering the continuity of the presentation from memory
  - backchecking the presentation
  - fixing specific expressions, turns and terms
  - limiting filler words and sounds
  - faster and smoother lecturing
  - gaining self-confidence

Presentation tips

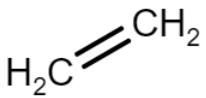
- using notes (only visible to the presenter, not the audience)
  - hard-to-remember abbreviations, foreign terms, etc. can be written down in the notes under the picture in question to be sure, so that a person does not forget or distort what it is about under stress
- backup images
  - explaining things that someone is likely to ask (usually the opponent's questions in BP and DP) insert as separate thank you slides at the end of the presentation and be prepared to use them
  - if someone asks them, you have a solid ground for an answer, plus you look like a dude/oracle
  - if no one asks for them, no one will know that you had them ready at all (they're only after the thank you) and they won't disturb you
- choose appropriate clothing
  - a Hawaiian shirt with flip-flops is usually not appropriate, as is too much cleavage or an astronaut costume
- be active and discuss, but don't get into bigger arguments with the assessors
  - even if you win the argument, some evaluators will not take it well and step on you
  - but if you don't mind: "Hrr to them!" (A professor is only human too, and if you're right, he doesn't have the right to treat you rudely just because you're a student.)

Selected information from organic chemistry

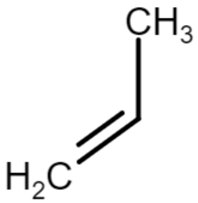
Important organic compounds with trivial names



vinyl

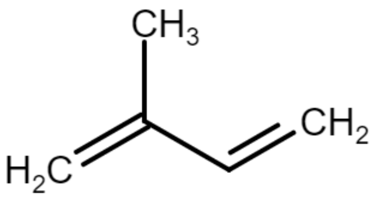


ethylene

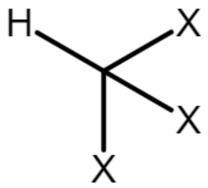


propylene

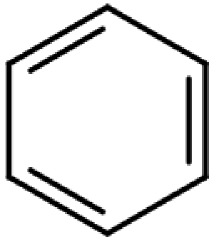
acetylene



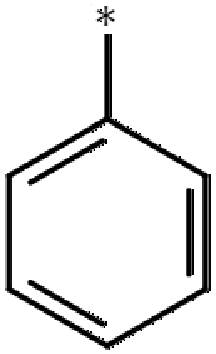
isoprene



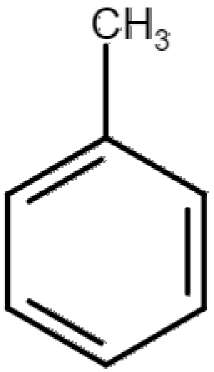
haloform



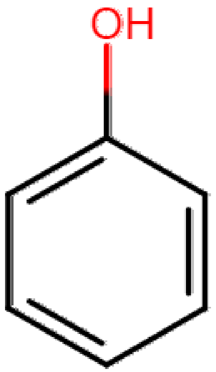
benzene



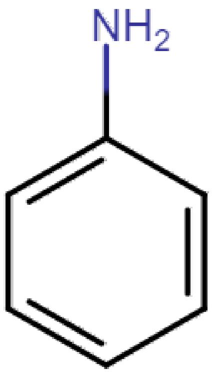
phenyl



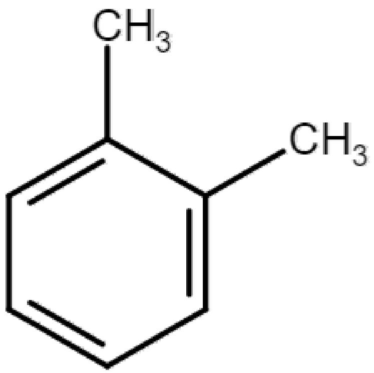
toluene



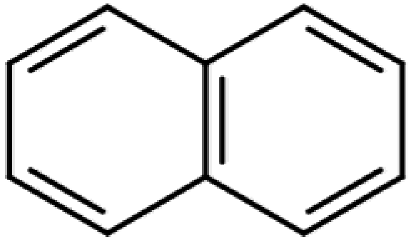
phenol



aniline

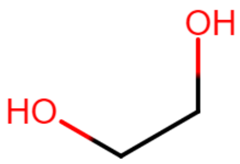


xylene

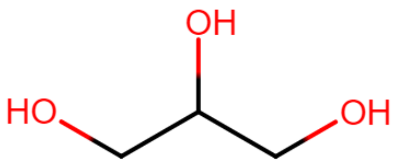


naphtalen

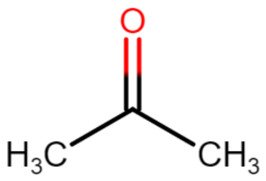
Important organic compounds with trivial names



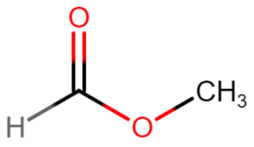
glycol



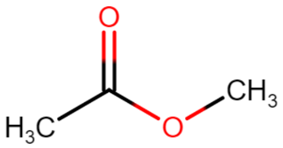
glycerol
(glycerin)



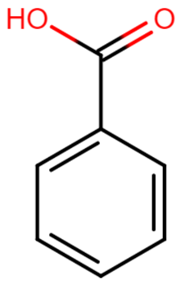
acetone



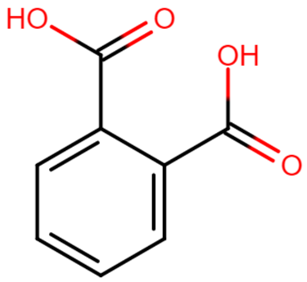
formic acid



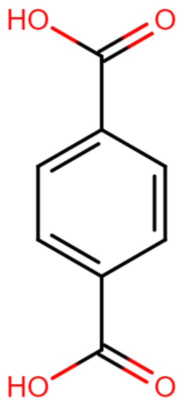
acetic acid



benzoic
acid



phthalic
acid

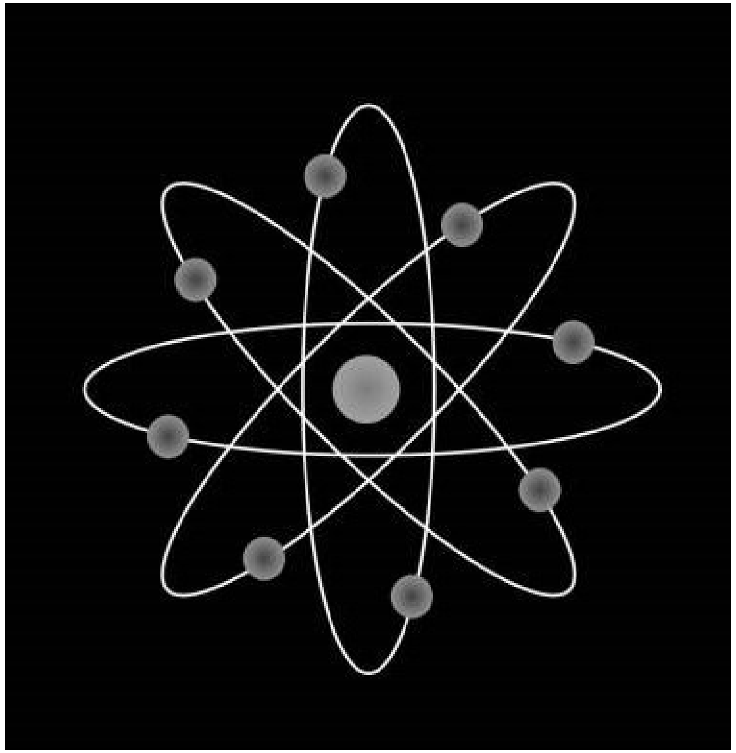


terephthalic
acid

Atom

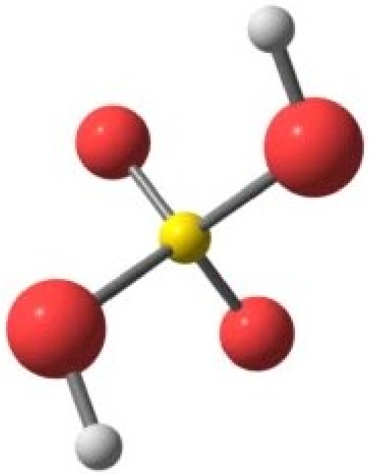
- the smallest part of matter, a fully characterizing element
- Democritus: átomos = indivisible, uncut
  - from a- (negative) and témnō (cut)*

- core
  - nucleons
    - protons (+) and neutrons (0)
  - not bulky
  - most matter
  - atomic shell
- electrons (-)
  - very bulky
  - small amount of matter



Molecule

- a particle formed by atoms connected to each other by a chemical bond fully characterizing a chemical substance

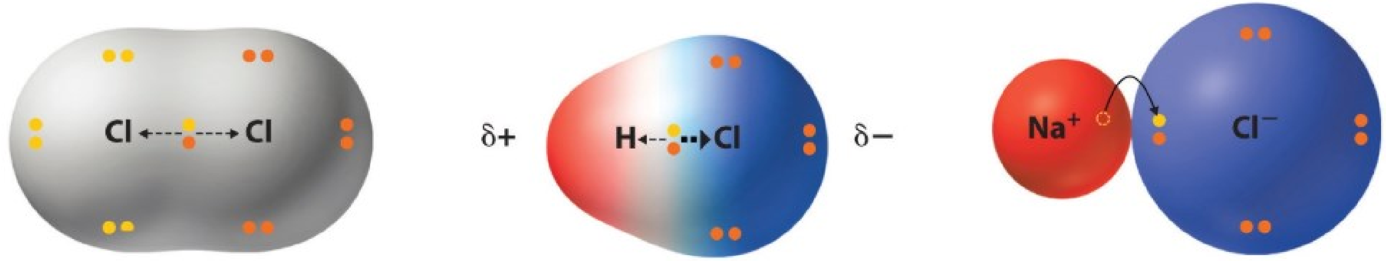


Chemical bond

- a strong bond between atoms ensured by the interaction of their valence electrons
- division
  - covalent
    - non-polar ($\Delta < 0.3$)
    - polar ($0.3 < \Delta < 1.7$)
  - ionic ($\Delta > 1.7$)
  - metal
    - sharing of free electrons (the so-called electron cloud)

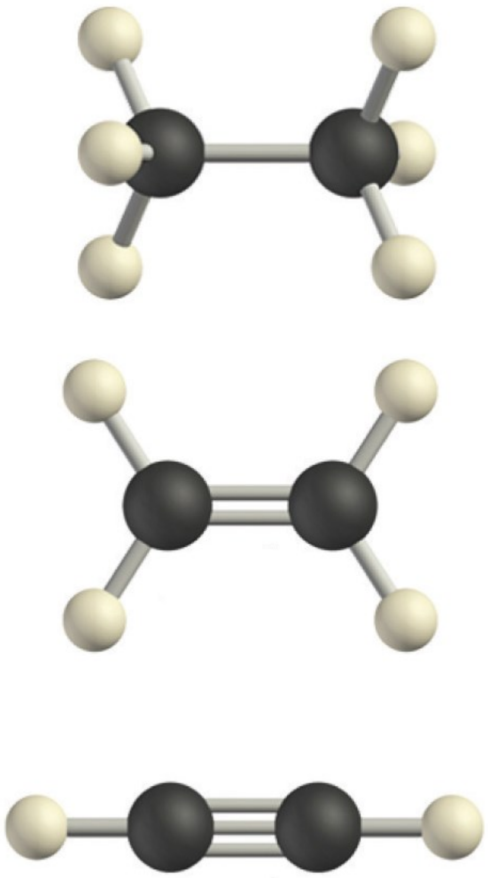
Charge distribution

nonpolar polar ionic

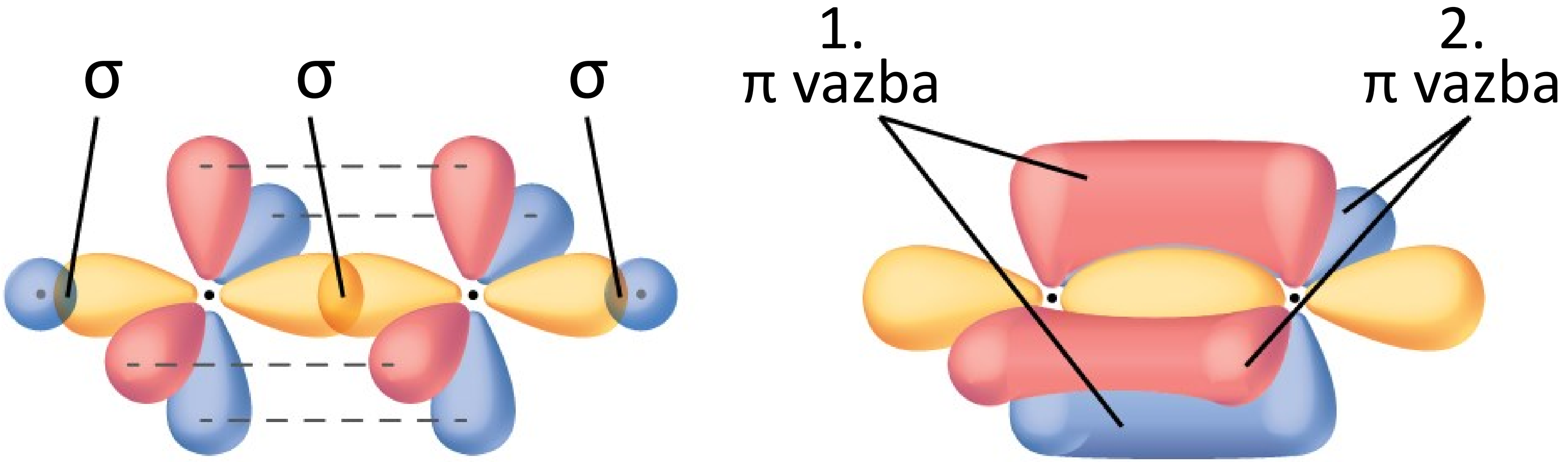


C-C bond

- simple
    - 1 σ-bond (1 electron pair per nuclear bond)
    - spatial
    - allows free rotation around its axis
    - saturated
    - about 1.54 Å
- double
    - 1 σ-bond
    - 1 π-bond (1 electron pair outside the nuclear bond)
    - flat
    - does not allow free rotation around its axis
    - unsaturated
    - about 1.34 Å
- triple
    - 1 σ-bond
    - 2 π-bonds (total of 3 electron pairs)
    - linear
    - does not allow free rotation around its axis
    - unsaturated
    - about 1.20 Å



Triple bond



Physical (secondary) bonds

- = secondary forces = nonbonding interactions
  - they manifest at a very small distance
  - force decreases with the 6th power of distance

- types:
  - dispersive (London's)
    - given by the slight polarization caused by the movement of the e-
    - unaffected by temperature
  - induced dipole
    - formed in the vicinity of the action of a permanent dipole
  - permanent dipole
    - arising in the vicinity of the polar bond (effort for mutual orientation)
    - affected by temperature
  - hydrogen bond (bridge)
  - H bonded to a more electronegative element (F, O, N, C, ...) and unbonded to another electronegative element with a free electron pair (F, O, N)

Van der Waals forces

bond strength

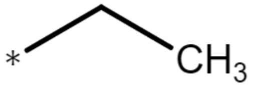
Approximate bond strength*

bond		approximate dissociation energy [kJ/mol]
covalent	C-C	340
	C=C	620
	C≡C	810
	C-H	420
ionic		400 až 1000
metalic		100 až 400
H-bond		10 až 40
other Van der Waals		2 až 15

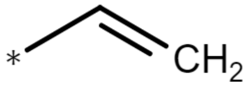
bond	approximate dissociation energy [kJ/mol]	bond length
H–H	436	0,074
C–C	347	0,154
C=C	611	0,133
C≡C	837	0,121
C–O	380	-
Si–O	370	-
B–O	500	-
S–S	214	-
C-H	413	-
C-F	552	-

* individual values vary by source

Characteristic groups

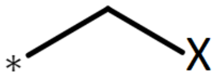


alkane (–an)

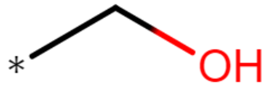


alkene (–en)

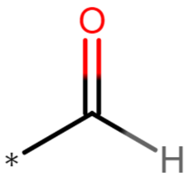
alkyne (–yn)



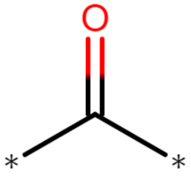
alkyl halide



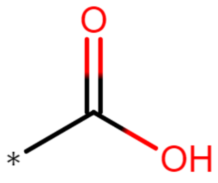
alkohol (–ol)



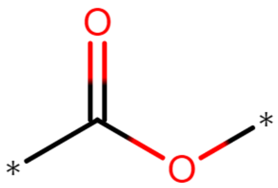
aldehyde (–al)



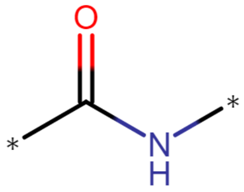
keton (on)



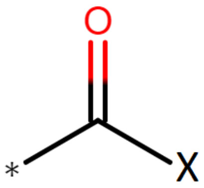
carboxylic acid



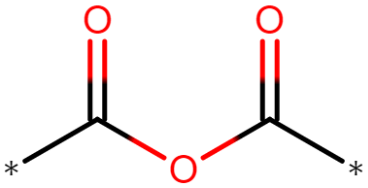
ester (-ate)



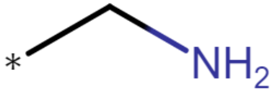
amide (–amid)



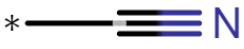
acyl halide



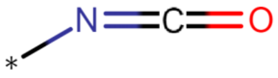
anhydride



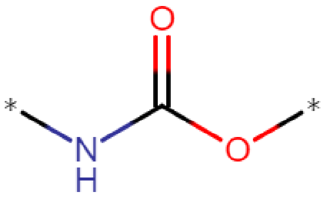
amine (–amine)



nitrile



isocyanate



urethane

Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

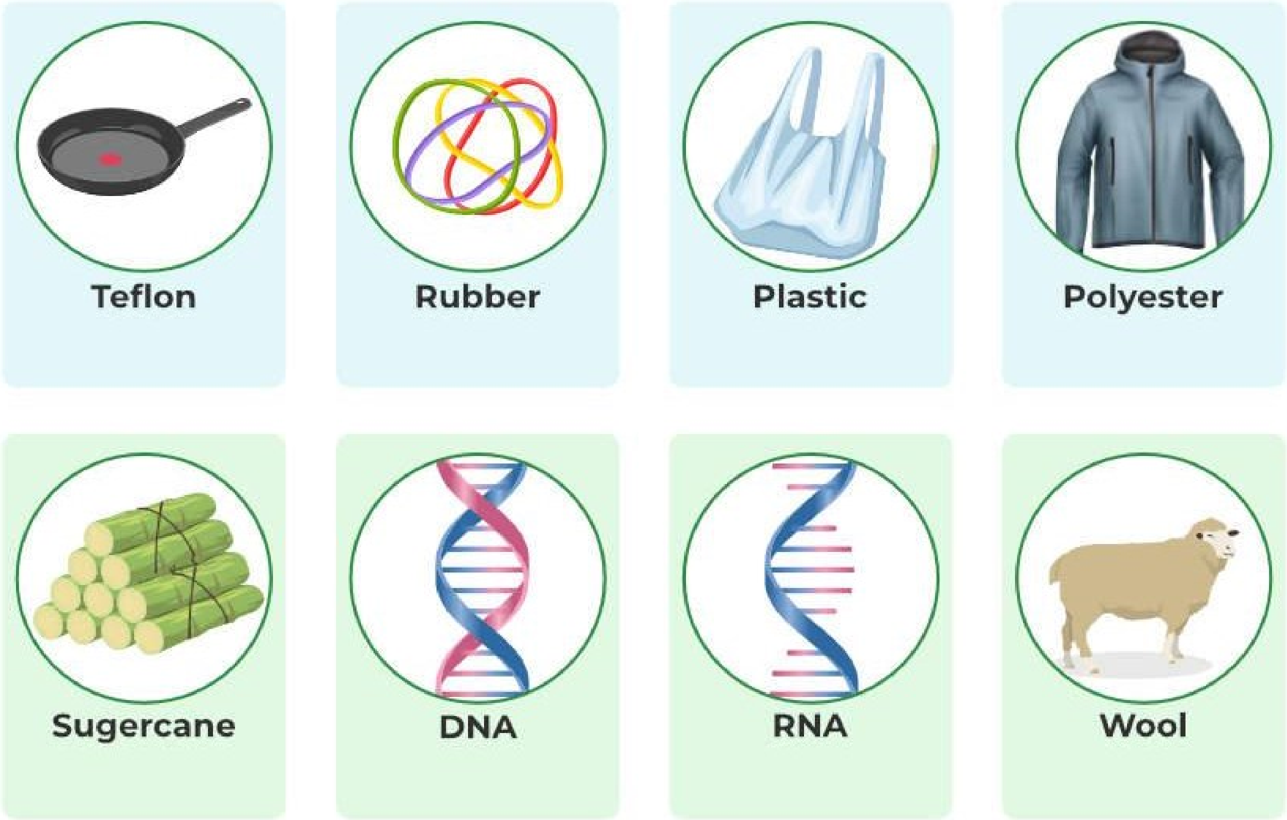
Národní plán obnovy

MŠMT
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Polymers

Introduction, basic terms
and
base materials for their synthesis

Polymers around us



Macromolecular chemistry

The science about

- preparations
- structures
- properties

of macromolecular substances and systems in which these substances are the main component.

History of macromolecular chemistry

- to the beginning of the 19th century – processing available natural polymers
- 1st half of the 19th century – attempts at scientific research into the structure of polymers
- 1811 – the first natural rubber processing factory (Vienna)
- 1839 – discovery of vulcanization of rubber (Goodyear)
- 1852 – concept of chemical bonding (Frankland)
- 1857 – tetravalent carbon and the theory of chemical structure (Kekulé and Kolbe)
- 1862 – celluloid (Hyatt)
- 1865 – artificial silk
- 1872 – synthesis of phenol-formaldehyde resins

History of macromolecular chemistry

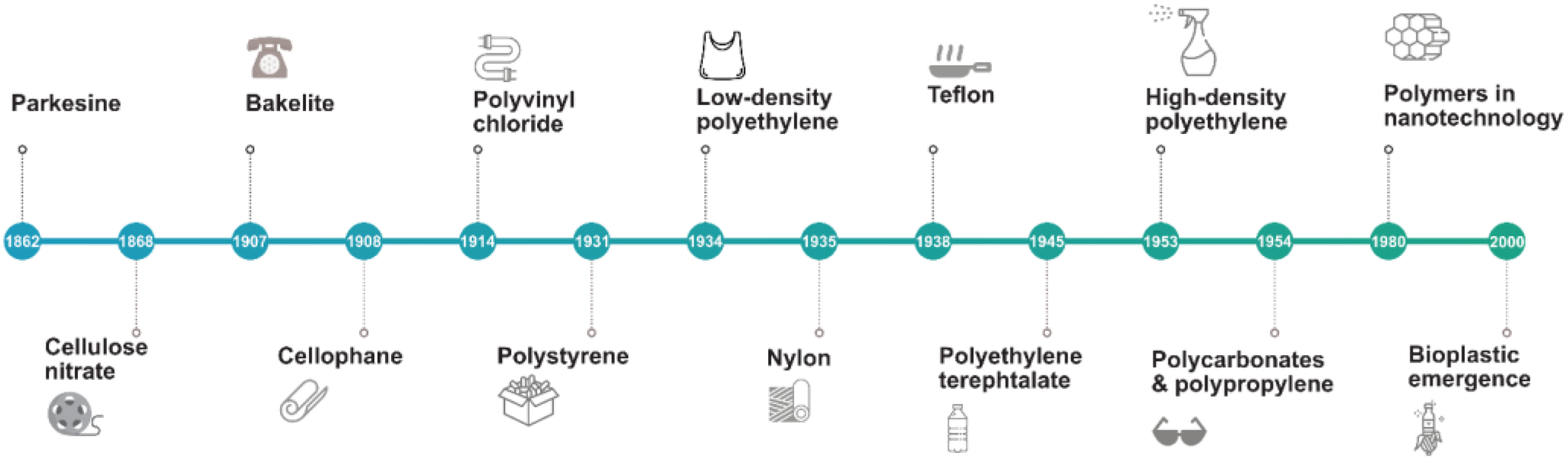
- 2nd half of the 19th century – colloidal theory, stagnation of structure research
- beginning of the 20th century – chain theory
- 1907 – industrial production of Bakelite
- 1909 – synthetic rubber
- 1920 to 1930 – PVA, PVC, PS, rubbers
- 1928 – unraveling the structure of proteins based on the chain theory
- The 1930s – the definitive victory of the chain theory, the beginnings of macromolecular chemistry
- 1930 to 1940 – polyesters, polyethylene, chloroprene
- 1940 to 1950 – rapid development of polymer research
- 1954 – polypropylene (Ziegler-Natta)
- so far – other new technologies, discoveries, possibilities, but also problems (e.g. plastic microparticles in drinking water)

Properties of polymers

- extraordinary modifiability of input materials
- high speed and volume of production
- cheap (relatively) processing of raw materials
- cheap (relatively) processing of products

- usually not very heat resistant
- often poorly degradable

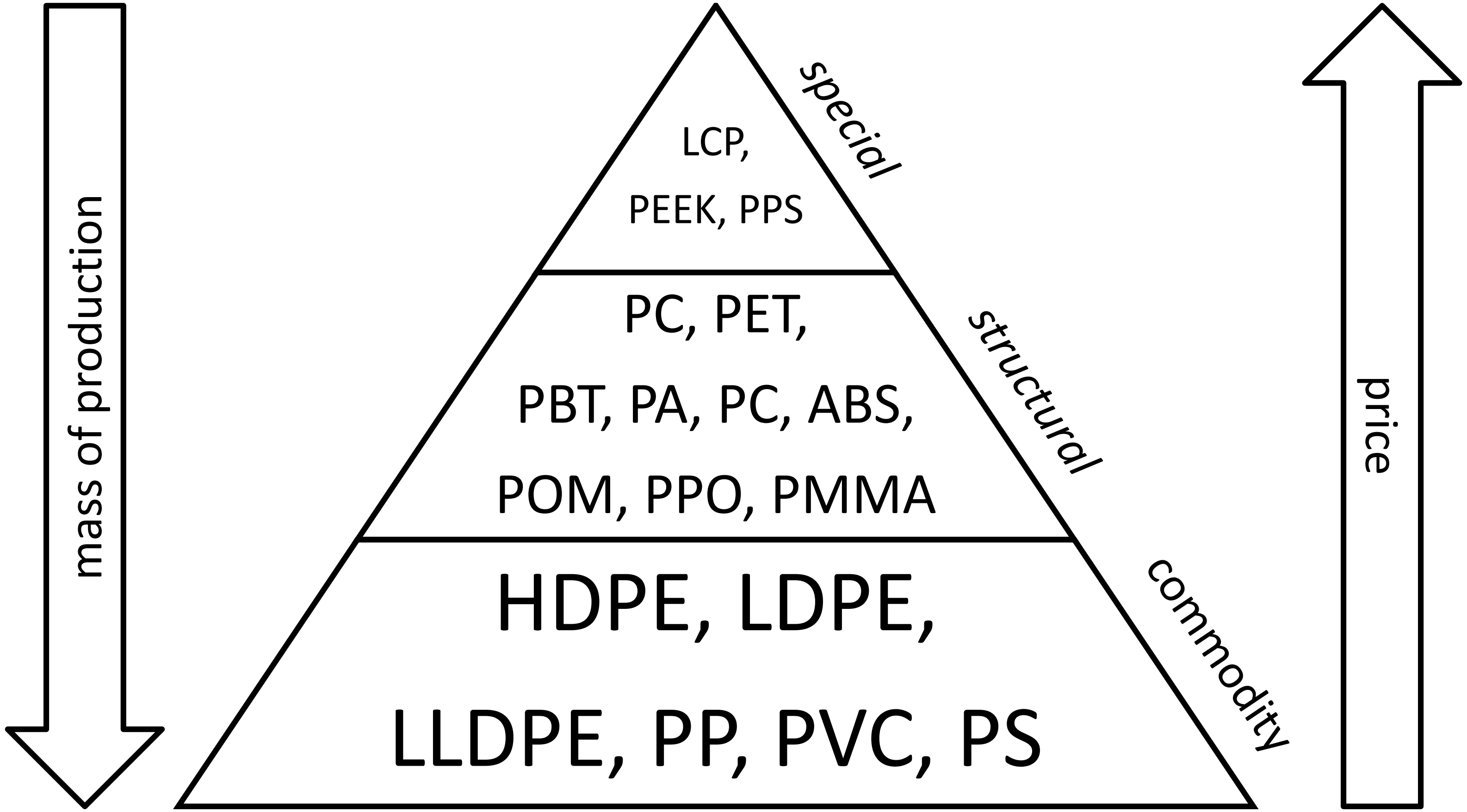
History of polymers timeline



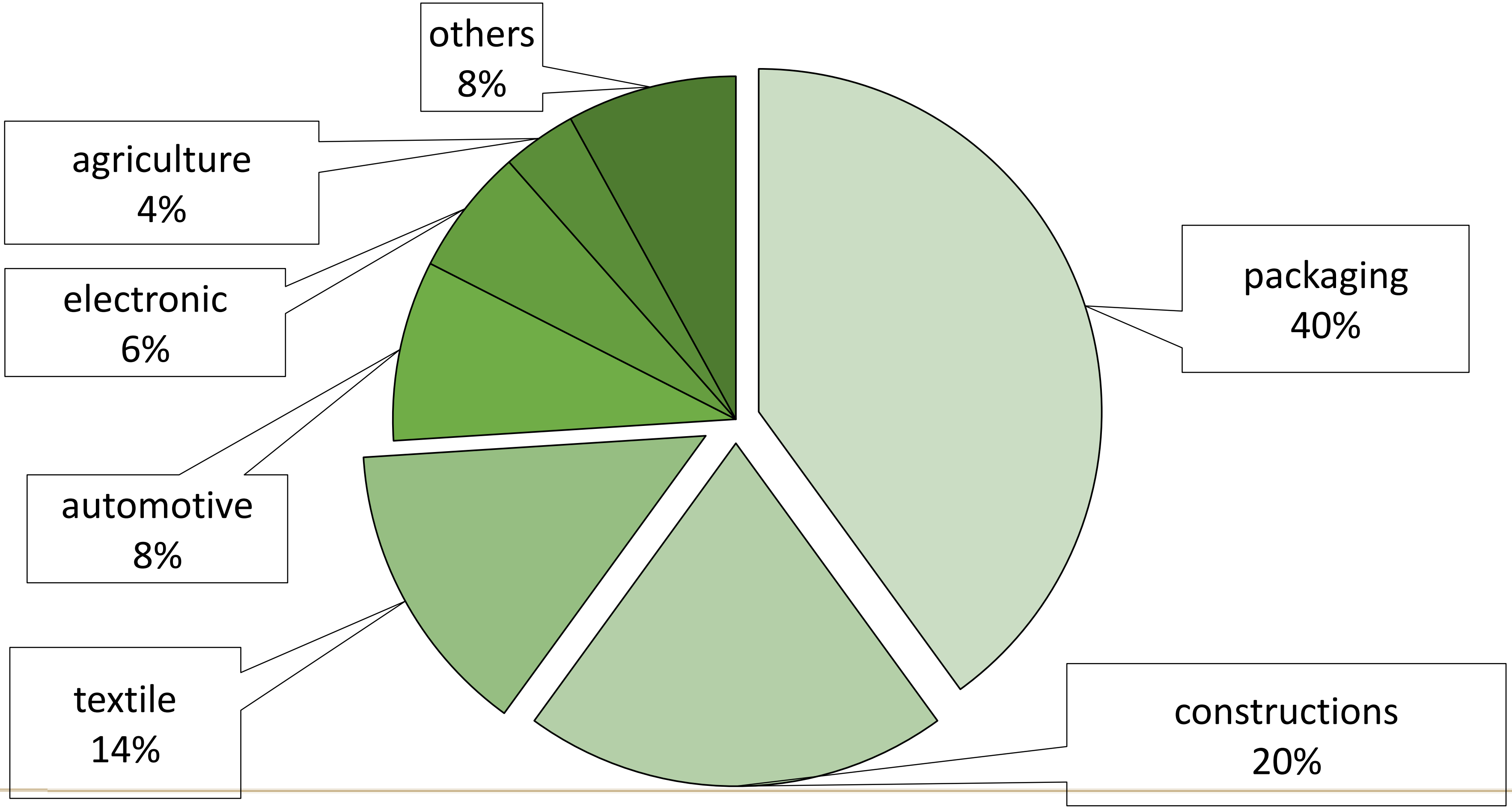
Classification according to production

- mass production
  - packaging, construction, textiles, automotive, agriculture
  - PE, PP, PVC, PS, PET, PA
- special
  - electrical engineering (insulation, batteries)
  - liquid crystals
  - polymer membranes
  - medical technology

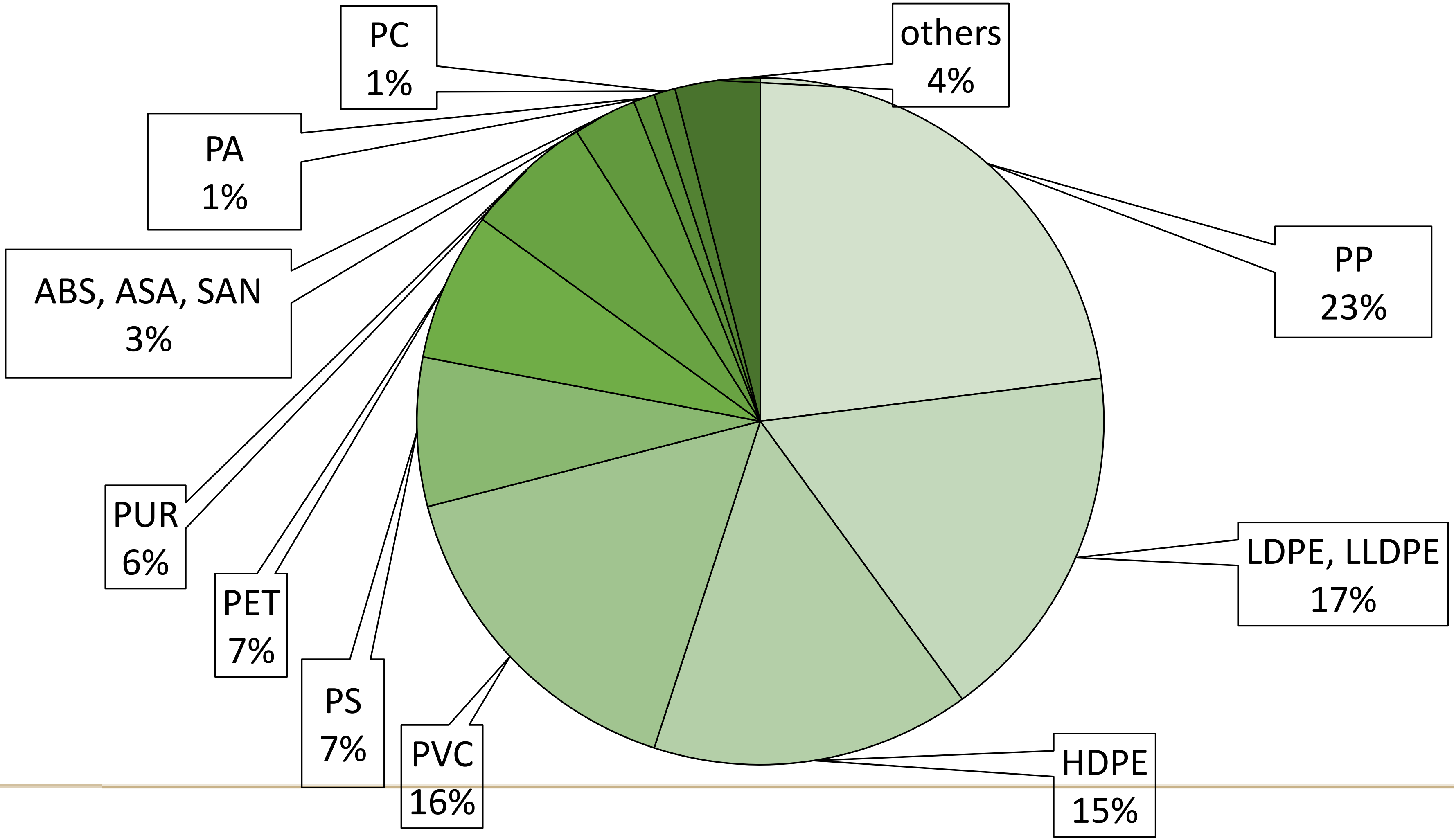
Polymers and price



World consumption of polymers

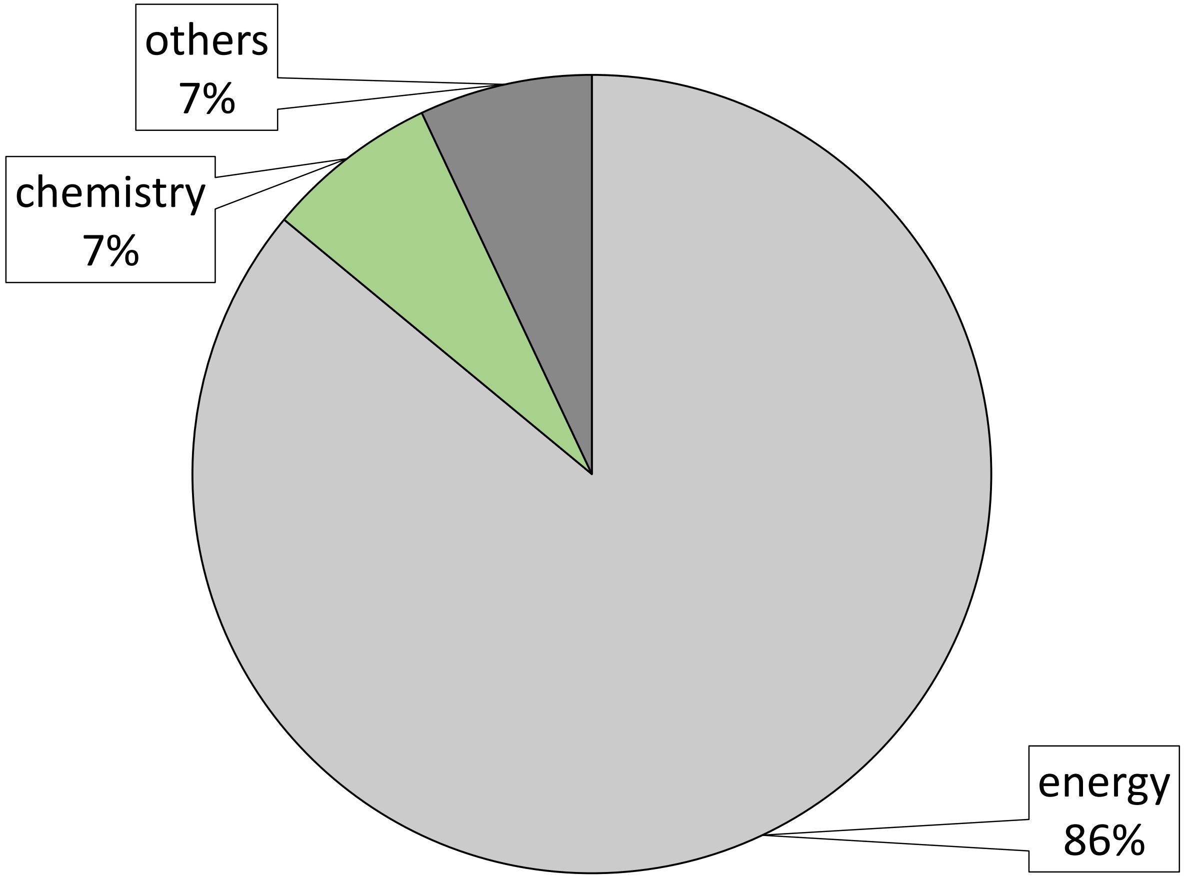


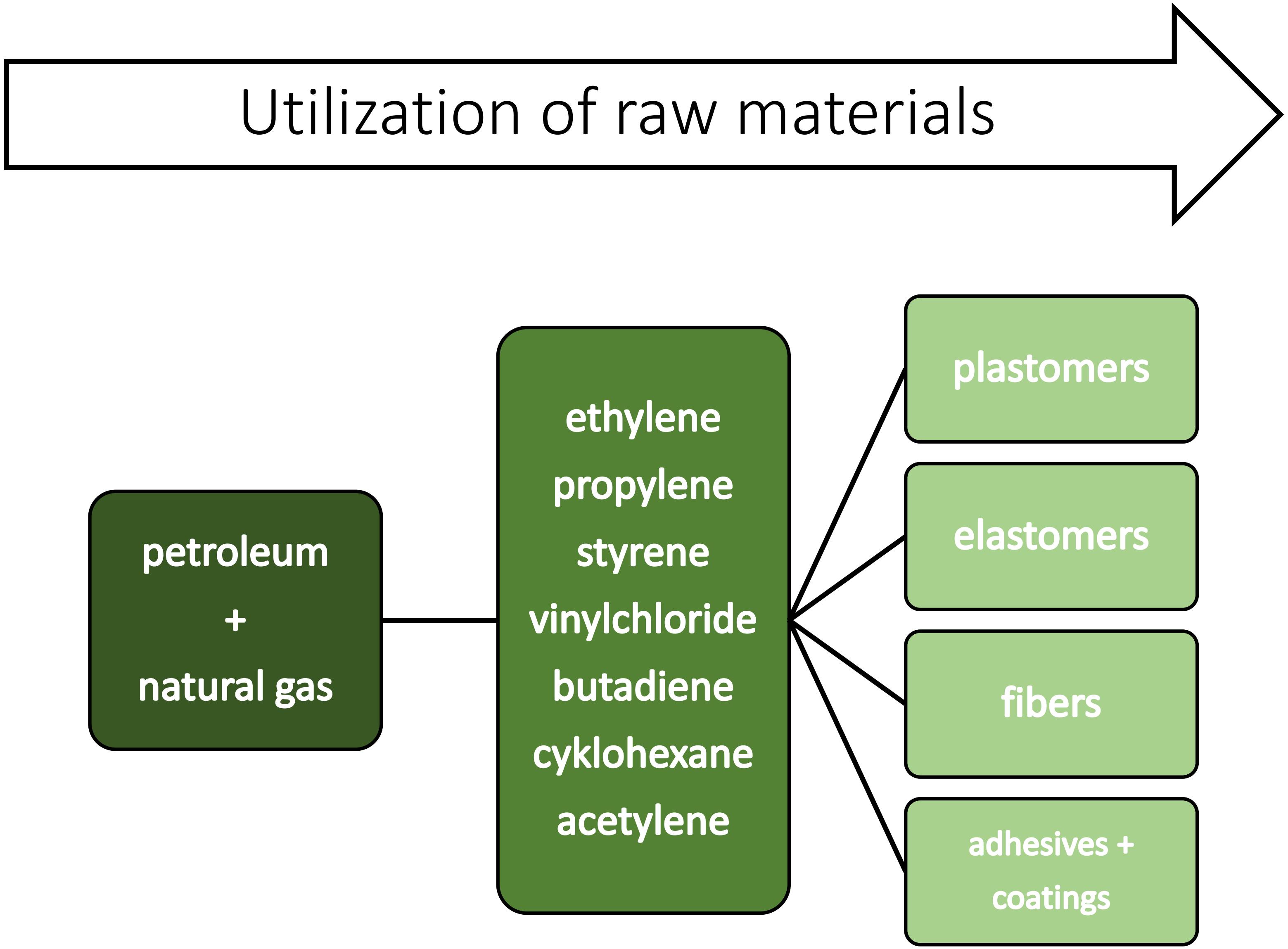
World consumption of polymers



Raw materials

- oil (60%)
- coal (18%)
- biomass (10%)
- other





Utilization of raw materials

petroleum
+
natural gas

ethylene
propylene
styrene
vinylchloride
butadiene
cyklohexane
acetylene

plastomers

elastomers

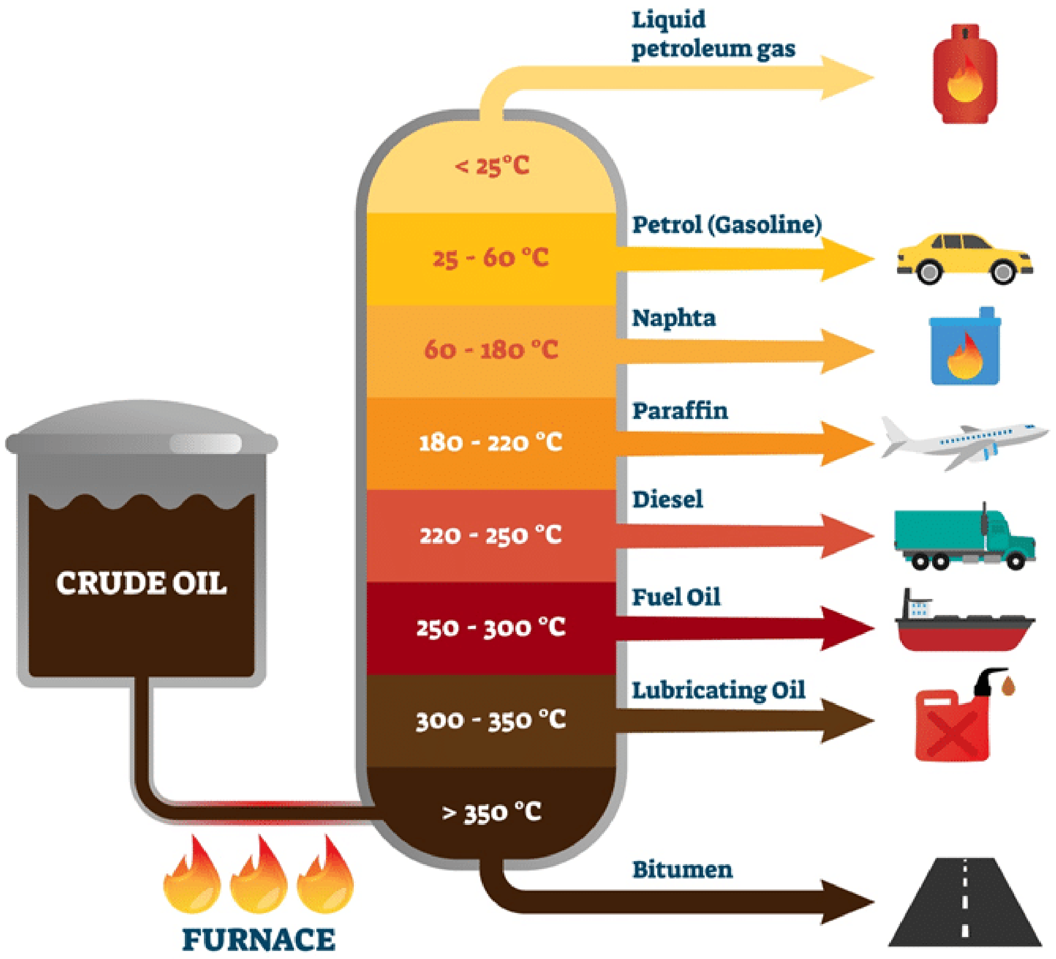
fibers

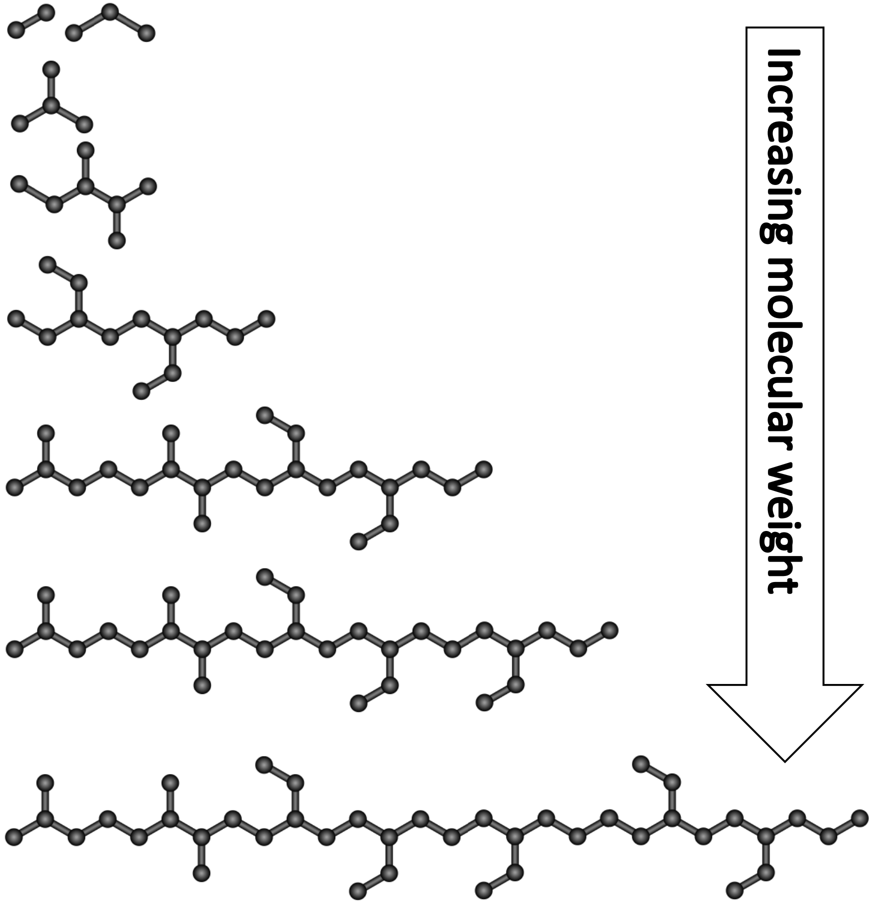
adhesives +
coatings

Petroleum

- a dark oily mixture of mostly organic substances
  - accompanied by deposits of natural gas
- it arises from dead parts of plants and animals in the absence of air, higher pressures and temperatures
- a source of monomers for the polymer industry
  - fractional distillation

Fractional distillation of crude oil





Basic terms

- POLYMER
  - a substance consisting mainly or entirely of macromolecules
  - is formed by a polyreaction
- MACROMOLECULE
  - a compound with a high molar mass formed by the repetition of one or more types of atoms or groups of atoms bonded to each other by a chemical bond in such a large number that the addition or subtraction of one or more units (from the ends of the molecule) does not change a whole range of properties
  - molecular weight greater than about 10^4 g/mol (there is no sharp transition between low and high molecular weight substances)

Basic terms

- OLIGOMER
  - a compound with a not too high molar mass formed by the repetition of one or more types of atoms or groups of atoms bound to each other by a chemical bond, whereby the properties are changed by the addition or subtraction of one or more units (from the ends of the molecule)

- MONOMER
  - a compound (most often organic) capable of forming macromolecules by reaction
- MONOMER (STRUCTURAL) UNIT
  - measure, measure
  - the largest constitutional unit formed during polymerization from a single monomer molecule

Basic terms

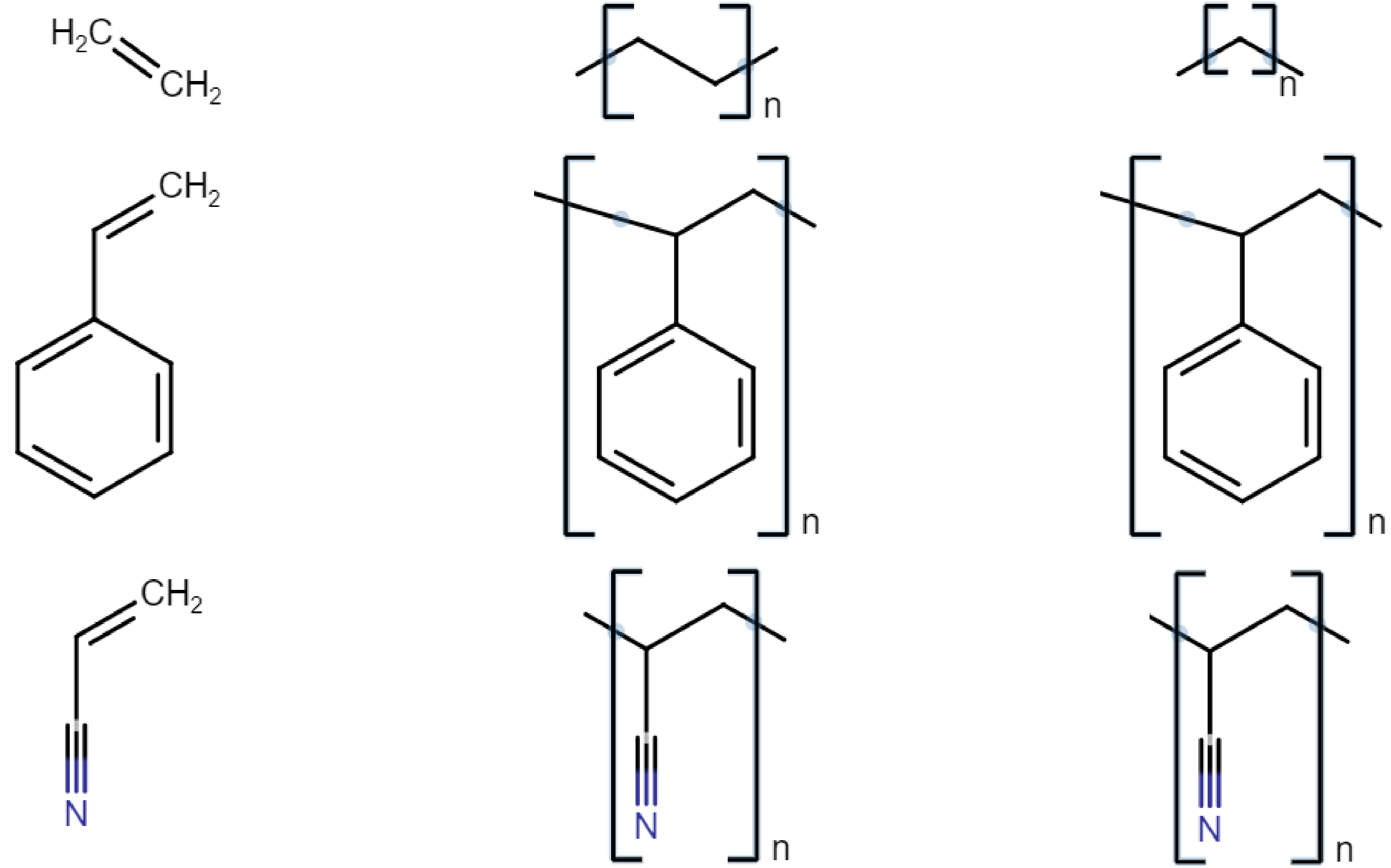
- DEGREE OF POLYMERIZATION
    - the total number of monomer units in the macromolecule

- CONSTITUTIONAL REPEATING UNIT (CRP)
    - the smallest constitutional unit whose repetition describes a regular polymer
        - a structure oriented from left to right is usually preferred, when the condition of the lowest locant of substitution according to the rules of nomenclature of organic chemistry is met
        - *from other point of view:* in the formula, there will usually be a group with a heteroatom on the left, and then carbon chains and other heteroatoms

Monomer

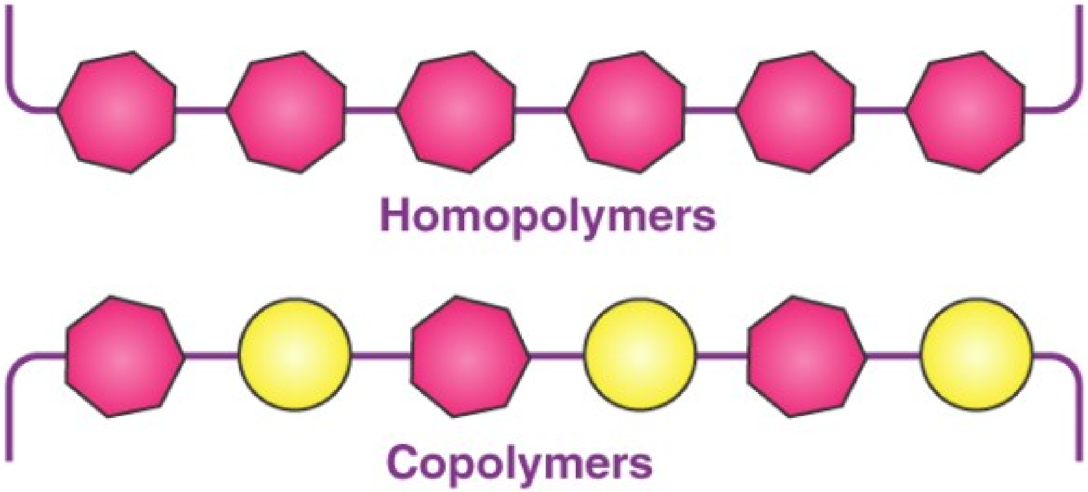
Monomer unit

CRP



Basic terms

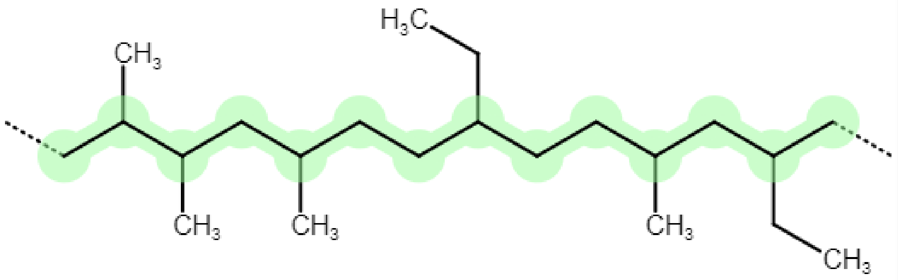
- HOMOPOLYMER
  - formed by only one type of mer
- HETEROPOLIMER or COPOLYMER
  - made up of several types of mers
  - statistical -S-S-T-S-T-T-T-S-T-S-S-T-
  - alternating -A-L-A-L-A-L-A-L-A-L-A-
  - periodic -P-E-R-P-E-R-P-E-R-P-E-
  - block -B-B-B-L-L-L-B-B-B-L-L-L-
  - grafted -G-G-G-G-G-G-G-G-G-G-
    -R-R -R-R -R-R



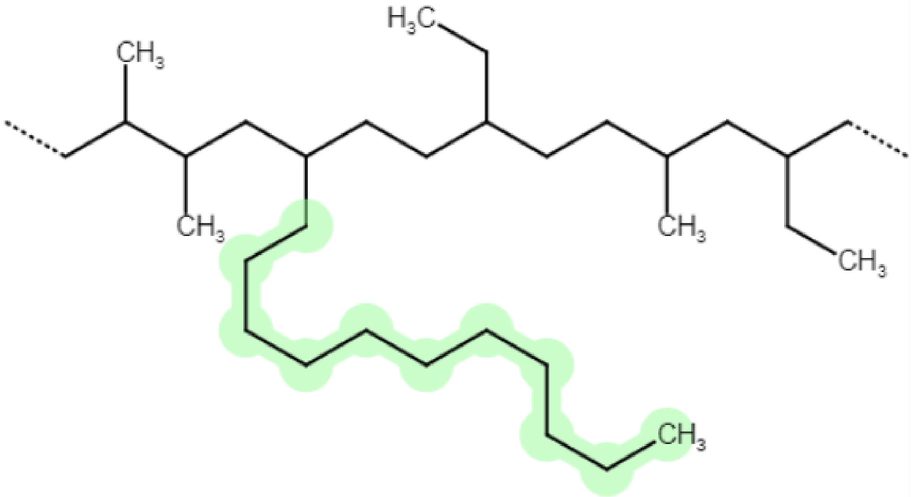
Basic terms

- MAIN CHAIN
  - the longest chain of a macromolecule
- SUBSTITUTE
  - structures bound to the main chain
- LINEAR POLYMER
  - consisting of only one simple string
- BRANCHED POLYMER
  - made up of one main chain and chemically bonded side chains (usually shorter)

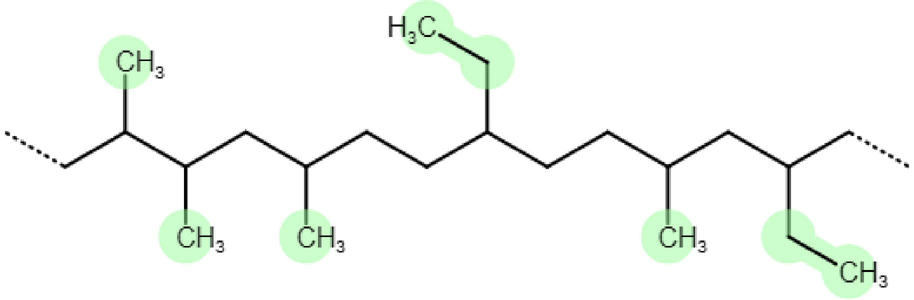
main chain



side chain



substituent



Exceptional behavior of polymers

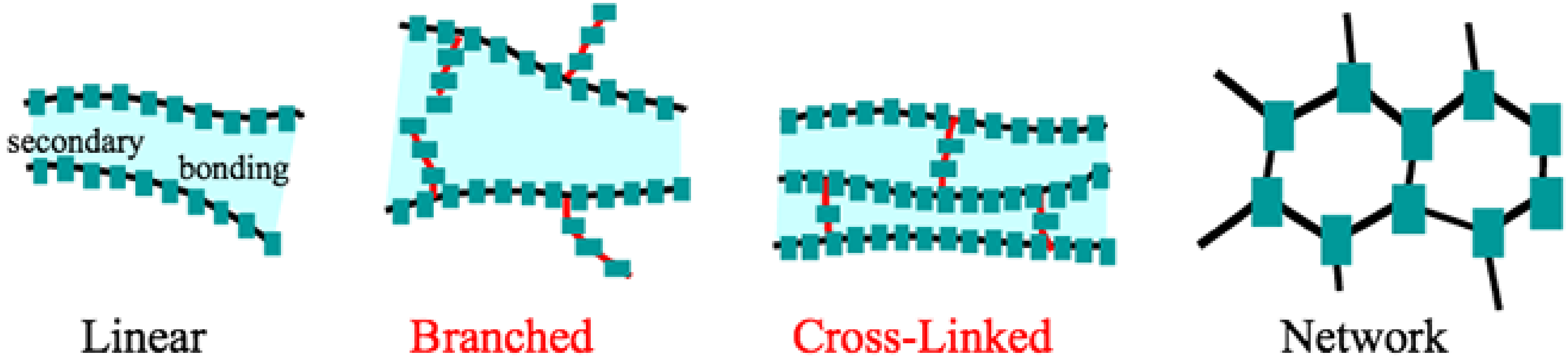
- the combined action of intermolecular forces
- string entanglement
- time-dependent movement

- the disproportion between the length and the width of the chain
- usually not all molecules (of the same polymer) are the same

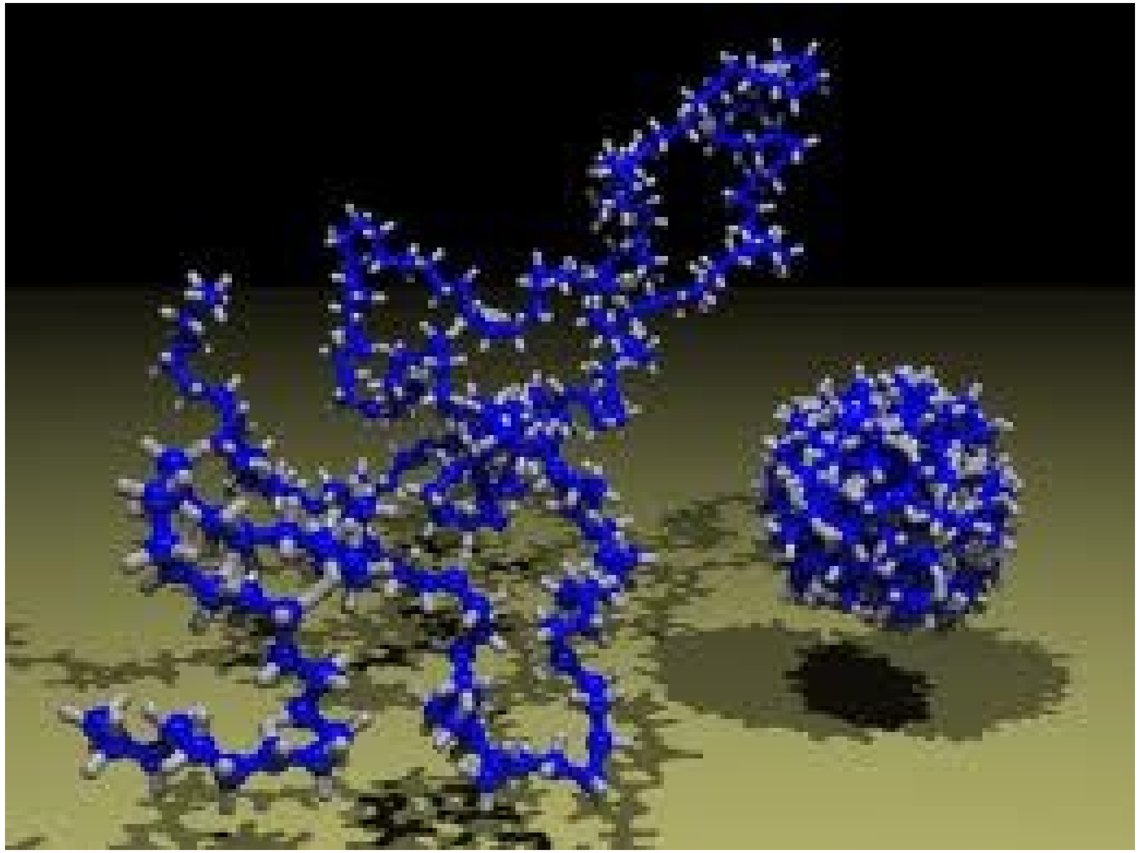
Structure of macromolecules

- given by the functionality of the monomers
  - linear
  - branched
  - cross-linked

- linear
  - soluble
- cross-linked
  - insoluble
  - swell

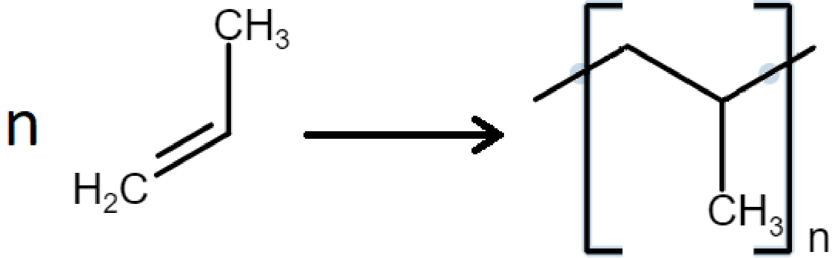


Shapes of macromolecules



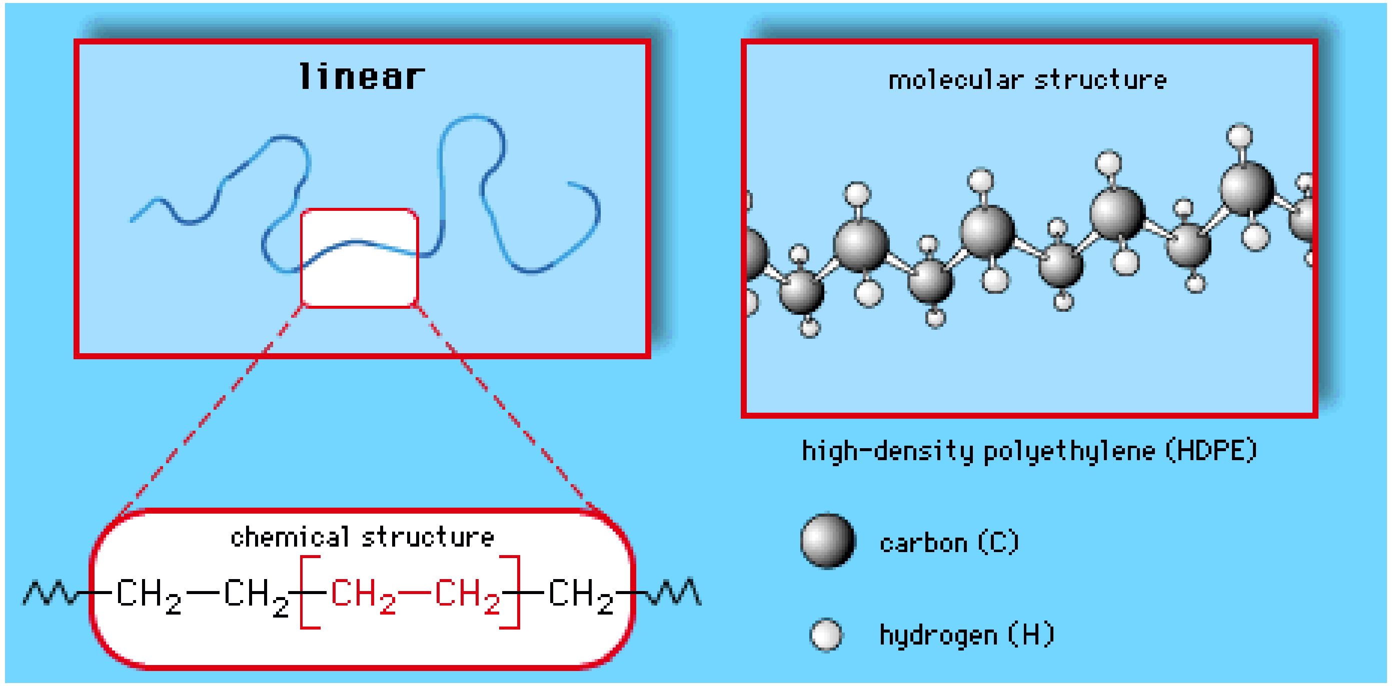
Polymerization

- the reaction in which small molecules become macromolecules
- the opposite is depolymerization (sometimes it can be traced back to the starting monomers)



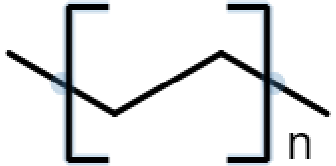
Polymers and chemical structures

- polyolefins
- vinyl polymers
- polyethers
- polyesters
- polyamides and aramids
- polyurethanes
- butadiene polymers

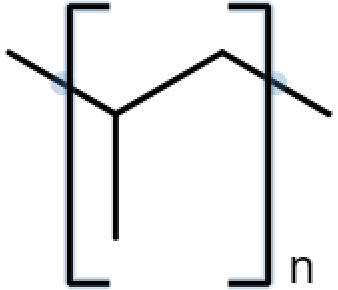


Polyolefins

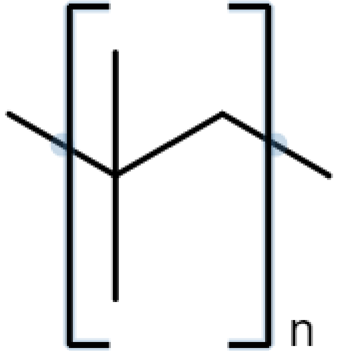
PE



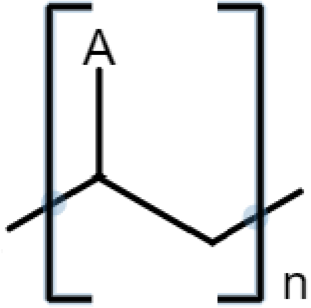
PP



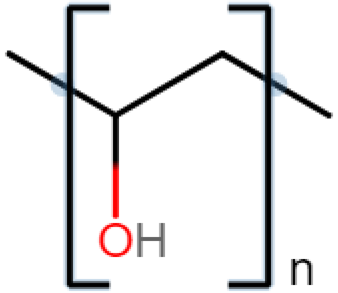
PIB



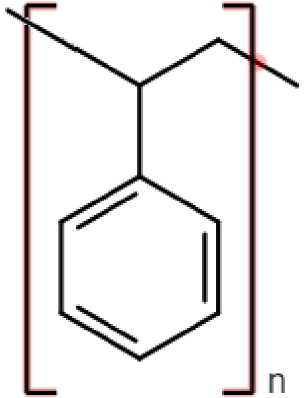
Vinyl polymers



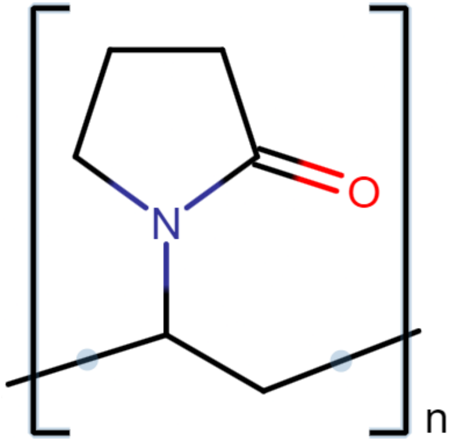
PVA



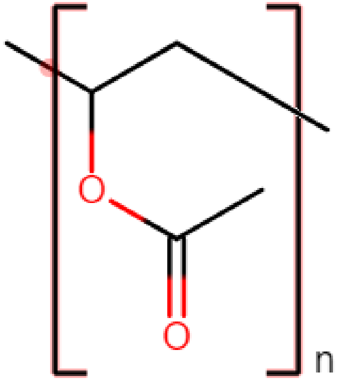
PS



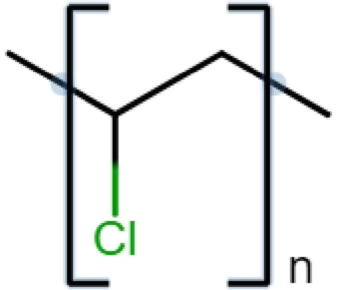
PVP



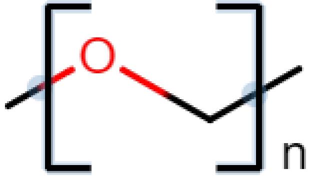
PVAc



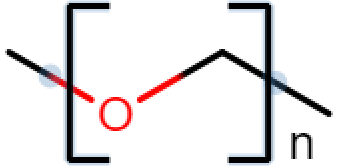
PVC



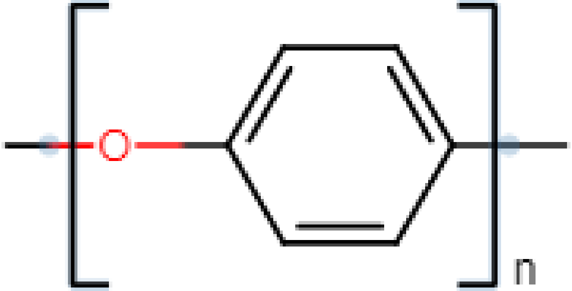
Polyethers



POM

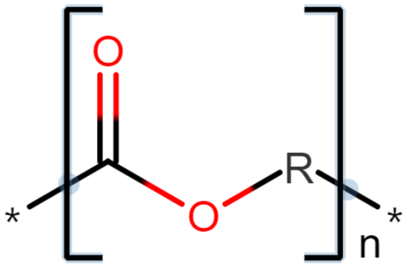


POPh

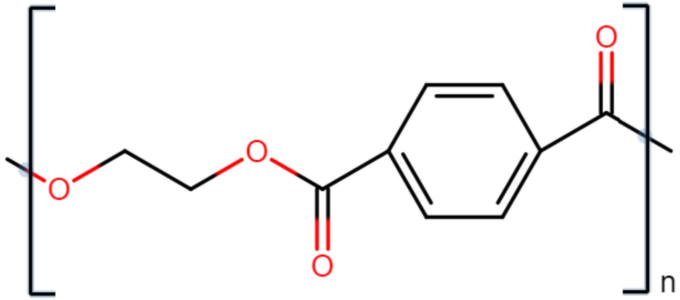


POE

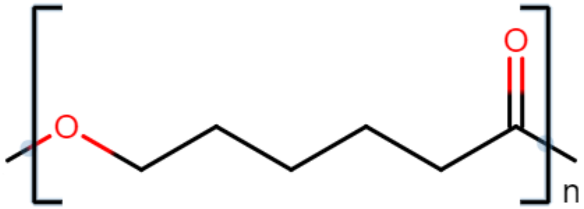
Polyesters



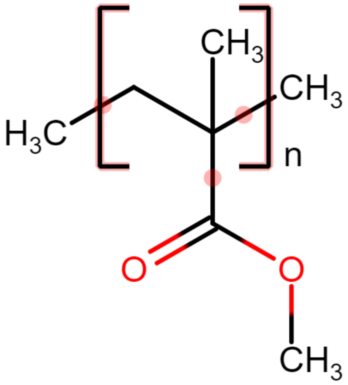
PET



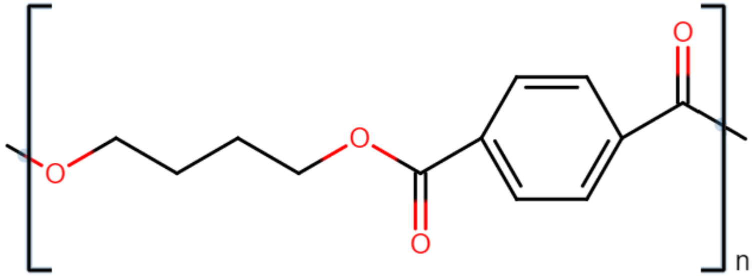
PCL



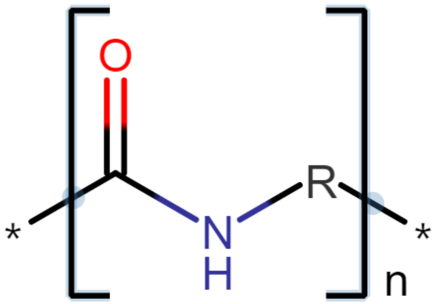
PMMA



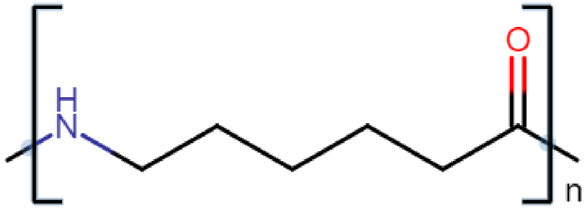
PBT



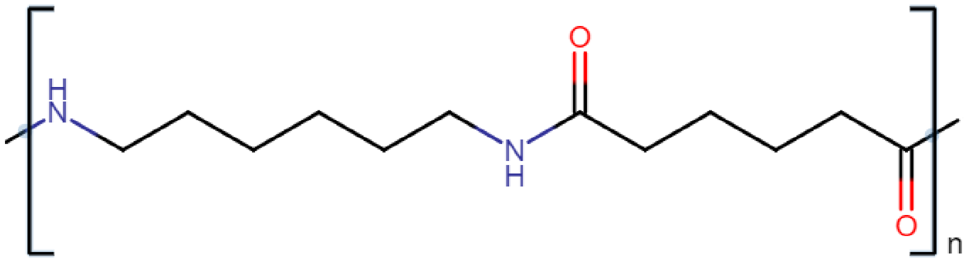
Polyamides



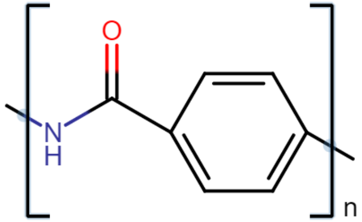
PA 6



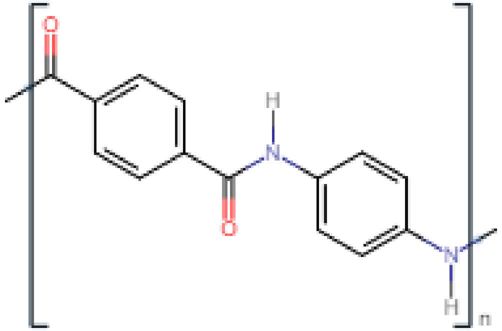
PA 66



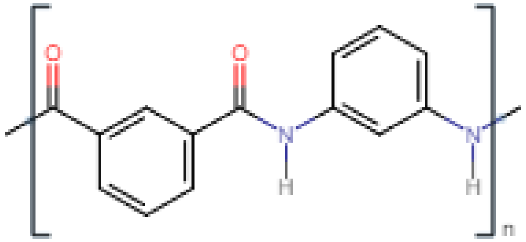
Aramides (aromatic polyamides)



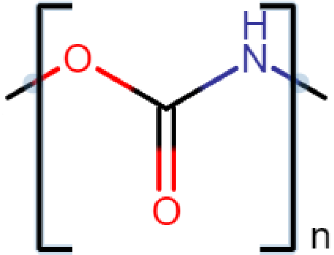
Kevlar

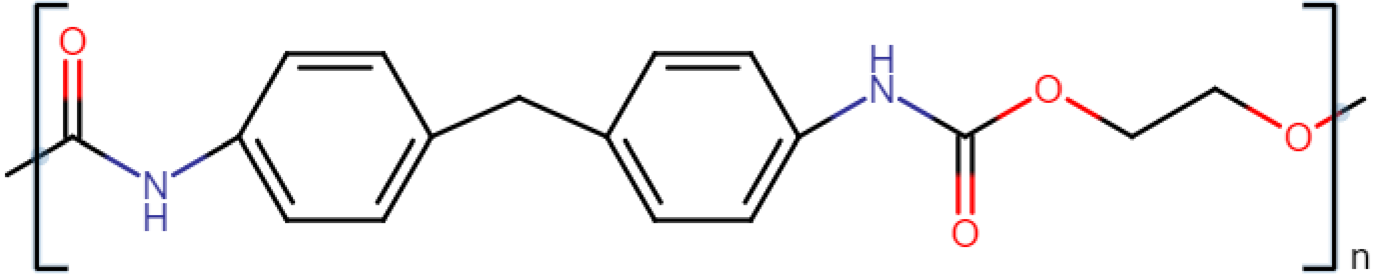


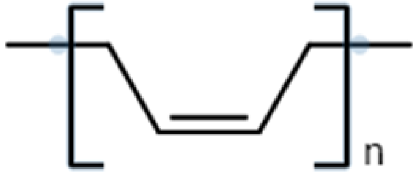
Nomex



Polyuretans

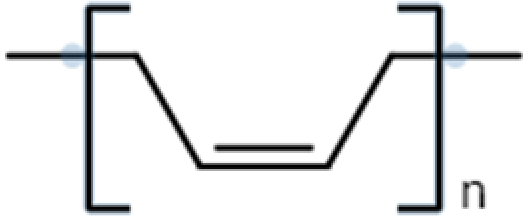




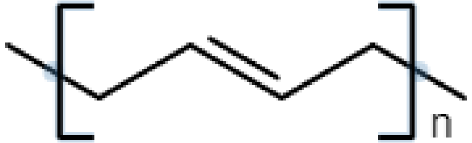


Butadiene polymers

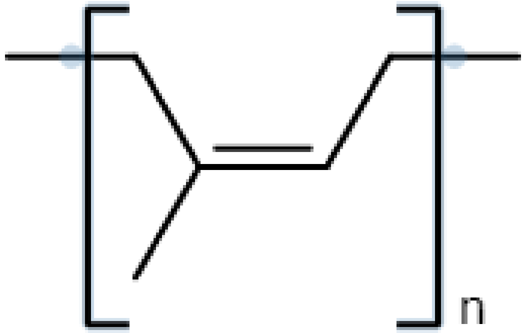
BR



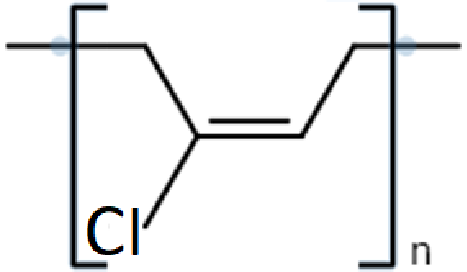
trans-

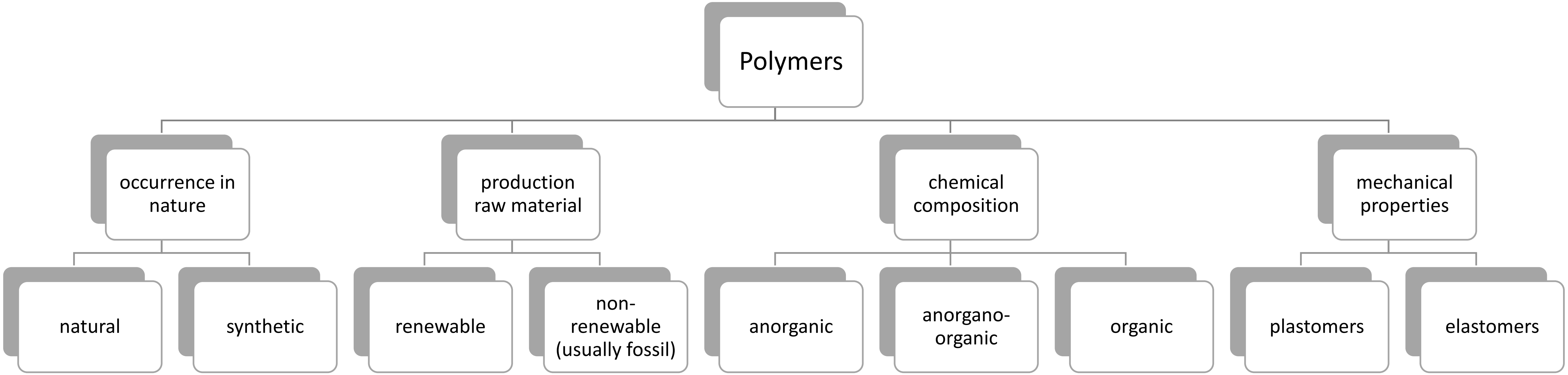


NR



CR




Polymers
occurrence in nature
production raw material
chemical composition
mechanical properties
natural
synthetic
renewable
non-renewable (usually fossil)
anorganic
anorgano-organic
organic
plastomers
elastomers

Plastomers - Thermoplastics

- they soften and become malleable when heated
- upon re-cooling, they solidify and lose malleability
- the process can be repeated many times (recycling)

- temperature changes here affect only intermolecular attractive forces
  - they do not cause chemical reactions

Plastomers - Reaktoplasty

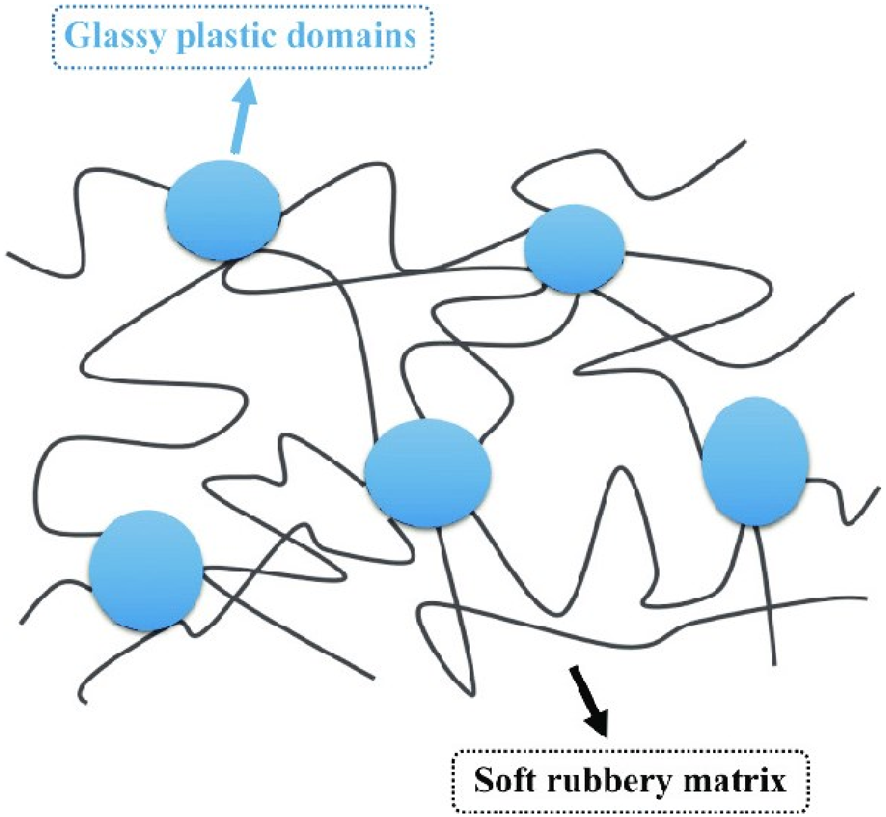
- before final processing, they contain chains with reactive functional groups
  - they harden chemically and form (most often spatially) cross-linked macromolecules
- changes are irreversible

- THERMOSETS
  - a reasonably long heating is sufficient to cure

Elastomers

- a weak force action causes a large reversible deformation

- rubbers
  - crosslinked rubbers
- thermoplastic elastomers
  - non-crosslinked linear molecules formed by alternating glassy and rubbery phases



Thank you for
your attention

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Chemical structure of polymers

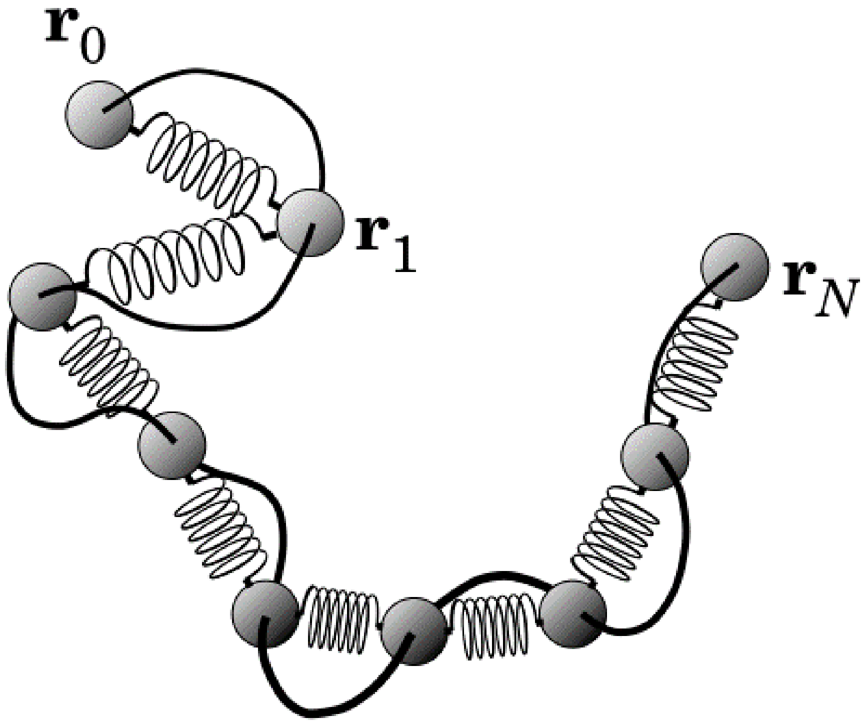
Effect of molecule structure on polymer properties

- polymer properties given (among others)
  - chemical structure
  - shape of macromolecules
  - by the number of interactions between macromolecules
- generally two phases
  - amorphous
    - always present to some extent
    - can be a completely amorphous polymer (common)
  - crystalline
    - great influence on mechanical properties, chemical resistance, resistance to solvents, etc.
    - may not be present (depending on chemical structure)
    - there cannot be a completely crystalline polymer (non-uniform)

Relationships between the chemical composition of a polymer and its properties

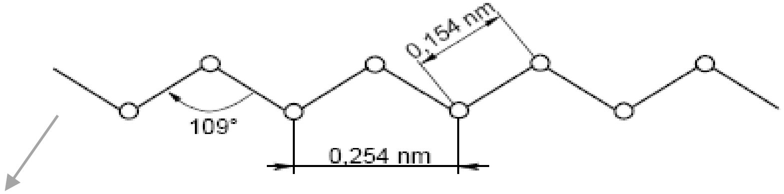
general feature		*effect on the polymer property*
bond strength	…	thermal stability
crystallinity	…	firmness, opacity
cross-linking	…	insolubility, rigidity
similarity of atoms, groups, polarity	…	solubility, miscibility
content of volatile substances (monomers, plasticizers)	…	flammability, toxicity
halogens in the structure	…	higher resistance to burning
conjugated systems	…	colour, sensitivity to UV, lower chemical resistance
conjugated systems along the backbone	…	electric conductivity

1. Models of the macromolecular chain

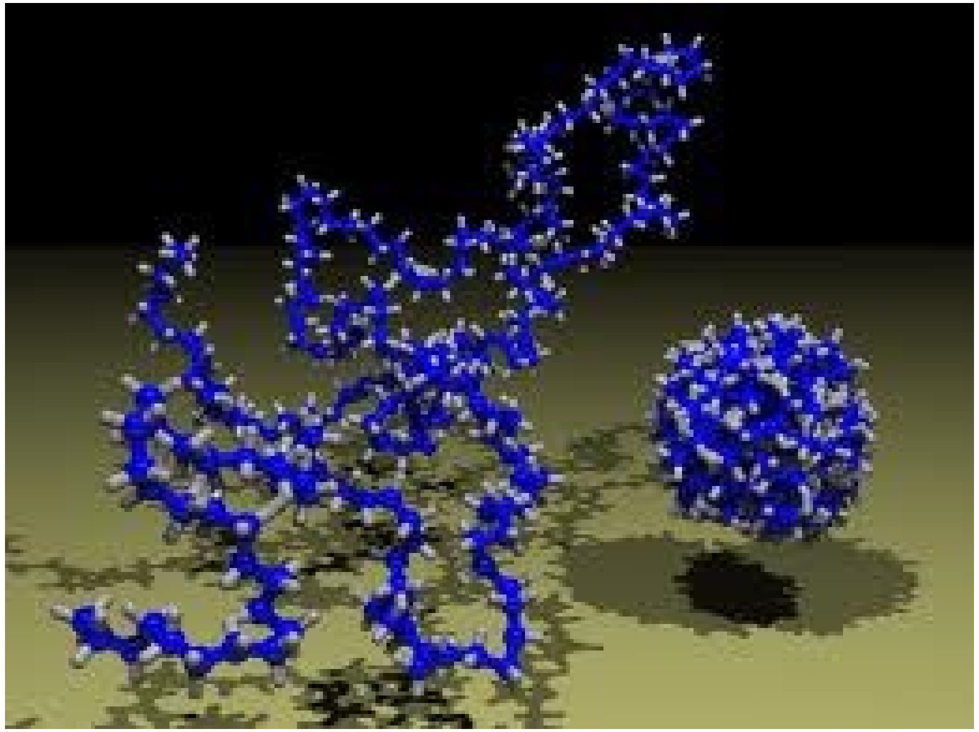


Shapes of macromolecules

- What is the shape of the molecule?

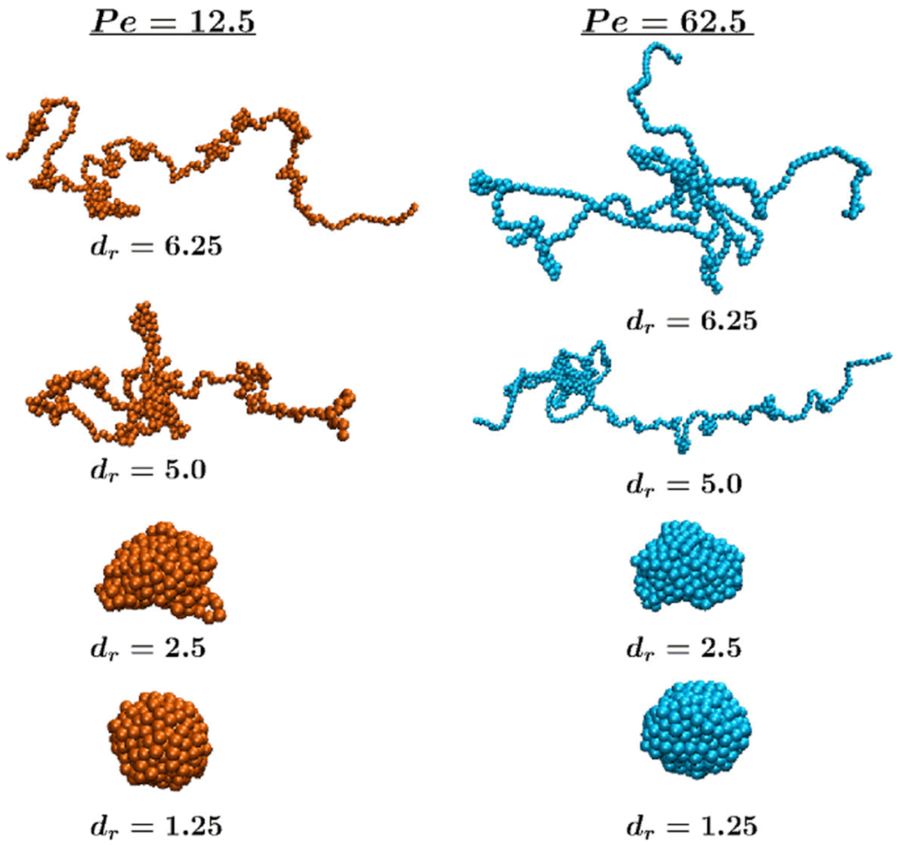


  - could be, but that's not usually how it looks like
- molecules are mostly not straightened
  - most often in the form of a statistic (Gaussian coil)
  - given the ability to rotate around single bonds



Shapes of macromolecules in solution

- globules
  - tightly coiled polymer chains
  - interaction with the solvent only on the surface of the globule
  - chemical or physical bonds ensure a more permanent shape of the globule
- coil
  - not very tightly coiled polymer chains
  - polymer chains interact with other chains and with solvent molecules
- developed chains
  - polymer chains interact almost exclusively with solvent molecules (applies to good solvents – i.e. those that dissolve the given polymer well)



The size of the macromolecular bulcoil

- must be determined statistically
  - coil differently wound (i.e. their dimensions are generally different)
  - similarly to the average molecular weight (in the sense of describing the entire polydisperse* system with a single value)
- dimensional characteristics used
  - mean radius of gyration $<s^2>^{1/2}$
  - mean distance of chain ends $<r^2>^{1/2}$
- mutual relationship (according to statistics)

$$< s^2 >= 6 < r^2 >$$

$$< s^2 >^{\frac{1}{2}} = 0{,}408 < r^2 >^{\frac{1}{2}}$$

---

* of a system with generally different particles of the dispersion fraction

Mean radius of gyration

- radius of gyration s^2
  - in foreign literature also R_g (Radius of gyration)
  - generally used particle size of the dispersion fraction
  - if we divide a particle of the dispersion fraction into very small segments (practically into mass points), the following will apply:

$$s^2 = \frac{1}{m_c}\sum_{i=1}^{n} m_i s_i^2$$

m_c … the total mass of the split particle

m_c … mass of the i-th segment

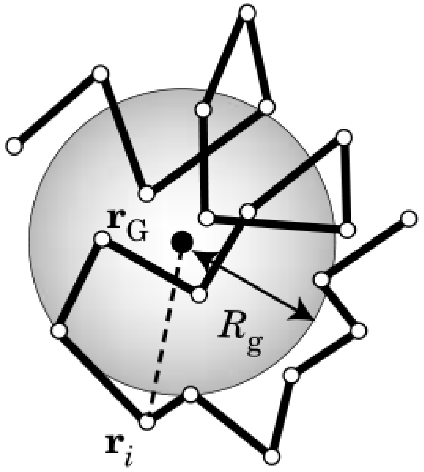
s_c … the distance of the i-th segment from the center of gravity of the particle

  - for segments of the same weight:

$$s^2 = \frac{1}{n}\sum_{i=1}^{n} s_i^2$$

n … the number of segments of the split particle

- mean radius of gyration $\langle s^2 \rangle^{1/2}$
  - the average value of the gyration radii of the system
  - a realistically measurable value that is used in practice



r_G … center of gravity of the macromolecule
R_g … radius of gyration (s)
r_i … the distance between the centroid and the i-th segment (s_i)

End-to-End distance

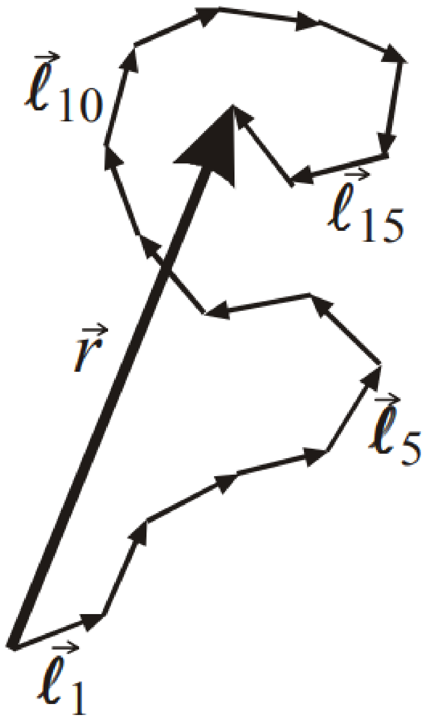
- end-to-end distance
  - in foreign literature also R_F (end-to-end distance)
  - only for linear strings (so we only have 2 ends)
  - we consider dividing the entire chain into segments that are described by vectors
  - a theoretical value used especially in theoretical calculations and modeling

$$\vec{r} = \sum_{i=1}^{n} \vec{l}_i$$

n … total number of segments

l_i … vector of the i-th segment

- mean end-to-end distance $\langle r^2 \rangle^{1/2}$
  - average value

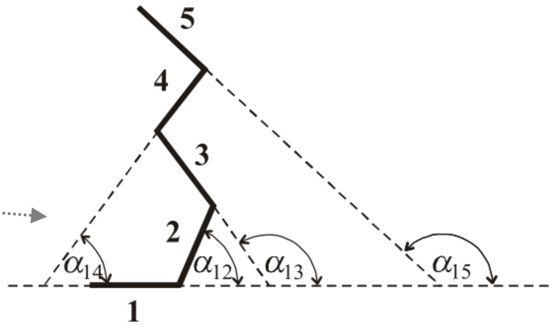


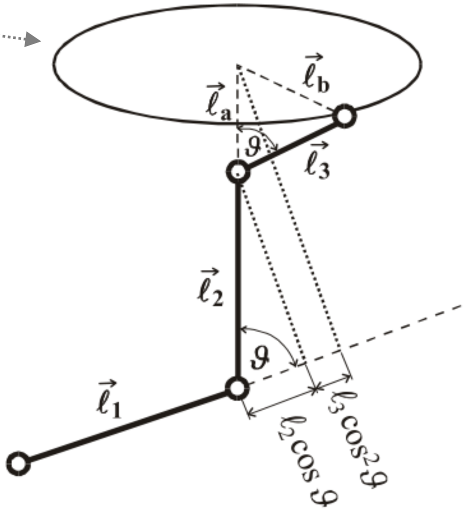
---

* for more on the issue of the ends of linear structures, see Werich+Voskovec – Pudr a benzín (link 2:07 to 2:59): https://www.youtube.com/watch?v=xluP9lIzBr8

Macromolecular coil models

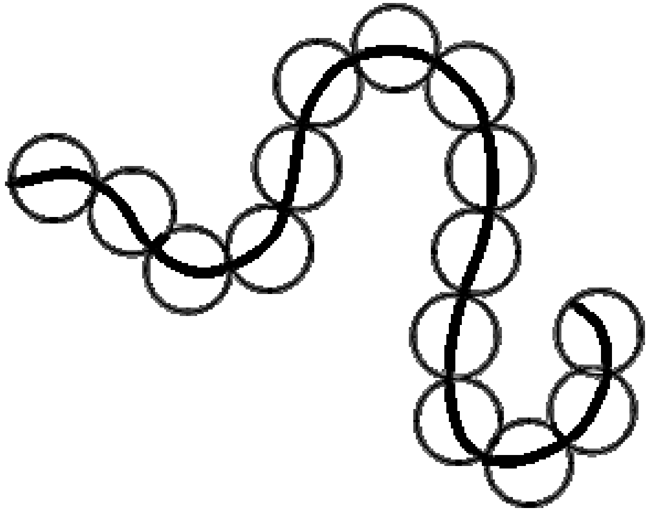
1. loosely coupled chain
    - bonds of the same length l_i
    - segments rotate with equal probability in the range α_{ij} (-180°; 180°)
2. freely rotating chain with a fixed valence angle
    - bonds of the same length l_i
    - free rotation with a constant valence angle between the bonds
3. a restricted rotatable chain with conformationally independent neighboring bonds
    - bonds of the same length l_i
    - rotation with a constant valence angle between the bonds
        - limited by energy barriers of microconformations
4. a restricted rotatable chain with conformationally dependent neighboring bonds
    - bonds of the same length l_i
    - rotation with a constant valence angle between the bonds
        - limited by energy barriers of microconformations
        - limited by energy barriers microconformations of neighboring bonds



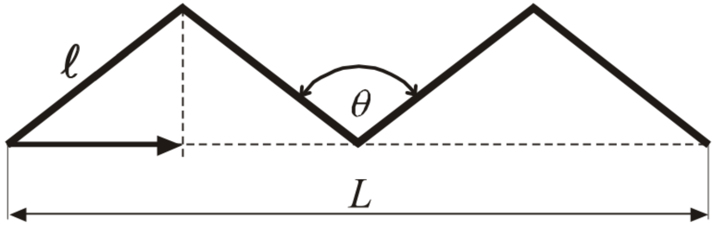


Macromolecular coil models

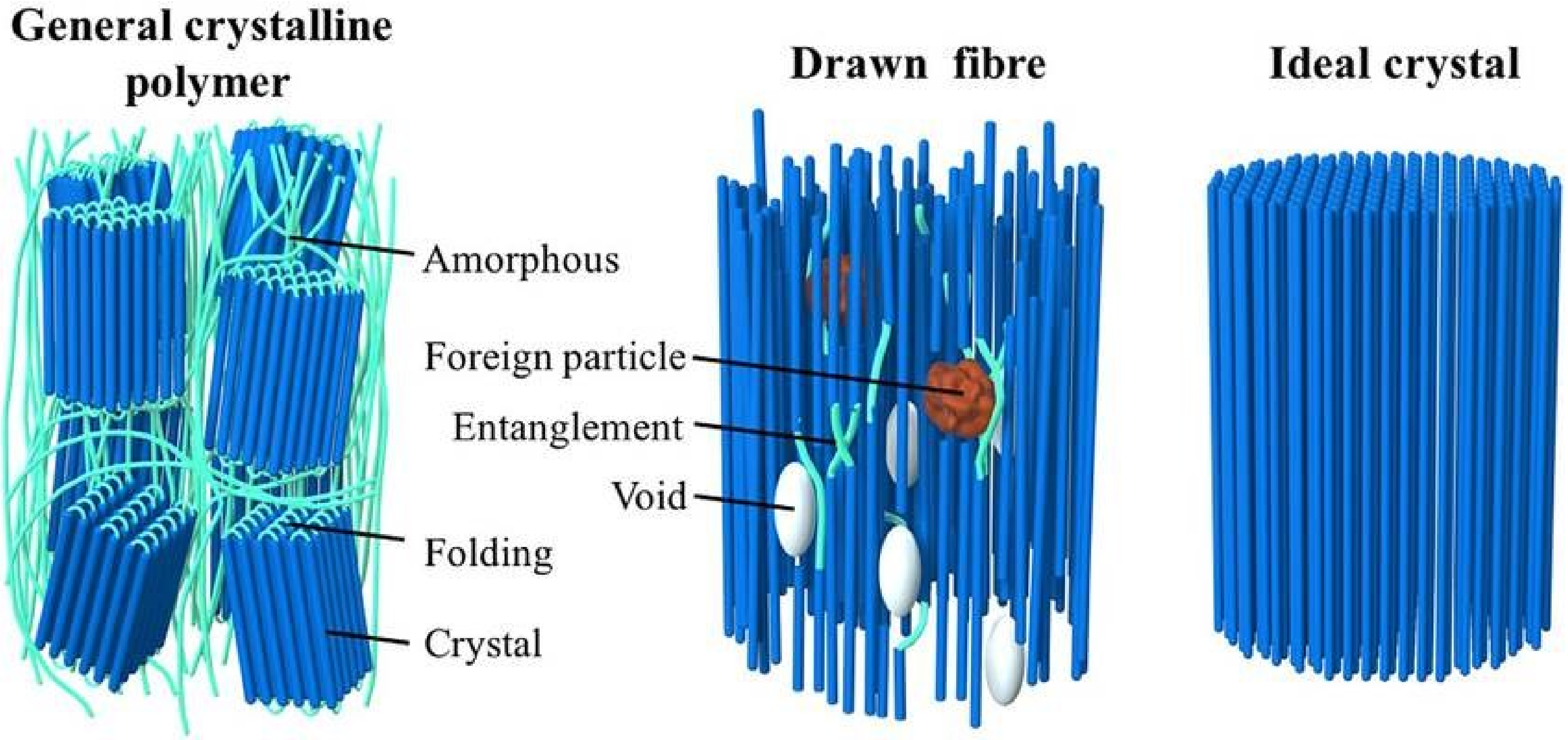
- previous models valuable for theory, too complex for practi



- equivalent chain
  - replacement of individual bonds with imaginary larger segments
    - they consist of as many adjacent links as possible so that even adjacent segments are mu
    - the whole then behaves again like a loosely jointed chain
  - with the original loosely coupled chain, they match in:
    - mean distances of chain ends $<r^2>^{1/2}$
    - contour length L
      - the maximum length of a theoretically stretched chain

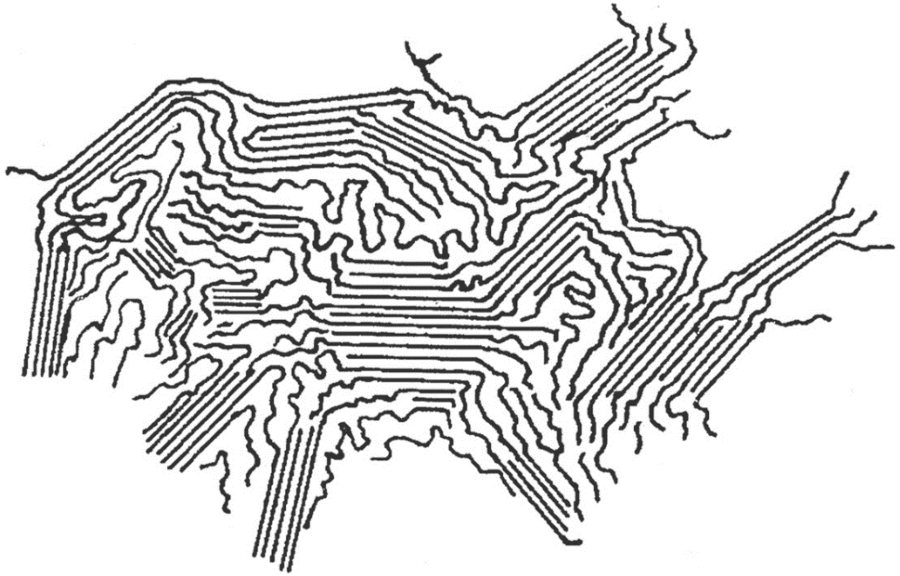


2. Amorphous and crystalline phase



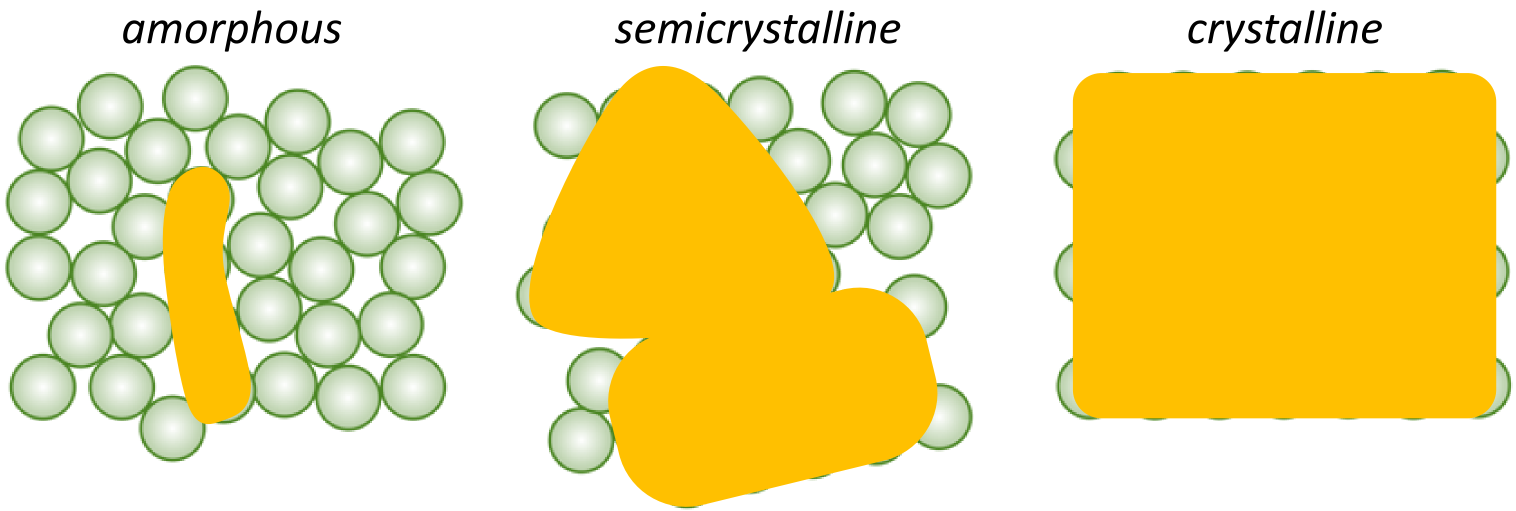
Morphology of polymers

- deals with the mutual arrangement of macromolecules in the entire polymeric substance
- two basic phases can be found
  - amorphous and crystalline
  - both phases differ significantly in their properties



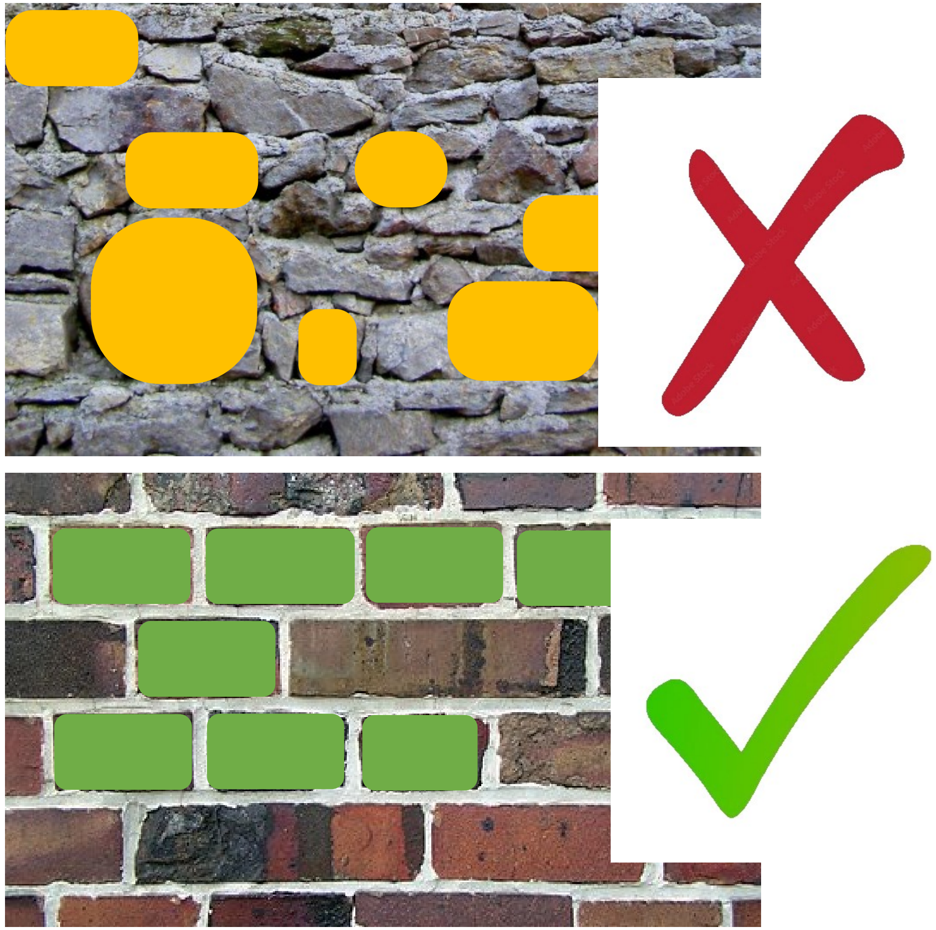
Crystallinity of polymers

- shockingly, many polymeric substances are partially crystalline
  - however, they are never 100% crystalline (maybe 99%)
  - therefore they are referred to as semi-crystalline (i.e. partially crystalline)
  - the individual crystalline structures in a given polymer are called crystallites
- a crystal in general is a structure that is regular over long distances


amorphous
semicrystalline
crystalline

Crystallinity of polymers

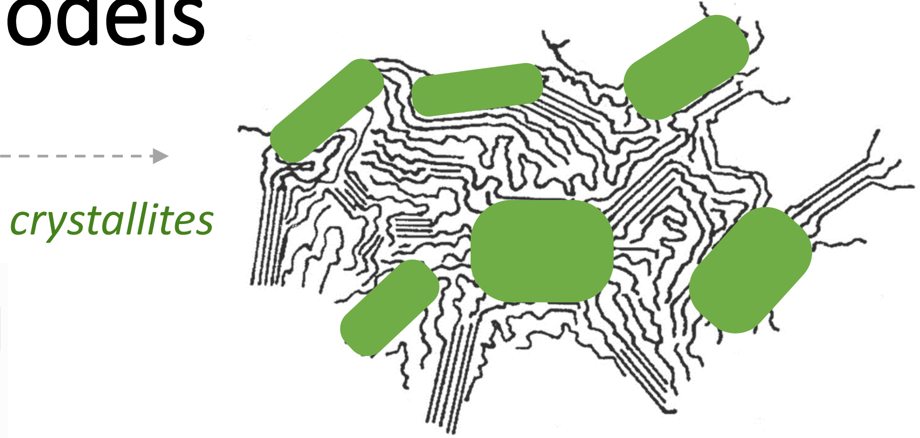
- in order for a regular structure to emerge, regular building blocks must be present
- I need for crystallization
  - regularity
  - (optionally) tactical
  - sufficiently strong secondary bonds
- example: masonry
  - regularity = bricks (stones) as similar as possible
  - secondary bonds = enough mortar



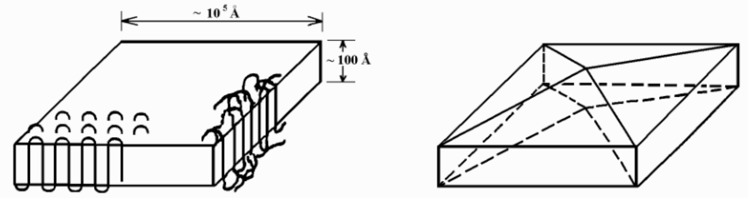
Sufficiently strong secondary bonds

- it is the sum of the forces (energies) of all secondary bonds holding the given crystallite together
  - I can have several strong (polar) bonds (PA)
  - or I may have many weaker bonds (PE, PP)
- the dissociation energy of secondary bonds must be smaller than the energy of thermal motion of molecules (entropic character)
  - thus, when the temperature increases sufficiently, the crystallites generally melt, because the thermal motions overcome the secondary bonds and the crystallite breaks up

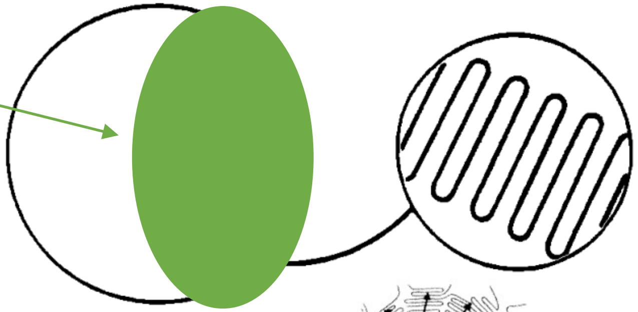
Crystallites structure models



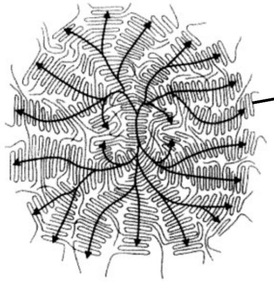
- lamellar fibrils
    - the oldest, probably survived today
- chain folded structure
    - from dilute solutions
    - broken pyramid
    - bends about 5-6 carbons long

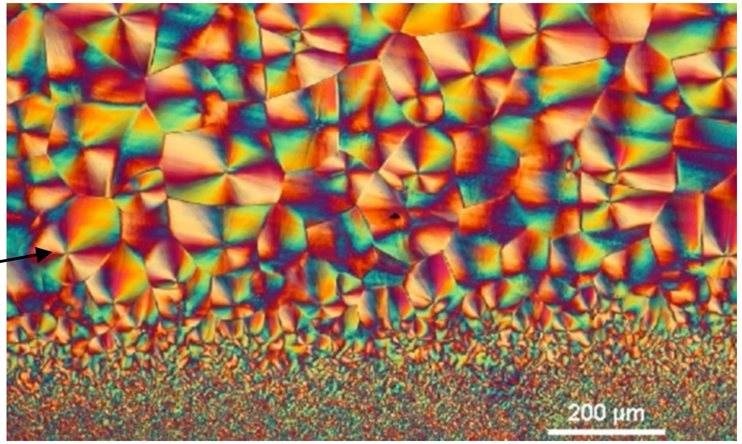


- dendrites (tree-like)
    - from more concentrated solutions
    - crystallites grow more easily in folds, grooves and corners (need to cover less surface energy)
    - that's why they start to grow everywhere, even on a different crystallite



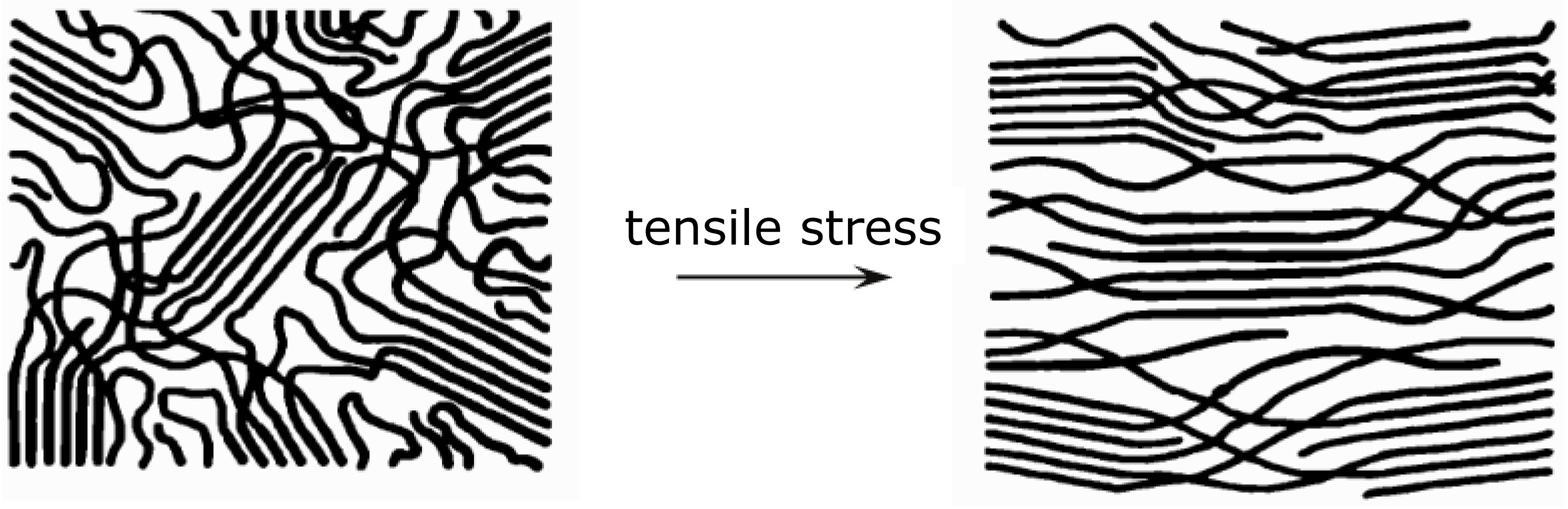
- spherulites
    - crystallization from the melt
    - least regular crystallites
    - typical Maltese cross in section under a polarizing microscope



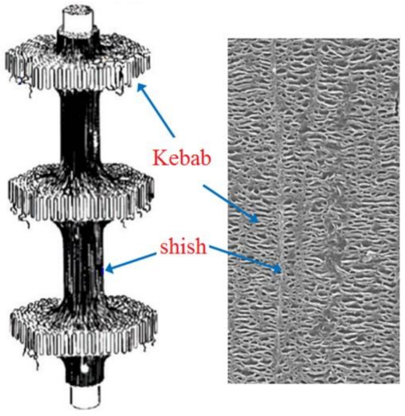


Orientation of crystallites

- generally random
- however, the external force is plural to orient them to some extent
  - e.g. when in filament drawing



tensile stress



shishkebab

Effect of crystallinity on the properties of polymers

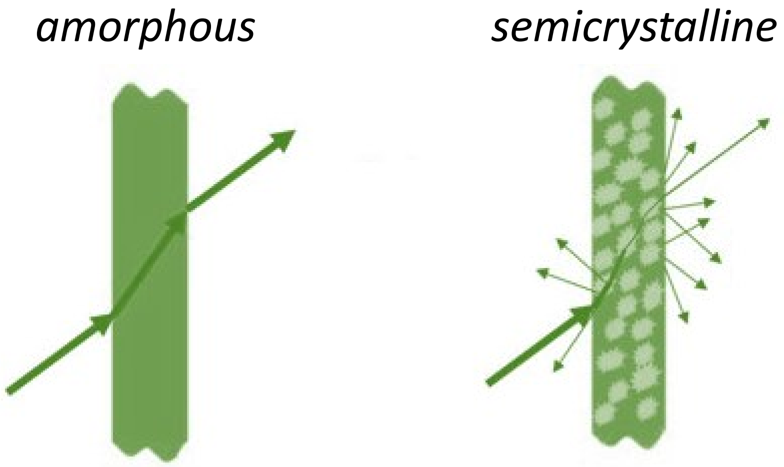
- higher density of the crystalline phase
  - macromolecules are regularly and tightly assembled (secondary bonds only act over short distances).
  - if you clean your clothes in the closet, they usually take up less space, although the mass is still there
    - i.e. the density is higher
- one polymer can show several types of crystal structure (e.g. PA 6)
  - similar to some inorganic substances

Effect of crystallinity on density

	density (g/cm^3)	
polymer	*crystalline phase*	*amorphous phase*
PA 6	1,24	1,07
PA 6|6	1,23	1,08
POM	1,54	1,25
PET	1,50	1,33
PTFE	2,35	2,00
PP (izotaktic)	0,95	0,85
HDPE	1,00	0,85

Effect of crystallinity on the properties of polymers

- other molecules do not penetrate between tightly arranged chains (reactions thus take place mainly on the surface)
  - higher resistance to chemicals (degradation)
  - higher resistance to dissolution
- crystalline polymer (without additives) is not clear, but only translucent
  - individual crystalline domains refract and reflect light in different directions
  - How is it that inorganic crystals tend to be clear and semi-crystalline polymers are not?
  - caused by more phase transitions
    - an amorphous polymer has only medium-polymer optical transitions, whereas a crystalline polymer has many transitions inside the polymer, amorphous-crystalline
    - this causes multiple scattering and reflection (if we grind a clear amorphous polymer into a powder, it will no longer be clear but will appear white)
    - e.g. foamed PS is completely amorphous and appears white only because of the large number of air-polymer transitions



Effect of crystallinity on the properties of polymers

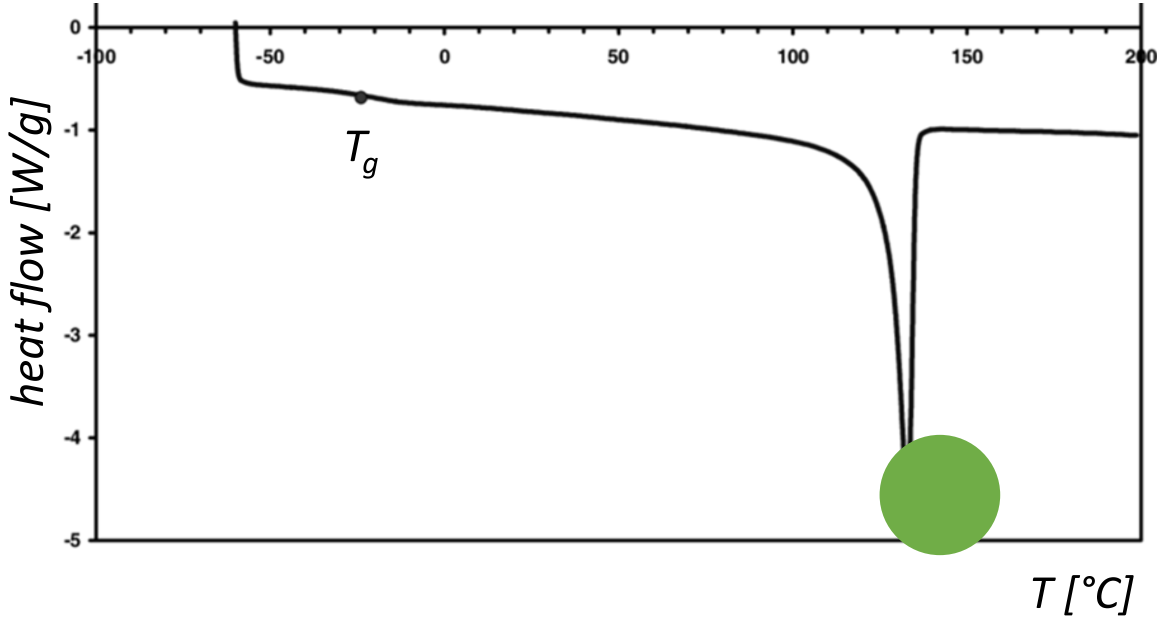
- as the degree of crystallinity increases, the strength of the polymer usually increases
  - in crystallites there are a number of secondary bonds that must be overcome
  - can completely change the character of the material
    - e.g. tactical PP is very mechanically resistant, while atactic is a waxy (even oily at low molecular weights) substance
    - LDPE is much less mechanically resistant than HDPE or even UHMWPE

Crystallinity really matters. Mainly it results in the difference between a PE bulletproof vest and a PE plastic bag for a snack.

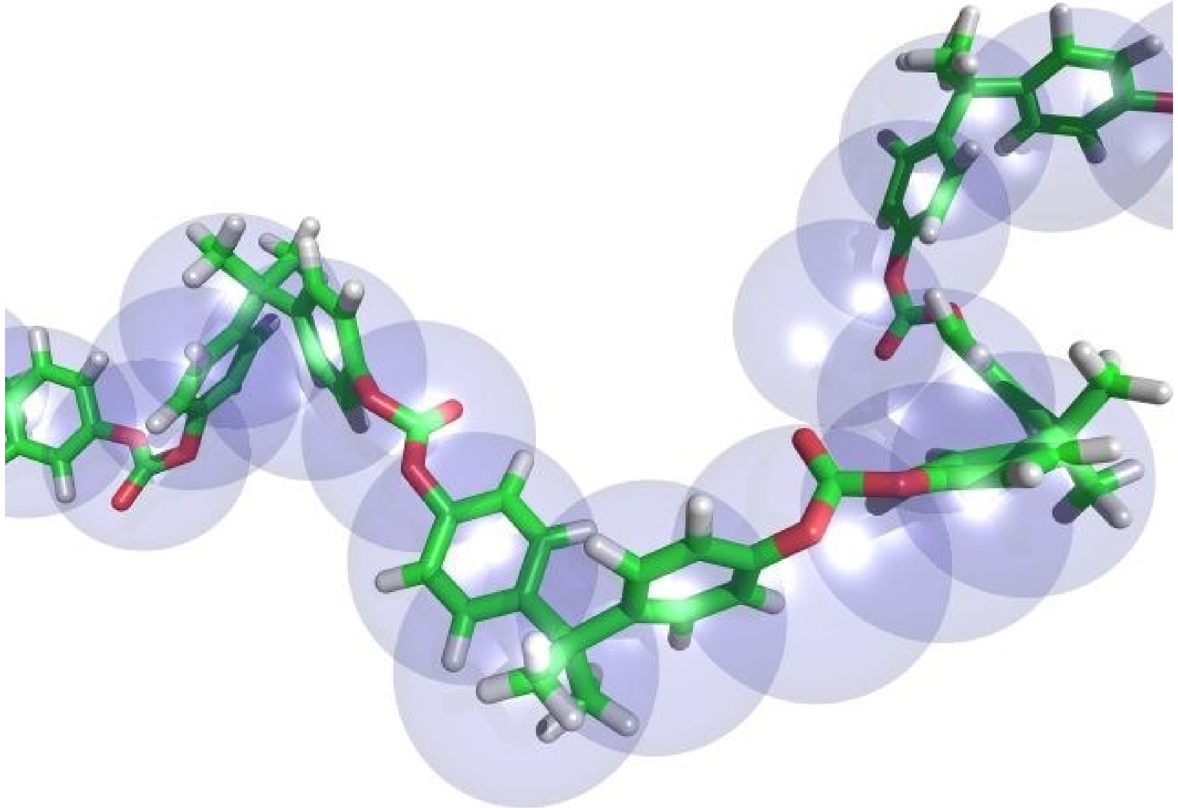
Melting temperature of crystallites T_m

- crystallites are held together by secondary bonds
- increasing the temperature of the polymer means supplying energy to its molecules
    - if this is greater than the strength of the secondary bonds, they may split - the crystallite melts
    - the melting point Tm of the crystallites means the temperature above which all the crystallites melt and the polymer becomes amorphous

differential scanning calorimetry (DSC)



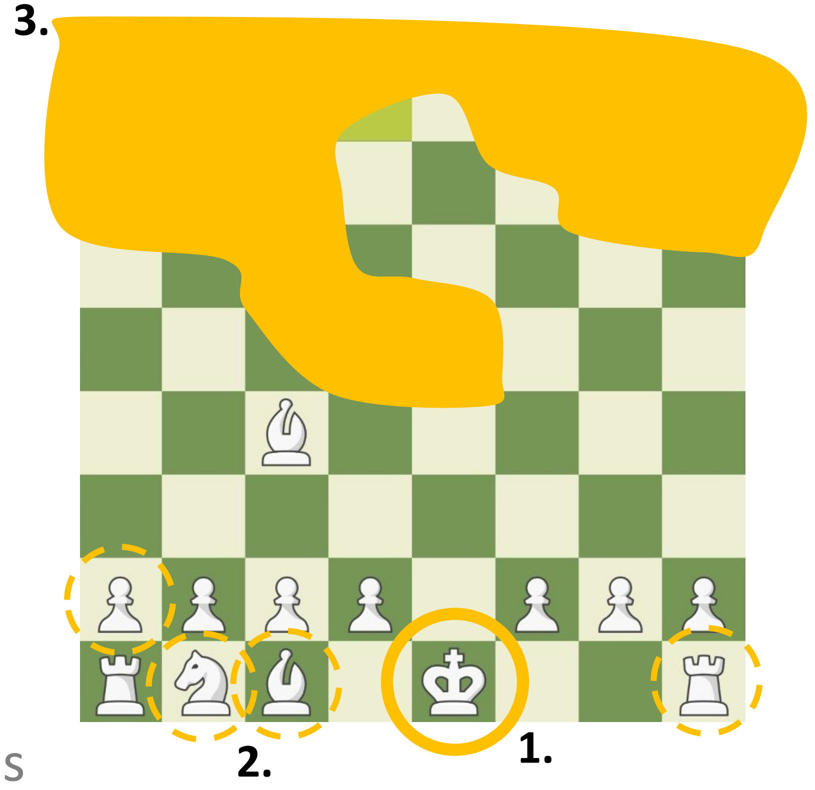
3. Chemical structure of polymers



Chemical structure of macromolecules

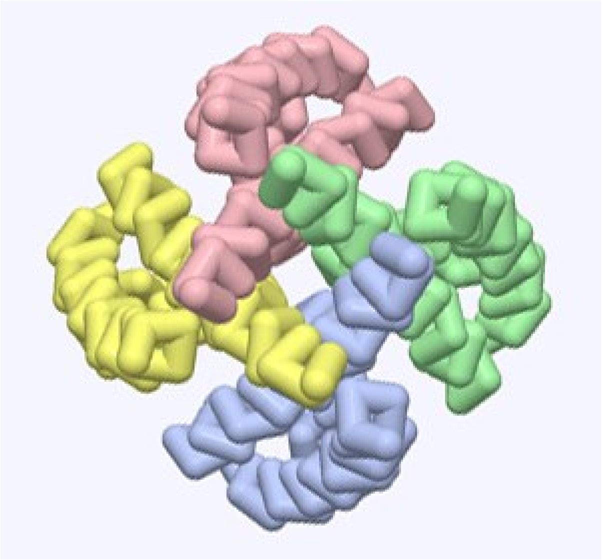
- it is based on the structure of organic substances
  - primary (constitution)
  - secondary (configuration)
  - tertiary (conformation)
  - quaternary

- example: chess
  - the most important is the king (constitutional monarchy)
  - the figure I'm currently pulling is also important (configuration)
  - in the end, I decide what the layout of the figures is, what is the formation of my army
  - I don't because it's an obscure biochemical matter



Structure and isomerism of organic substances

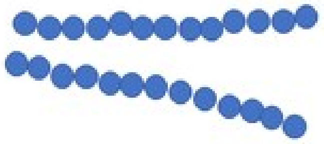
- constitution (primary)
  - the order of atoms and the types of bonds between them
- configuration (secondary)
  - spatial arrangement of the molecule
  - cis-/trans-, c-/t-, Z-/E-
  - regularity and tacticity of polymers
- conformation (tertiary)
  - the spatial arrangement of the atoms of a molecule around a single bond
  - cause of internal rotation of macromolecules
- supramolecular structure (quaternary)
  - relative position of macromolecules to others
  - can be found mainly in enzymes or proteins

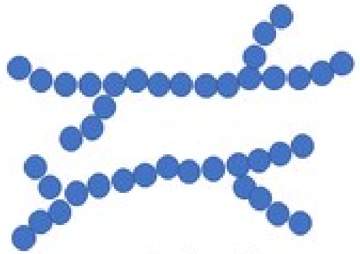


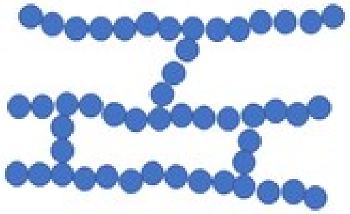
supramolecular structure of sodium channel formed by four identical proteins (each color represents a different molecule)

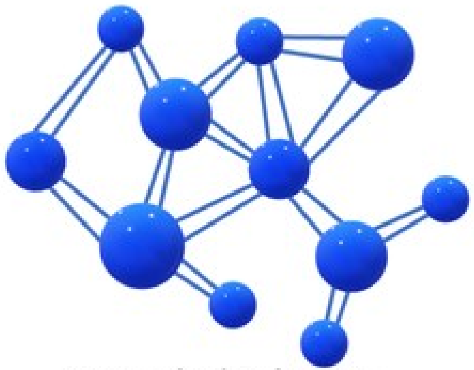
1. Constitution

- given by the functionality of the monomers
  - linear
  - branched
  - netted
    - lightly
    - strongly (or fully)
- linear and branched
  - can be soluble
- cross-linked
  - insoluble
  - could swell


Linear Polymers

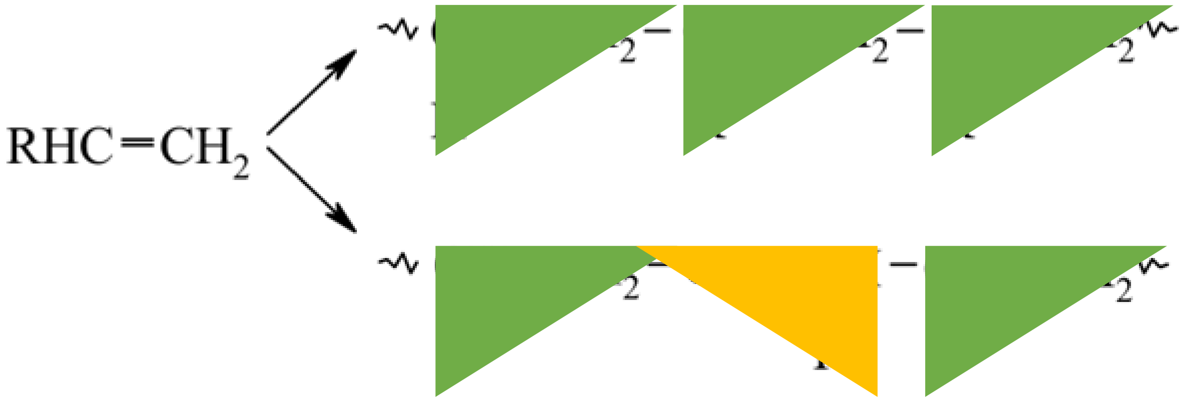

Branched Polymers


Crosslinked Polymers


Networked Polymers

1. Constitution (regularity)

- regular macromolecule
  - obtained by regular repetition of the constitutional unit
  - head-to-heel arrangement only
- only regular polymers can (but don't have to) be semicrystalline

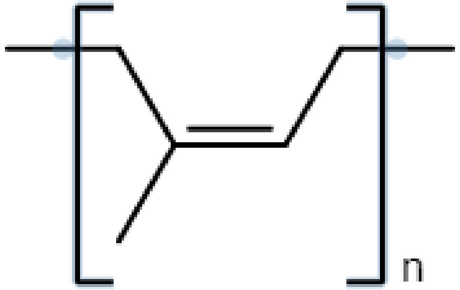


head-to-tail

head-to-head (or tail-to-tail)

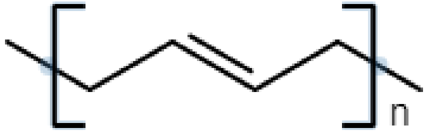
2. Configuration (cis- trans- arrangement)

- characteristic of buta-1,4-diene polymers
- depends on whether a cis- or trans- arrangement is formed at the double bond
  - sometimes also marked Z (Zusammen) and E (Entgegen)



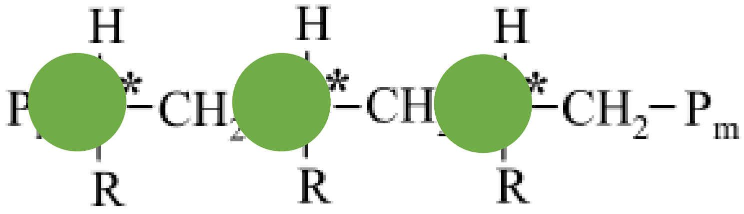
cis-
Z-

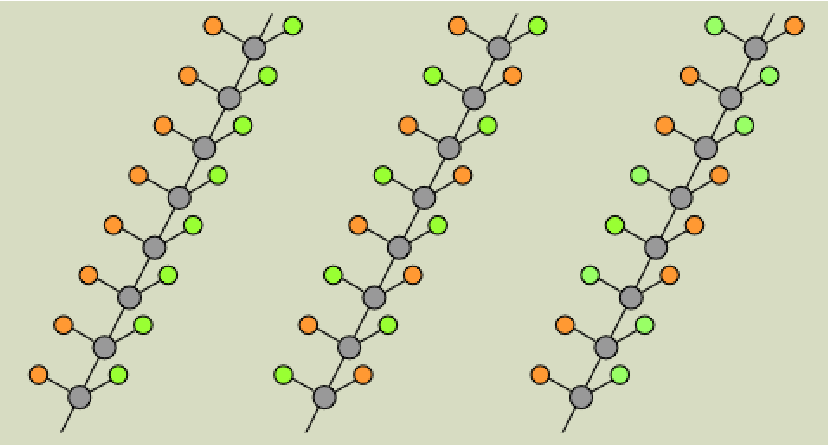
trans-
E-



2. Configuration (tacticity)

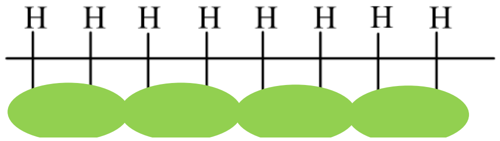
- the arrangement of stereoisomeric centers in the main chains of macromolecules
    - stereoisomerism – occurs in asymmetric molecules with carbons with different substituents (marked by C*) on all four bonds
- fundamentally affects crystallinity
    - and thus also mechanical properties, temperature behavior, etc.



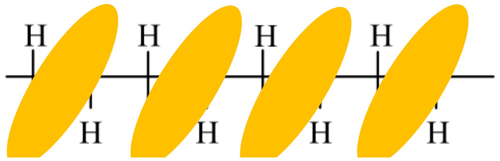

isotactic syndiotactic atactic

2. Configuration (multiple tactics)

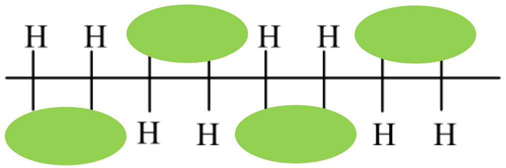
- several types of stereoisomeric centers alternate
  - if there are two, it is ditacticity
  - the prefixes erythro- and threo- are used
- erythro-ditacticity
  - the stereoisomeric centers are next to each other
- threo-ditacticity
  - the stereoisomeric centers are opposite each other



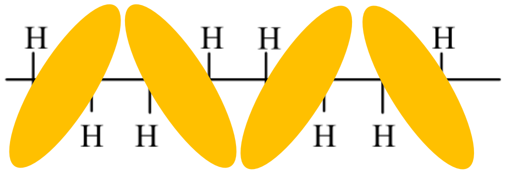
erythro-diisotactic



threo-diisotactic



erythro-disyndiotactic

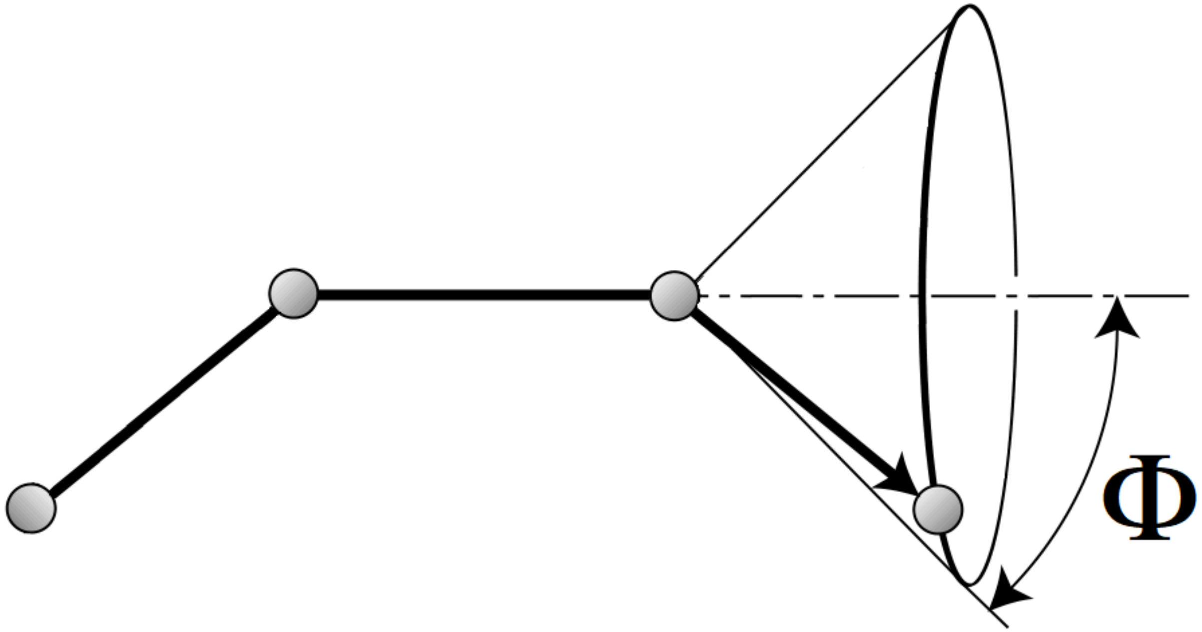


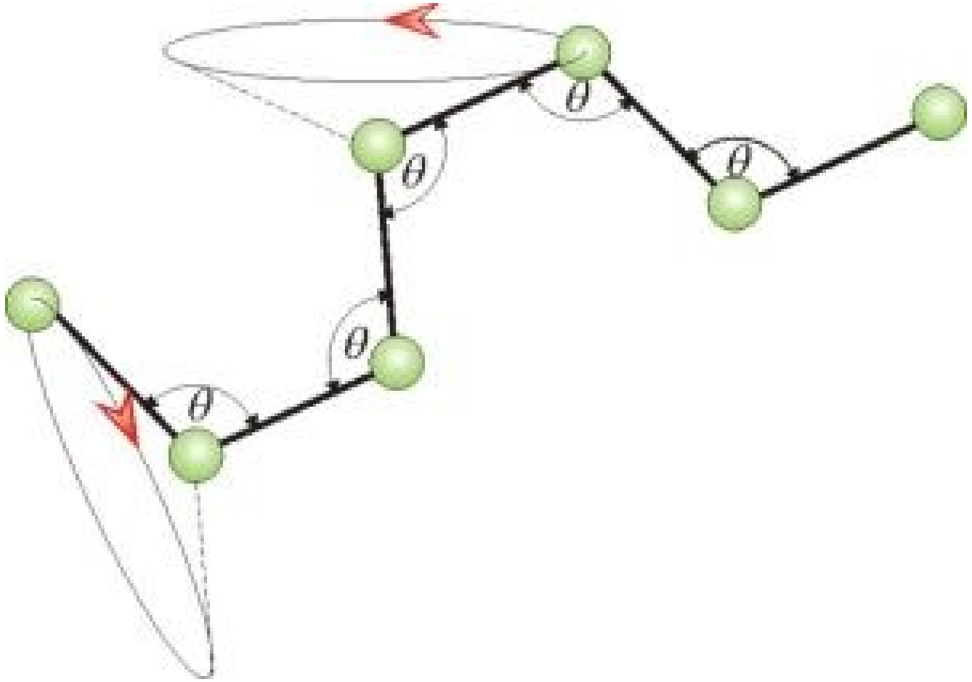
threo-disyndiotactic

3. Conformation (internal rotation)

- otherwise also intramolecular rotation
- only for long flexible chains (e.g. cyclic structures or macromolecules)
- rotation around single bonds
  - in the case of macromolecules, we mainly examine the rotation of the atoms of the main chain (substituents and hydrogens do not bother us so much)
- responsible for different chain conformations
  - are refundable
  - they generally cannot be isolated
- it is described by the **torsional (dihedral) angle** ϕ (capital phi)

3. Conformation (torsion angle)

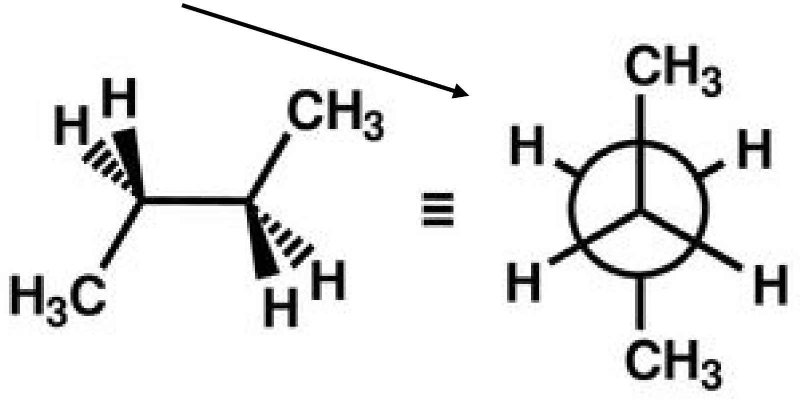




3. Conformation (local)

- also microconformation
  - describes only a certain part (segment) of the whole molecule
- conformation affected by steric repulsion
  - electricity the packages have a negative charge and when they get too close they start to repel each other
- usually illustrated on butane in the Newman projection

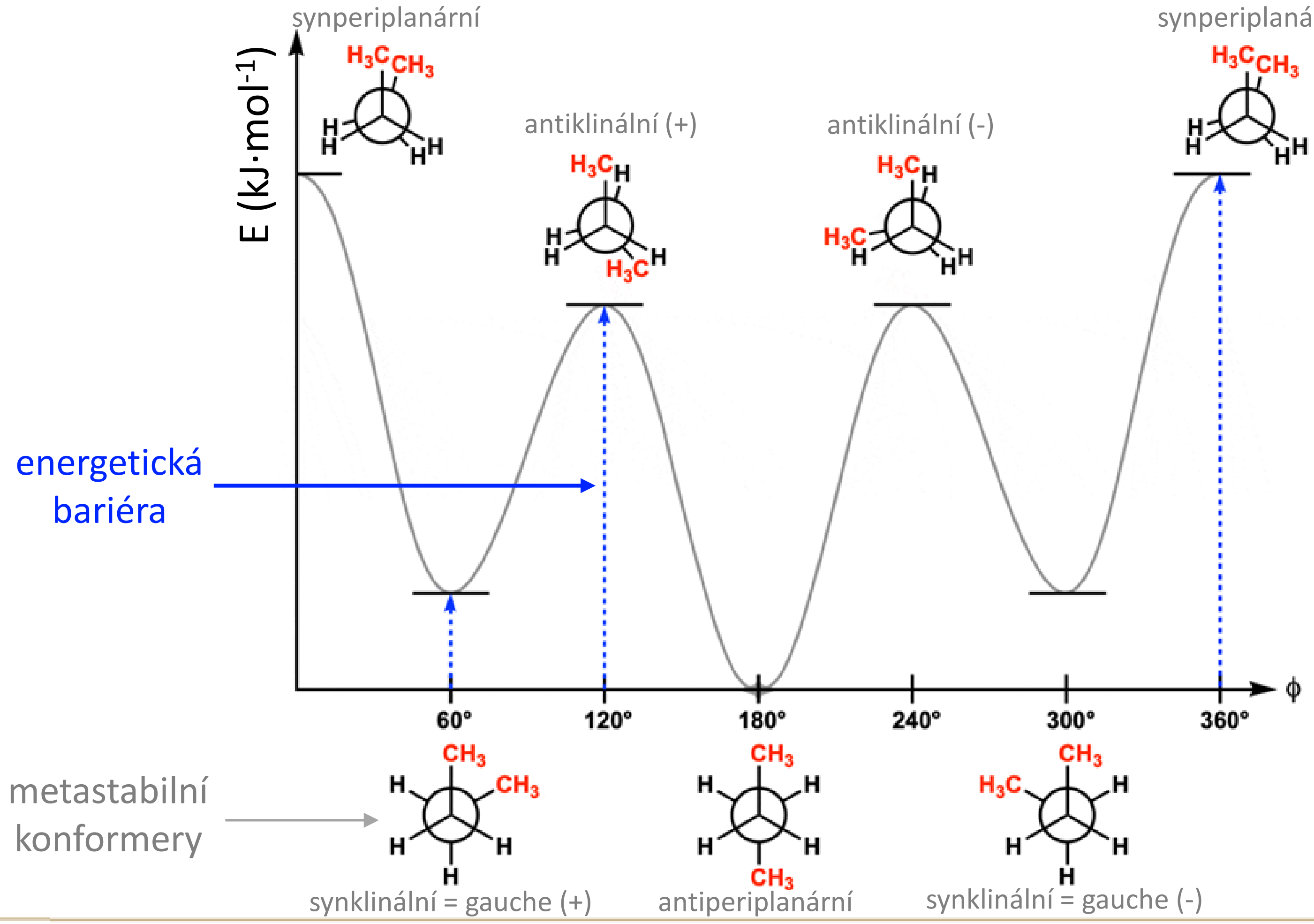
torsion angle Φ	*name*	*relative energy** *(kJ·mol^{-1})*
0	trans (antiperiplanar)	0
± 120 °	gauche (synclinal)	2,1
± 180 °	cis (coplanar)	> 15

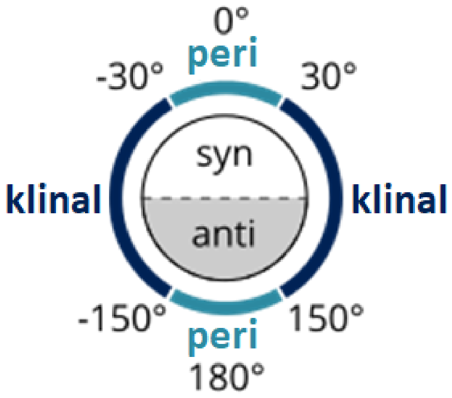


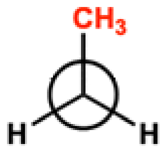
---

* referred to the contractual minimum of 0 kJ·mol^{-1} in the trans configuration (0 °)

3. Konformace (stabilita lokálních konformací)

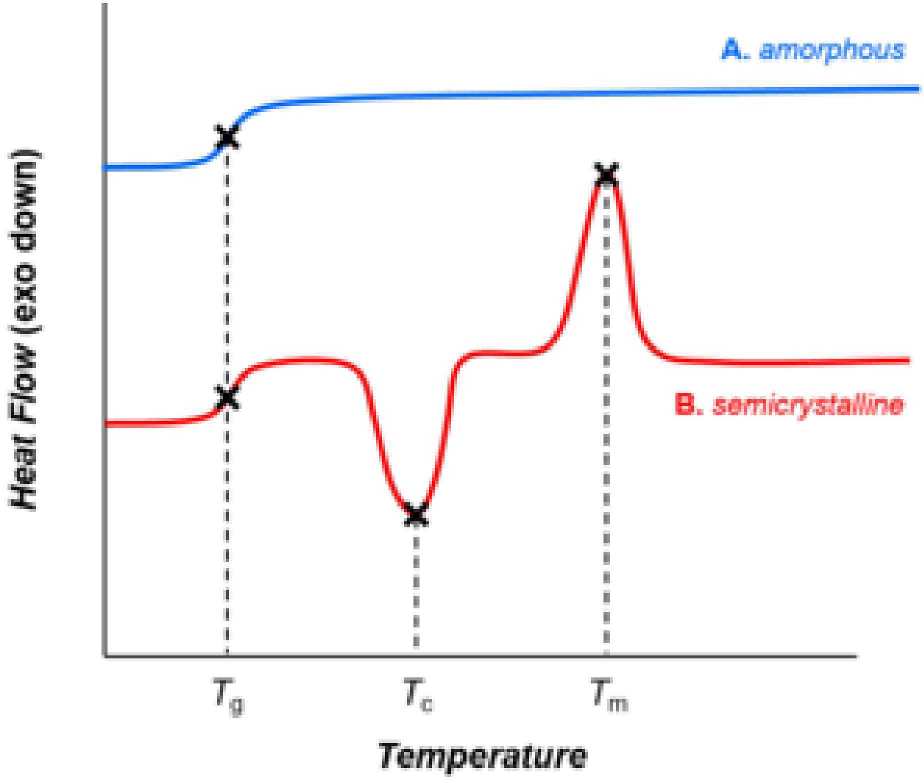






koplanární

Thermal behavior of polymers

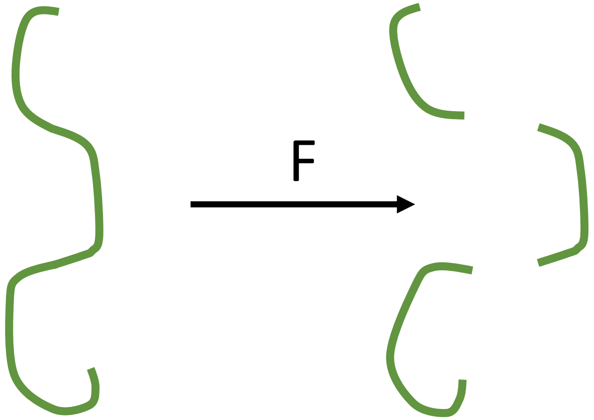


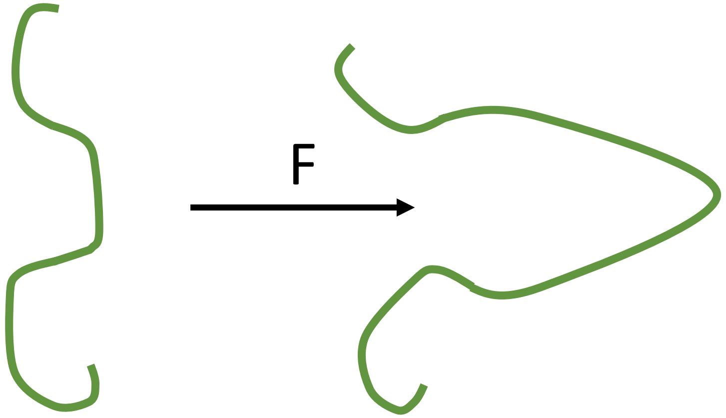
Thermal behavior of polymers

- most polymers behave differently at different temperatures
  - at a lower temperature they tend to be glassy
    - less flexible
    - more fragile
    - harder
      - at a very low temperature, for example, a rubber tube can be so hard that its fragments can be hammered into wood like a nail (it is possible, but to the disappointment of the audience and the demonstrator, these usually shatter)
  - at higher temperatures they tend to be rubbery
    - more flexible
    - tougher
    - less hard
  - caused by the so-called **glass transition** temperature (T_g)

Glass transition temperature T_g

- temperature interval in which the state of the polymer changes from glassy to rubbery (and vice versa)
  - refers ONLY to the amorphous phase of the polymer
- the glassiness of the polymer is determined by the limited possibility of reaction of macromolecular chains to mechanical stress
  - the chains are frozen and cannot move relative to each other
- the rubber-like properties, on the other hand, is given by the possibility of movement of parts of the chains relative to each other





Glass transition temperature

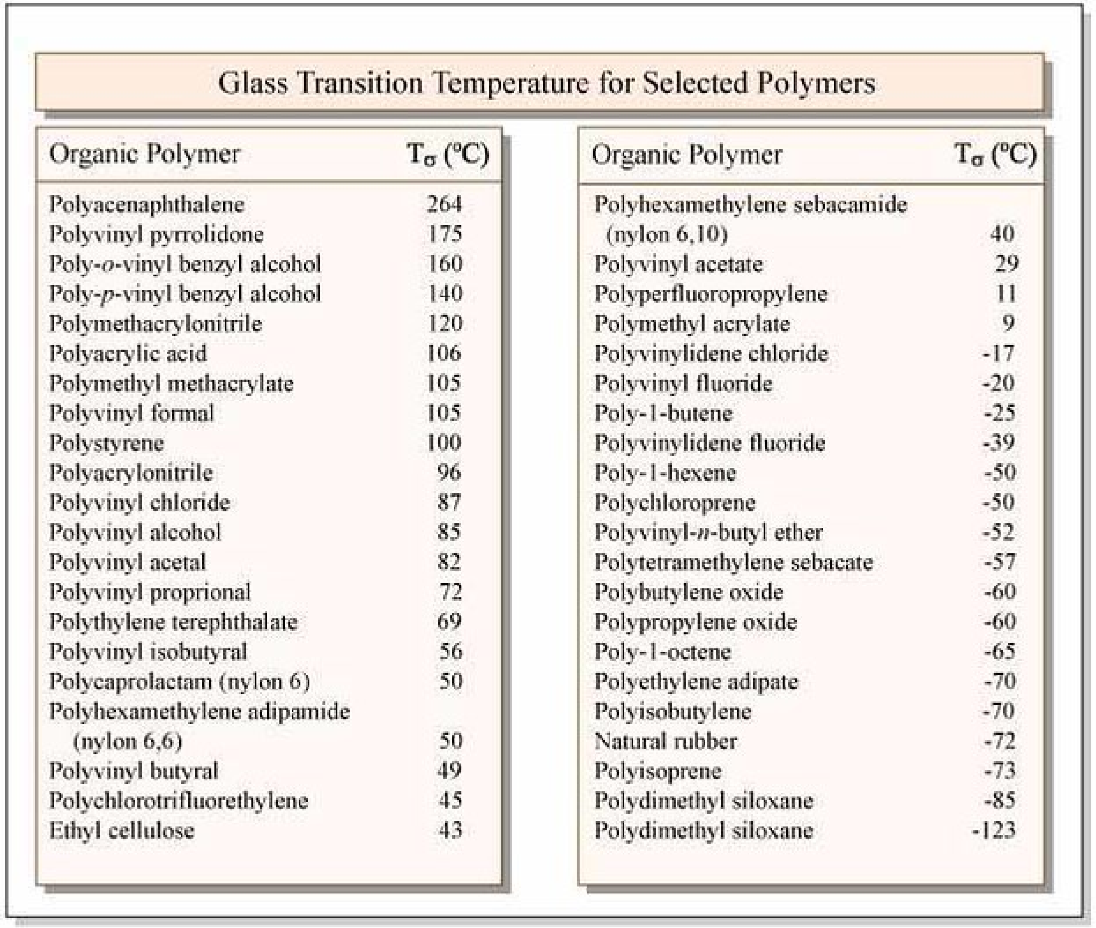
- mobility of parts of macromolecules made possible by temperature movements (overcoming secondary bonds)
  1. vibrations of atoms
  2. internal rotation
     - movements of a pair of neighboring atoms of the molecule
  3. external rotation
     - movements of larger segments of molecules
     - allows to respond elastically to external influences
     - rubbery behavior
  4. translation
     - sliding of molecules over others
     - the flow of molecules in the form of a melt
     - plastic behavior
- even outside these temperatures, movements may occur, but they are either unlikely or too slow

required energy

Glass transition temperature

- the temperature at which the movement of segments of macromolecules begins in a reasonable amount and speed
    - when exceeded, a large number of physical properties change
    - fortress
    - hardness
    - tenacity
    - thermal expansion
    - heat capacity
    - density
    - refractive index of light
    - dielectric constants
    - …
- it is not a specific temperature, but an interval (depends on the heating speed, etc.)
- it is most simply determined by the differential calorimetric method (DSC)

Polymer	[redacted]	Tm (°C)
PET	[redacted]	250 to 260
LDPE	[redacted]	100 to 110
PVC	[redacted]	-
PP	[redacted]	160 to 165
PS	[redacted]	-
HDPE	[redacted]	125 to 135
ABS	[redacted]	-
PC	[redacted]	-
PMMA	[redacted]	-
PA6	[redacted]	225 to 235
PA66	[redacted]	225 to 265
PA610	[redacted]	210 to 230
POM	[redacted]	175 to 790
PBT	[redacted]	220 to 230



Glass Transition Temperature for Selected Polymers

Organic Polymer	T_g (°C)
Polyacenaphthalene	264
Polyvinyl pyrrolidone	175
Poly-*o*-vinyl benzyl alcohol	160
Poly-*p*-vinyl benzyl alcohol	140
Polymethacrylonitrile	120
Polyacrylic acid	106
Polymethyl methacrylate	105
Polyvinyl formal	105
Polystyrene	100
Polyacrylonitrile	96
Polyvinyl chloride	87
Polyvinyl alcohol	85
Polyvinyl acetal	82
Polyvinyl proprional	72
Polythylene terephthalate	69
Polyvinyl isobutyral	56
Polycaprolactam (nylon 6)	50
Polyhexamethylene adipamide (nylon 6,6)	50
Polyvinyl butyral	49
Polychlorotrifluorethylene	45
Ethyl cellulose	43

Organic Polymer	T_g (°C)
Polyhexamethylene sebacamide (nylon 6,10)	40
Polyvinyl acetate	29
Polyperfluoropropylene	11
Polymethyl acrylate	9
Polyvinylidene chloride	-17
Polyvinyl fluoride	-20
Poly-1-butene	-25
Polyvinylidene fluoride	-39
Poly-1-hexene	-50
Polychloroprene	-50
Polyvinyl-*n*-butyl ether	-52
Polytetramethylene sebacate	-57
Polybutylene oxide	-60
Polypropylene oxide	-60
Poly-1-octene	-65
Polyethylene adipate	-70
Polyisobutylene	-70
Natural rubber	-72
Polyisoprene	-73
Polydimethyl siloxane	-85
Polydimethyl siloxane	-123

Effect of polymer structure on T_g

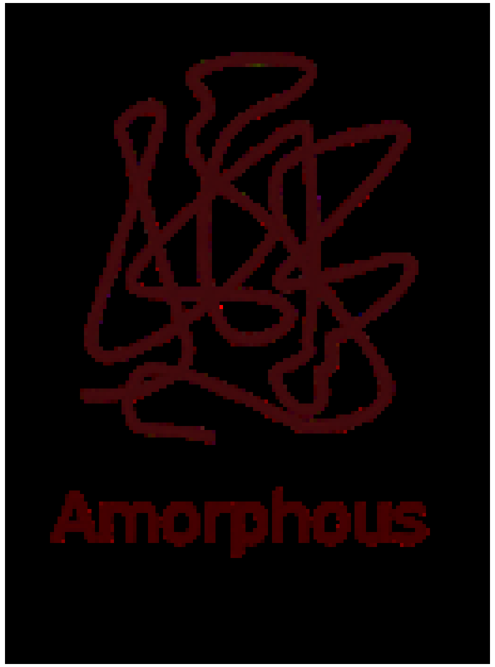
- T_g grows with:
  - backbone stiffness of the chain
    - rigid chains, e.g. ladder-like, aromatic part of the backbone, multiple bonds in the backbone
  - volume of substituents
    - e.g., phenyl PS is quite bulky, as are the long side chains
  - polarity
    - the more polar bonds, the more strong secondary bonds restricting motion
    - the more polar the bonds are, the harder they are to break
  - by branching
    - analogous to voluminous substituents
  - by the length of the macromolecular chain
    - multiple entanglements and secondary bonds (like branching)
  - by networking
    - preventing movement of macromolecules relative to each other
  - increasing content of rigid structures
    - e.g. PS blocks in SBS thermoplastic elastomer
    - fillers (e.g. carbon black in rubber)

- T_g decreases with:
  - the flexibility of the backbone of the chain
  - with decreasing size of substituents
  - decreasing polarity
  - with decreasing degree of branching
  - with decreasing length of the macromolecular chain
  - decreasing rate of cross-linking
  - decreasing content of rigid structures
  - increasing content of plasticizers
    - low-molecular substances inside the polymer preventing the formation of secondary bonds between the chains (in short, they interfere there)
    - e.g. water for cotton (cellulose has a high T_g, so it cannot be ironed dry very well, but after moistening it decreases dramatically)

Amorphous polymer states

- generally three basic ones
  - glassy
  - rubbery
  - plastic

1. glassy state
   - below T_g
   - the movement of macromolecules is greatly restricted
   - chain spines crack under stress



Amorphous polymer states

2. rubbery = viscoelastic
    2. between T_g and T_f (flow temperature) or $T_{degradation}$
    3. only for macromolecules with a sufficient number of nodes (whether chemical or physical)

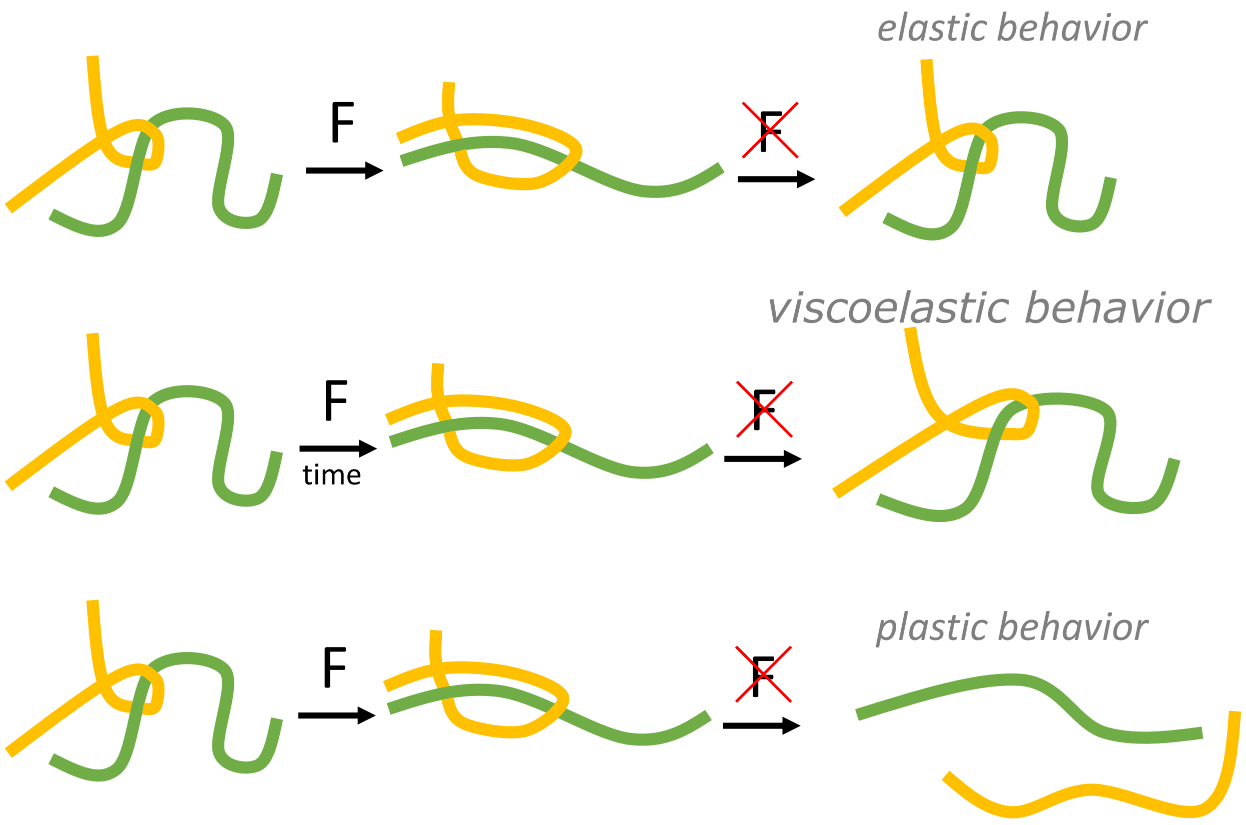
- viscous behavior (irreversible deformation)
  - during long-term mech. stress, macromolecules are deformed and do not return to their original state after the stress is over (not completely)
  - the macromolecules managed to flow into a different form and new secondary bonds are formed, which ensure a new changed shape of the polymer
- elastic behavior (reversible deformation)
  - during short-term mech. stress, macromolecules deform and return to their original (most probable) state after the stress is over
  - the macromolecules did not have time to flow into another form and the secondary bonds did not fundamentally change (they keep their original shape)

Amorphous polymer states

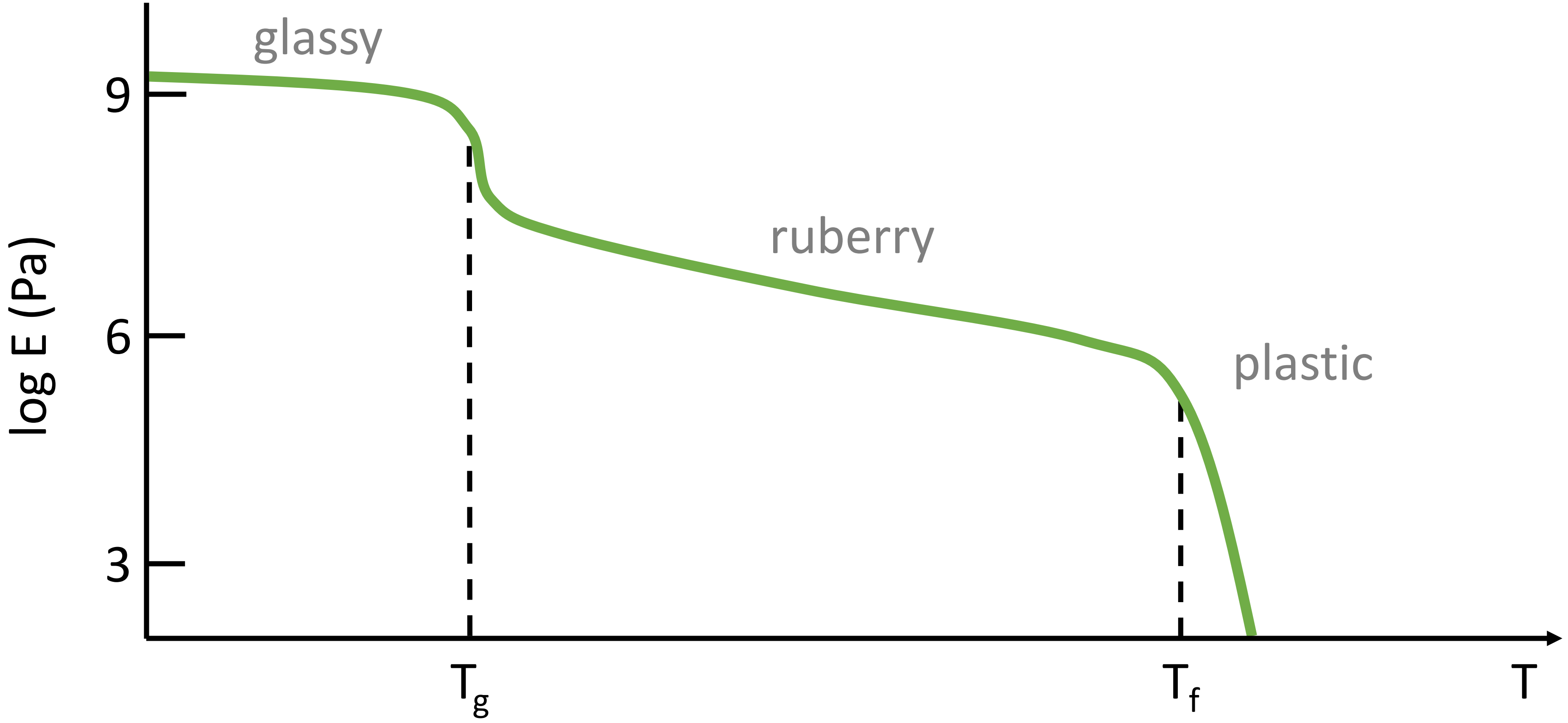
3. plastic state
   - occurs after the creep temperature Tf is exceeded
   - secondary bonds between molecules are practically non-existent (too short-lived) and macromolecules flow after each other → I got a melt
   - the deformation is completely irreversible
   - not all polymers can reach a plastic state
     - they either decompose before they flow
     - or they are so cross-linked that they cannot flow

Amorphous polymer states

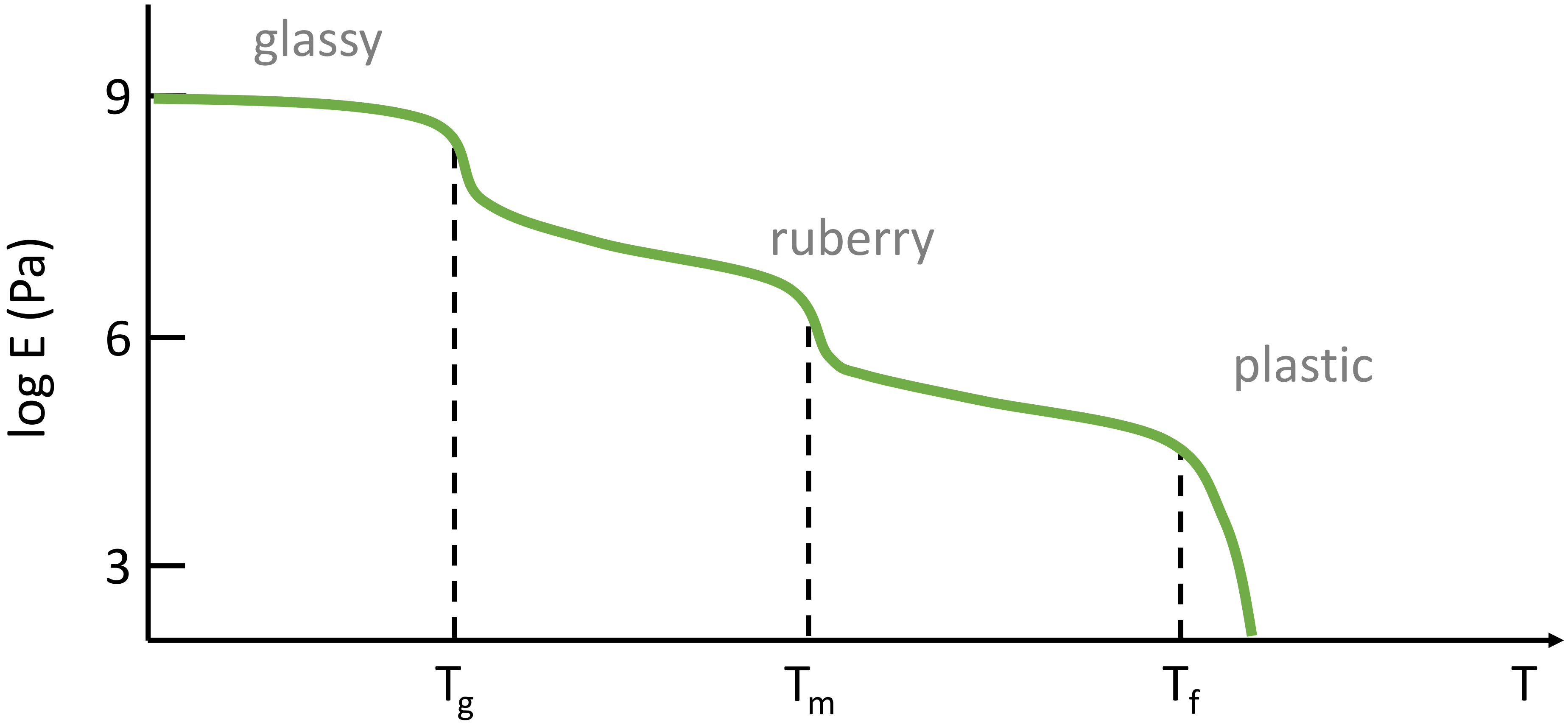
state	*temperature range*	*deformation*
glassy	$0 – T_g$	reversible (to a small extent)
ruberry	$T_g – T_f$	partially reversible
plastic	$T_f – T_{degradation}$	irreversible



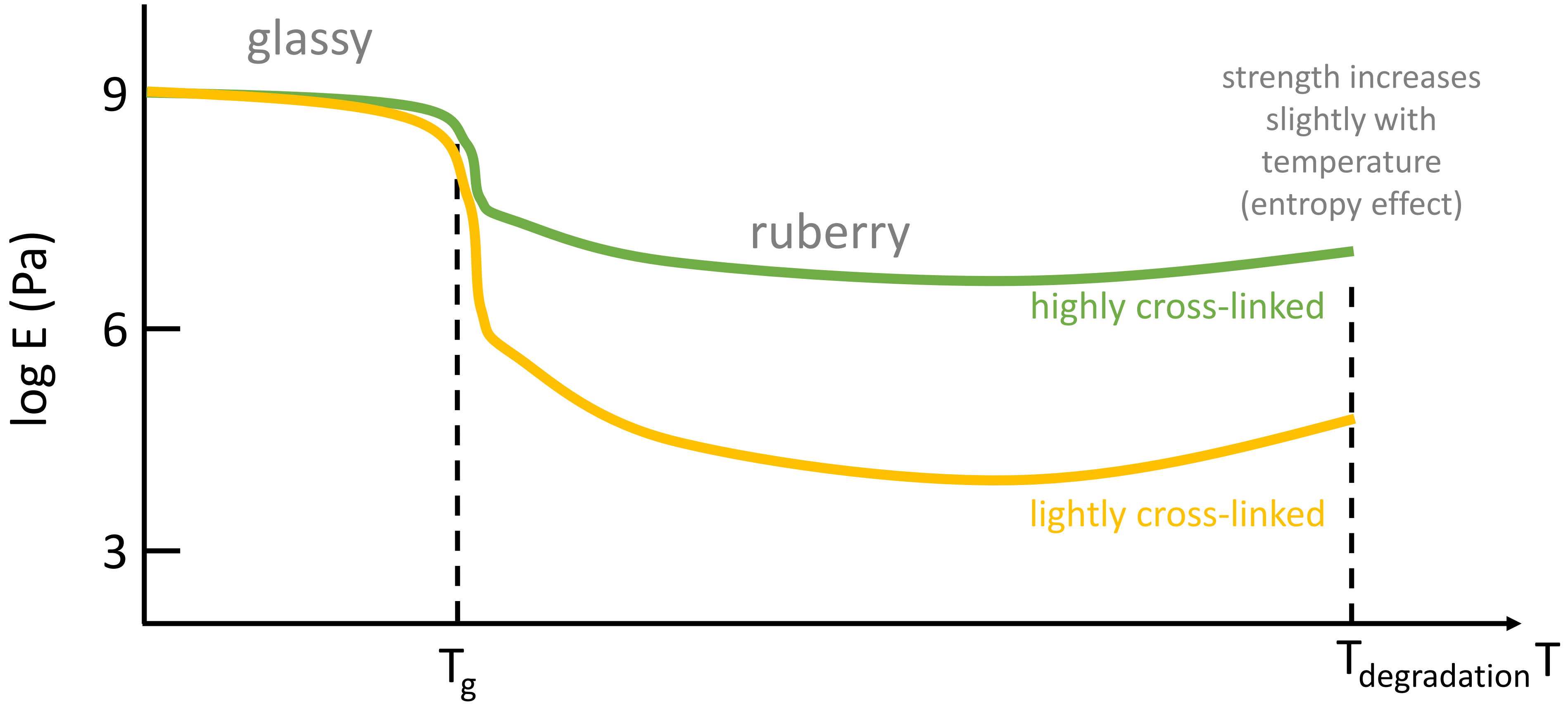
Dependence of modulus of elasticity on temperature for an amorphous polymer



Dependence of modulus of elasticity on temperature for a semicrystalline polymer



Dependence of the modulus of elasticity on temperature for a cross-linked polymer



Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií NextGenerationEU

Národní plán obnovy

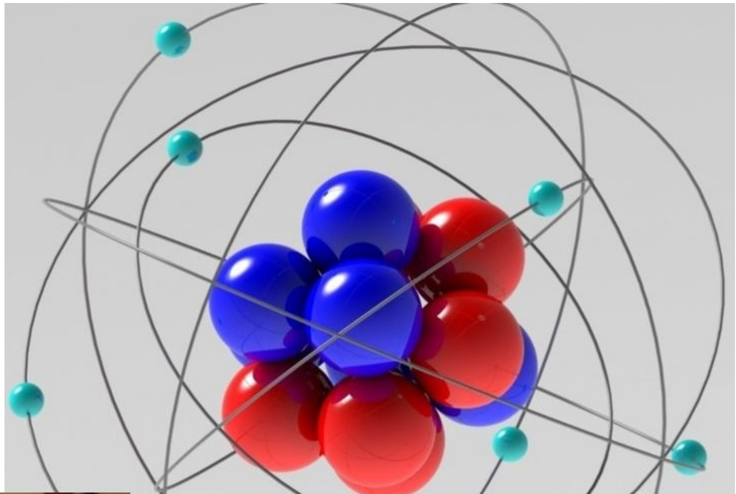
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Molar mass distribution

Molar and relative molecular weight

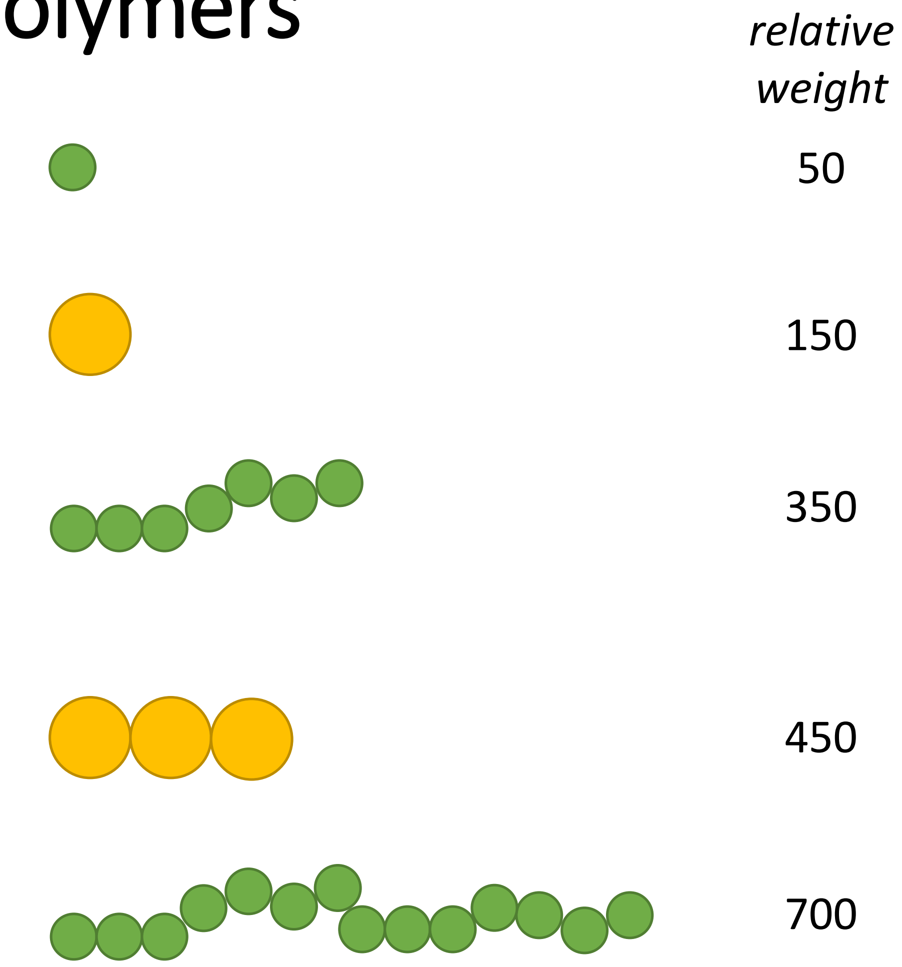
- molar weight
  - molar mass
  - mass of 1 mole of given molecules [g/mol]

- relative molecular weight
  - molecular weight
  - dimensionless number
    - expresses how many times the given molecule is heavier than $\frac{1}{12}$ of the isotope ${}^{12}_{6}C$
  - somewhat imprecisely it can be viewed as comparing the mass of a molecule to the mass of 1 proton (or 1 neutron)
  - Dalton unit
    - Da
    - in polymer practice usually kDa
    - corresponds to the mass of $\frac{1}{12}$ of the isotope ${}^{12}_{6}C$ because a dimensionless unit is not scientific enough



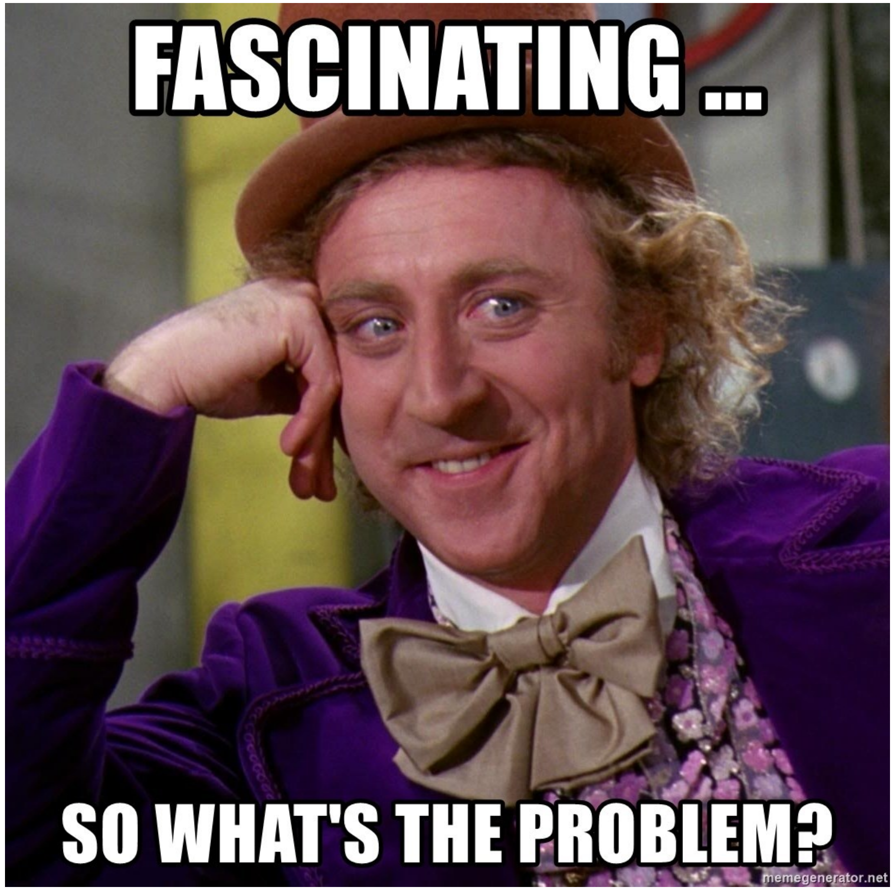
Molecular weight of polymers

- usually in 10^3 to 10^6
- Why is it important?
  - gives information about the size/length of strings
  - size/length of strings
    - the higher the weight, the (usually) longer chain
    - individual polymers can only be compared after conversion (according to measured weights)
      - e.g. the yellow trimer is heavier but shorter than the green heptamer
      - the molecular weight is thus directly related to the degree of polymerization P
- this is not unambiguous information (badly includes branching or cyclic structures)
  - however, usually the higher the number, the larger (longer) the string



A few definitions

- macromolecules of synthetic polymers usually do not have the same size (molar mass)
  - are so-called **non-uniform** (polydisperse)
  - are a mixture of **polymer homologues**
    - macromolecules with the same chemical composition but different molar masses
  - weight distribution more or less continuous
- some polymers (usually natural substances, e.g. proteins) can be made up of precisely sized macromolecules
  - a polymer of macromolecules of uniform molar mass is called **uniform** (mondisperse)



Why do we care about molar mass?

- fundamentally affects the physical, physico-chemical and chemical properties of materials
  - the nature of the material
    - oligomers tend to be liquid
    - short polymers tend to be waxy and non-solid
    - extremely long tend to be stiffer to rigid
  - dissolution rate
  - viscosity of the solution or melt
  - elasticity
  - reactivity
    - the shorter the chains, the greater the relative number of end groups

When stirring, boiled penne is easier to handle than boiled spaghetti due to the difference in their length.

Average molar mass of polymers

- molar mass of non-uniform polymers (each macromolecule generally has a different one)
  - it is solved by appropriate averaging
- there are several types of averages
  - numerous
  - viscosity
  - mass
  - z
    - supposedly centrifugal - from the German centrifuge
    - then z+1 (expansion of the z-mean)
- each kind of diameter gives emphasis to differently sized molecules
  - e.g. z-averages mainly consider the longest fibers

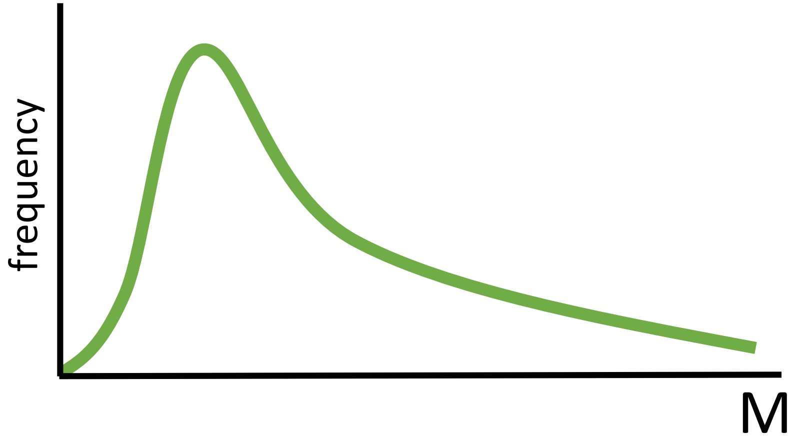
Table of average molar masses

name		*symbol*	*expression*		
number…	average molar mass	$\overline{M_n}$	$\sum x_i M_i$	$\frac{\sum n_i M_i}{\sum n_i}$	$\frac{\sum n_i}{\sum n_i}$ [redacted]
viscosity…		$\overline{M_v}$	$\sqrt[a]{w_i M_i^a}$	$\sqrt[a]{w_i M_i^a}$	$\sqrt[a]{\frac{\sum n_i M_i^{1+a}}{\sum n_i M_i}}$
mass…		$\overline{M_w}$	$\sum w_i M_i$	$\frac{\sum n_i M_i^2}{\sum n_i M_i}$	$\frac{\sum n_i}{\sum n_i}$ [redacted]
z… (centrifugal)		$\overline{M_z}$	$\frac{\sum w_i M_i^2}{\sum w_i M_i}$	$\frac{\sum n_i M_i^3}{\sum n_i M_i^2}$	$\frac{\sum n_i}{\sum n_i}$ [redacted]
z + 1…		$\overline{M_{z+1}}$	$\frac{\sum w_i M_i^3}{\sum w_i M_i^2}$	$\frac{\sum n_i M_i^4}{\sum n_i M_i^3}$	$\frac{\sum n_i}{\sum n_i}$ [redacted]

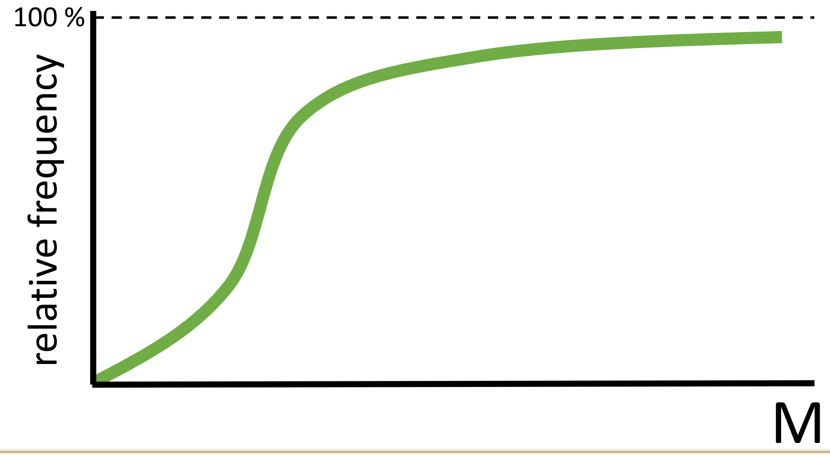
x_i … molar fraction; w_i … mass fraction; a … Mark-Houwink constant

Visualization of molar mass distributions

- basically two options
  - differential curve
    - shows how many molecules have a given molar mass

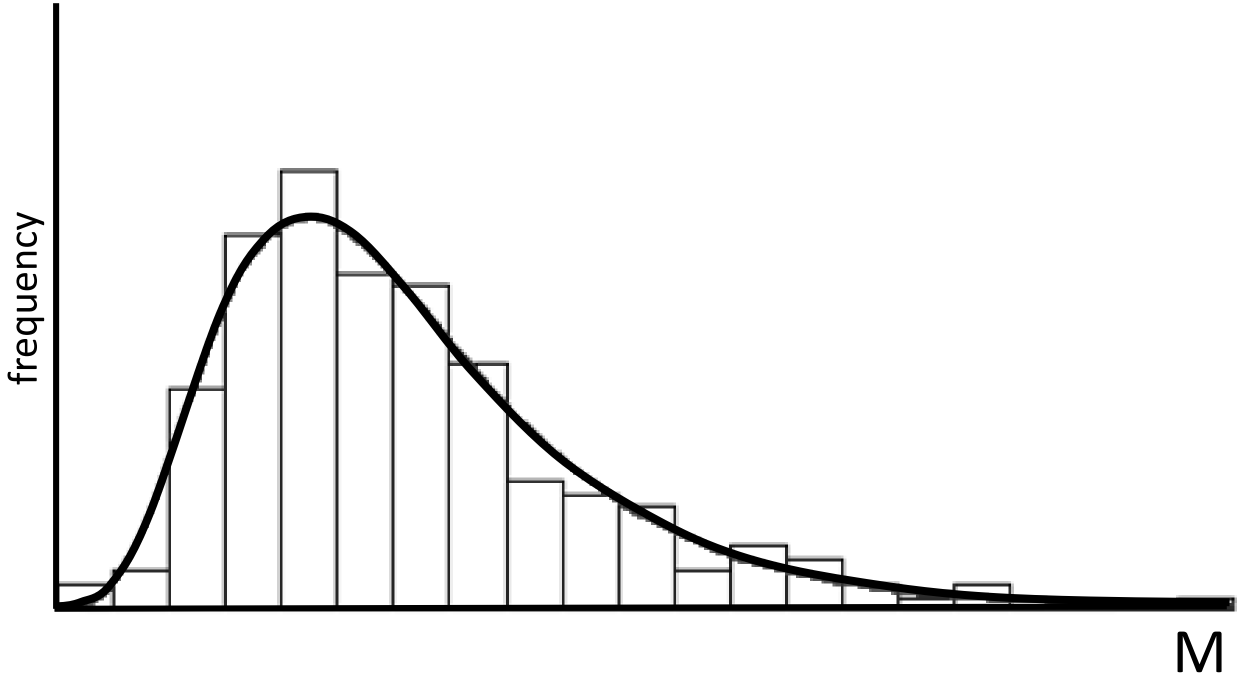


  - integral (cumulative) curve
    - shows how many molecules have a given molar mass and smaller



Differential distribution curve of molar masses

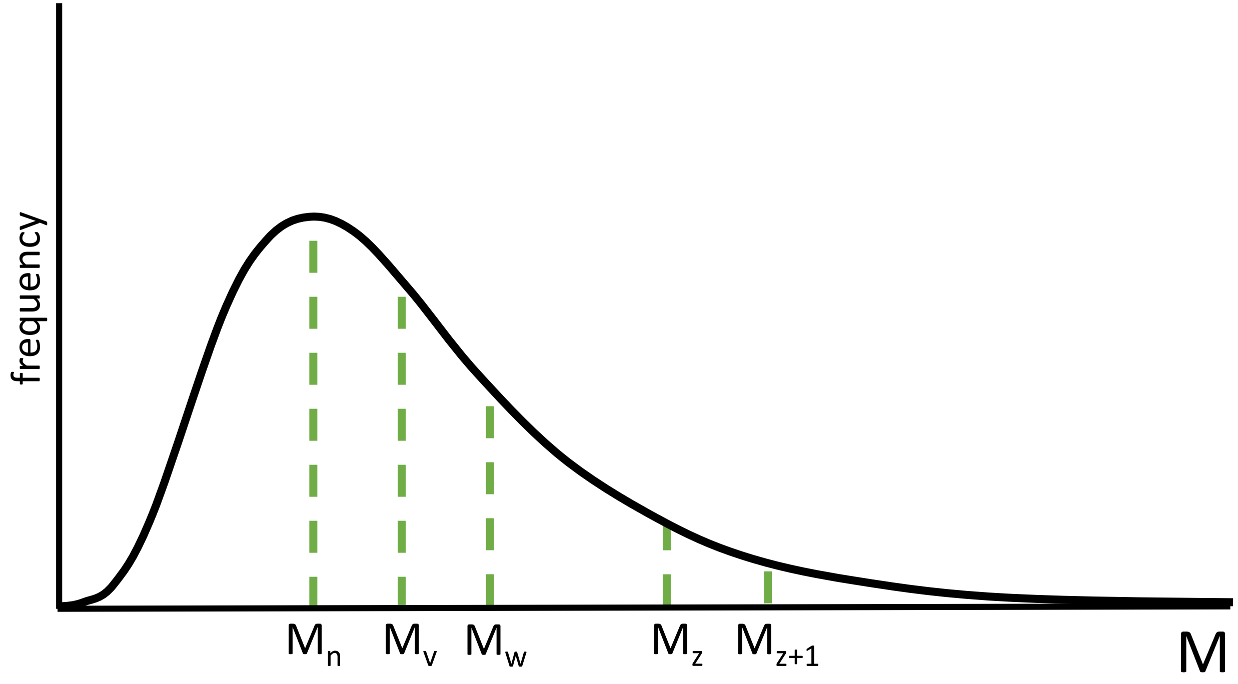
- shows how many macromolecules have a given molar mass
- usually some variant of the log-normal distribution
  - however, it can also be other (e.g. double-peaked, etc.)



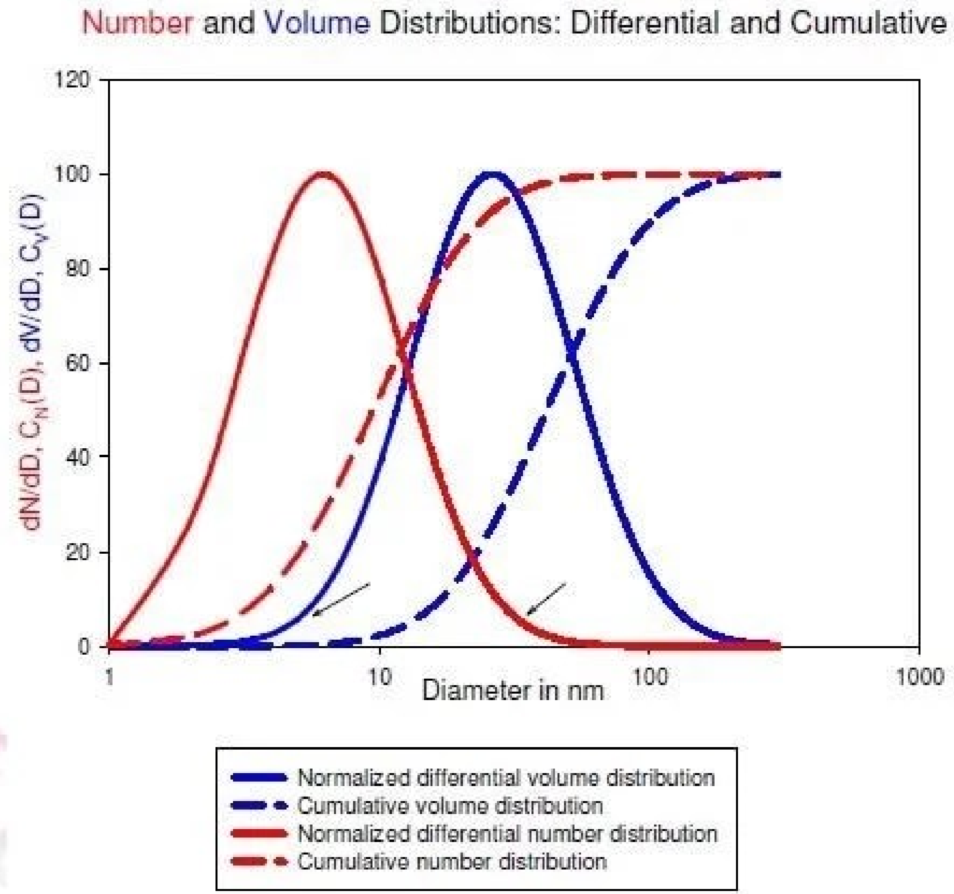
Differential distribution curve of molar masses

- the numerically averaged mass curve is shown
- then other diameters on it
- it is always true that

$$\overline{M_n} \leq \overline{M_v} \leq \overline{M_w} \leq \overline{M_z} \leq \overline{M_{z+1}}$$



Distribuční křivky molárních hmotností

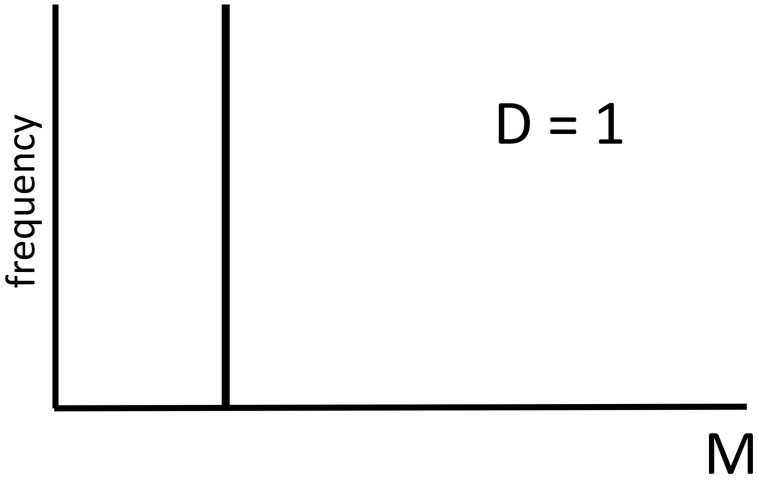


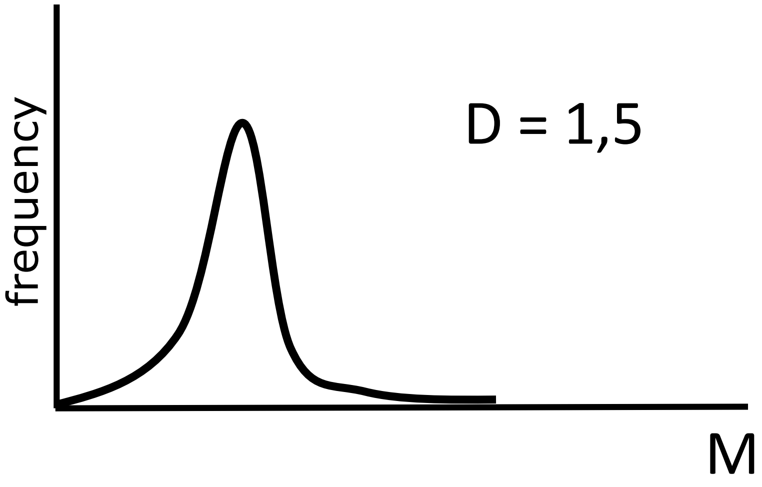
Dispersity index

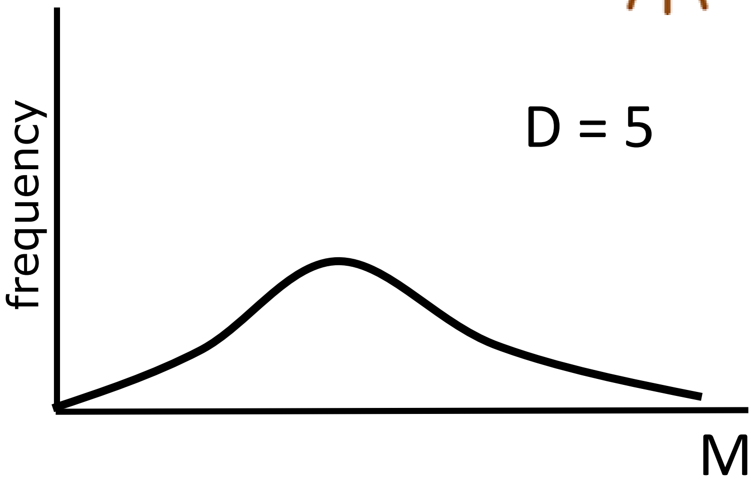
- formerly called polydispersity
- corresponds to the proportion of mass centers of mol. hmm compared to numerically medium
  - since the numerator (Mw) is always greater than or equal to the denominator (Mn), the non-uniformity index is always greater than 1

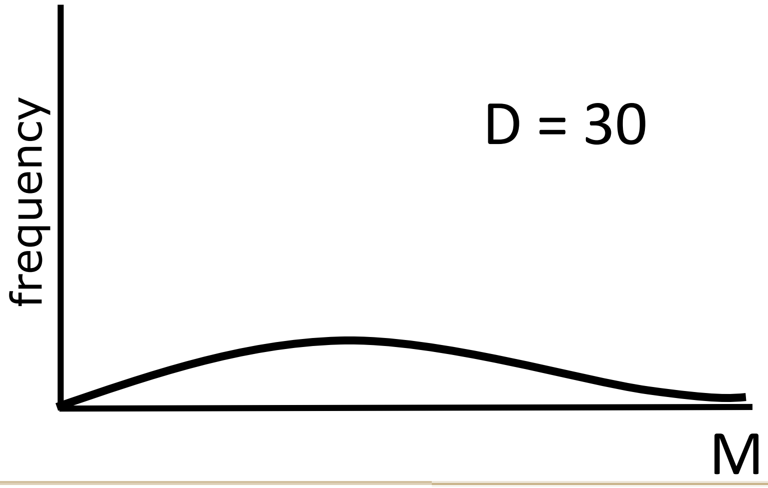
$$\mathrm{D} = \mathrm{Đ} = \mathrm{Z} = \mathrm{PI} = \mathrm{PDI} = \frac{\overline{\mathrm{M_w}}}{\overline{\mathrm{M_n}}} \geq 1$$

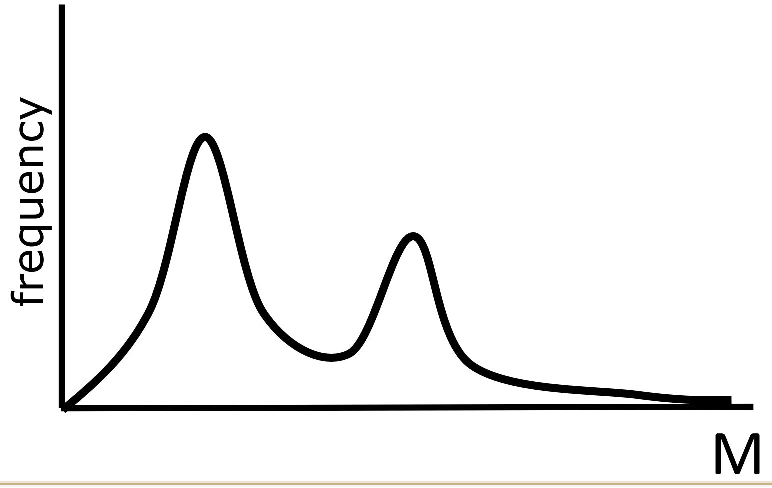
- gives information about how non-uniform the system is
  - if it is close to 1, then the molecules are similar in length
    - Đ around 1.1 to 1.3 are still considered practically uniform
  - if 50 is needed, we have a decently non-uniform system


frequency
D = 1
M


frequency
D = 1,5
M


frequency
D = 5
M


frequency
D = 30
M


frequency
M

An example of calculating molecular weights

Let us have 7 moles of uniform polybutylene terephthalate (PBTF) with a molar mass of 654 g/mol, 3 moles of PBTF with a molecular weight of 210 g/mol and 9 moles of PBTG with a mass of 87 g/mol. Calculate the number average, weight average, z and z+1 average molar mass of a given PBTF as well as the non-uniformity index. Discuss the result.

polymer homolog	*amount of substance (mol)*	*molecular weight*
A	7	6540
B	3	2100
C	9	870

$$\overline{M_n} = \sum x_i M_i = \frac{n_A}{n_A + n_B} M_A + \frac{n_B}{n_A + n_B} M_B + + \frac{n_C}{n_C + n_C} M_C \cong 3153\ g/mol$$

$$\overline{M_w} \cong 5332\ g/mol$$

$$\overline{M_z} \cong 6235\ g/mol$$

$$\overline{M_{z+1}} \cong 6461\ g/mol$$

Example 2

polymer homolog	*amount of substance (mol)*	*molecular weight*
A	1	4000
B	1	100000

$$\overline{M_n} = \sum x_i M_i = \frac{1}{1+1}4000 + \frac{1}{1+1}10^6 \cong \mathbf{52000\ g/mol}$$

$$\overline{M_w} = \sum w_i M_i = \frac{1 \cdot 4000}{1 \cdot 4000 + 1 \cdot 10^6}4000 + \frac{1 \cdot 10^6}{1 \cdot 4000 + 1 \cdot 10^6}10^6 \cong \mathbf{96307\ g/mol}$$

$$\overline{M_z} = \frac{\sum w_i M_i^2}{\sum w_i\, M_i} = \frac{\frac{1 \cdot 4000}{1 \cdot 4000 + 1 \cdot 10^6}4000^2 + \frac{1 \cdot 10^6}{1 \cdot 4000 + 1 \cdot 10^6}(10^6)^2}{\frac{1 \cdot 4000}{1 \cdot 4000 + 1 \cdot 10^6}4000 + \frac{1 \cdot 10^6}{1 \cdot 4000 + 1 \cdot 10^6}10^6} \cong \mathbf{99847\ g/mol}$$

$$\overline{M_{z+1}} = \frac{\sum w_i M_i^3}{\sum w_i\, M_i^2} = \frac{\frac{1 \cdot 4000}{1 \cdot 4000 + 1 \cdot 10^6}4000^3 + \frac{1 \cdot 10^6}{1 \cdot 4000 + 1 \cdot 10^6}(10^6)^3}{\frac{1 \cdot 4000}{1 \cdot 4000 + 1 \cdot 10^6}4000^2 + \frac{1 \cdot 10^6}{1 \cdot 40 + 1 \cdot 10^6}(10^6)^2} \cong \mathbf{99994\ g/mol}$$

$$D = \frac{\overline{M_w}}{\overline{M_n}} = \frac{96307}{52000} \cong \mathbf{1,9}$$

Example 3

polymer homolog	*amount of substance (mol)*	*molecular weight (kDa)*
A	5	4
B	2	100

$$\overline{M_n} = \sum x_i M_i = \frac{5}{5+2}40 + \frac{2}{5+2}1000 \cong \mathbf{31{,}4\ kg/mol}$$

$$\overline{M_w} = \sum w_i M_i = \frac{5 \cdot 40}{5 \cdot 40 + 2 \cdot 1000}40 + \frac{2 \cdot 1000}{5 \cdot 40 + 2 \cdot 1000}1000 \cong \mathbf{91{,}3\ kg/mol}$$

$$\overline{M_z} = \frac{\sum w_i M_i^2}{\sum w_i\, M_i} = \frac{\frac{5 \cdot 40}{5 \cdot 40 + 2 \cdot 1000}40^2 + \frac{2 \cdot 1000}{5 \cdot 40 + 2 \cdot 1000}1000^2}{\frac{5 \cdot 40}{5 \cdot 40 + 2 \cdot 1000}40 + \frac{2 \cdot 1000}{5 \cdot 40 + 2 \cdot 1000}1000} \cong \mathbf{99{,}6\ kg/mol}$$

$$\overline{M_{z+1}} = \frac{\sum w_i M_i^3}{\sum w_i\, M_i^2} = \frac{\frac{5 \cdot 40}{5 \cdot 40 + 2 \cdot 1000}40^3 + \frac{2 \cdot 1000}{5 \cdot 40 + 2 \cdot 1000}1000^3}{\frac{5 \cdot 40}{5 \cdot 40 + 2 \cdot 1000}40^2 + \frac{2 \cdot 1000}{5 \cdot 40 + 2 \cdot 1000}1000^2} \cong \mathbf{1000\ kg/mol}$$

$$D = \frac{\overline{M_w}}{\overline{M_n}} = \frac{913}{314} \cong \mathbf{2{,}9}$$

Example 4

polymer homolog	amount of substance (mol)	molecular weight (kDa)
A	5	4
B	1	120

$$\overline{M_n} = \sum x_i M_i \cong \mathbf{20,3\ kg/mol}$$

$$\overline{M_w} = \sum w_i M_i \cong \mathbf{103,4\ kg/mol}$$

$$\overline{M_z} = \frac{\sum w_i M_i^2}{\sum w_i\ M_i} \cong \mathbf{119,4\ kg/mol}$$

$$\overline{M_{z+1}} = \frac{\sum w_i M_i^3}{\sum w_i\ M_i^2} \cong \mathbf{120\ kg/mol}$$

$$D = \frac{\overline{M_w}}{\overline{M_n}} \cong \mathbf{4,4}$$

Example 5

polymer homolog	*amount of substance (mol)*	*molecular weight (kDa)*
A	250	4
B	1	1000

$$\overline{M_n} = \sum x_i M_i \cong \mathbf{8\ kg/mol}$$

$$\overline{M_w} = \sum w_i M_i \cong \mathbf{502\ kg/mol}$$

$$\overline{M_z} = \frac{\sum w_i M_i^2}{\sum w_i\ M_i} \cong \mathbf{996\ kg/mol}$$

$$\overline{M_{z+1}} = \frac{\sum w_i M_i^3}{\sum w_i\ M_i^2} \cong \mathbf{1000\ kg/mol}$$

$$D = \frac{\overline{M_w}}{\overline{M_n}} \cong \mathbf{63}$$

Example 6

polymer homolog	amount of substance (mol)	molecular weight (kDa)
A	171	4
B	71	12
C	37	24
D	23	46
E	11	112

$$\overline{M_n} = \sum x_i M_i \cong \mathbf{15,1\ kg}$$

$$\overline{M_w} = \sum w_i M_i \cong \mathbf{46,9\ kg}$$

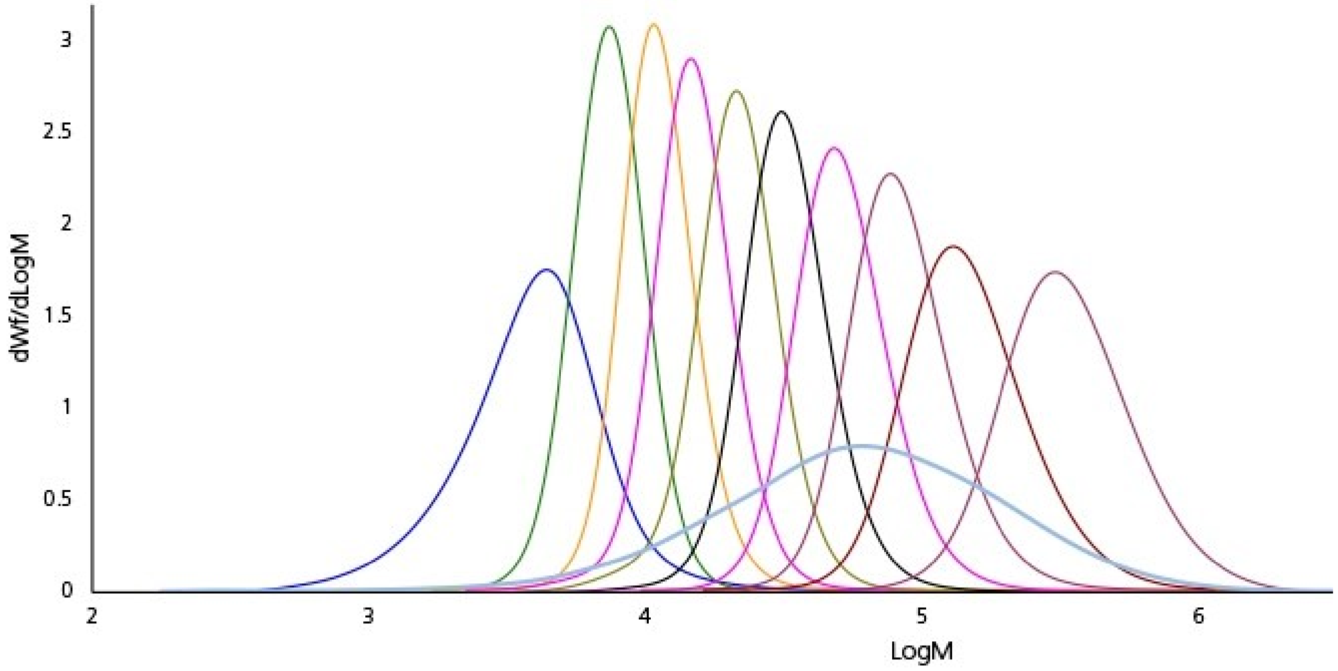
$$\overline{M_z} = \frac{\sum w_i M_i^2}{\sum w_i\ M_i} \cong \mathbf{83,0\ kg}$$

$$\overline{M_{z+1}} = \frac{\sum w_i M_i^3}{\sum w_i\ M_i^2} \cong \mathbf{100,8\ kg}$$

$$D = \frac{\overline{M_w}}{\overline{M_n}} \cong \mathbf{3,1}$$

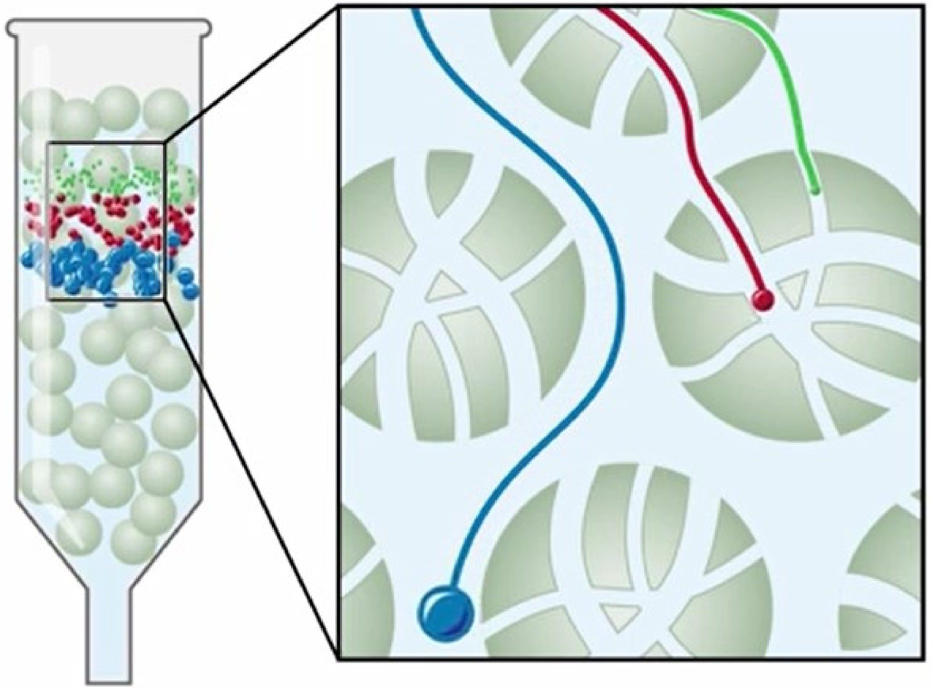
Fractionation of polymer homologues

- isolation of polymer homologues from a mixture
    - individual polymer homologs can almost never be isolated
        - remember the definitions of a polymer (removing a few units won't affect their properties - So how could I isolate them if I can't find any property in which they differ physically or chemically?)
    - rather, polymer molecules with a very narrow distribution (e.g. Đ = 1.1) are obtained



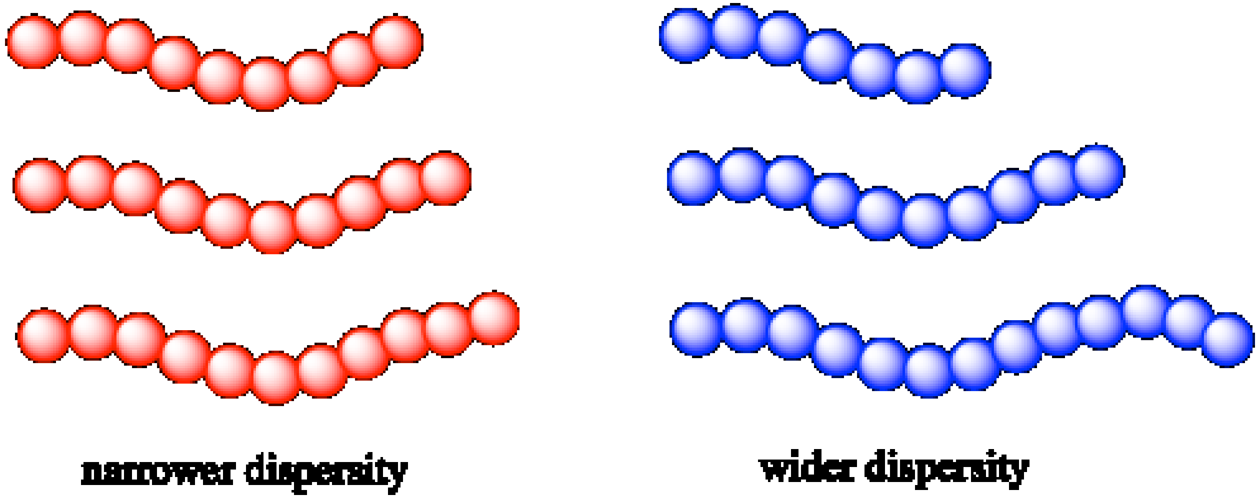
Fractionation methods

- precipitation
  - the longer the chain, the more easily it is precipitated by the addition of the wrong solvent
  - I dilute the initially perfect polymer solution with a non-solvent and gradually remove the precipitated polymer
- dissolution
  - the opposite of the precipitating technique
- gel permeation chromatography (GPC)
  - the polymer solution flows through a column (tube) in which there is a gel with defined pores and the whole thing is carried by a suitable liquid (the so-called mobile phase in which the polymer is soluble)
  - small macromolecules flow into the pores during this and stay behind the large ones that do not fit into the pores
  - the smaller the molecule, the slower it flows
  - at the end of the column, I gradually remove the polymer solution with a narrower distribution



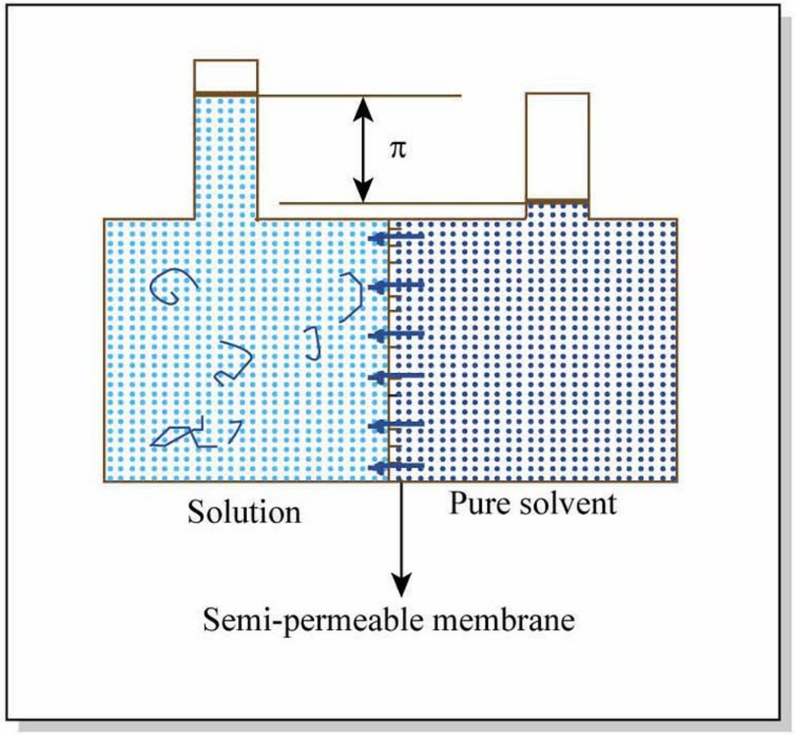
Determination of molar mass

- can be divided by
  - output values
  - absolute
    - by measuring I get the molar mass value
  - relative
    - I need a standard to determine the exact value
- output (which average value you get)
  - M_n
    - end group method
    - osmometry
    - ebuloscopy
    - cryoscopy
    - mass spectroscopy
  - M_v
    - rheometry
  - M_s
    - light scattering
    - sedimentation
- practically always only for soluble polymers



Methods measuring M_n

- end group method
  - absolute method of determination
  - each (unbranched) macromolecule has two ends (often reactive) → if I find the number of end groups, I get the exact number of macromolecules
  - I can, for example, use a dye (preferably green, because I like it the most), which binds only to the ends, and then spectrophotometrically determine how much of it binds
- osmometry
  - membrane or in the vapor phase
  - osmotic pressure depends on the size of macromolecules
  - we let the solvent penetrate into the polymer solution through the semi-permeable membrane and after equalizing the osmotic and hydrostatic pressures we determine the molar mass



Methods measuring M_n

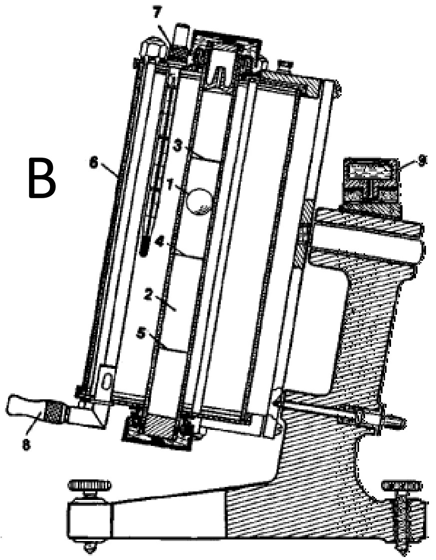
- ebuloscopy
  - a small addition of a nonvolatile solute to a solvent will lower its boiling point
  - this change in boiling point is proportional to the change in molar concentration
- cryoscopy
  - a small addition of a non-volatile solute to a solvent will lower its melting point
  - this change in melting point is proportional to the change in molar concentration

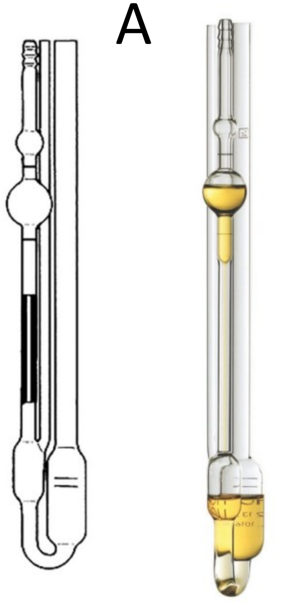
- mass spectrometry
  - absolute method

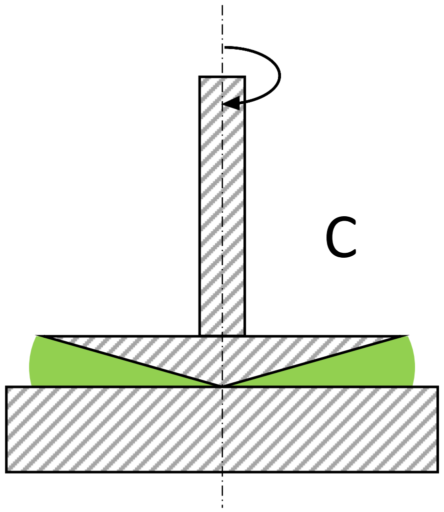
1. chop a macromolecule into pieces (by ionization)
2. I filter ions (e.g. through a quadrupole) according to the ratio of their charge and mass (z/m)
3. I will measure the frequency of ions with a given z/m ratio
4. I will find out the spectrum and from it the molar mass of the original macromolecule

Methods measuring M_v

- viscometry
  - relative method
  - viscosity dependent on concentration and molar mass
    - imagine that you are mixing 500 g of said penneis and 500 g of unbroken long spaghetti in a 5 l pot of hot water - one will surely be much harder to stir
  - multiple measurement methods
  - capillary
    - e.g. Ubbehlohde viscometer (A)
  - ball
    - the object descends through the solution and I measure the speed of descent
    - e.g. Höppler viscometer (B)
  - rotational
    - rotational viscometers or rheometers (C)
- flow index
  - for melts
  - how many (grams) of polymer melt will flow through a defined nozzle at a defined temperature and pressure
  - does not indicate the molar mass, but the flow properties of the polymer depending on the molar mass

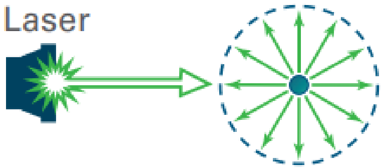


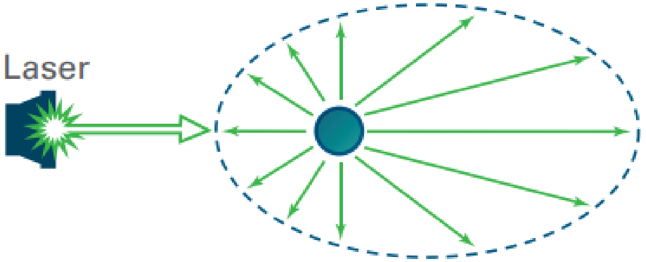




Methods measuring M_w

- light scattering
  - absolute
  - scattering of light on small particles (molecules)
  - very sensitive to dirt (dust, scratches on optical elements, etc.)
  - the wavelength of the radiation used must be
  - the intensity of the scattered radiation depending on the viewing angle, the concentration of the solution and the mass average molar mass
    - depending on the size of the macromolecular balls, different kinds of scattering occur





Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

MŠMT
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Synthesis of polymers

Three conditions of monomer polymerizability

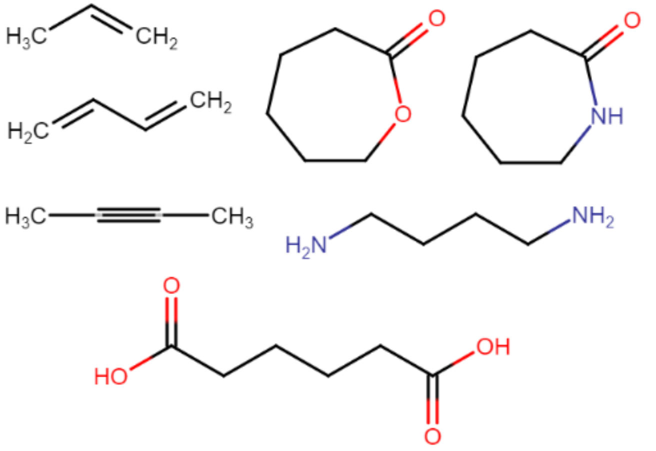
- in order for a monomer to polymerize, it must meet three conditions:

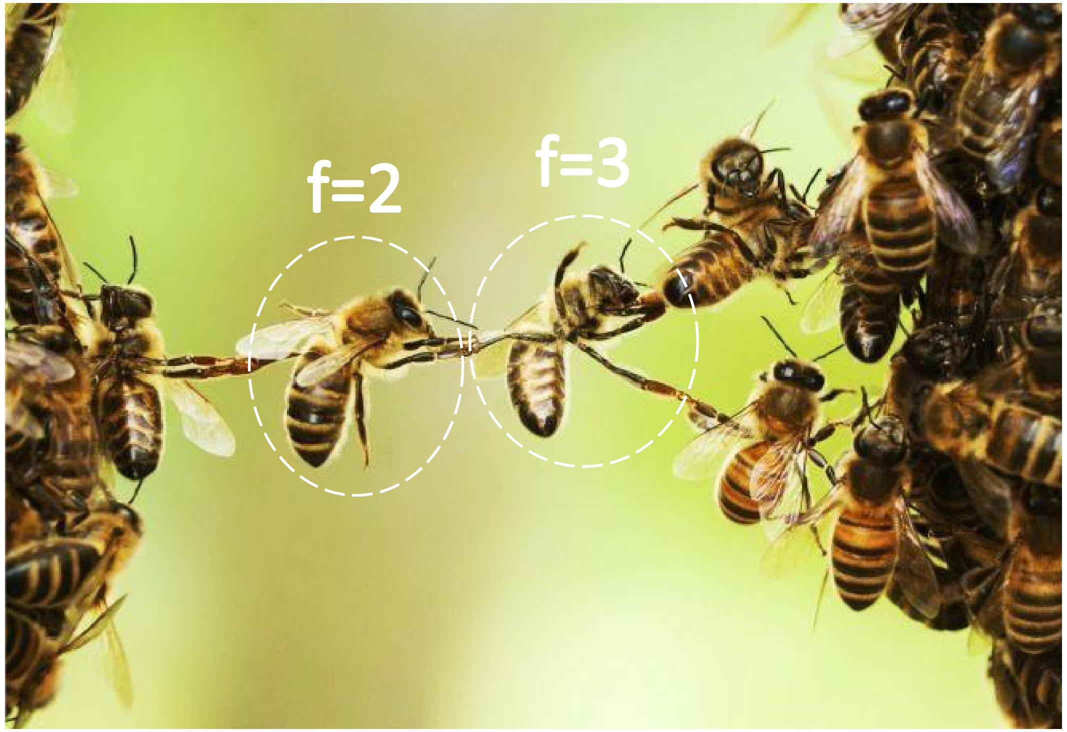
1. chemical
    - a structure capable of forming chains
2. thermodynamic
    - an appropriate reaction is taking place
3. kinetic
    - the polyreaction must be faster than the other reactions
    - system can be activated

1. Chemical condition

- monomers must be at least difunctional (f at least 2)
  - at least two groups capable of binding to other molecules

1. multiple bond
2. suitable functional groups
3. cycle with a heteroatom





2. Thermodynamic condition

- the Gibbs energy must decrease during the reaction
  - assumption of spontaneous reaction (lower energy of the resulting system)

$$\Delta G < 0$$

- ΔG … change in Gibbs (free) energy

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

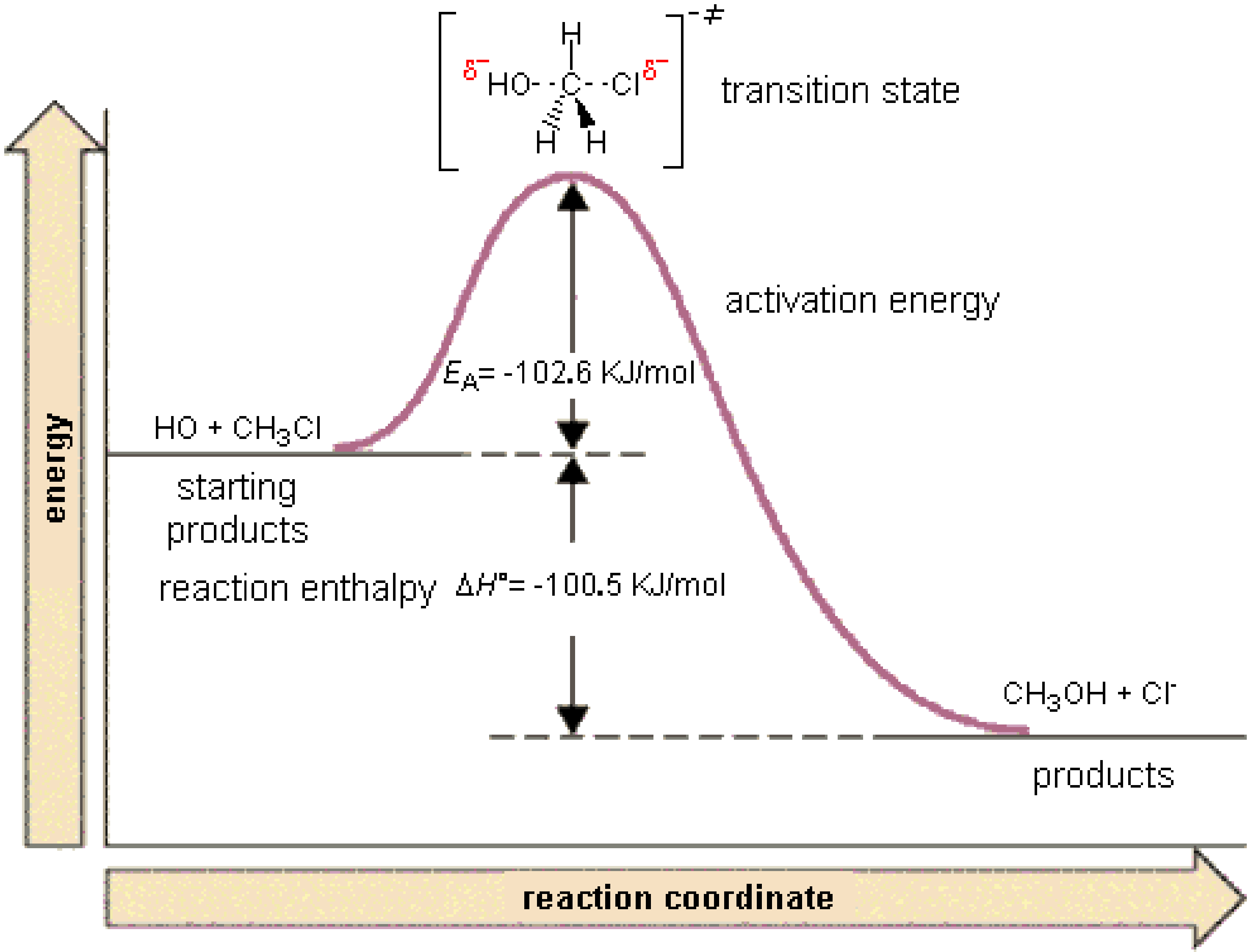
ΔH … enthalpy change
T … thermodynamic temperature
ΔS … entropy change

2. Thermodynamic condition

- ΔH … enthalpy change
  - transferred energy (heat) at constant pressure
    - exothermic reaction ($\Delta H < 0$) – energy leaves the system
    - endothermic reaction ($\Delta H > 0$) – energy enriches the system
  - fundamentally influenced by the structure of the monomer
  - usually energy is released (exothermic reaction)

Pieter Bruegl – The Fight Between Carnival and Lent (1559)

- ΔS … entropy change
  - degree of system disorder (the larger, the more disordered)
  - usually $\Delta S < 0$
    - monomers arrange themselves into chains
    - the exception is the tearing of large cycles, where ΔS is slightly higher than 0


H
δ− HO- -C- -Cl δ−
H H
-‡
transition state
activation energy
E_A= -102.6 KJ/mol
HO + CH_3Cl
starting products
reaction enthalpy $\Delta H°$= -100.5 KJ/mol
$CH_3OH + Cl^-$
products
energy
reaction coordinate

2. Thermodynamic condition

- $\Delta G = 0 = \Delta H - T\Delta S$

ΔH	< 0	< 0	> 0	> 0
ΔS	< 0	> 0	< 0	> 0
	T_c	**always**	**never**	**T_f**

- T_c … ceiling temperature
  - after exceeding it, polymerization stops, because $\Delta G>0$
- T_f … floor temperature
  - the reaction does not run until it is exceeded, since $\Delta G>0$

ceiling vault in Kladruby (Santiny)

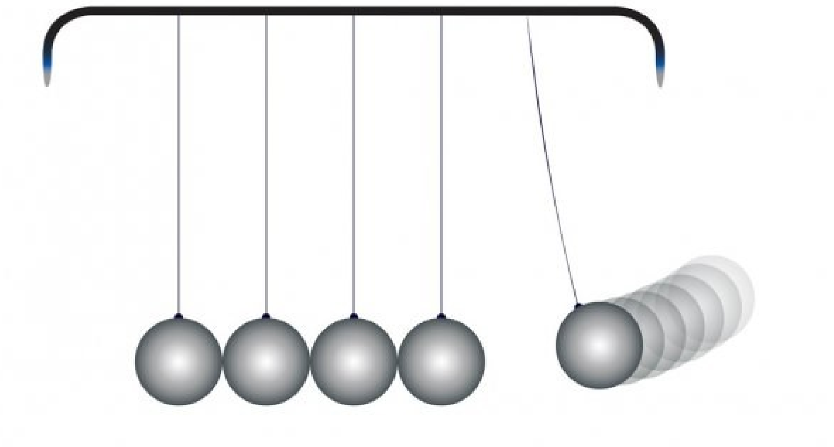
paving in the rotunda of St. Wenceslas in Prague (MatFyz)

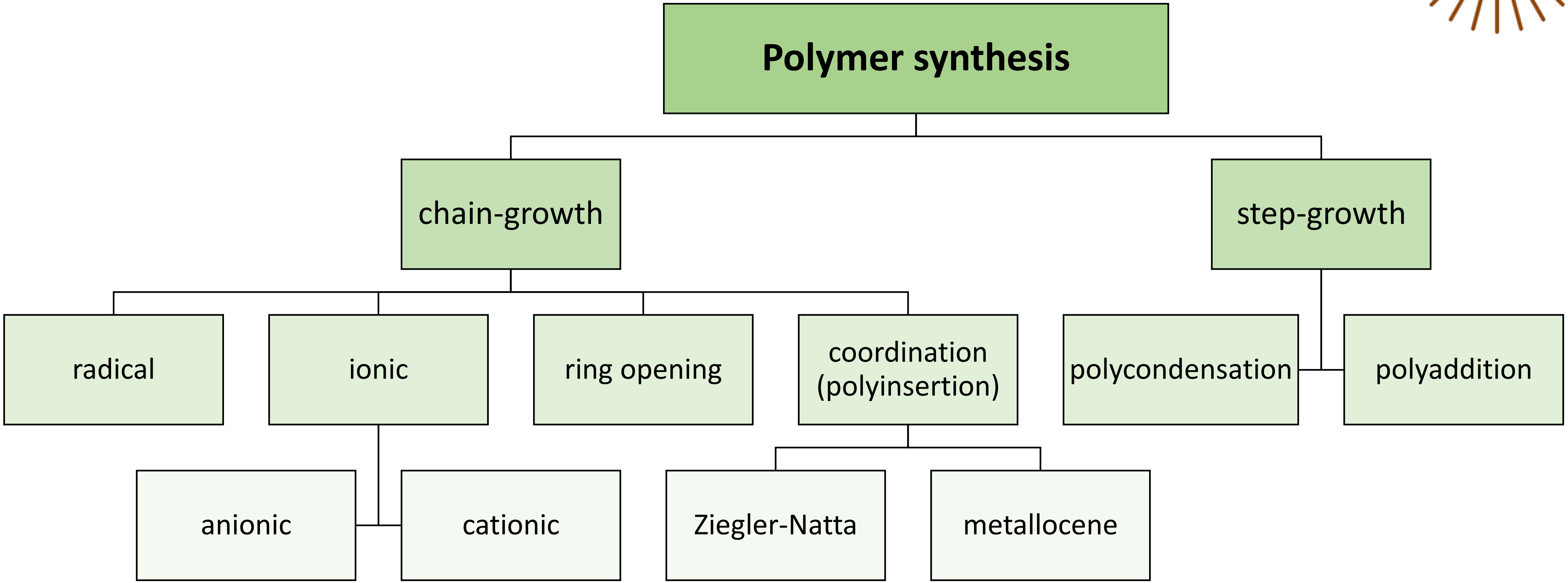
3. Kinetic condition

- the polyreaction must be faster than other reactions (e.g. termination of growth, depolymerization, etc.)
  - monomers must preferentially grow into macromolecules and not something else

$$v_{growth} \gg v_{rest}$$

- the monomer must be activatable
  - a reactive intermediate must be formed
    - dependent on the monomer structure
  - activation
    - radicals
    - ions
    - complexes





Polymer synthesis

chain-growth

step-growth

radical

ionic

ring opening

coordination (polyinsertion)

polycondensation

polyaddition

anionic

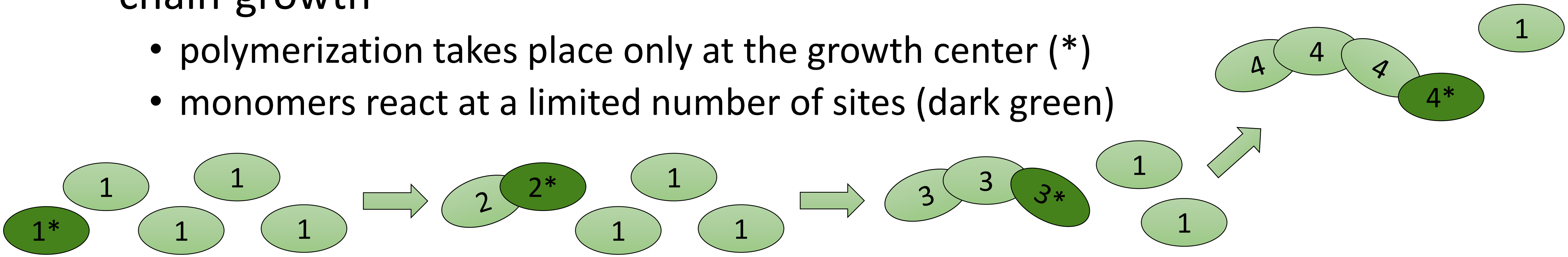
cationic

Ziegler-Natta

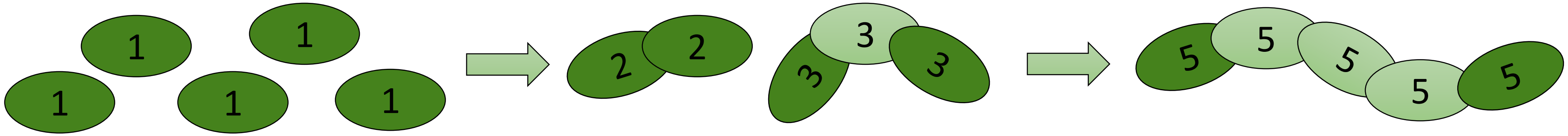
metallocene

Chain and step reactions

- chain-growth
  - polymerization takes place only at the growth center (*)
  - monomers react at a limited number of sites (dark green)

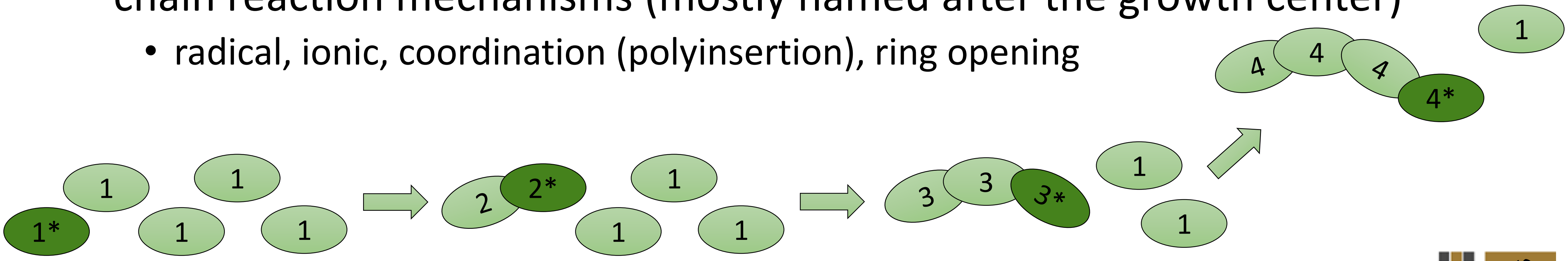


- step-growth
  - monomers can react with monomers, oligomers and polymers



Chain-growth polyreaction

- repeated attachment of monomer molecules to growth centers (radicals, ions, complexes)
- three groups of reactions are usually repeated (it is not always a single reaction, but rather a series of reactions): initiation, propagation, termination
- chain reaction mechanisms (mostly named after the growth center)
  - radical, ionic, coordination (polyinsertion), ring opening

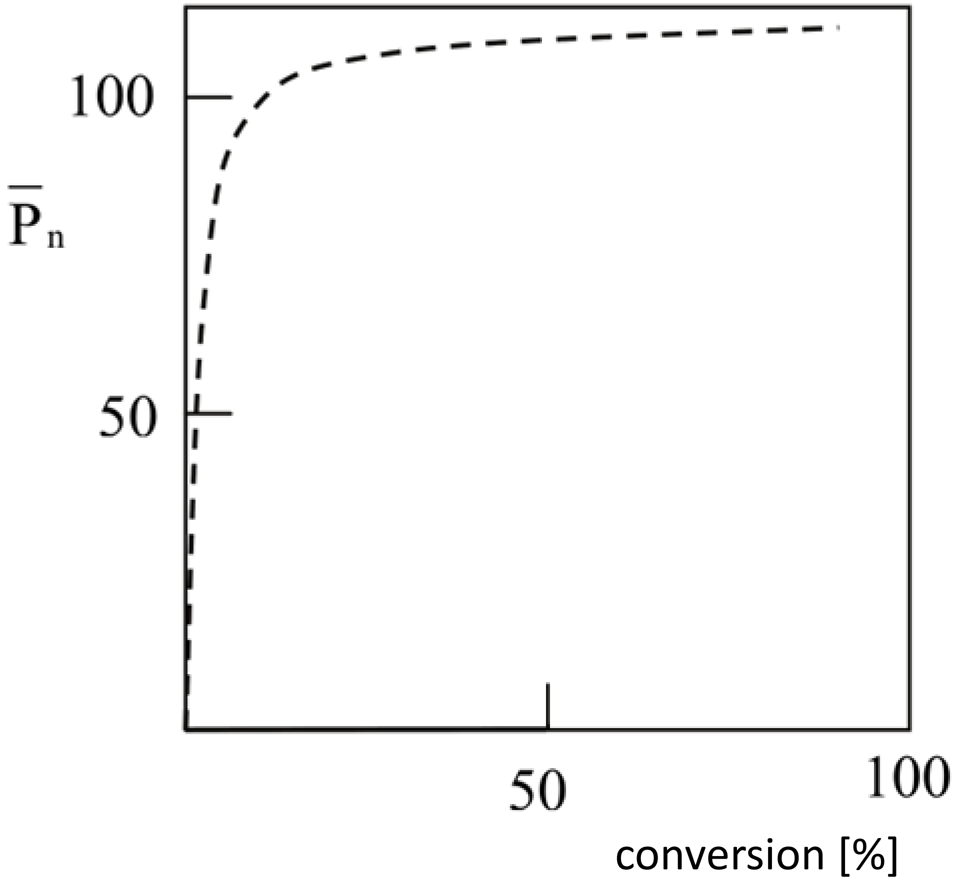


The chain reaction mechanism is influenced by:

- chemical structure of monomers
  - multiple bonds
    - usually double, but triples can also be found
  - bond polarization
  - size of substituents
    - bulky substituents may sterically hinder the reaction
  - stress in circles (if I have cyclic monomers)
- mechanism of initiation and or catalysis
  - monomer dependent
- ability to stabilize reaction intermediates
  - dependent on the monomer and reaction mechanism

Dependence of polymerization chain reaction degree on conversion

- polymerization degree P
  - = number of monomeric units in the macromolecule
- monomer conversion
  - = proportion of reacted monomer units
  - 100% conversion therefore means complete reaction of the reaction mixture
- chain polyreactions
  - capital P even with a small conversion
  - it no longer increases much at higher conversions



Characteristic features of chain polyreaction

- molecules grow by repeated addition to the active site
- the monomer concentration decreases gradually during the polymerization
  - the concentration of growing molecules is small (10^{-8} to 10^{-3} mol)
- long reaction times are not necessary for the formation of a high molecular weight polymer
  - the time required to form a long macromolecule is on the order of a few seconds

Chain-growth polyreactions - radical

- one of the most widespread synthetic polyreactions
- LDPE, PS, PMMA, SR, PVAc

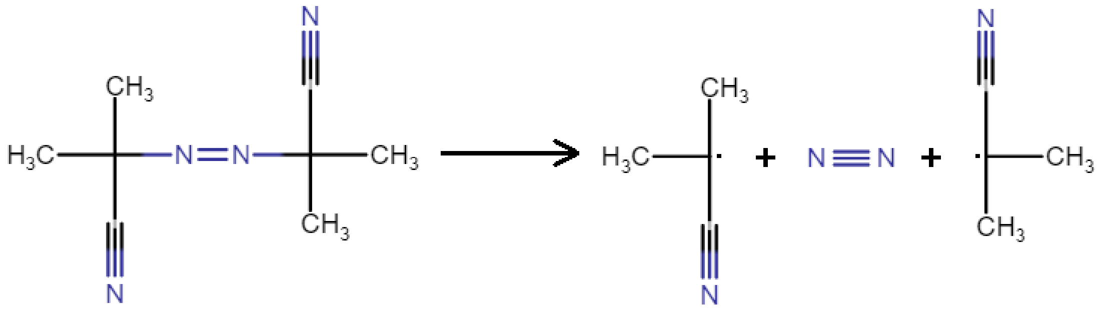
- the general course of a radical reaction
  1. initiation
  2. promotion
  3. termination

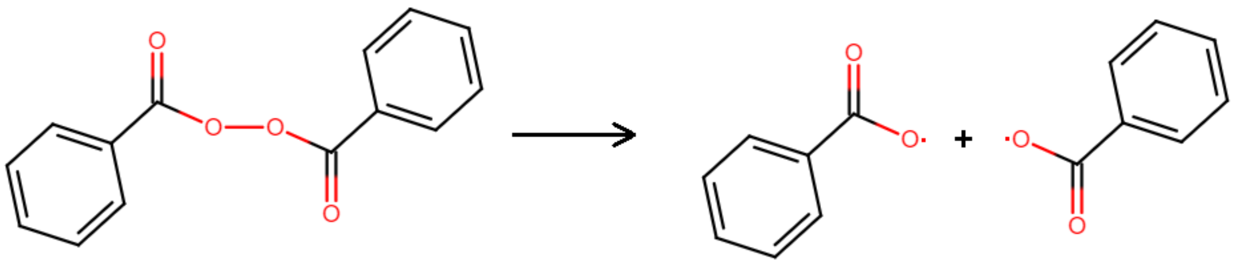
"The concept of free radicals was unknown in 1920.
Well, maybe in politics, but not in chemistry."
Herman Francis Mark

Initiation (radical polyreactions)

- initiation = formation of a growth center
- usually homolytic cleavage of the initiator bond to form radicals
  - radical = a molecule with an unpaired electron
    - is marked with a dot (lone electron)
    - generally extremely reactive (unstable)
- cage effect
  - after homolytic cleavage, it can happen that the resulting radicals located close to each other react together and the radicals thus disappear
- such reactions do not lead to the formation of initiator molecules
- with reactive monomers, the polyreaction sometimes takes place spontaneously
- they must therefore be stabilized (so that they do not react already in the storage container)

ABIN

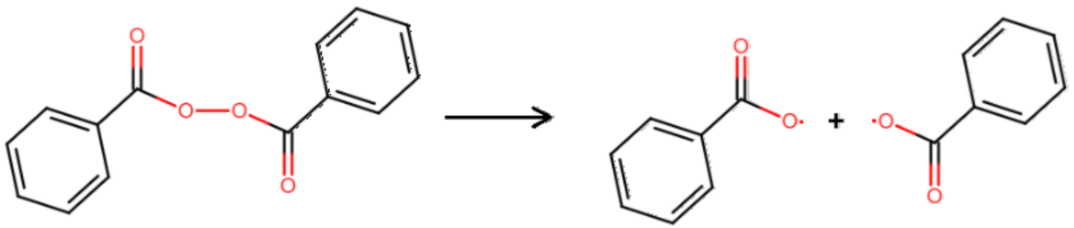




dibenzoylperoxide

1. Initiation

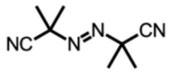
- the radical's electron is highly reactive
  - electrons always want to be in pairs (remember gas molecules, e.g. H2)
- it wants to make an electron pair with any other electron
- it also pulls it out of an already existing electron pair
  - the more weakly bound such an electron is, the easier it will be
    - eg π electrons of a double bond



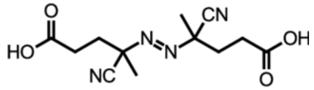
1. *initiator cleavage* $\text{Ini-Ini} \rightarrow \text{Ini}\cdot + \cdot\text{Ini}$
2. *the creation of a growth center* $\text{Ini}\cdot + H_2C{=}CH_2 \rightarrow \text{Inic-}CH_2$

Ways of initiation

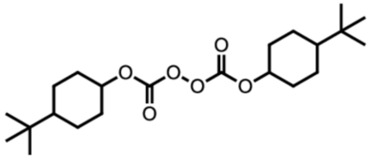
- thermal
- radiation
  - photoinitiation (visible radiation)
  - high-energy (X-ray, α, β, γ, n0)
- oxidation-reduction
- electrochemical



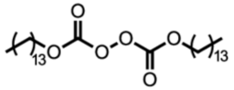
α,α'-azoisobutylronitrile
AIBN
$T_{1/2,\,10h}$= 65 °C



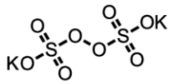
4,4'-azobis(4-cyanovaleric acid)
ACVA
$T_{1/2,\,10h}$= 69 °C



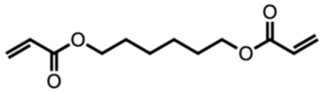
bis(tert-butylcyclohexyl)peroxydicarbonate
BCPC
$T_{1/2,\,10h}$= 48 °C



di-tetradecyl peroxydicarbonate
PODIC
$T_{1/2,\,10h}$= 48 °C

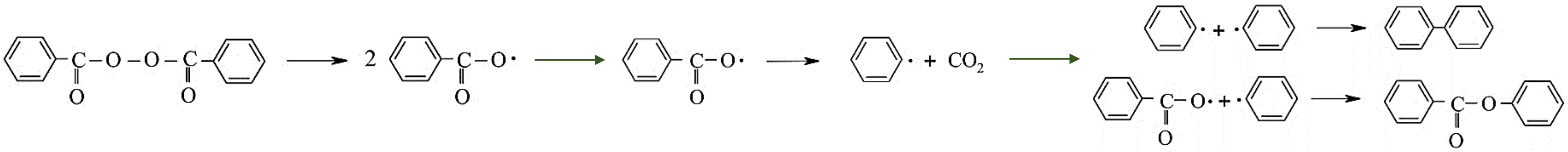


potassium persulfate
KPS
$T_{1/2,\,10h}$= 70 °C



1,6-hexanediol diacrylate
HDDA

non-initiating reaction (influence of the cage effect)



2. Propagation

- represents the growth of the (macro)molecule itself
- the growth center is still transferred to the end of the chain


Ini-🟩 + 🟨 → Ini-🟩-🟨

Ini🟩-🟨 + 🟧 → …

3. Termination

„I‘ll be back.“

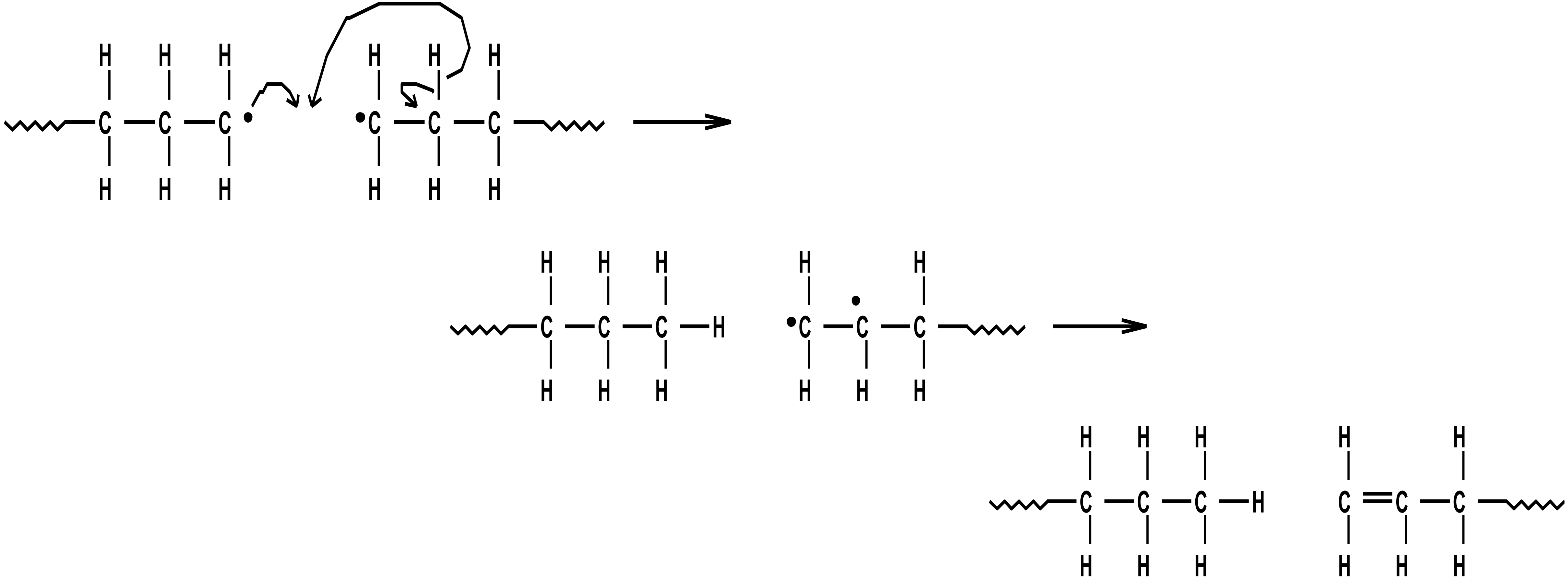
- the disappearance of the growth center (given molecule)
  - two radicals form an electron pair (the radical disappears)
  - radical jumps to another molecule (radical does not disappear)
- recombination (pairing)
  - a single bond is formed between the radicals

$$[CH_2]_n\cdot + \cdot[CH_2]_m \rightarrow [CH_2]_{n+m}$$

- disproportion
  - one molecule will provide a hydrogen and the other an electron to the radical

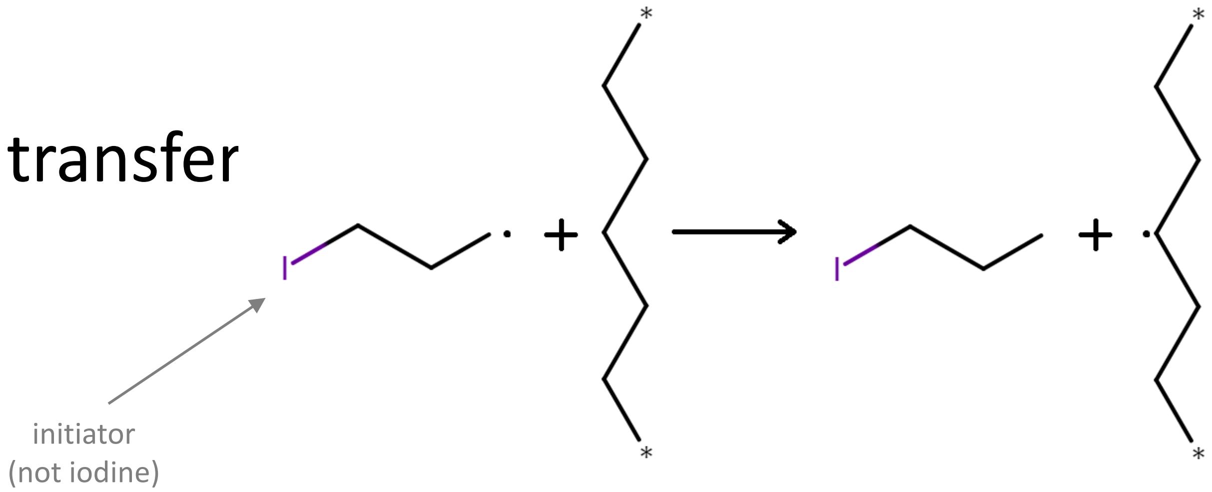
$$[CH_2]_n\cdot + \cdot CH_2\text{-}CH_2[CH_2]_m \rightarrow [CH_2]_n + CH_2{=}CH_2\text{-}[CH_2]_m$$

Mechanism of disproportionation



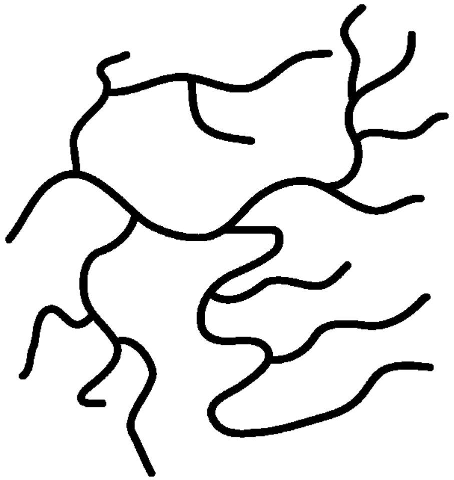
Transfer reactions

- there is no disappearance of the reaction center
- the reaction center is transferred to a new location on the macromolecule or to a new macromolecule
  - intramolecular
  - intermolecular
- always accompanied by hydrogen transfer
- creation of branched structures
  - e.g. LDPE



LDPE

- low density (low density) PE
- highly branched structure
  - How is it possible that the difunctional monomer ethylene is able to form branched structure?
    - transfer reactions
- produced under high pressures by radical polymerizati
- chemically resistant, mechanically weak



Chain-growth polyreactions - ionic

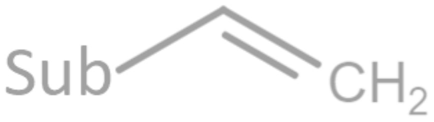
Chain-growth polyreactions - ionic

- varies with the type of growing active center
    - cationic (polyisobutylene)
    - anionic (formaldehyde)

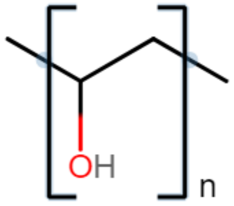
- comparison with radical polymerization
    - more selective
    - sensitive to the presence of impurities (e.g. water)
    - more expensive (more complicated)
    - chain growth cannot be terminated by recombination or disproportionation (equally charged active centers repel each other)

Kinetic condition for vinyl monomers

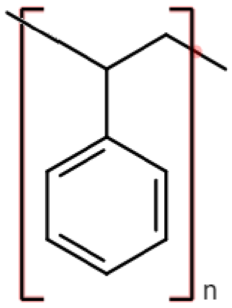
- the substituent stabilizes the reactive intermediate (macroion)
  - thus determines the mechanism of the polyreaction
- a combination of inductive and mesomeric effects
  - inductive effect
    - electron displacement along the σ bond
    - caused by the different electronegativities of the atoms
  - mesomeric effect
    - electron displacement along the π bond
    - caused by the conjugation of the π electrons of the substituent and the vinyl double bond
    - usually stronger than inductive effect



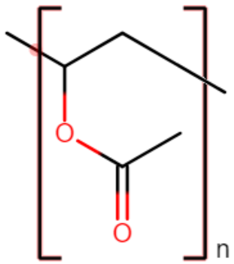
PVA



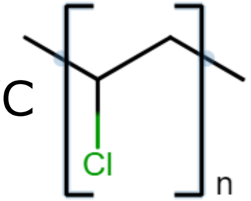
PS

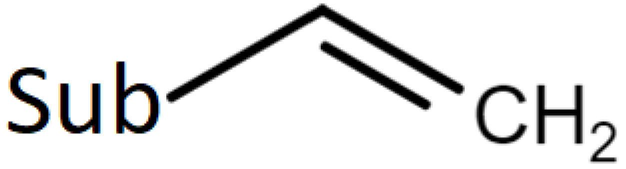


PVAc



PVC





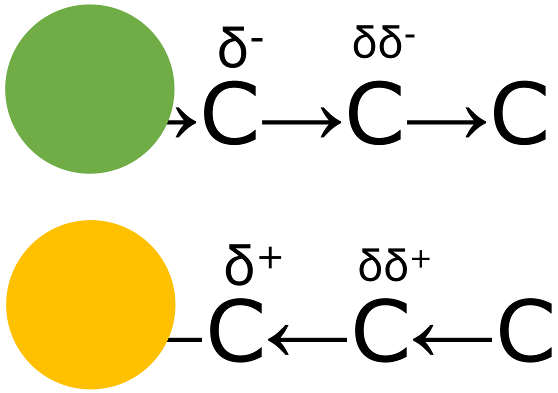
Inductive and mesomeric effect

- the resulting shift of electrons from or to the substituent (Sub) given by a combination of inductive and mesomeric effects
- the mesomeric effect is usually stronger than the inductive one
  - the exception is for the –X halides, which have such a strong inductive and such a weak mesomeric that they generally behave more according to the inductive
- due to the I and M substituent on vinyl, electrons are pushed to the double bond or, conversely, pulled away from the double bond
  - this will subsequently affect whether the double bond will be partially positively charged (has less electron density) or partially negatively charged (higher electron density)
  - depending on whether it will react cationically or anionically

Inductive effect (I)

- given by the different electronegativity of neighboring atoms

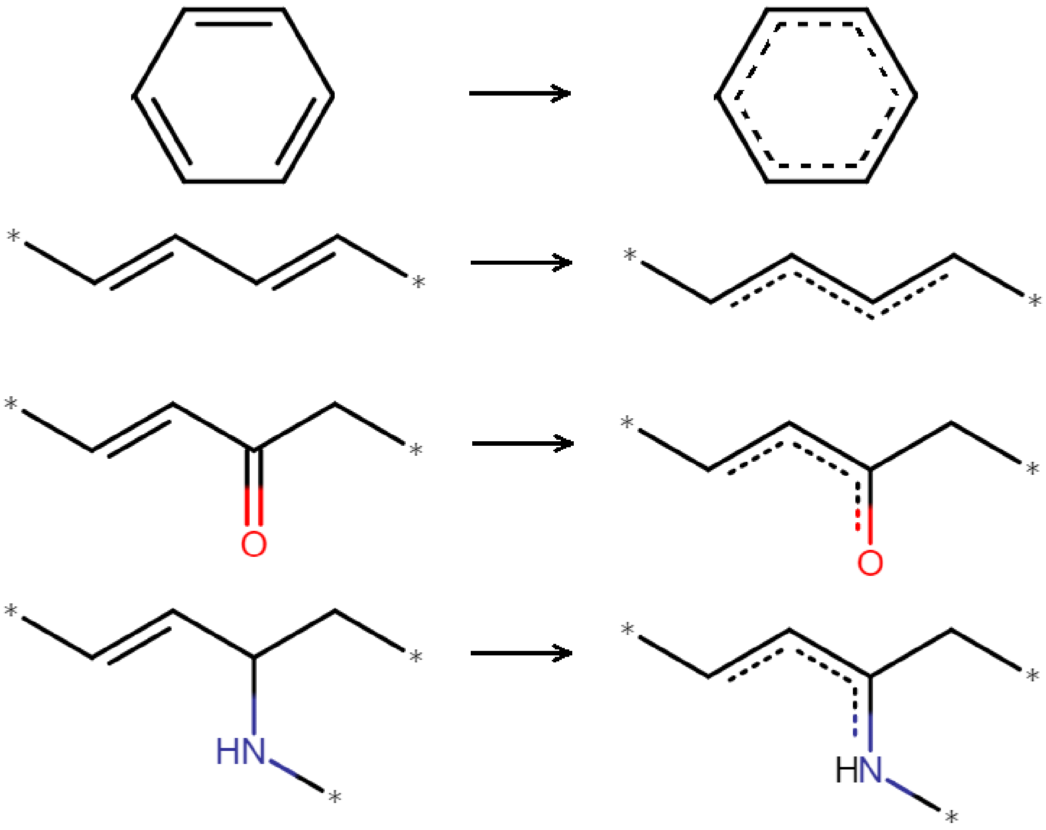
- positive (+I)
  - alkyl, alkenyl, phenyl, ether, amine
- negative (-I)
  - halogen, carbonyl, nitro



Electron acceptoric substituents (I-)	Electron donating substituents (I+)
-X, $-OCH_3$, $-NH_2$, $-NO_2$, -CN, $-SO_2R$, -COR, $-NH_3^+$	$-CH_3$, -Alkyl, $-\ddot{\underset{..}{O}}:^{\ominus}$, $-\ddot{\underset{..}{S}}:^{\ominus}$, $-Si(CH_3)_3$

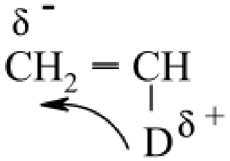
Mezomeric effect (M)

- electron displacement along the π bond
  - M+ pushes electrons to, M- on the contrary, away
  - caused by the conjugation of the π electrons of the substituent and the vinyl double bond
  - conjugation
    - stabilization caused by overlapping of neighboring π electrons or a lone electron pair
  - identification in the molecule
    - double bonds or double bond and free elec. a pair of atoms next to each other
- usually stronger than inductive
  - except for the halides, which are more inductive because π e- are much more mobile than σ e-

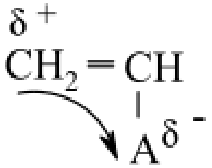


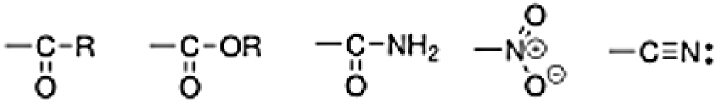
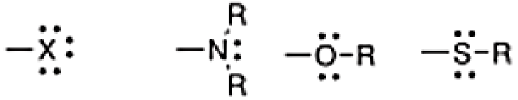
Mezomeric effect (M)

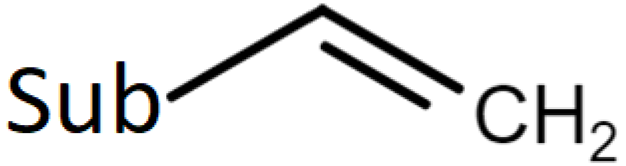
- positive (+M)
    - increasing electron density
    - it can be recognized by the fact that a less electronegative atom is attached to a more electronegative atom (e.g. ←O←C- or ←S ←C-))



- negative (-M)
    - decreasing electron density
    - it can be recognized that a more electronegative atom is bound to a less electronegative atom (e.g. →C→O- or →C→S-)



Electron acceptoric substituents (M-)	Electron donating substituents (M+)
 R = alkyl or H	 (X = F, Cl, Br, I) R = alkyl or H

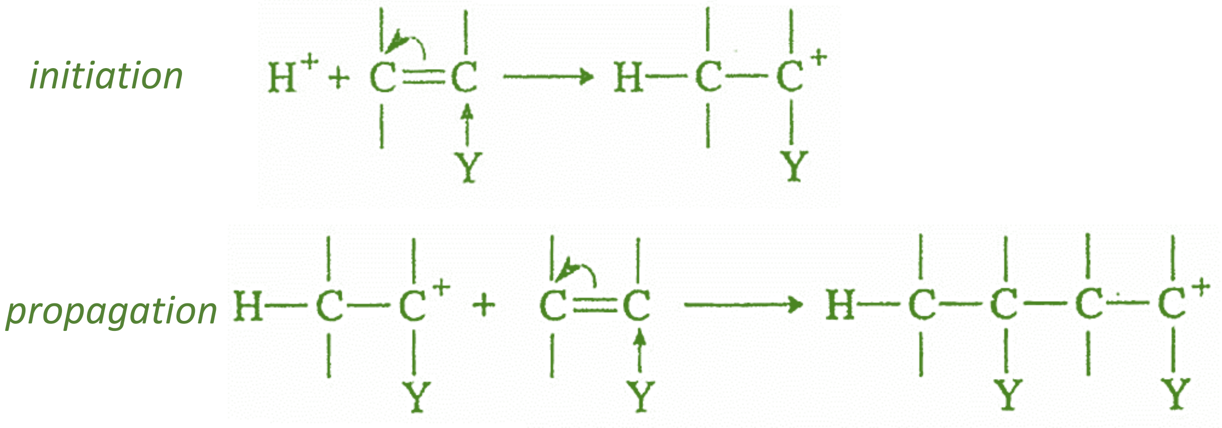


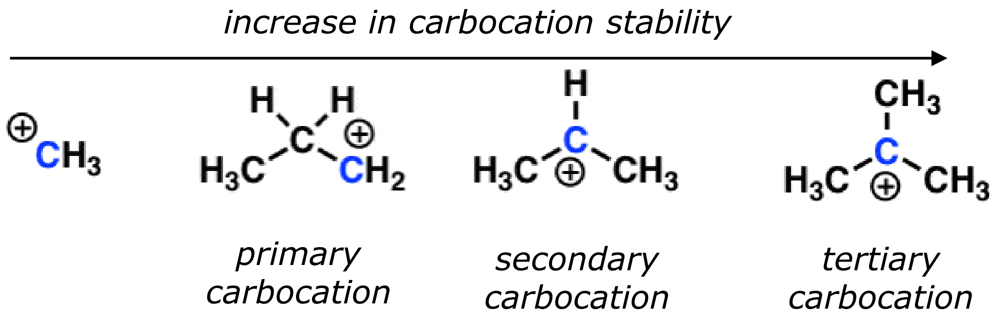
Examples of action of I and M

- styrene
  - phenyl certainly has I+ and M+, so the whole will push electrons towards the vinyl double bond
  - however, the benzene nucleus is capable of stabilizing many things, so it can behave in several ways
- vinyl chloride –Cl
  - chloride has a strong I- and a weak M+, so the whole will withdraw electrons from the double bond towards the chloride (except when M is weaker than I)
- nitrile –CN
  - nitrile induces both I- and M-, so the unit must withdraw electrons from the double bond
- methyl ether –O–CH_3
  - the oxygen of the methyl ether will provide I-, but the methyl ether has M+, so the whole will push the electrons towards the double bond (M is stronger than I here)

Cationic polymerization

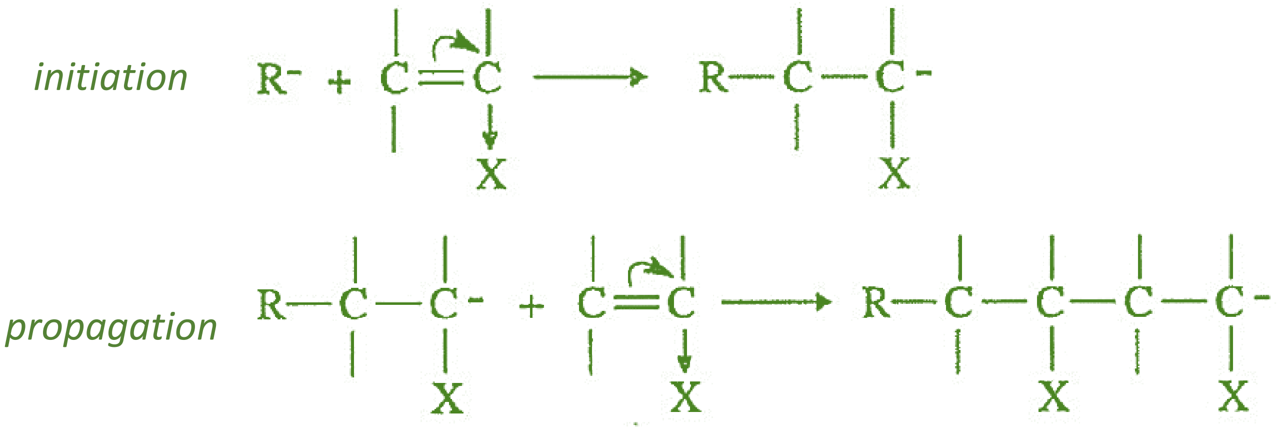
- the growth center has a positive charge (carbocation)
- the Y substituent pushes electrons to the vinyl double bond
    - the latter is therefore more electron-rich and can attack with an electron-acceptor initiation particle
- little used in industry
    - too much reactivity
    - macroion instability
    - solvent costs
- examples
    - polyisobutylene
    - poly(1,1-dimethylethylene)
- termination usually by a transfer reaction

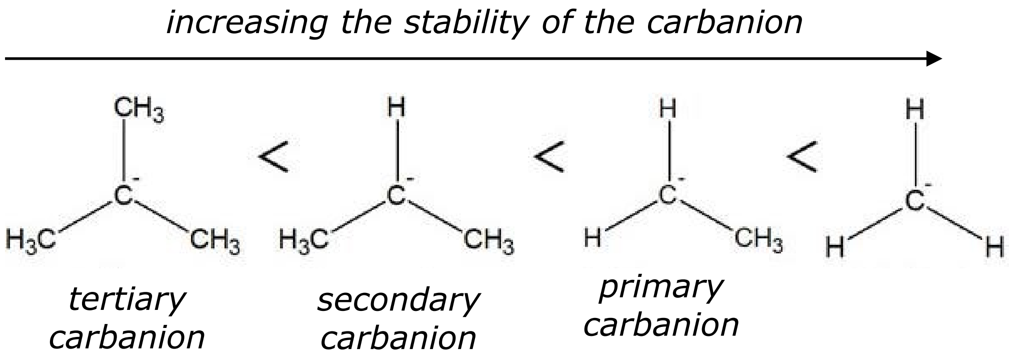




Anionic polymerization

- the growth center has a negative charge (carbon anion)
- the X substituent withdraws electrons from the vinyl double bond
  - the double bond is thus electron-poor and more easily attackable by an electron-donating particle
- used more in industry
  - costs of solvents and initiators
- examples of reacting monomers
  - styrene, butadiene, isoprene, vinyl ester, methacrylate, cyanoacrylate, cyclic monomers
  - a typical example is instant glue (cyanoacrylates)
- usually ending in a transfer reaction

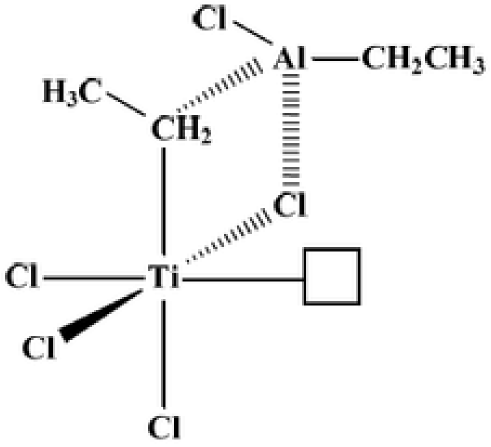


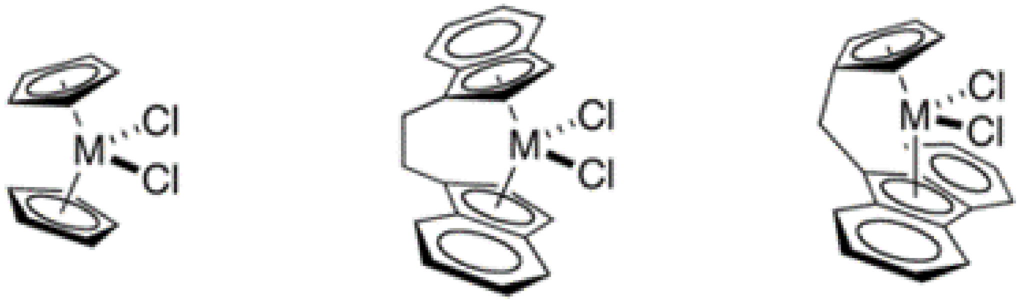


Chain-growth polyreactions - coordination

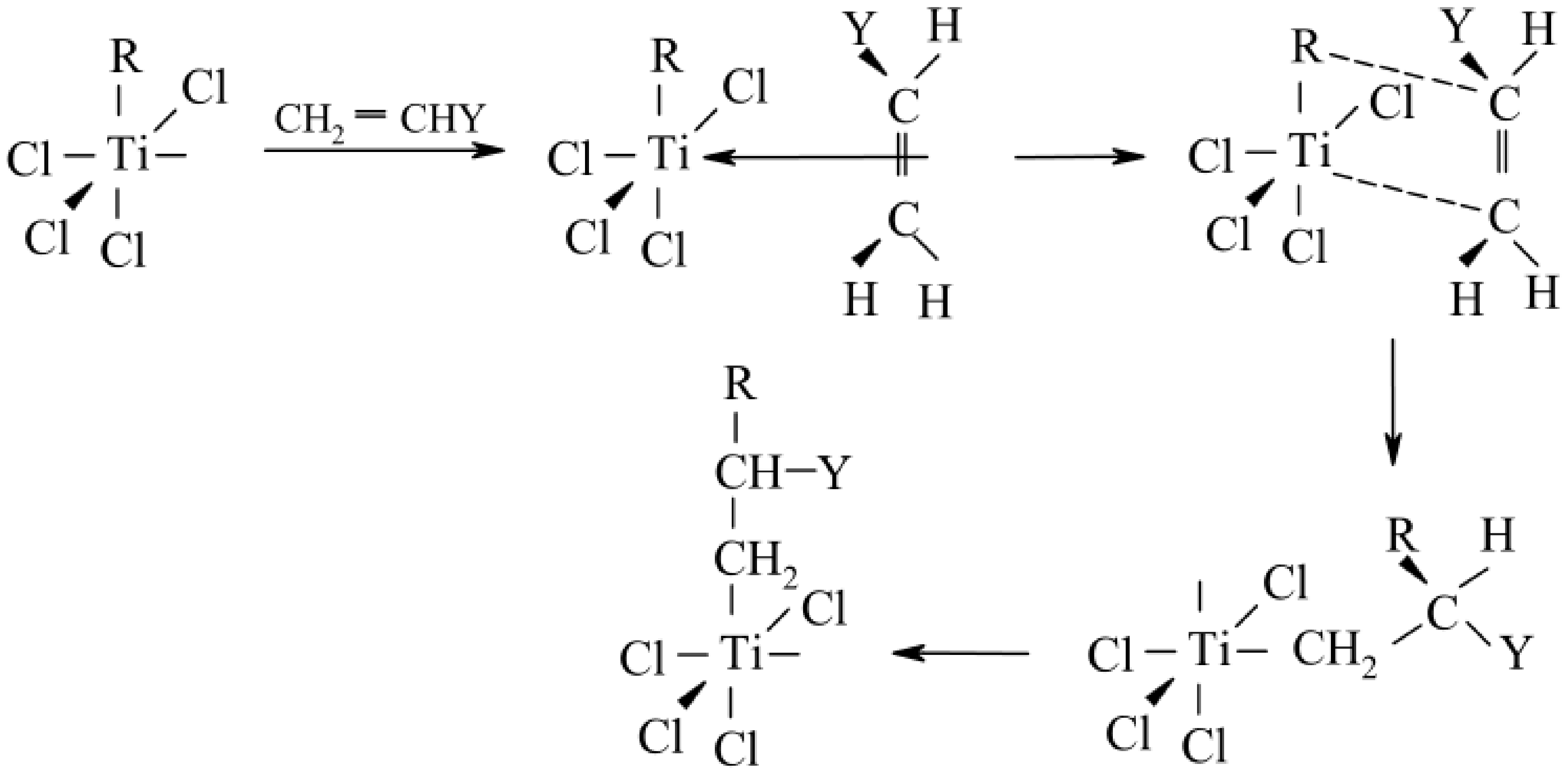
Chain-growth polyreactions - coordination

- otherwise also polyinsertion
  - production of tactical polymers
  - other methods are usually short on this
- Ziegler-Natt catalysts
  - a transition metal salt (eg $TiCl_4$) and an organometallic compound of element III. main groups (e.g. $Al(CH_2CH_3)_3$)
  - isotactic polymers
- metallocene catalysts
  - sandwich molecules (metal cation is enclosed between aromatic anions)
  - isotactic or syndiotactic polymers



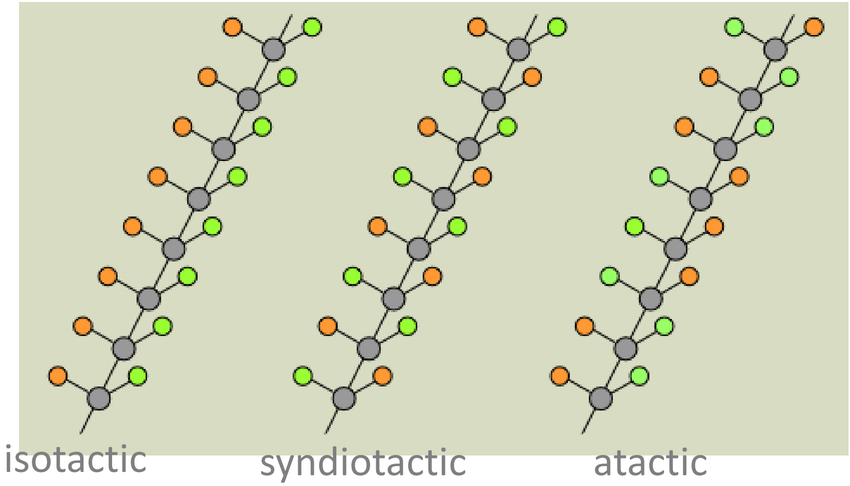


Ziegler-Natta catalyst



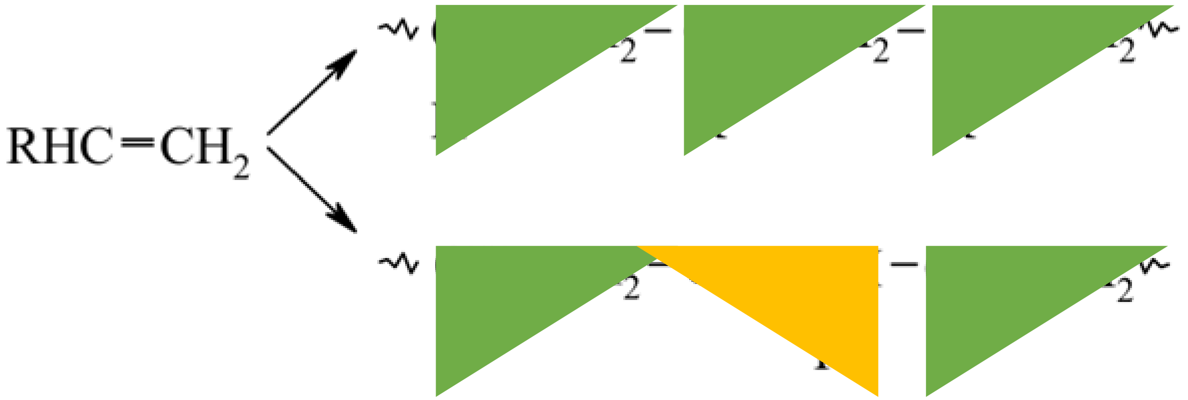
Tacticity of macromolecules

- the arrangement of stereoisomeric centers in the main chains of macromolecules
  - stereoisomerism - occurs in asymmetric molecules with carbon having different substituents on all four bonds
- fundamentally affects crystallinity
  - and thus also mechanical properties, temperature behavior, etc.



1. Constitution (regularity)

- regular macromolecule
  - obtained by regular repetition of the constitutional unit
  - head-to-heel arrangement only
- only regular polymers can (but don't have to) be semicrystalline

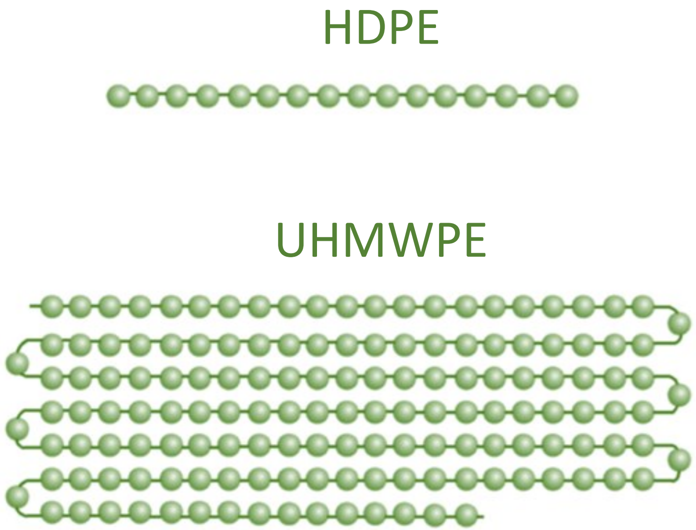


head-to-tail

head-to-head (or tail-to-tail)

HDPE, UHMWPE

- linear macromolecules
- high crystallinity and therefore also density
- extraordinary mechanical properties
- HDPE – 200,000 to 500,000 g/mol
  - high density (high density) PE
- UHMWPE – 6,000,000 g/mol
  - Ultra high molecular weight PE
  - chains contain over 200,000 mers



Polypropylene (PP)

- exclusively isotactic
  - atactic is practically not used because it is an unusable waxy substance
- fibers, pipes, packaging material, disposable products
- semicrystalline

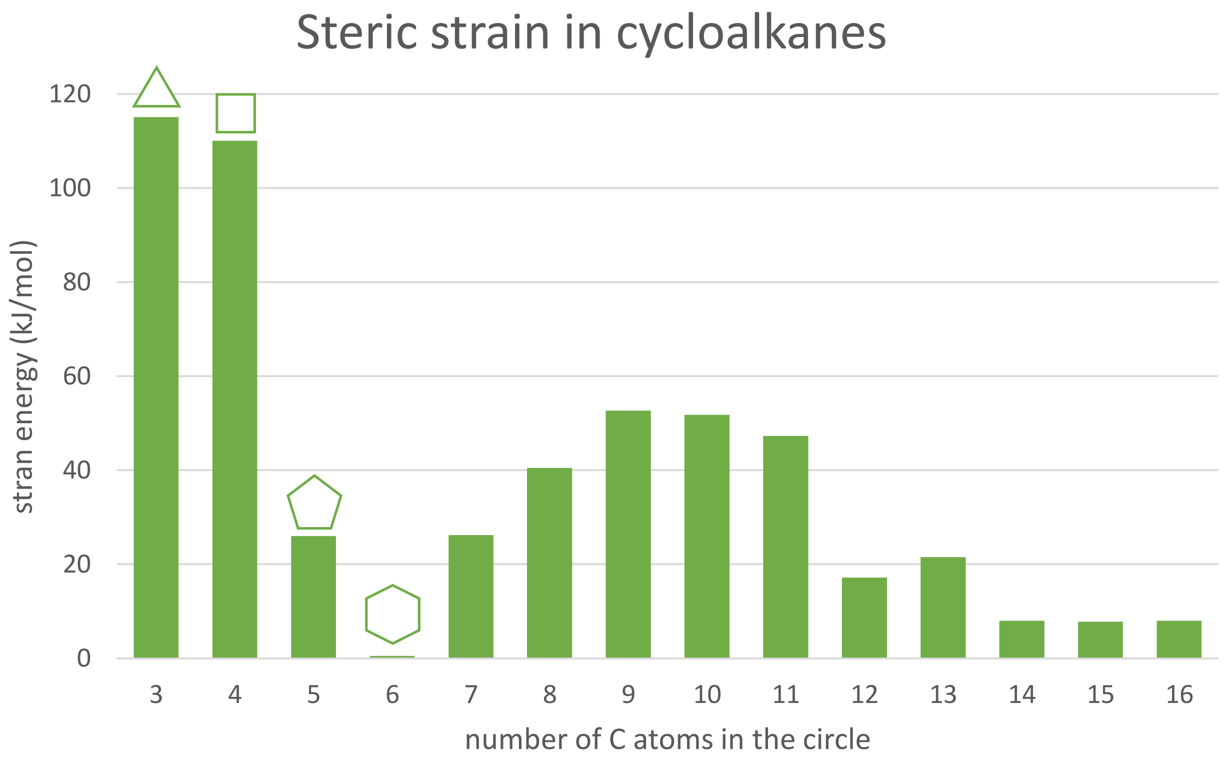
Chain-growth polyreactions – Ring opening

Chain-growth polyreactions - Ring opening

- denoted by the abbreviation ROP
  - in principle, it is not a reaction mechanism itself, but a group of different reactions (radical or ionic) that have in common that they start from cyclic monomers
- thermodynamics plays a big role
  - usually the most important thing is the tension in the circle (the larger the circle, the less stable the circle and the more likely we will be able to activate it)
  - the least stable rings are 3 and 4 membered, then around 9
  - the presence of a heteroatom or a multiple bond is required
  - with large circles almost without steric stran
    - the entropy change ΔS also starts to play a role in them
      - it can be even higher than 0, because the opening of the ring increases the mobility of the new ends and so the entropy increases

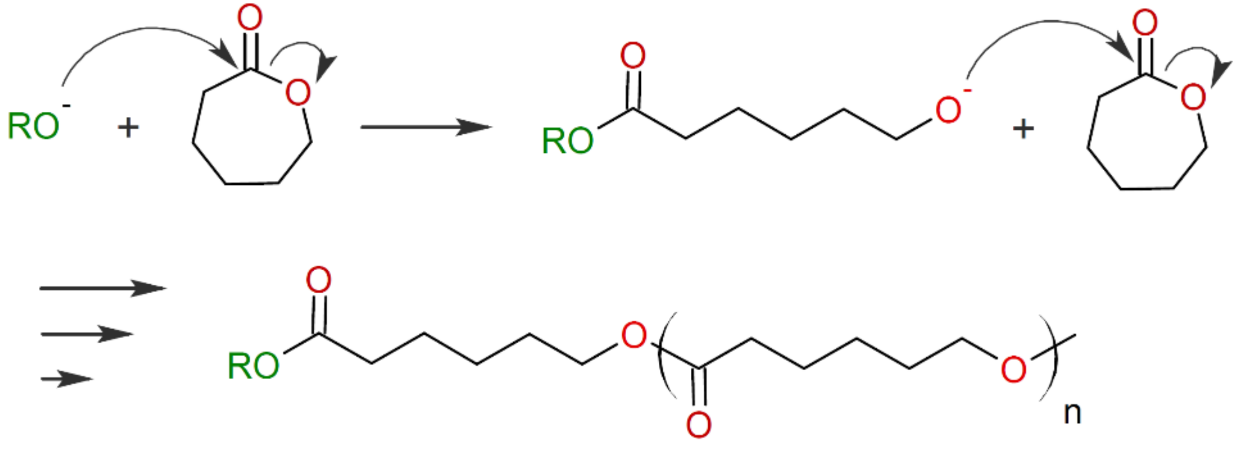
Chain-growth polyreactions - Ring opening

- can be polymerized radically (unsaturated heterocycles) or ionically
- cyclic monomers
  - lactones
  - lactams
  - heterocycles with sulfur or silicon



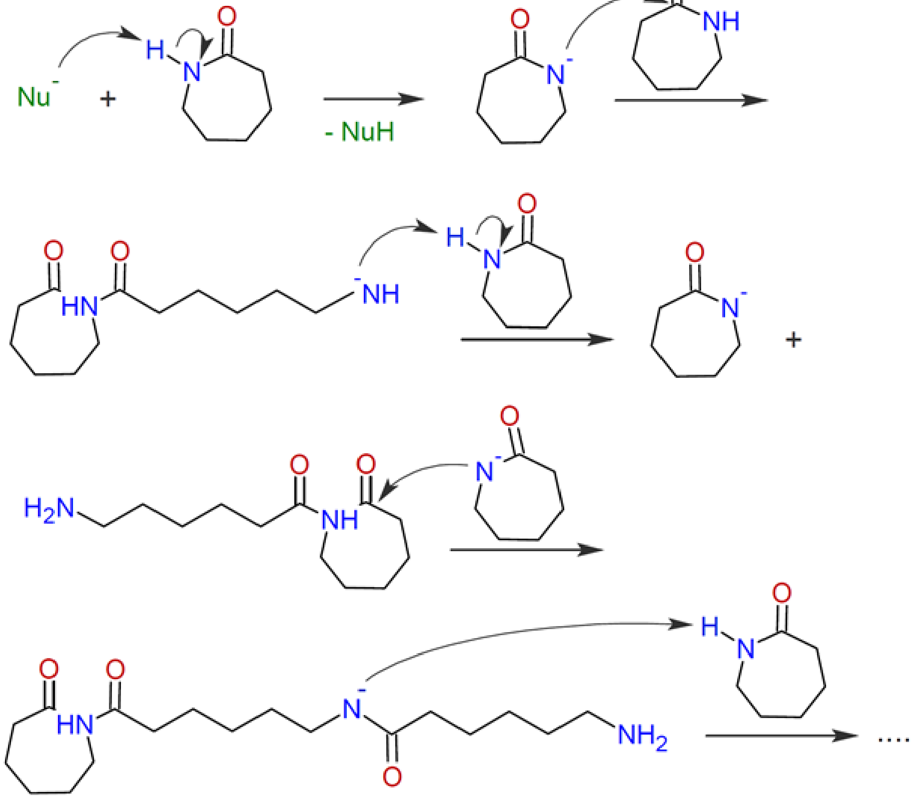
Reaction of caprolactone and caprolactam

caprolactone
(cyclic ester)



polycaprolactone (PCL)

caprolactam
(cyklic amide)

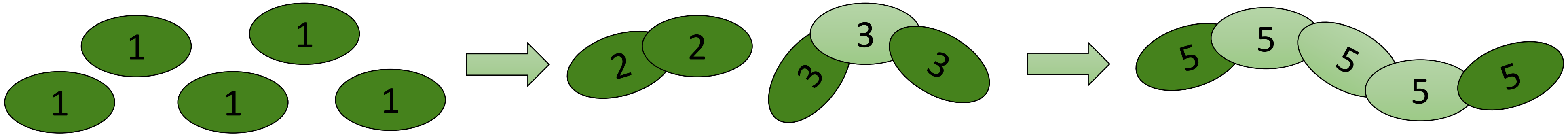


polyamide 6 (PA 6)

Step-growth polyreactions

Step-growth polyreactions

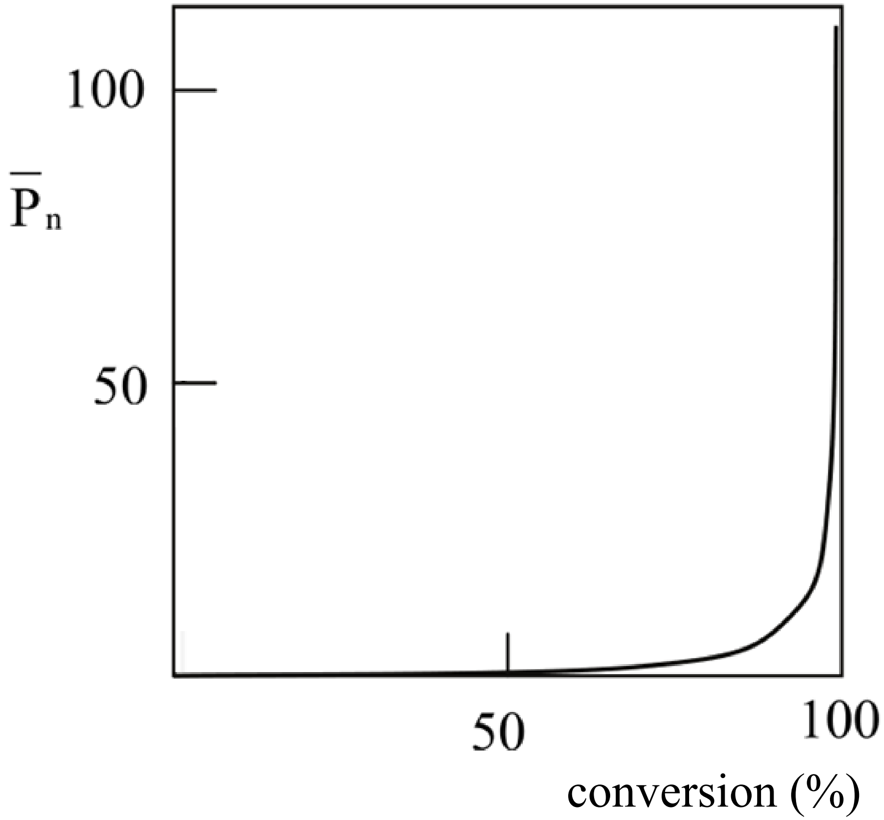
- mutual reaction of functional groups of monomers, oligomers and polymers in an "all with all" way
- the reaction mixture contains chains of various lengths, from monomer to finished macromolecules
- can be divided into
  - polycondensation
  - polyadiction



Dependence of degree of polymerization of stepwise polyreactions on conversion

- polymerization degree P
  = number of monomeric units in the macromolecule
- monomer conversion
  = proportion of reacted monomer units
  - 100% conversion therefore means complete reaction of the reaction mixture

- stepwise polyreactions
  - slow growth of the polymerization degree
  - higher degree of polymerization only at high conversions



Step-growth polyreactions

- a low molecular weight product is **always** formed
  - low molecular weight product (d) is usually water, hydrogen halide, methanol or ammonia

$$A + B \rightarrow C + d$$

- often equilibrium reactions (must affect equilibrium)
  - it means that the yield of such reactions tends to be low

- homopolymerization
  - hydroxycarboxylic acids (PES), aminocarboxylic acids (PA)
- heteropolymerization
  - e.g. dicarboxylic acid with diol (PES) or diamine (PA)

Carothers equation (for linear polymerization)

- let's have a bifunctional monomer A-B (where A reacts only with B)
  - the number of monomer molecules before the reaction starts is $N_{beginning}$
    - during the polyreaction, N decreases
    - monomers react to become oligomers or polymers
  - the number of unreacted monomer molecules is $N_{unreacted}$
  - the degree of conversion p corresponds to the proportion of reacted monomer molecules to their original number

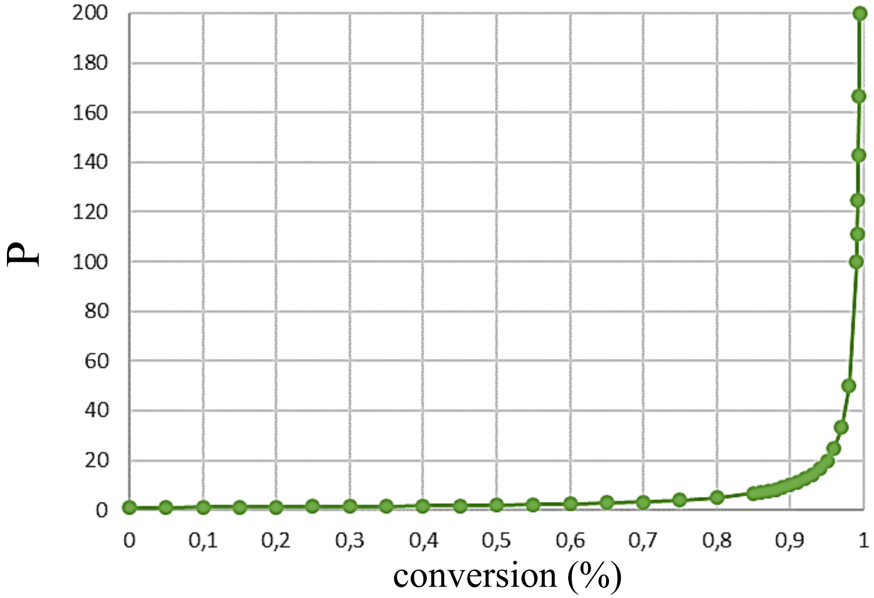
$$p = \frac{N_{reacted}}{N_{beginning}} = \frac{N_{beginning} - N_{unreacted}}{N_{beginning}}$$

  - (numerically) the average degree of polymerization $\mathbf{P_n}$ corresponds to :

$$\overline{P_n} = \frac{N_{beginning}}{N_{unreacted}}$$

  - from this follows the so-called Carothers equation of the dependence of the degree of polymerization on the degree of conversion of the monomer:

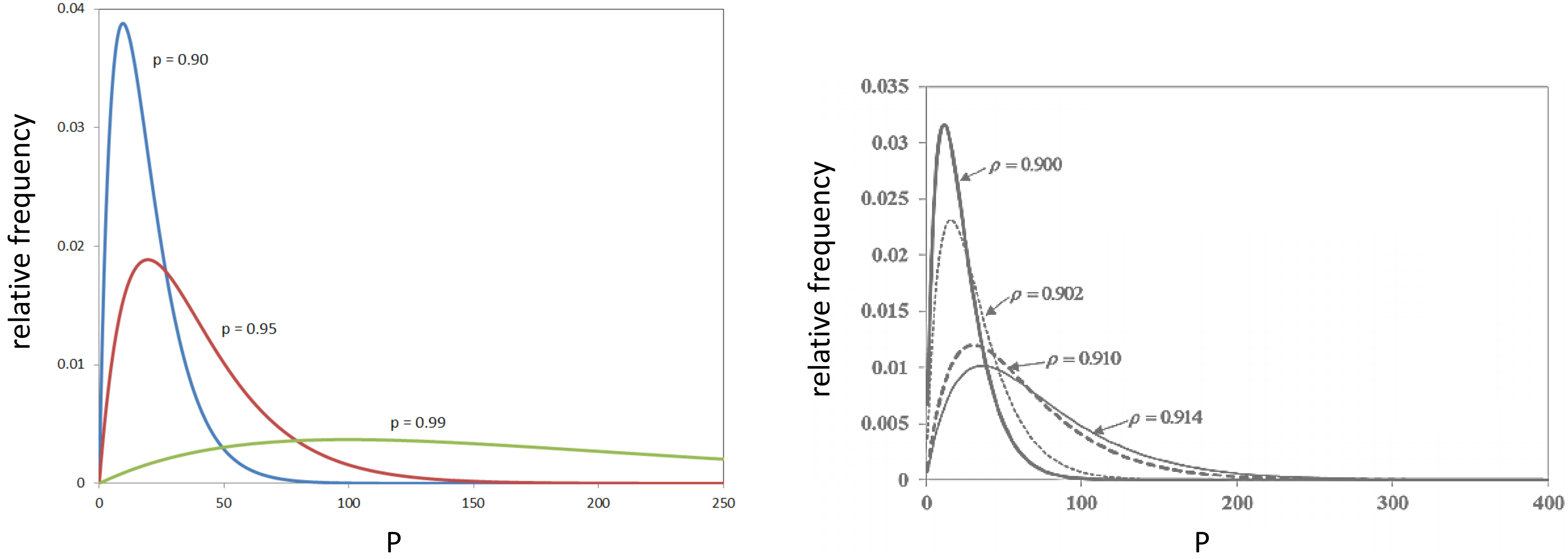
$$\overline{P_n} = \frac{1}{1-p}$$



Consequence of the Carothers equation

If we want to prepare macromolecules of high molar mass, we have to drive the reaction to extreme degrees of conversion

Dependence of the molecular size distribution on the degree of conversion p (Flory distribution curves)



Equilibrium constant I

- usually, equilibrium reactions
  - equilibrium given for the const. temperature by the **equilibrium constant K**
    - in common esterifications they are from 0.1 to 10
  - unbalanced above 10000, balanced up to 100

$$K = \frac{\prod[product]}{\prod[reactant]}$$

e.g. $A + B \rightarrow C + d$

$$K = \frac{[C] \cdot [d]}{[A] \cdot [B]}$$

- a small equilibrium constant means that the degree of monomer conversion will be low

  → a low degree of conversion means that the degree of polymerization will be low

  → a low degree of polymerization means that the useful properties of the polymer will be poor
    - it is necessary to break the equilibrium of the reaction (usually by removing a low-molecular-weight product)

Equilibrium constant II

- if amino acid molecules react (forming water and amide -CONH-) with each other, the following applies to their functional groups (-NH$_2$ for amino, -COOH for carboxylic):

$$K = \frac{[-CONH-]\cdot[H_2O]}{[-NH_2]\cdot[-COOH]}$$

  - where (among other things) the concentration of amine groups must match the concentration of carboxyl groups, so that:

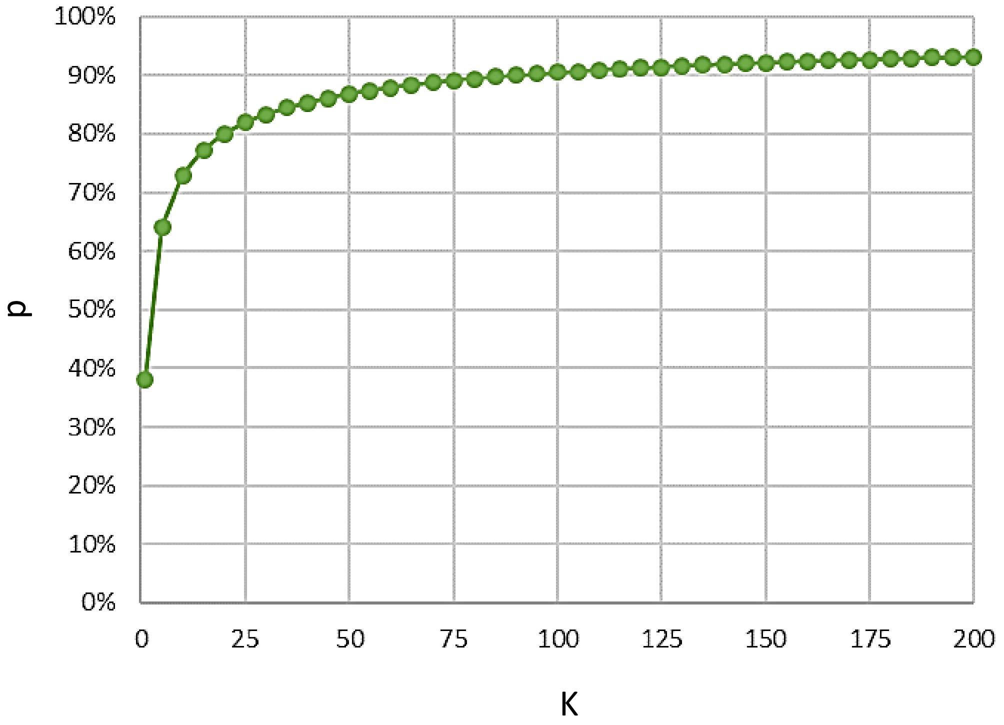
$$K = \frac{[-CONH-]\cdot[H_2O]}{[-NH_2]^2}$$

  - the concentration of the resulting amide groups -CONH- is equal to the degree of conversion p of the original reacting groups:

$$K = \frac{p\cdot[H_2O]}{[-NH_2]^2}$$

  - at the same time, the concentration of reacting groups corresponds to the amount of unreacted groups (i.e. 1-p):

$$K = \frac{p\cdot[H_2O]}{[1-p]^2}$$



Equilibrium constant III

$$K = \frac{p \cdot [H_2O]}{[1-p]^2}$$

- after adjustment:

$$\frac{K}{[H_2O]} = \frac{p}{[1-p]^2}$$

- the number average molar mass **P$_n$** is:

$$\overline{P_n} = \frac{1}{1-p}$$

- Then:

$$\frac{K}{[H_2O]} = \overline{P_n}^2 p$$

$$\overline{P_n} = \sqrt{\frac{K}{p[H_2O]}}$$

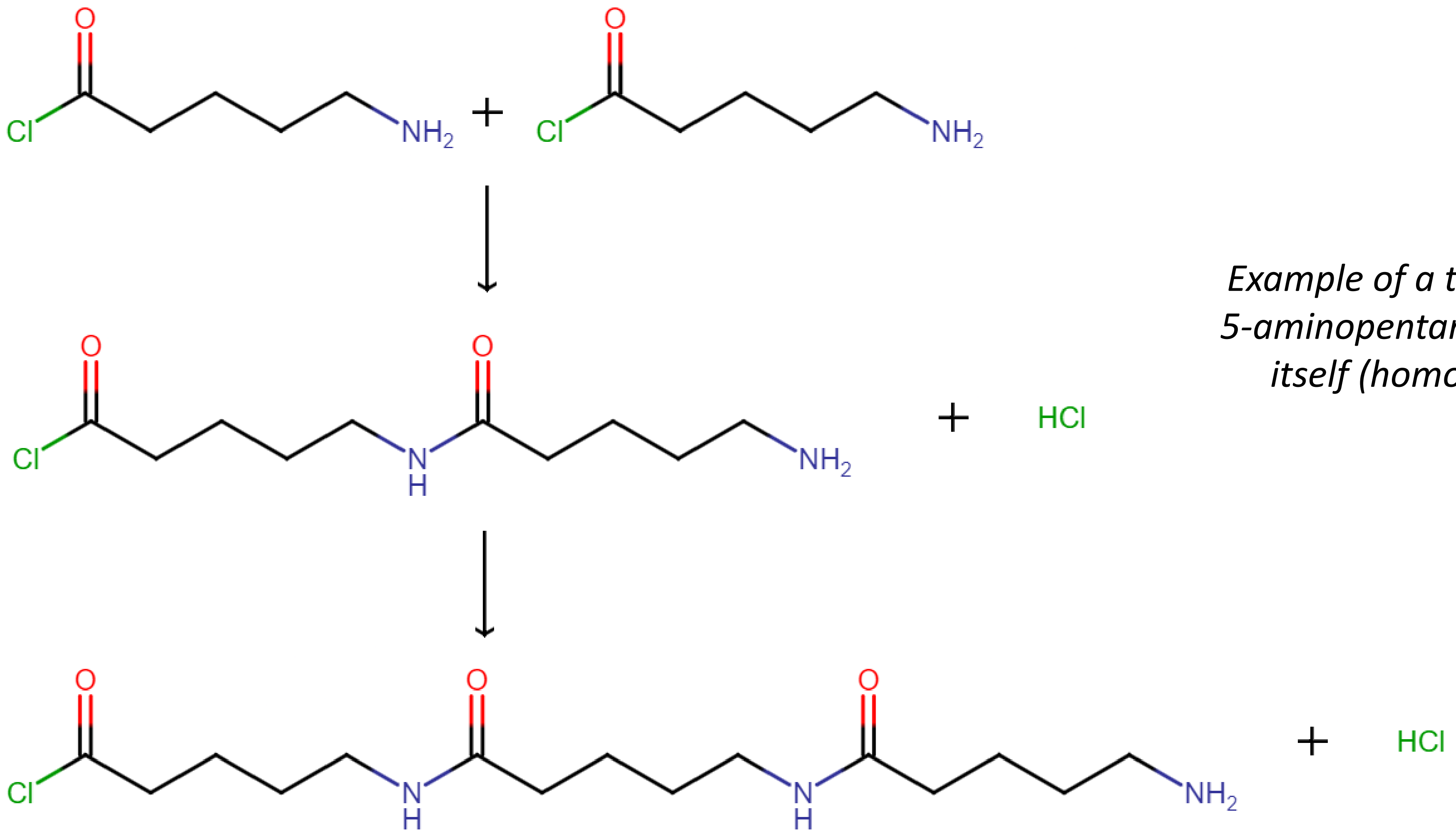
- at high conversion (p approaches 1) we can write:

$$\overline{P_n} = \sqrt{\frac{K}{[H_2O]}}$$

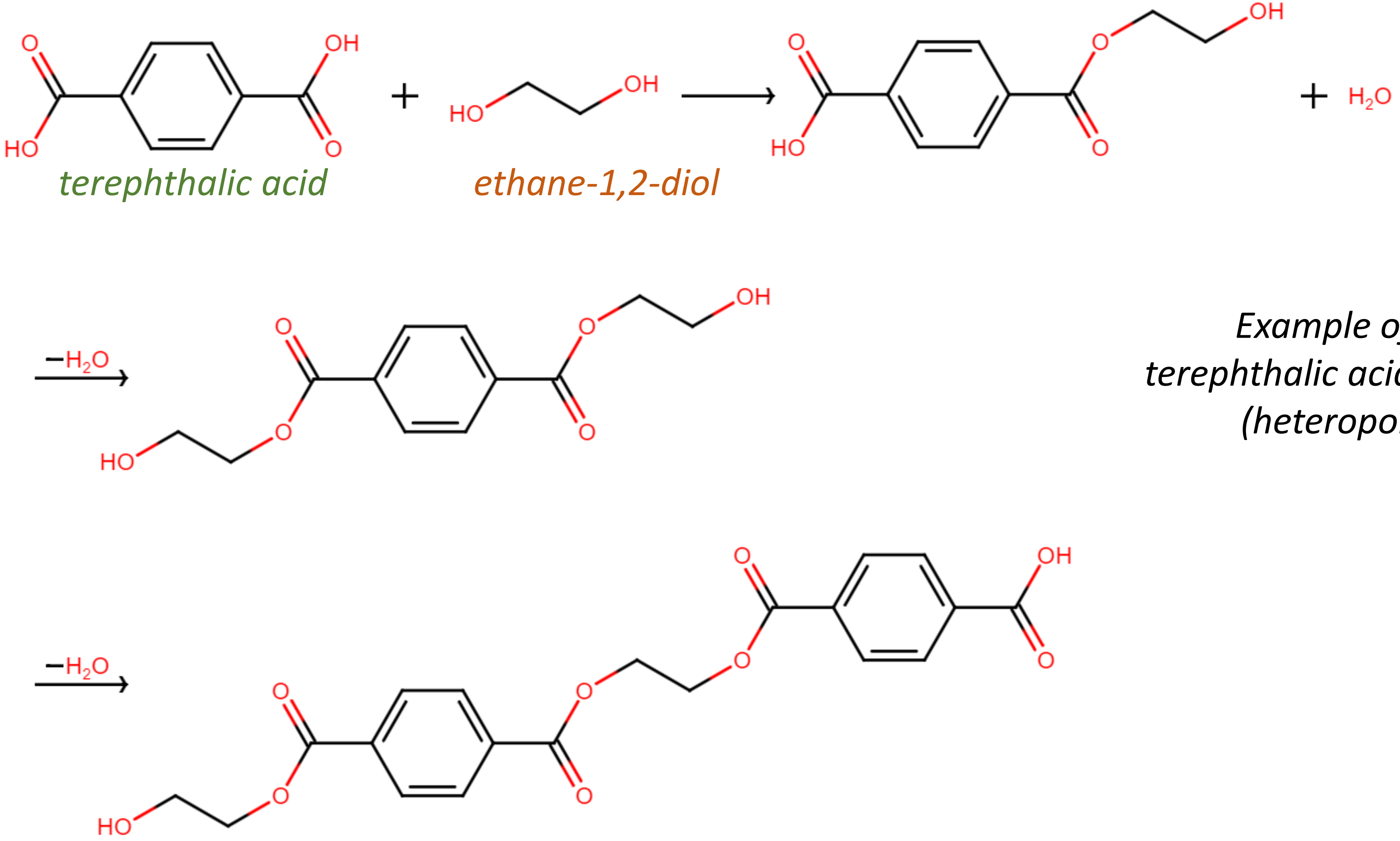
Equilibrium constant IV

$$\overline{P_n} = \sqrt{\frac{K}{[H_2O]}}$$

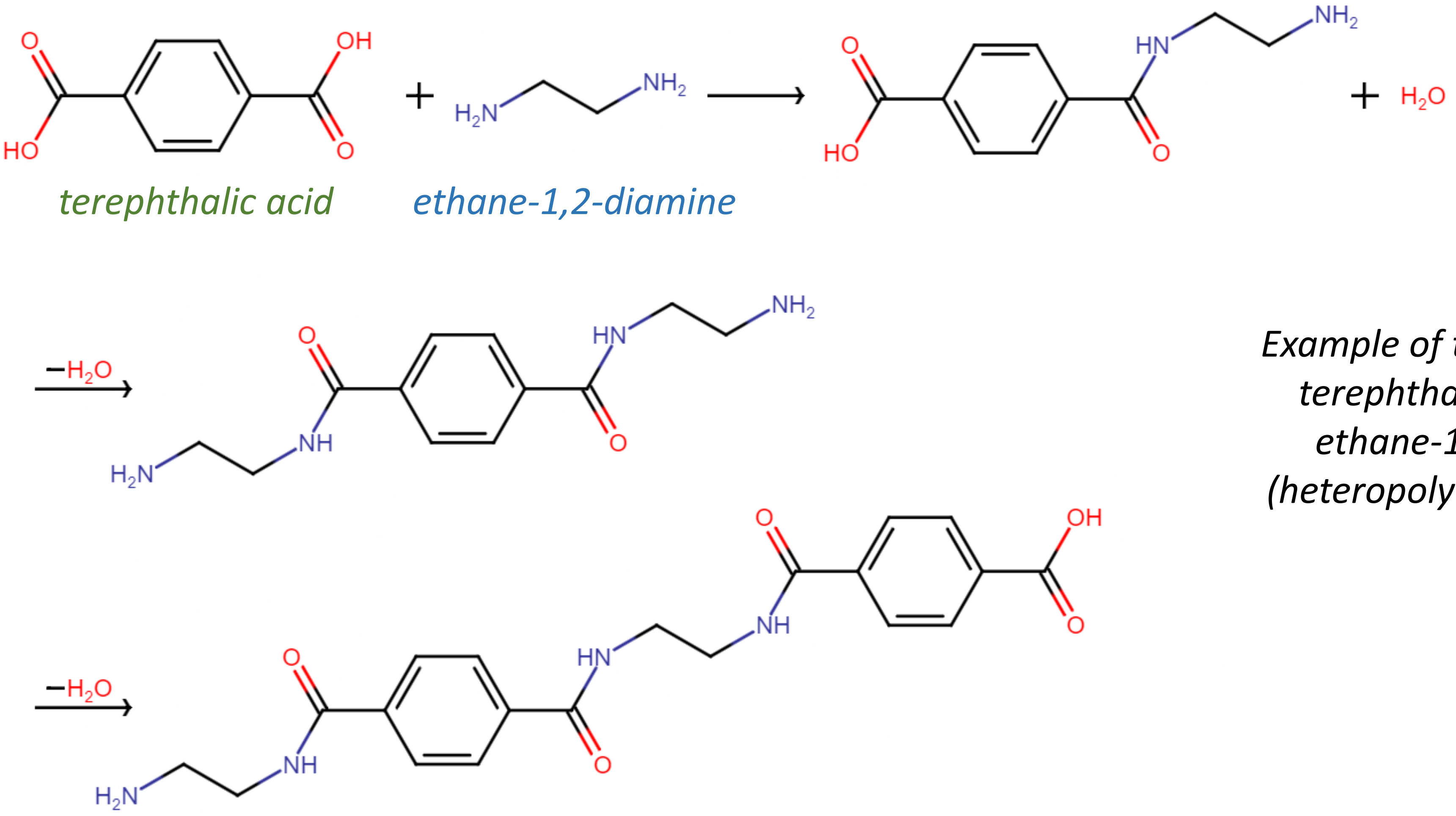
- a consequence of the problem of low equilibrium constants
  - enabling the formation of macromolecules always with a low degree of polymerization even at (theoretically) 100% conversion p
- solution:
  - removal of low molecular weight product (concentration reduction)



Example of a theoretical reaction of 5-aminopentanoic acid chloride with itself (homopolycondensation)



Example of the reaction of terephthalic acid with ethane-1,2-diol (heteropolycondensation)



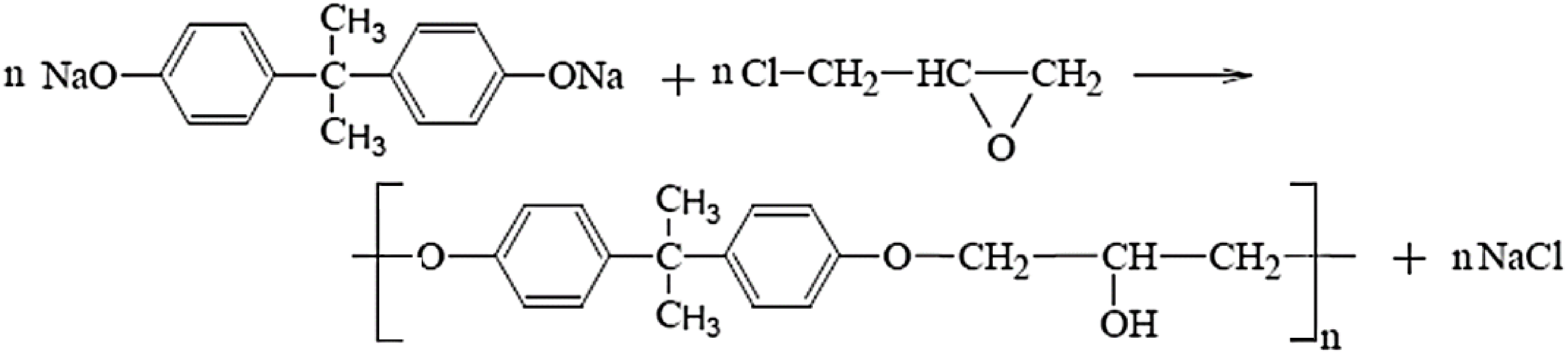
Example of the reaction of terephthalic acid with ethane-1,2-diamine (heteropolycondensation)

Polycondensates - PET

- can be derived from terephthalic acid or its chloride
  - terephtaoyl chloride is used more often because the low molecular weight HCl product is more easily distilled off

Polycondensates - epoxy resins

- reaction of bisphenols and epichlorhydrin (known locally as epic)
- modeling, grinding and grinding, dental medicine

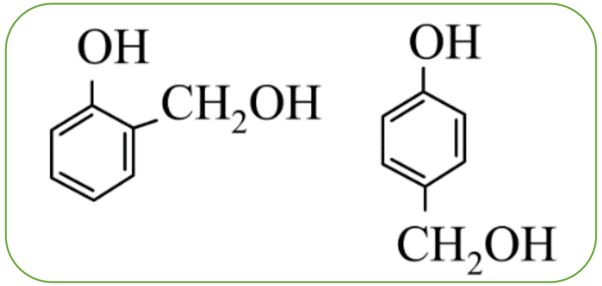


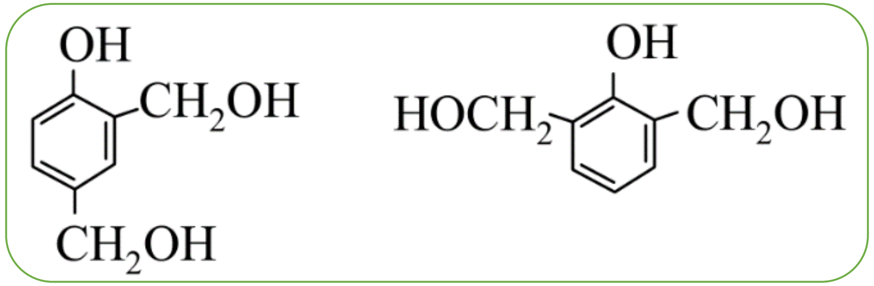
Polycondensates - phenoplasts

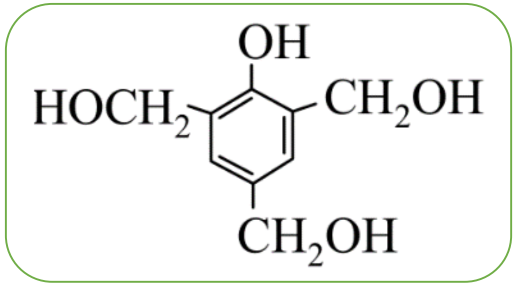
- synthetic resins based on phenol and aldehydes
- phenol (trifunctional - 2× ortho, 1× para) + formaldehyde (bifunctional)
- depending on the phenol:formaldehyde ratio, temperature and pH, the following are formed:
  - alkaline pH + excess formaldehyde → resol → resit (after cross-linking)
  - acidic pH + excess phenol → novolac
- the most famous is Bakelite

Resol

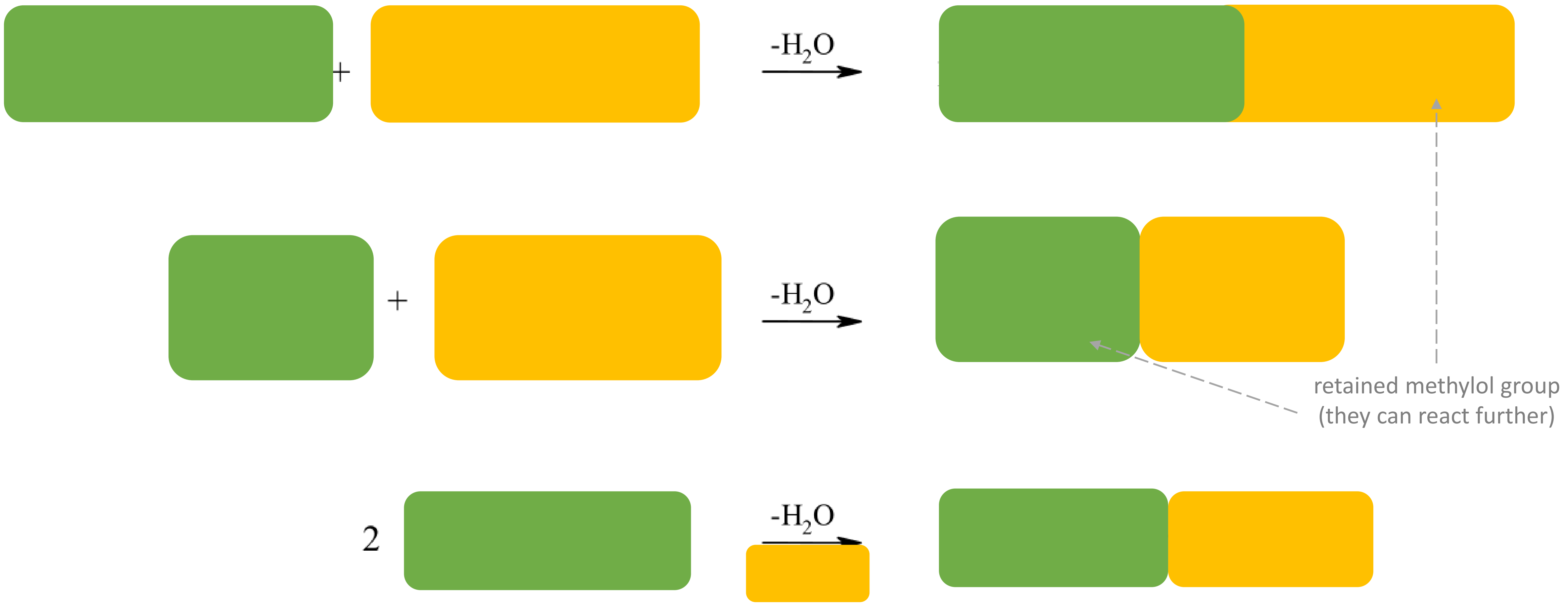
- mixture of oligomers with reactive methylol groups (-CH_2OH)
    - molar mass around 500 to 2000 g/mol (from 2 to about 10 mers)
- the hydroxyl group of the phenol directs the substitution on the aromatic nucleus to the ortho and para positions
    - base-catalyzed reaction of phenol with formaldehyde
        - molar ratio less than 1 (usually 0.8 - 0.9)
        - mono-, di- and trimethylolphenols are formed
- liquid or solid substances (according to structure)
- may be water soluble (generally not)







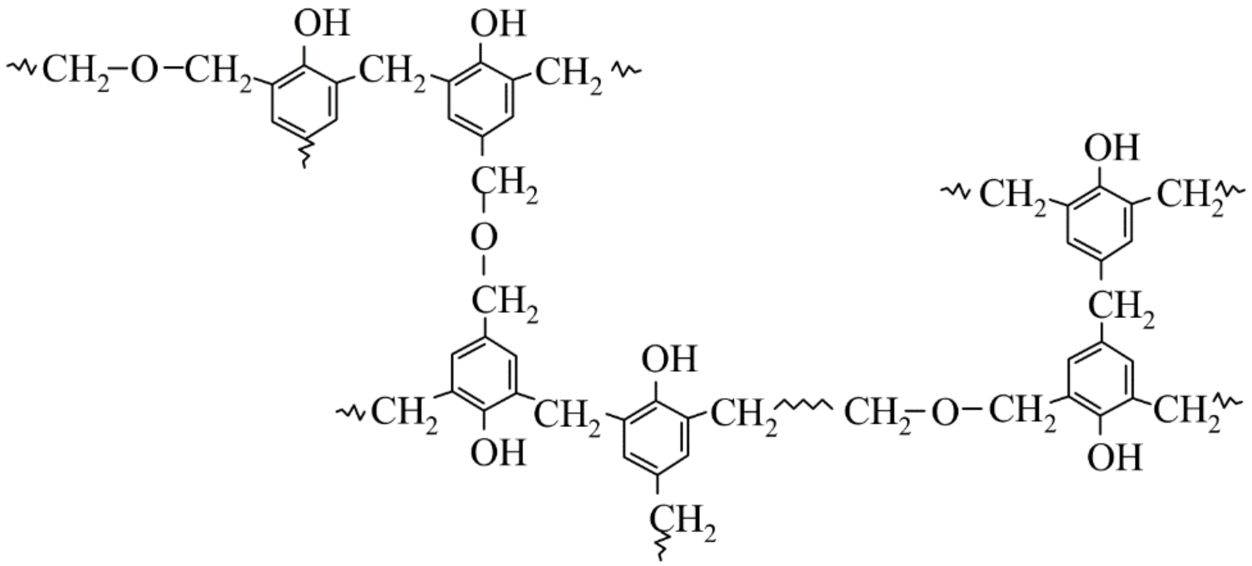
Examples of condensations of methylolphenols

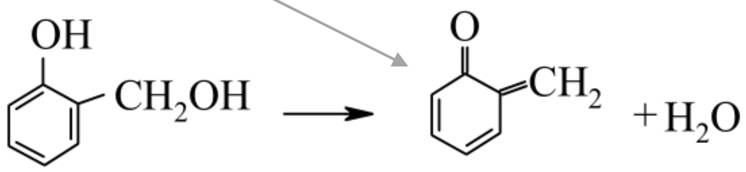


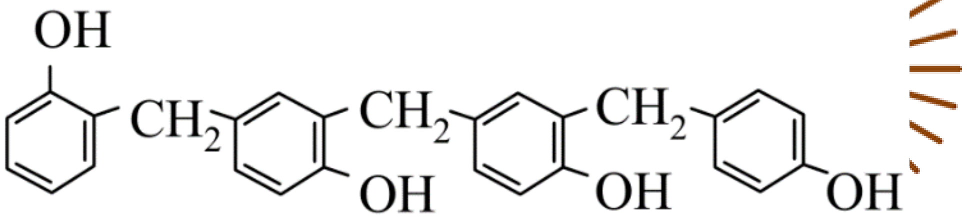
retained methylol group
(they can react further)

Resins

- resins are formed by cross-linking resols
  - takes place in an acidic environment at higher temperatures (180 °C)
    - methylene ($-CH_2-$) or methyl ether bridges ($-CH_2-O-CH_2-$)
    - the higher the temperature, the more methylene bridges prevail over methyl ether bridges
- brown-red coloration caused by the formation of quinone methides (their conjugated double bonds absorb visible radiation) during the thermal splitting of water from methylolphenols during cross-linking





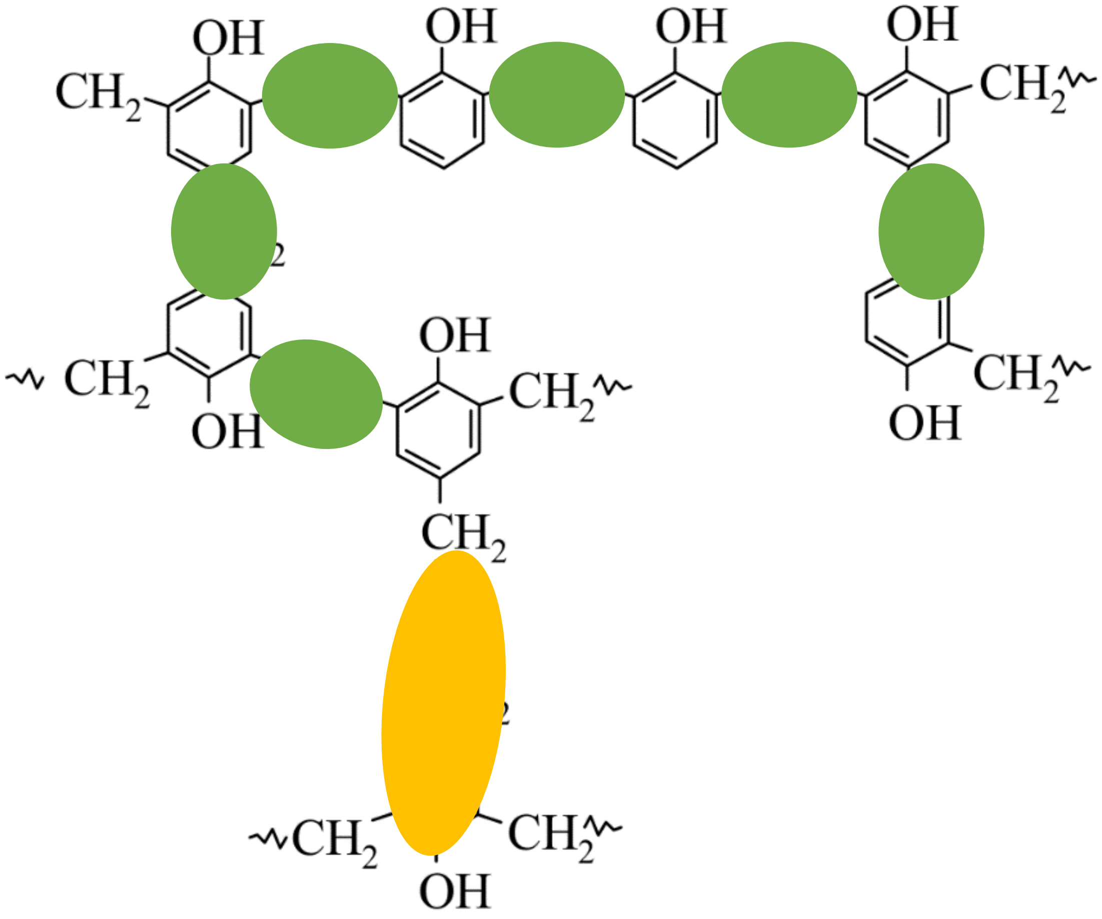


Novolac

- oligomers resulting from the acid-catalyzed reaction of formaldehyde with phenol, with an excess of phenol
  - formaldehyde:phenol ratio = 0.75 to 0.85:1
  - molar mass up to approximately 1000 g/mol (again units to lower tens of mers)
- do not contain methylol groups
  - there is an excess of phenol, so the formaldehyde will react all of it
  - thanks to their absence, they are more stable
- they are thermoplastic substances
- their cross-linking produces phenol-formaldehyde resins

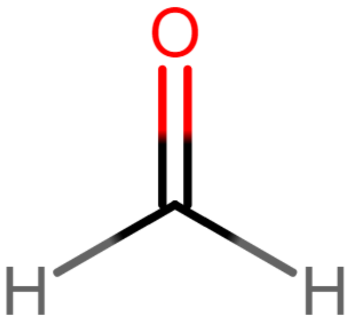
Polycondensates - phenol-formaldehyde resins

- cross-linking of novolacs with formaldehyde-releasing substances (e.g. hexamethylenetetramine with water) at higher temperatures (160 °C)
  - 🟩
  - 🟨 (Ph-CH_2-NH-)



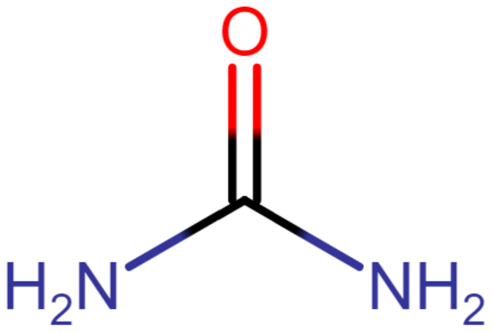
Polycondensates - aminoplasts

- again, one reactant is formaldehyde (as in phenoplasts)
  - the second is a nitrogenous compound:
    - urea (up to tetrafunctional)
    - melamine (up to six functions)



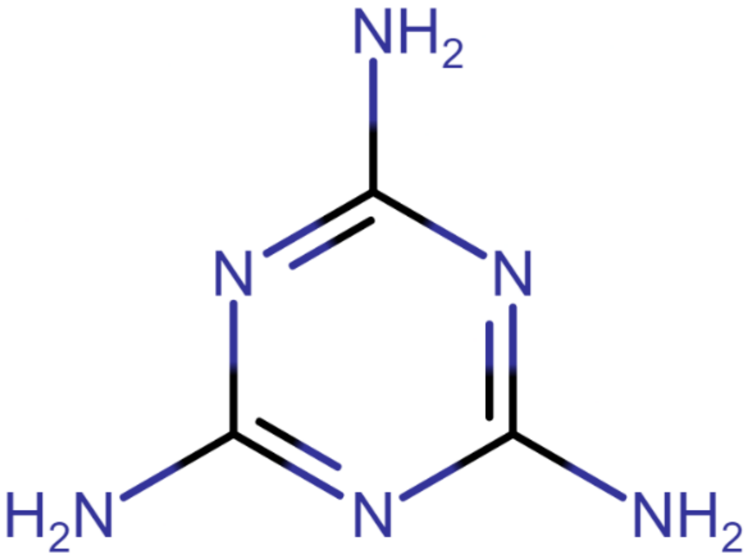
formaldehyde

+



urea

nebo

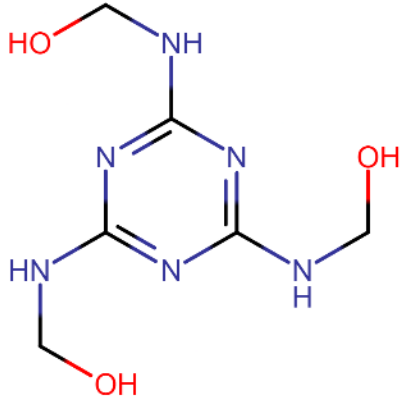


melamine

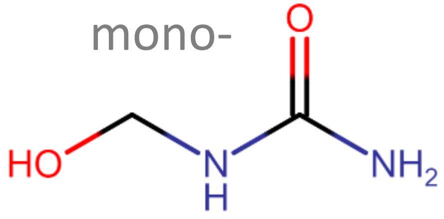
Reaction of formaldehyde with urea or melamine

- depending on the reaction conditions:
  - mono- to tetramethylolurea
  - mono- to hexamethylolmelamine

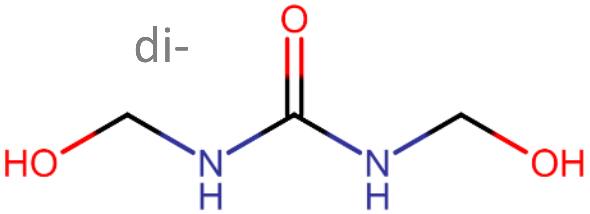
tri-



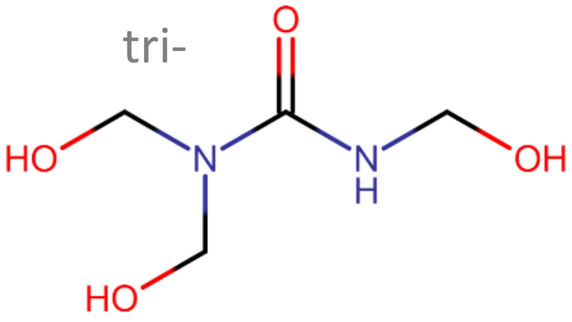
mono-



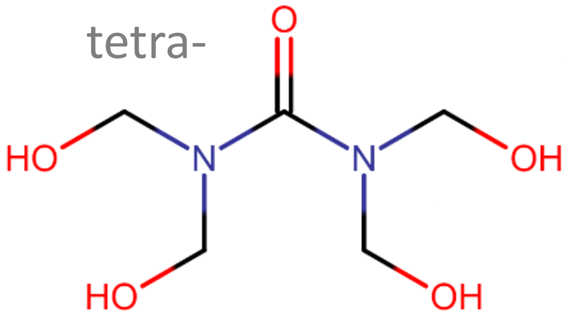
di-



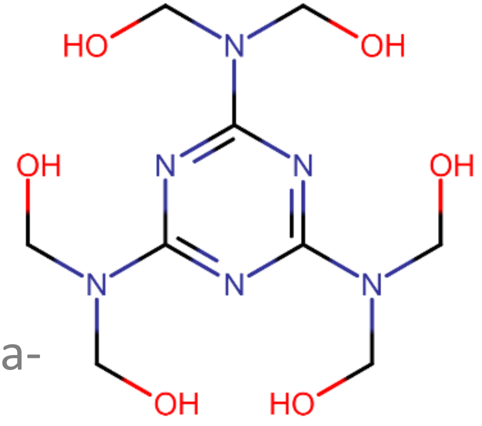
tri-



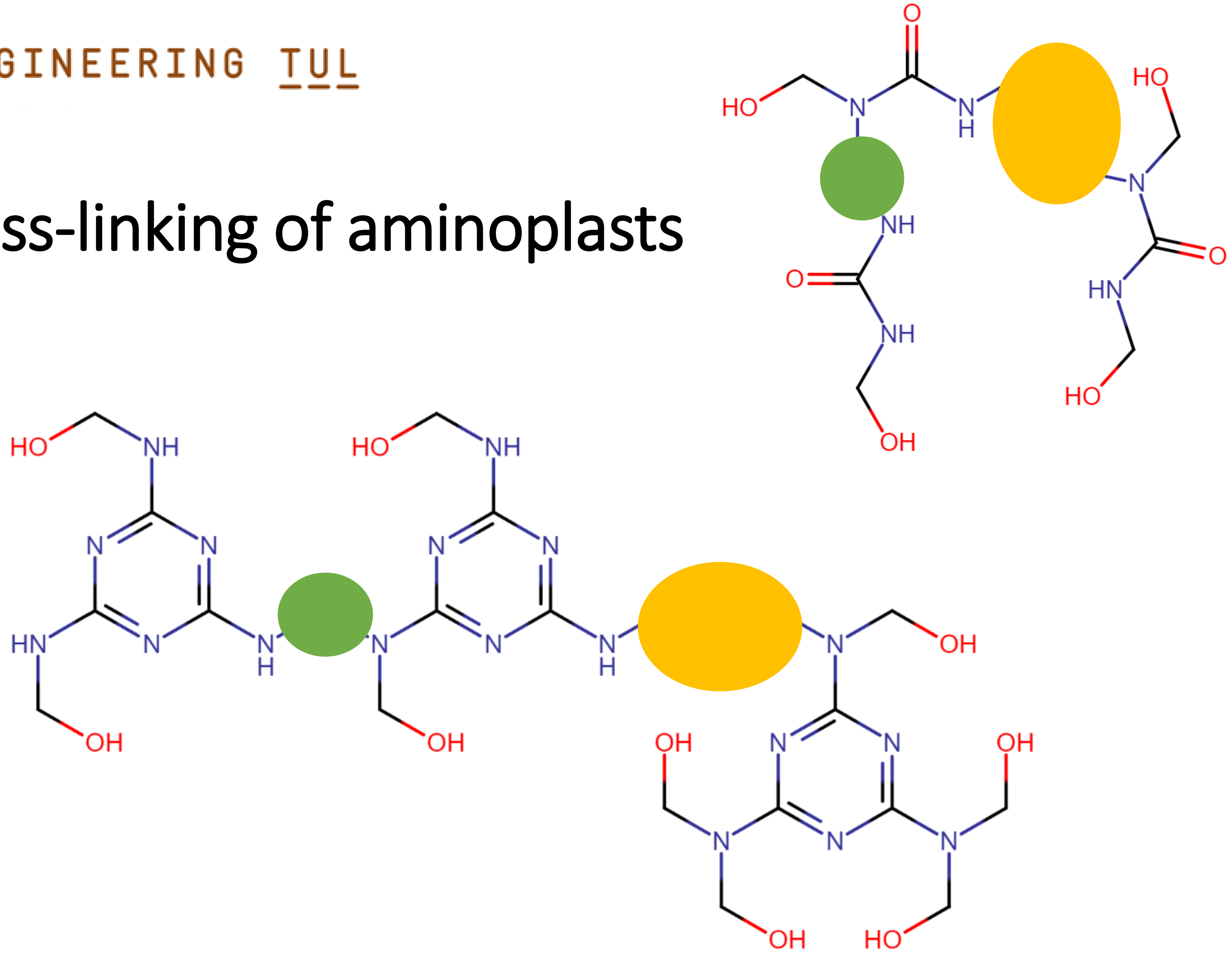
tetra-



hexa-



Cross-linking of aminoplasts



- again increased temperature and acidic environment
- again 🟩 and 🟨 bridges
- due to the high functionality of urea and melamine, a very dense network is created

Polycondensates - polysulphide rubber

- reaction of alkyl dihalides with inorganic polysulfides
- oil-resistant rubbers, the torment of students during laboratory work

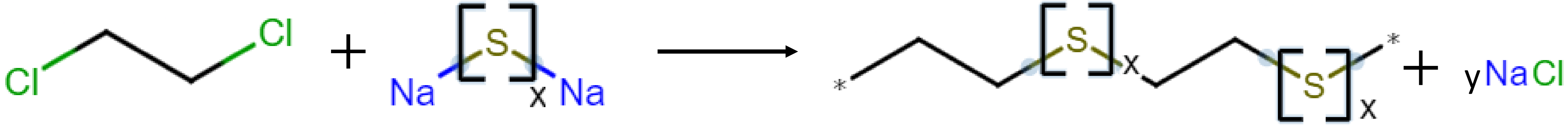


Table of reaction groups and their polycondensation products

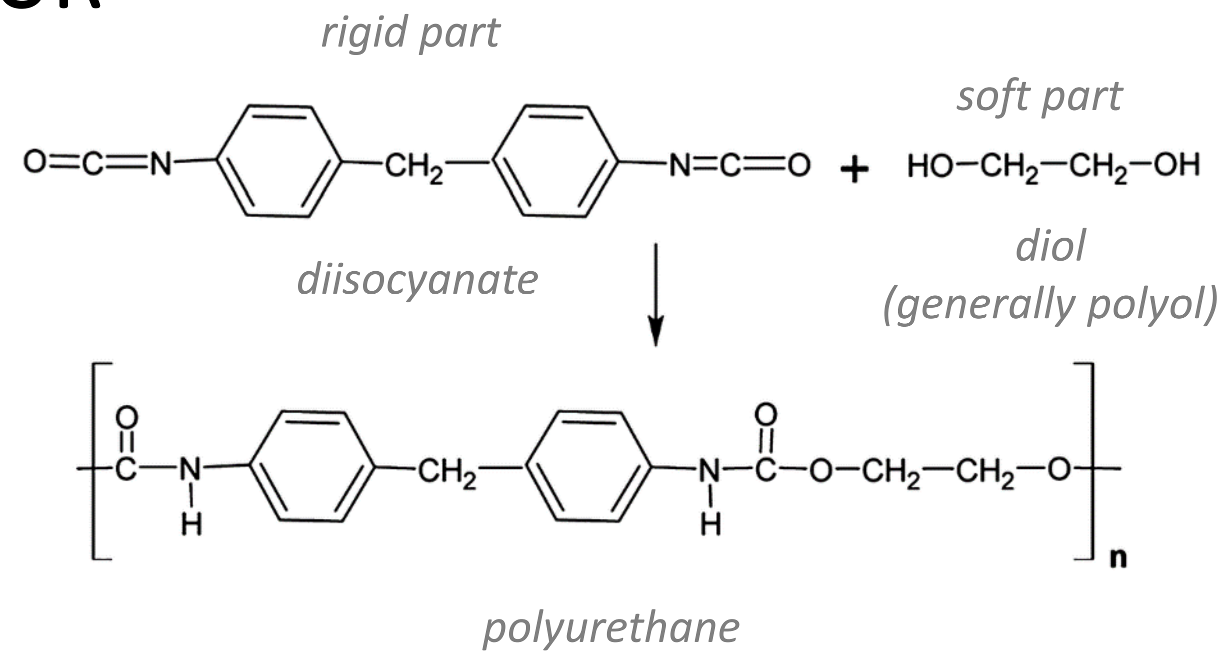
-OH	-COOH -COOR -COOX	polyester
	-X -OH	polyether
$-NH_2$ (may also apply to secondary)	-COOH -COOR -COOX	polyamide
-SiOH	-SiOH	polysiloxane
-CHO	aromatic alcohol	phenol-formaldehyde resins
	urea derivates	urea-formaldehyde resins

Step-growth polyreactions - polyaddition

- reaction without the formation of by-products
  - without changing the total composition of the product (only a change in structural units)
    - in a sense the simplest reaction to invent
    - I will evaluate the type of new bond and describe the rest so that there is nothing left
- the balance of such reactions is usually strongly shifted in favor of the products
- ring-opening polymerization (ROP) is sometimes also classified here
  - however, they show signs of chain polymerization

PUR

- insulation, adhesives, mounting foams, artificial leather



- many possible side reactions:
  - foam PUR
    - isocyanate + water

$$\sim NCO + H_2O \longrightarrow \sim NH_2 + CO_2$$

  - cross-linked PUR
    - isocyanate + amine

$$\sim NCO + H_2N \sim \longrightarrow \sim NH-CO-NH \sim$$

Industrial methods of polymerization

Industrial methods of polymerization

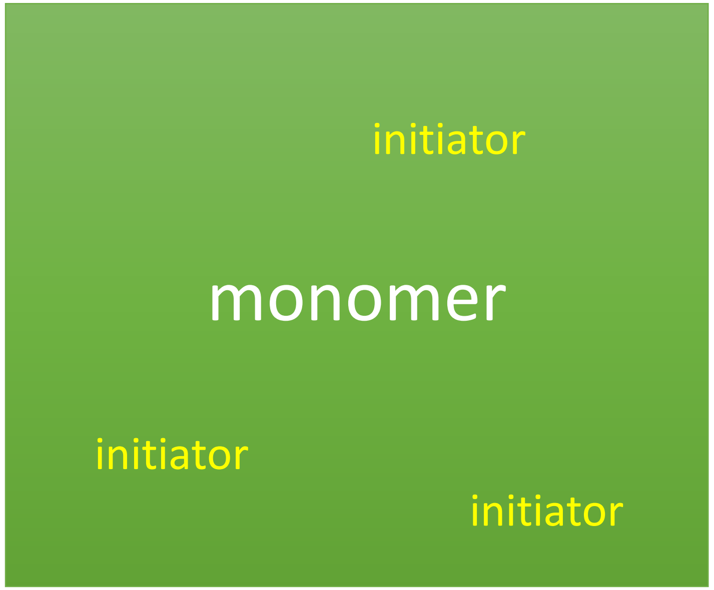
- not only the reaction mechanism affects the polymerization outcome
- during polyreactions, heat is usually generated (sometimes so high that the whole thing can catch fire or explode)
  - given that the conversion of most monomers to polymer has a negative enthalpy change ΔH and the temperature increases during the reaction
- generally four methods of polymerization:

Industrial methods of polymerization

- bulk (in the monomer phase)
- solution
- suspension
- emulsion

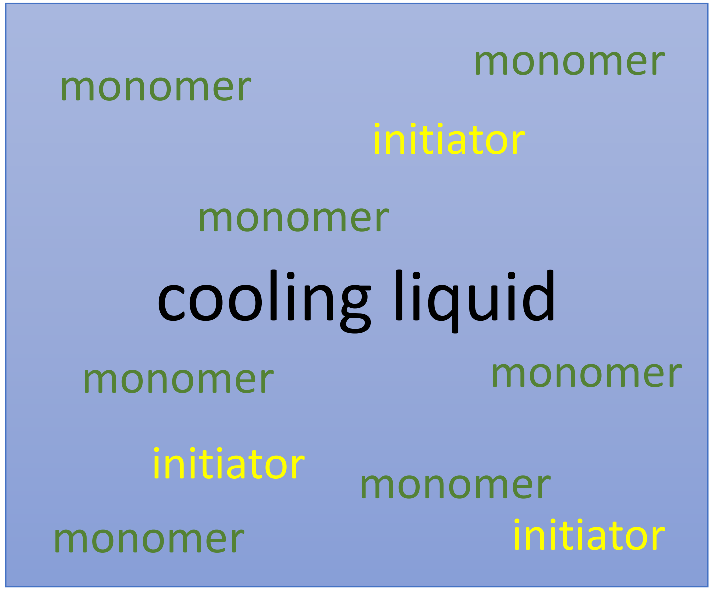
1. Bulk polymerization

- takes place directly in the monomer phase
  - I add an initiator to the monomer and let it react
  - radical or ionic
- if the resulting polymer is soluble in its monomer, I get an increasingly viscous solution, which eventually solidifies (a real block of polymer - hence the older name of the method)
- if the emerging polymer is not soluble in its monomer, a fine powder precipitated in the monomer is formed (I get a powder, so the label block polymerization is not entirely appropriate)
- high product purity
  - there is nothing else except the initiator
- difficult cooling
  - the reaction usually produces a lot of heat and I may not be able to cool it down inside the growing polymer
  - thermal decomposition of the resulting polymer or boiling of the monomer may occur (possibly catching fire)



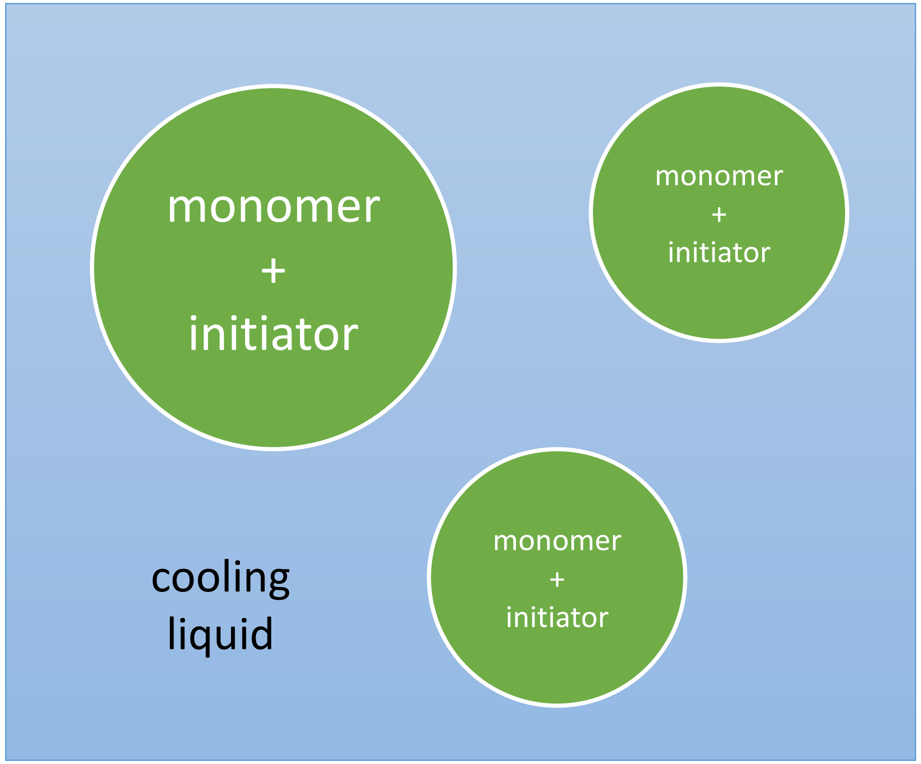
2. Solution polymerization

- in order to dissipate the reaction heat and cool the whole, I dissolve the monomer in a suitable cooling liquid and add the initiator
    - the monomer must therefore be soluble in the liquid
    - radical, ionic or coordination polymerization
- easy cooling
    - lower product purity
    - there is a lot of solvent
- lower average molar mass
    - lots of solvent molecules reduce the chance of the growth center hitting another monomer
    - growth centers are transferred to solvent molecules
- if the polymer is soluble in the cooling liquid, I get a viscous solution
    - adhesives and coatings
    - or I can pour a non-solvent into the mixture and precipitate the polymer (precipitation reaction)
- if the polymer is insoluble in the cooling liquid, it precipitates and I get a fine powder



3. Suspension polymerization

- called pearl or bead polymerization
- at the beginning we have an emulsion of the monomer phase (monomer + initiator dissolved in it) in the immiscible phase of the cooling liquid
    - monomer phase mostly non-polar, cooling liquid polar (e.g. water)
- the polyreaction creates a suspension of solid spherical polymer particles in a cooling liquid (therefore suspension or bead)
- I stabilize the emulsion by stirring
- as with the soup with oil meshes, by stirring I make sure that the meshes stay small and do not combine into larger ones
    - if the droplets made a big drop, I wouldn't cool it
    - the droplet size is usually around 1 mm
    - the amount and size of the droplets depends mainly on the mixing speed

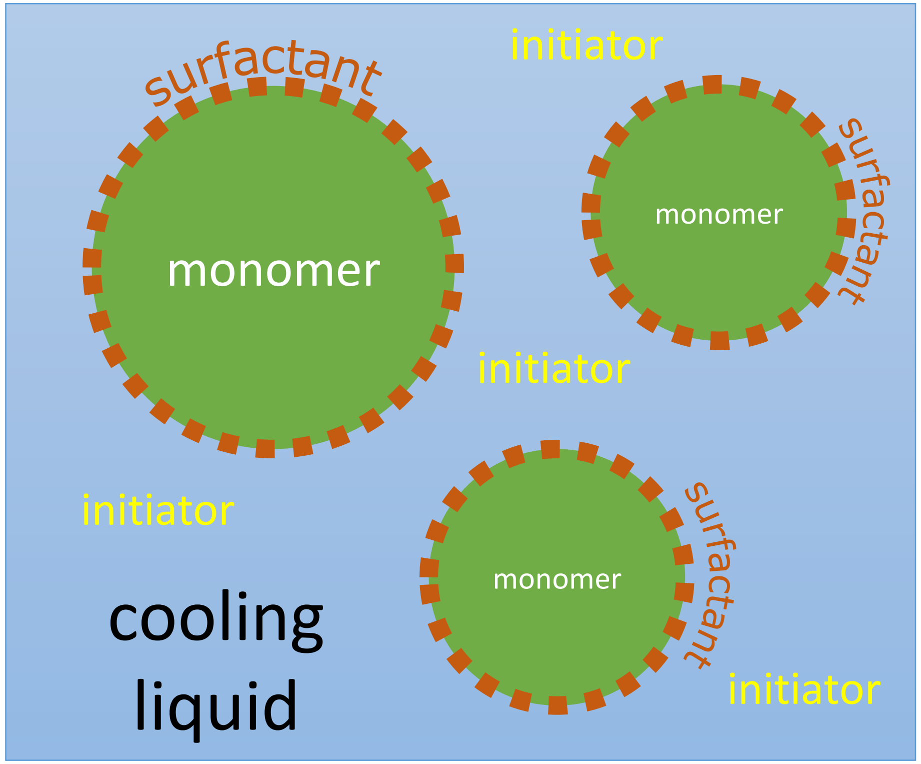


3. Suspension polymerization

- the amount of coolant makes it easy to cool down
- I have to add stabilizers
    - during the growth of the macromolecules the droplets become sticky and would stick together, so I cover them on the surface with something to prevent them from sticking together
        - either a substance clinging to the surface of the droplets (like flouring dough on a roll)
        - or something to increase the viscosity of the coolant so that the droplets cannot get close to each other
    - it reduces the purity of the product
- used e.g. for PS, PVC, PMMA

4. Emulsion polymerization

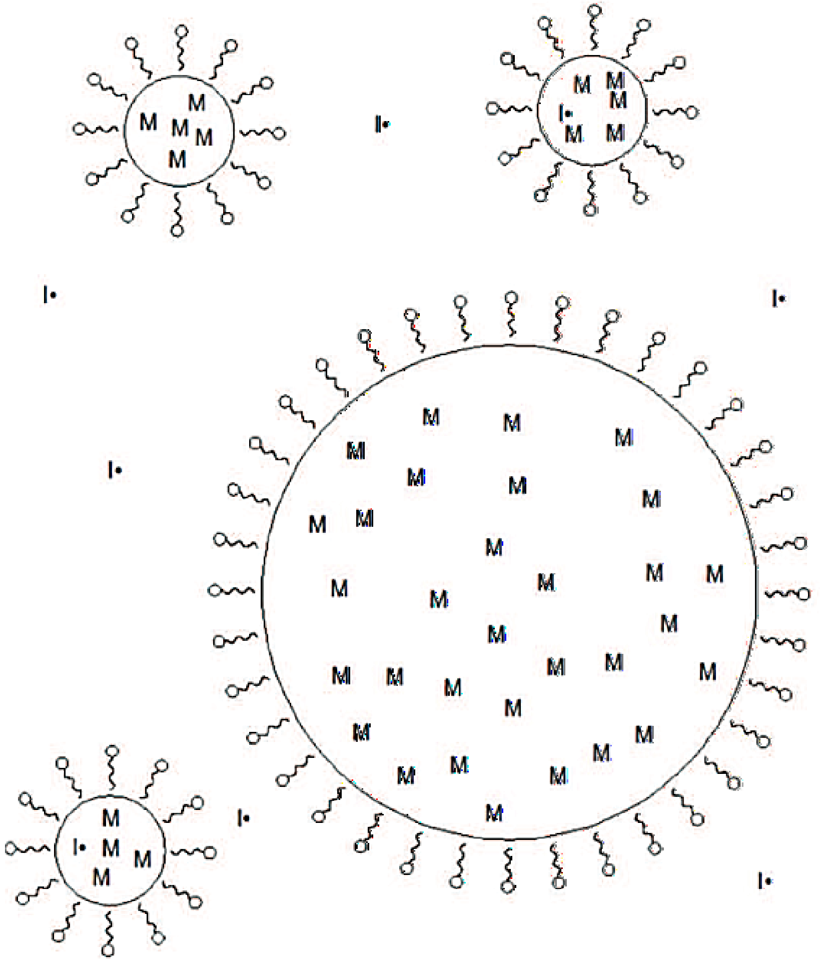
- based on a monomer immiscible with the cooling liquid, in which the initiator and emulsifier (= surfactant, surfactant) are dissolved
  - above the critical micellar concentration, the emulsifier forms micelles in which the monomer is enclosed (it doesn't want to be in the cooling liquid and likes to stuff itself inside the micelles)
  - compared to suspension micelles, the micelles are mainly stabilized by the emulsifier and not so much by mixing or additives
- the polyreaction takes place inside the micelles, where the monomer is practically pure
- micelle size is in units of µm (compared to 1 mm for suspension)
- the polyreaction starts when the initiator gets into the droplet

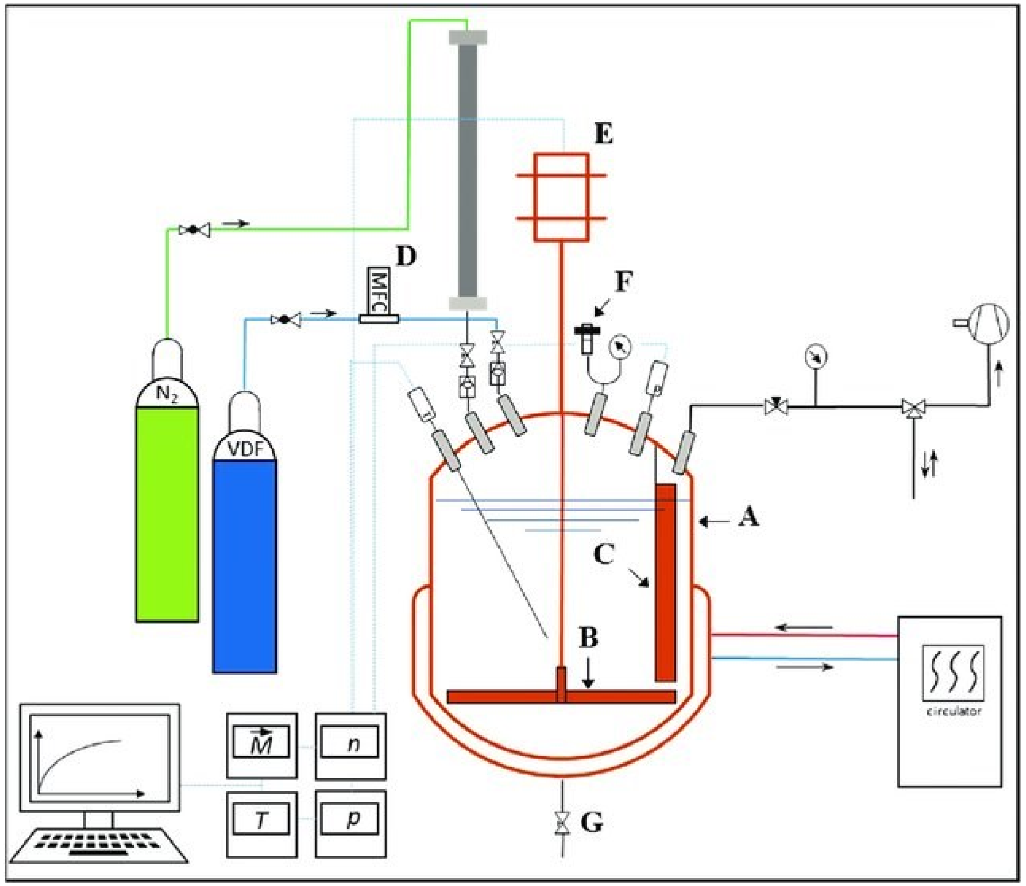


4. Emulsion polymerization

- higher average molar masses
- easy cooling
- after all, a less pure product
- the result of the polyreaction is the so-called latex

  = stable emulsion of polymer particles with a size of about 1 µm dispersed in a cooling liquid (hence emulsion polymerization)
  - suitable for paint materials
  - a polymer can be obtained by precipitation
- usually for latex/rubber





Emulsion polymerization reactor (here for PVDF aqueous emulsion)
A – Reactor, B – Stirrer, C – Stream splitter, D – Monomer dispenser, E – Stirrer motor with stirring resistance control, F – Safety sensors and fuses, G – Bottom valve

Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

MŠMT
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

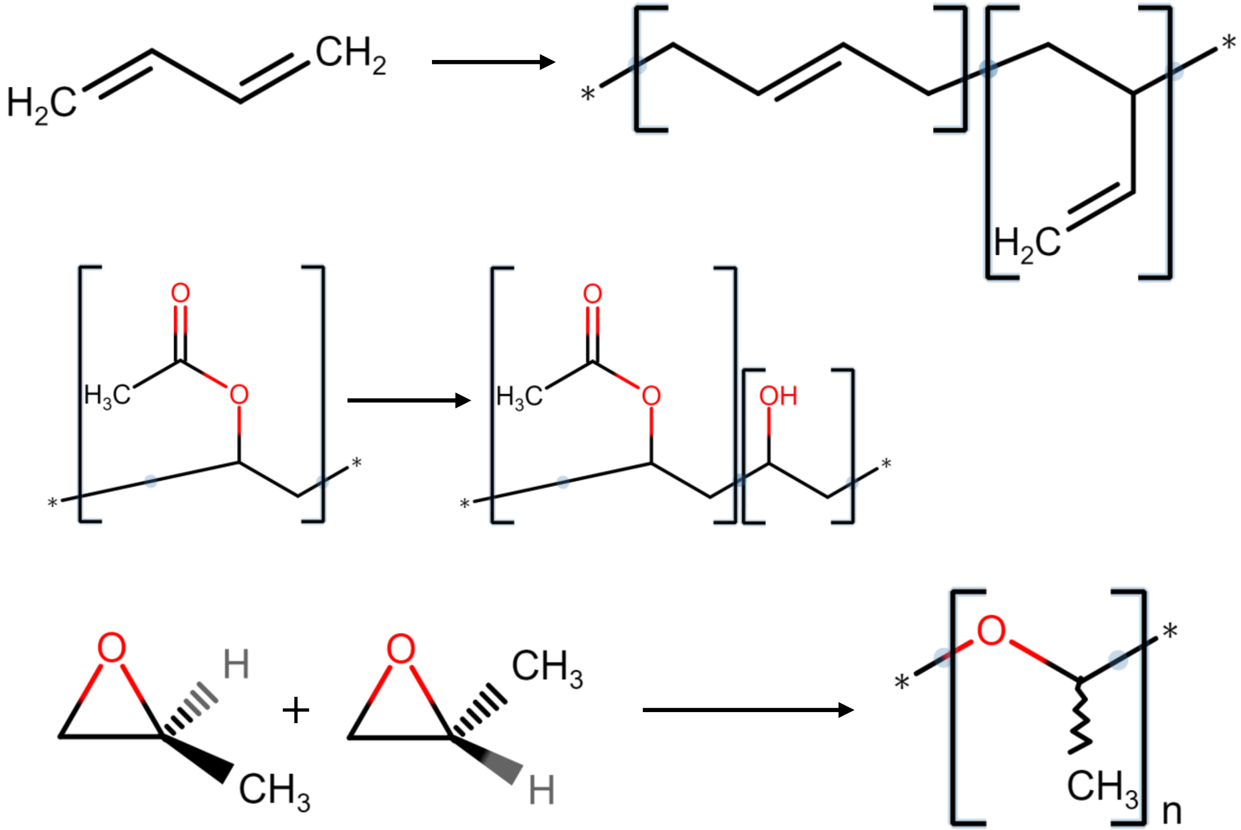
Copolymers

Copolymer

- otherwise also a heteropolymer
  - the opposite is a homopolymer
- macromolecular substance formed from at least two different types of monomers (usually 2 or 3 types)
  - individual monomers are called comonomers
- according to the number of comonomers, we distinguish bipolymerization (2), terpolymerization (3), etc.
- enantiomers are generally not considered different monomers
- common in natural polymers (heteropolysaccharides, proteins, lignin, etc.)
- they also have considerable technical significance
  - acrylonitrile-butadiene-styrene rubber (ABS)
  - butadiene styrene rubber (BSR)
  - copolymers of ethylene with vinyl acetate (EVA)

Pseudocopolymers

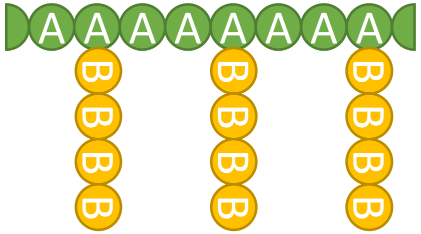
- there are polymers classified as homopolymers, although there are more different monomer units in their structure, which can be given by:
  - by different course of monomer reactions (e.g. 1,2 and 1,4 reactions of butadiene)
  - or an imperfect conversion (e.g. residues of acetate groups in PVA)
- enantiomers are not considered different monomers
  - e.g. the reaction of the reaction of the enantiomeric mixture of R-methyloxirane and S-methyloxirane leading to atactic polymethyloxirane is not taken as copolymerization



Importance of copolymers

- modification of the properties of the final product
  - solubility
  - tenacity
  - hardness
  - abrasion resistance
  - elasticity
  - optical properties
  - thermal stability
  - option to add networkable groups
  - improving the dispersibility of additives (pigments, etc.)

Types of polymers according to measurements

structure		*term*		*abbreviation*
	…	homopolymer	…	polyA
-	…	general copolymer	…	poly(A-co-B)
	…	random (statistical)	…	poly(A-stat-B)
	…	alternating	…	poly(A-alt-B)
	…	block	…	poly(A-block-B)
	…	grafted	…	poly(A-graft-B)

Polymerization leading to copolymer

copolymer		*polyreaction*
random (statistical)	…	radical
alternating	…	radical, polycondensation
block	…	ionic
grafted	…	radical, ionic

Copolymerization reaction

- polymerization of at least two different types of monomers
- e.g.:
  - poly(ethylene-co-propylene)
  - poly(styrene-co-butadiene)
  - poly(vinylidene chloride-co-vinyl chloride)
  - poly[imino(1,6-dioxohexane-1,6-diyl)iminohexane-1,6-diyl] (PA6,6)

Radical bipolymerization

- three types of reactions (same as for radicals)
  - initiation
  - promotion
  - termination
- in general, the rules of radical homopolymerization apply, but complicated by the possibility of a larger amount of reaction

Initiation of radical bipolymerization

- homolytic decay of initiator I produces 2 radicals R·

$$Ini - inI \rightarrow 2Ini\,\cdot$$

- however, two growth centers may arise
  - one on the M_1 monomer and the other on the M_2 monomer

$$Ini\cdot + M_1 \rightarrow IniM_1\,\cdot$$
$$Ini\cdot + M_2 \rightarrow IniM_2\,\cdot$$

Promotion of radical bipolymerization

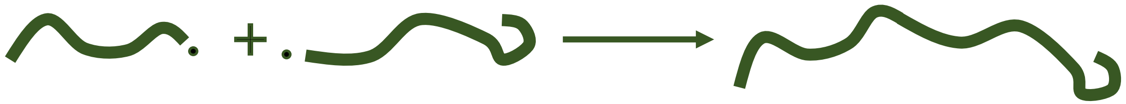
- thus, bipolymerization may appear to be not much more complicated than homopolymerization
  - however, the multiplication of possible reactions occurs again in the case of promotion
- if only the last unit of the growth chain affects the addition of a new measure, 4 reactions can occur
  - rate constants correspond to individual reactions k_{ij}

$$-M_1\cdot+M_1 \xrightarrow{k_{11}} -M_1M_1\cdot$$
$$-M_1\cdot+M_2 \xrightarrow{k12} -M_1\,M_2\cdot$$
$$-M_2\cdot+M_1 \xrightarrow{k21} -M_2\,M_1\cdot$$
$$-M_2\cdot+M_2 \xrightarrow{k22} -M_2\,M_2\cdot$$

Termination of radical bipolymerization

- this time the same as for homopolymerization
  - recombination (pairing)
    - a single bond is formed between the radicals

$[CH_2]_n\cdot + \cdot[CH_2]_m \rightarrow [CH_2]_{n+m}$



  - disproportion
    - one molecule will provide a hydrogen and the other an electron to the radical

$[CH_2]_n\cdot + \cdot CH_2\text{-}CH_2[CH_2]_m \rightarrow [CH_2]_n + CH_2{=}CH_2\text{-}[CH_2]_m$

The ratio of incorporated mers in the copolymer

- it is determined by the amount of incorporated mers or, conversely, the rate of decrease of the given monomers
- it's supposed, that
  - monomers are consumed only for the growth reaction (initiation is thus neglected)
  - the concentration of radicals is unchanged
    - if a new one arises, another must disappear (and vice versa)
    - it is referred to as the stationary state condition of bipolymerization
    - applies as follows:

$$k_{12}[-M_1\ \cdot][M_2] = k_{21}[-M_2\ \cdot][M_1]$$

    - the equation can be understood, for example, as the rate of disappearance of radicals -Mi· is the same as the rate of their formation

Constant concentration of radicals

- monomer is consumed only in growth reactions (theoretically)

growth reaction	radical balance of growth centers
$-M_1 \cdot +M_1 \xrightarrow{k_{11}} -M_1 M_1 \cdot$	• radical $-M_1\cdot$ of the growth center does not disappear, because it is replaced by another $-M_1$
$-M_1 \cdot +M_2 \xrightarrow{k12} -M_1\, M_2 \cdot$	• radical $-M_1\cdot$ of the growth center disappears, but a new radical is formed $-M_2\cdot$
$-M_2 \cdot +M_1 \xrightarrow{k21} -M_2\, M_1 \cdot$	• radical $-M_2\cdot$ of the growth center disappears, but a new radical is formed $-M_1\cdot$
$-M_2 \cdot +M_2 \xrightarrow{k22} -M_2\, M_2 \cdot$	• radical $-M_2\cdot$ of the growth center does not disappear because another one replaces it $-M_2\cdot$

When one perishes, the other must arise, and when the other perishes, the first arises again.

Radical ratio of growth centers

- the rate of incorporation of individual mers must somehow correspond to the representation of individual radicals -$M_1\cdot$ and –$M_2\cdot$
- can be simply derived from the steady state condition

$$k_{12}[-M_1\ \cdot][M_2] = k_{21}[-M_2\ \cdot][M_1]$$

$$\frac{[-M_1\ \cdot]}{[-M_2\ \cdot]} = \frac{k_{21}[M_1]}{k_{12}[M_2]}$$

The ratio of incorporated mers in the copolymer (Part II)

- it is determined by the amount of incorporated mers or, conversely, the rate of decrease of the given monomers
- the rate of decrease (concentration) of a given comonomer corresponds to the rate of all reactions that consume it (in a given time):

$$-\frac{d[M_1]}{dt} = k_{11}[-M_1\cdot][M_1] + k_{21}[-M_2\cdot][M_1]$$

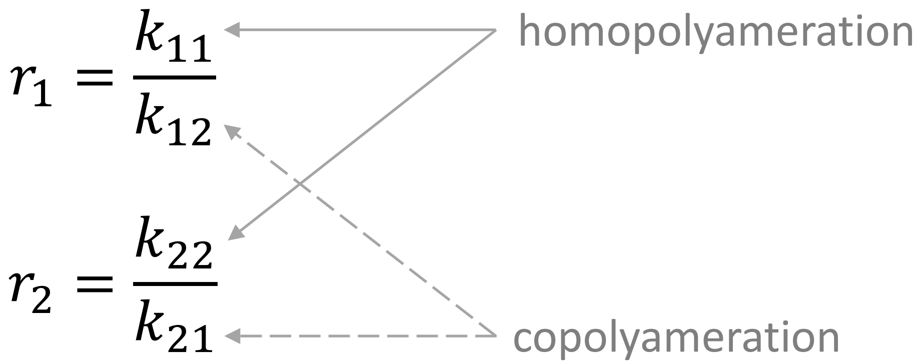
$$-\frac{d[M_2]}{dt} = k_{22}[-M_2\cdot][M_2] + k_{12}[-M_1\cdot][M_2]$$

The ratio of incorporated mers in the copolymer (Part III)

- share of rates of change in comonomer concentrations:

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[-M_1\ \cdot][M_1] + k_{21}[-M_2\ \cdot][M_1]}{k_{22}[-M_2\ \cdot][M_2] + k_{12}[-M_1\ \cdot][M_2]}$$

- copolymerization parameters
  - express the ratio of the rate of homopolymerization of comonomer i to the rate of copolymerization i and y



$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

homopolyameration

copolyameration

Copolymerization equation

- by adjusting the equation of the proportions of the rates of change of the comonomer concentrations using the copolymerization parameters r_i, the so-called copolymerization equation is created

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]}$$

- the resulting composition of the copolymer thus depends on:
  - proportional representation of comonomers M_1 and M_2 in the reaction mixture
  - copolymerization parameters r_1 and r_2
- applies in general, but since the ratio of comonomers usually changes over time, it is usually not possible to calculate the resulting polymer composition from it only according to the ratio of comonomers in the reaction batch

The ratio of incorporated mers in the copolymer (Part IV)

- the reactivity of the growth centers can depend not only on the last measure, but also on the penultimate one
  - the so-called penultimate effect

$$-M_1M_1\cdot \qquad -M_2M_1\cdot \qquad -M_2M_2\cdot \qquad -M_1M_2\cdot$$

- the whole process is then complicated by the necessity of using new copolymerization parameters r_i'

$$r_1 = \frac{\overset{-M_1M_1\cdot+M_1}{k_{111}}}{\underset{-M_1M_1\cdot+M_2}{k_{112}}} \qquad r_1' = \frac{\overset{-M_2M_1\cdot+M_1}{k_{211}}}{\underset{-M_2M_1\cdot+M_2}{k_{212}}} \qquad r_2 = \frac{k_{222}}{k_{221}} \qquad r_2' = \frac{k_{122}}{k_{121}}$$

The ratio of incorporated mers in the copolymer (Part V)

- the significance of the values of the copolymerization parameters r_i

$$\frac{k_{11}}{k_{12}} = r_1$$

> 1 … M_1 binds preferentially to the growth center ending in $–M_1·$

≈ 1 … M_1 binds to a growth center ending in –M1· about as fast as it binds to a growth center ending in $–M_2·$

< 1 … M_1 binds preferentially to the growth center ending in $–M_2·$

Copolymerization diagrams

- the product of the copolymerization parameters r_1r_2 is more often used to estimate the composition of the copolymer
    - it is expressed by so-called copolymerization diagrams
- axes of diagrams
    - mole fraction of the composition of the reaction mixture fi
        - number of comonomer molecules M_1 and M_2
    - by the molar fraction of mers incorporated into the growing F_i chains
        - number of built-in measures m_1 and m_2

$$f_1 = \frac{[M_1]}{[M_1]+[M_2]} \qquad F_1 = \frac{[m_1]}{[m_1]+[m_2]}$$

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Homopolymerization or block copolymerization

$$r_1 \cdot r_2 \gg 1$$

- when both r_1 and r_2 are significantly higher than 1
  - it means that mainly homopolymerizations occur
- in radical polymerization, two homopolymers are formed (this is not copolymerization)

- block copolymers may occur in the case of ionic ones

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Alternating copolymerization

$$r_1 \cdot r_2 = 0$$

- occurs in two (three) cases:

fň)

$$k_{11} = k_{22} = 0$$

bž)

$$k_{11} = 0; k_{22} \neq 0$$

dř)

$$k_{11} \neq 0; k_{22} = 0$$

fň) homopolymerization growth does not take place (comonomer M_1 does not react with growth center –$M_1\cdot$ and M_2 does not react with center –$M_2\cdot$)

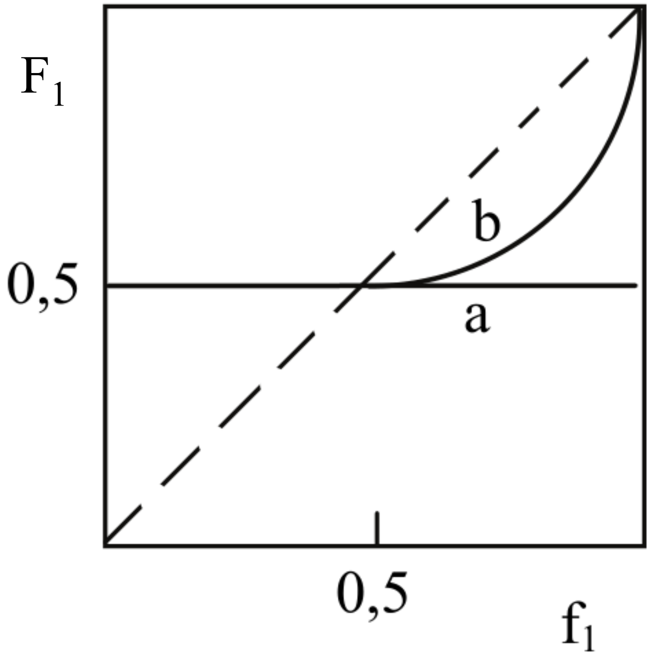
bž) M_1 incapable of homopolymeric growth (the comonomer M_1 does not react with the growth center –$M_1\cdot$)

dř) the same case as bž) – it is only a reversed labeling of comonomers

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Alternating copolymerization



$$r_1 \cdot r_2 = 0$$

a) $r_1 = r_2 = 0$

- perfectly (strictly) alternating
- comonomers are always able to react only with the other comonomer and not with themselves
- if one of the comonomers in the reaction mixture runs out, the reaction stops

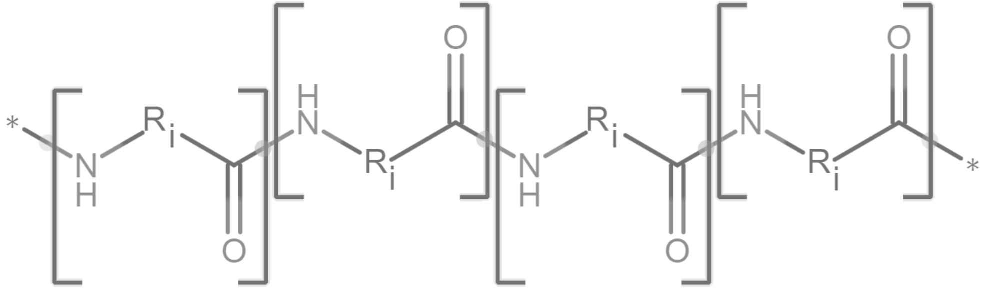
b) $r_1 = 0; r_2 = 0{,}1$

the homopolyreaction here takes place 10 times worse than the heteropolyreaction

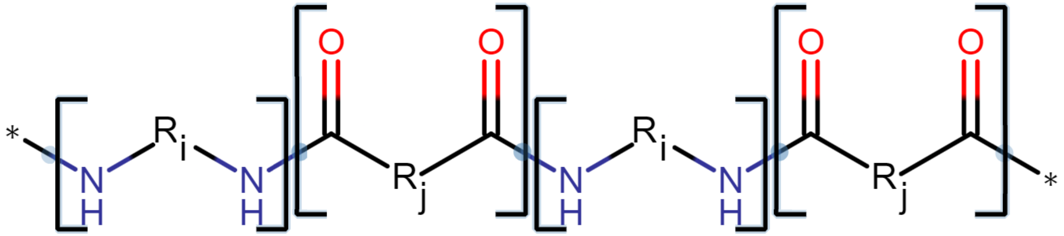
- mostly alternating
- comonomers react predominantly with the second comonomer
- it ceases to be perfectly alternating when the composition of the reaction mixture is deviated (e.g. it will only consist of comonomers)

Side topic: Heteropolyamides

- the case of strictly alternating copolymers
  - polycondensation reaction (not yet resolved radical)
- comonomers can (due to their chemical nature) only react with the opposite (not with each other)
- PA 46, PA 66, PA 69, PA 610, PA 612, PA1012
- they are copolymers because they are formed from two comonomers
  - some consider them homopolymers because these comonomers cannot be made into the corresponding homopolymers, but the general definition classifies them as copolymers



homopolyamide



heteropolyamide

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Statistical (ideal) copolymerization

$$r_1 \cdot r_2 = 1$$

- occurs when the preceding applies and at the same time:

lň) $r_1 > 1; r_2 < 1$

tž) $r_1 < 1; r_2 > 1$

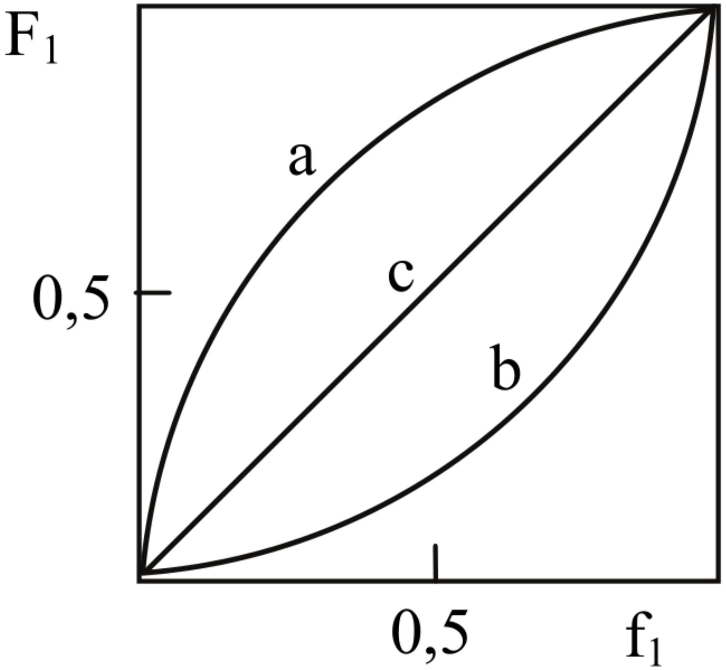
hř) $r_1 = 1; r_2 = 1$

lň) comonomer M_1 prefers homopolyreaction and M_2 prefers heteropolyreaction
tž) (similar to that) comonomer M_1 prefers heteropolyreaction and M_2 prefers homopolyreaction
hř) homopolyreaction and heteropolyreaction take place at the same speed for both comonomers

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Statistical (ideal) copolymerization



$$r_1 \cdot r_2 = 1$$

a) $r_1 = 5; r_2 = 0,2$
- ideal non-azeotropic copolymerization

b) $r_1 = 0,2; r_2 = 5$
- ideal non-azeotropic copolymerization

c) $r_1 = r_2 = 1$
- ideal azeotropic copolymerization
- the composition of the copolymer is dependent only on the composition of the reaction mixture
- not very common

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Non-ideal copolymerization

$$r_1 \cdot r_2 \in (0; 1)$$

- occurs when the preceding applies and at the same time:

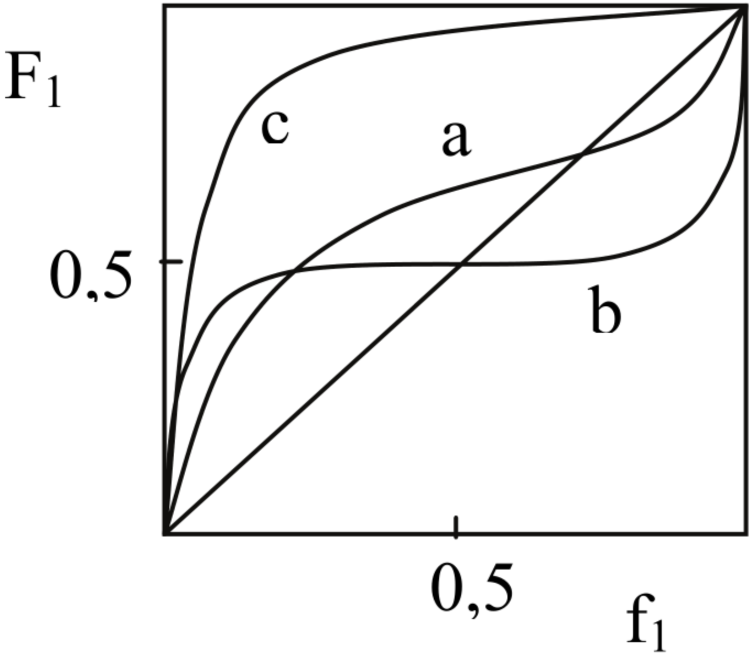
bň)	hž)	fř)
$r_1 > 0; r_2 < 0$	$r_1 < 0; r_2 > 0$	$r_1 < 0; r_2 < 0$

- the most common case of copolymerizations

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Non-ideal copolymerization



$$r_1 \cdot r_2 \in (0;1)$$

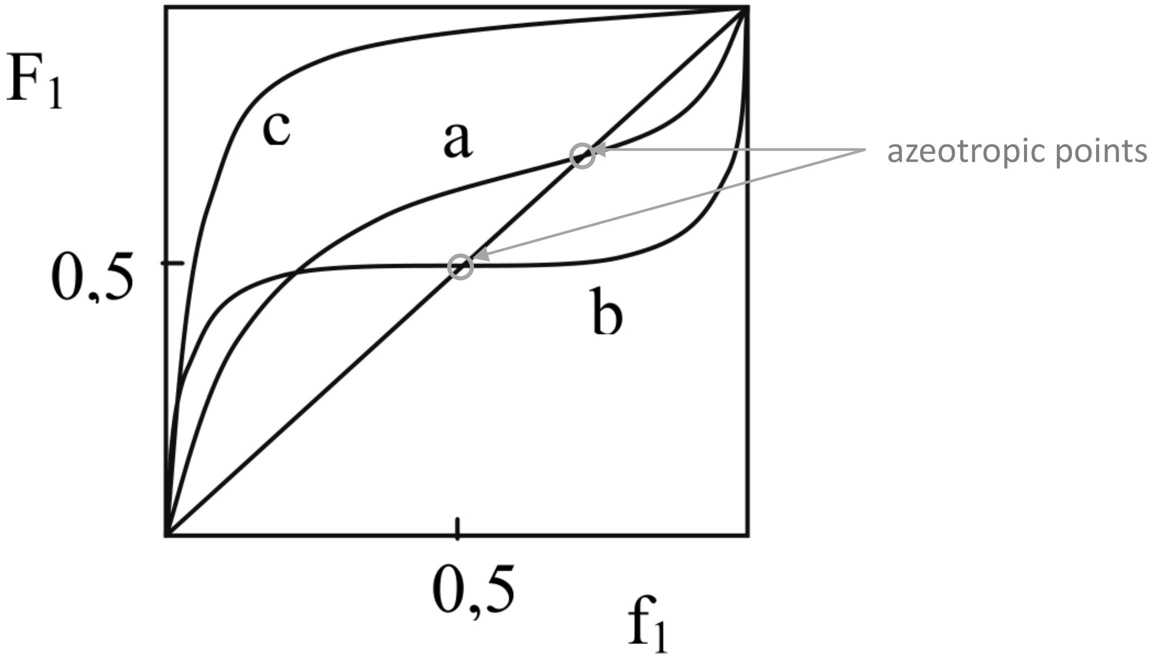
a) $r_1 = 0{,}52$; $r_2 = 0{,}12$
   - non-ideal azeotropic copolymerization

b) $r_1 = 0{,}04$; $r_2 = 0{,}01$
   - non-deal azeotropic copolymerization

c) $r_1 = 55$; $r_2 = 0{,}01$
   - non-ideal non-azeotropic copolymerization

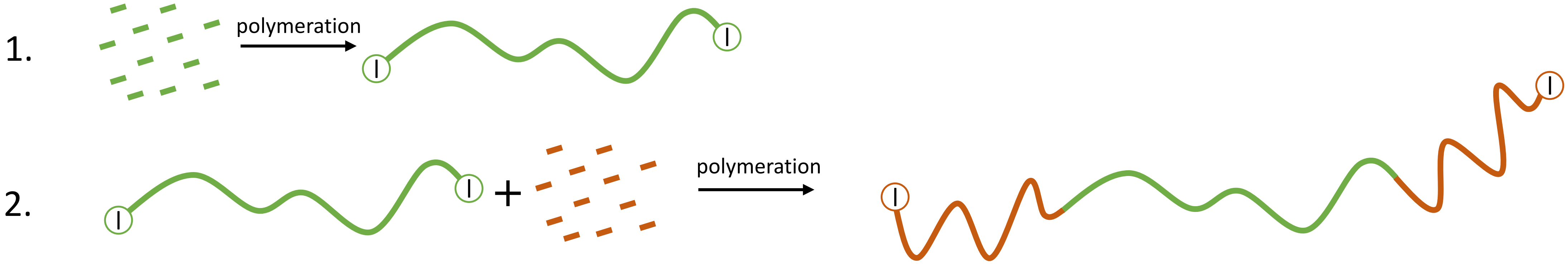
Azeotropic and non-azeotropic copolymerization

- azeotrope
  - the composition of the copolymer is identical to the composition of the handle (fce y = x)
- azeotropic copolymerization
  - its curve intersects the imaginary line segment of the ideal azeotropic copolymerization (at a point other than the starting or ending point)
- nonazeotropic copolymerization
  - its curve does not intersect the imaginary line segment of the ideal azeotropic copolymerization (at a point other than the starting or ending point)



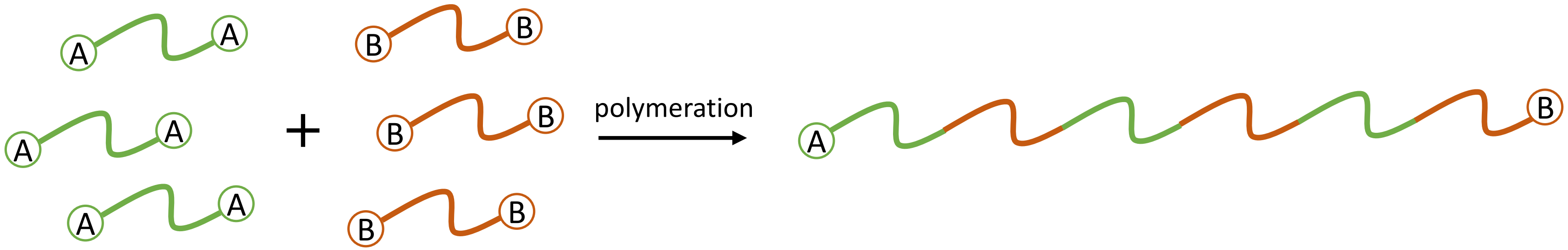
Block copolymerization (ionic)

- ionic copolymerization the most common
  - a homopolymer with **live ends** (capable of further reaction – **living polymerization**) of the chains is produced
  - after all the monomer is consumed, another suitable monomer is added and the reaction is continued
  - I can repeat with the same or new comonomers until I get bored



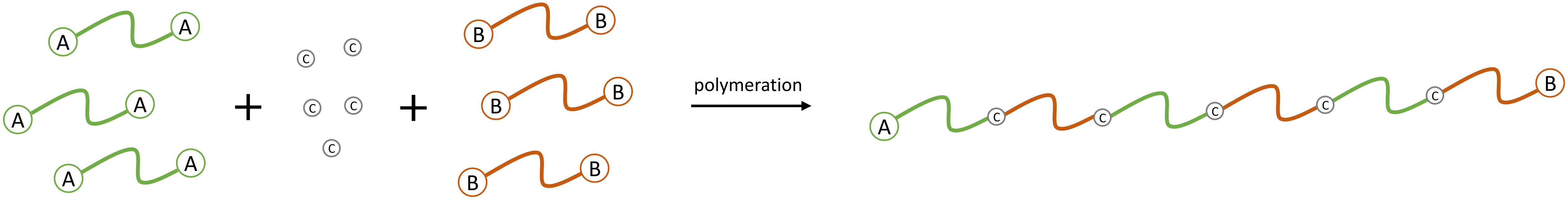
Block copolymerization – from prepolymers

- another possibility is the use of prepolymers
  - they are oligomers with end groups capable of further reactions
  - after they are mixed, a reaction occurs and a polymer is formed
- this is how e.g. poly(ester-block-urethane) is prepared
  - it is based on macrodiol and macrodiisocyanate
    - in the illustration below, A can be, for example, an –OH group and B can be an –NCO group



Block copolymerization – joining of chains

- another possibility is the linking of individual suitable prepolymers with bifunctional low molecular weight substances
  - these low molecular weight substances are called chain linkers

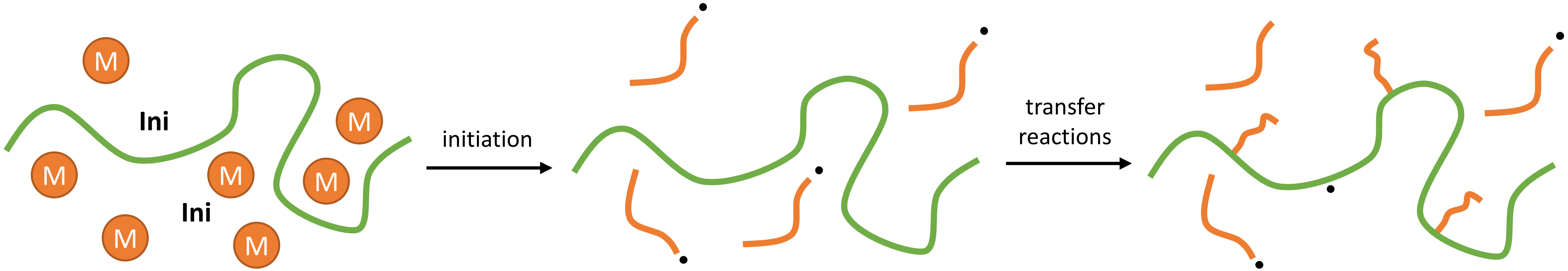


Block copolymerization - mastication

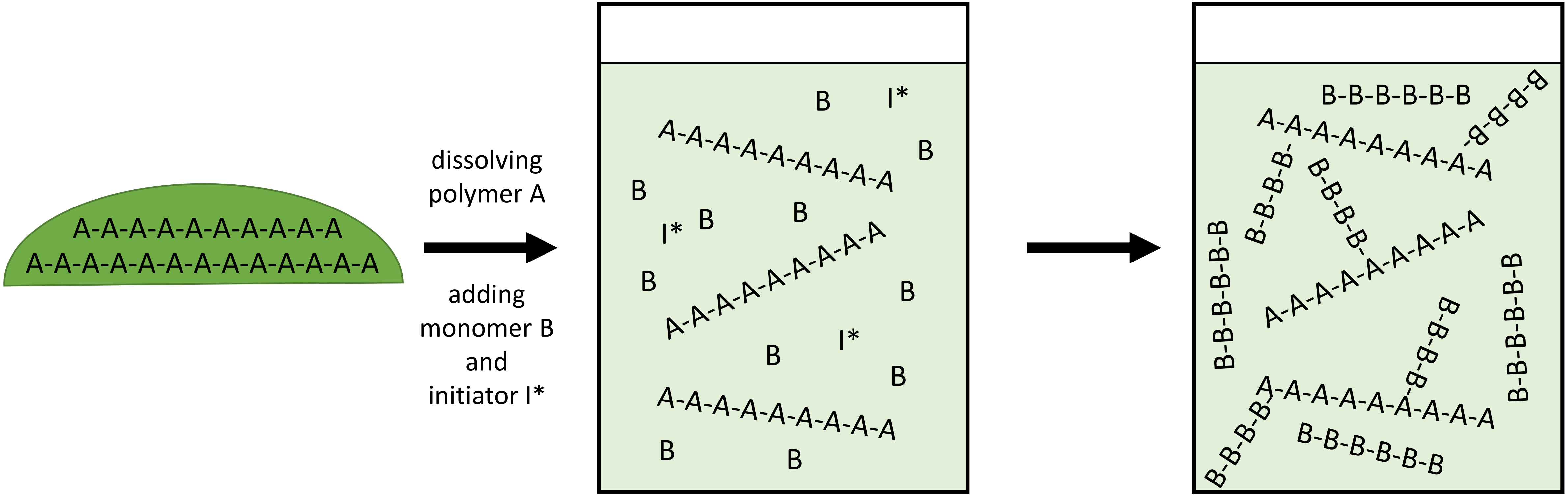
- mechanochemical syntheses can also be used
  - mechanically (for example on unevenly rotating calenders or by ultrasound) the chains of two or more homopolymers (all together) are broken, radicals are formed at the ends of the fragments and these cause their relinking
    - this is referred to as mastication
  - they are radicals, so not only recombination, but also other reactions take place
  - from two torn homopolymers, both homopolymers and a block copolymer are generally formed back

Grafting

- usually radical, sometimes ionic
- radicals
  1. uses transfer reactions (remember branching in LDPE)
  2. I dissolve the finished polymer with monomer (M) and initiator (I)
  3. initiate monomer polymerization (heat, UV, photoinitiation)
  4. with a sufficient concentration of radicals, transfer reactions and thus grafting begin to occur
- the products of such reactions are mixtures of both homopolymers and a graft copolymer
  - extra pure products are usually not needed (sometimes units of % grafted molecules in the polymer are sufficient)



A simplified scheme of graft polymer synthesis

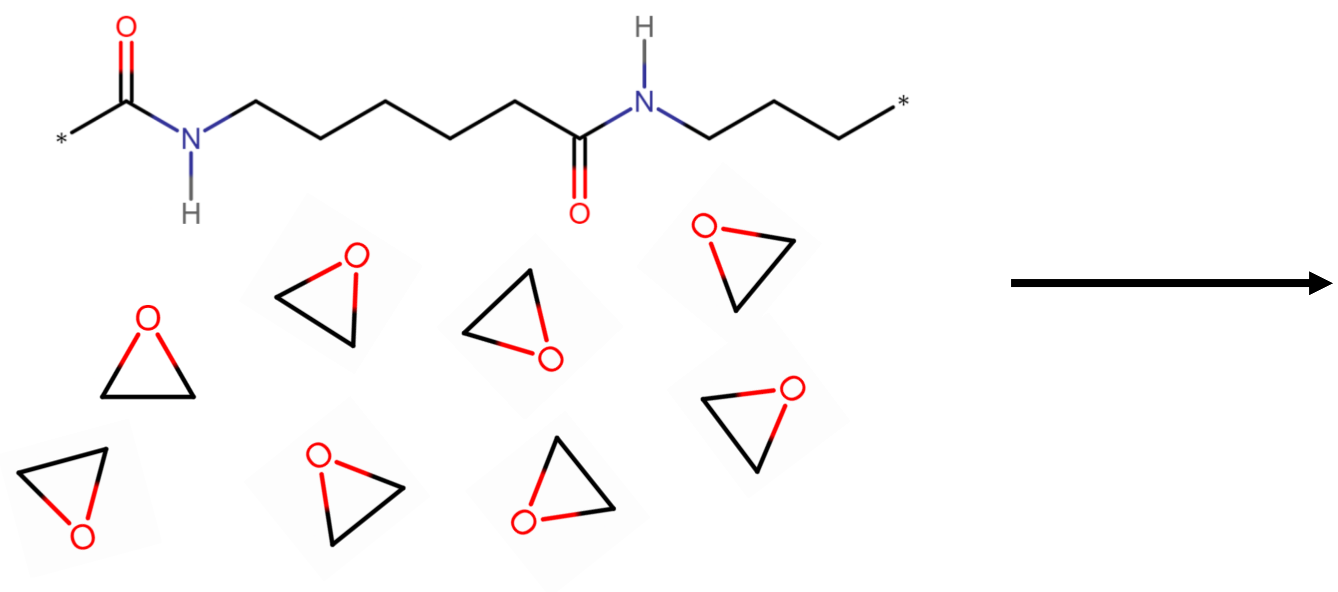


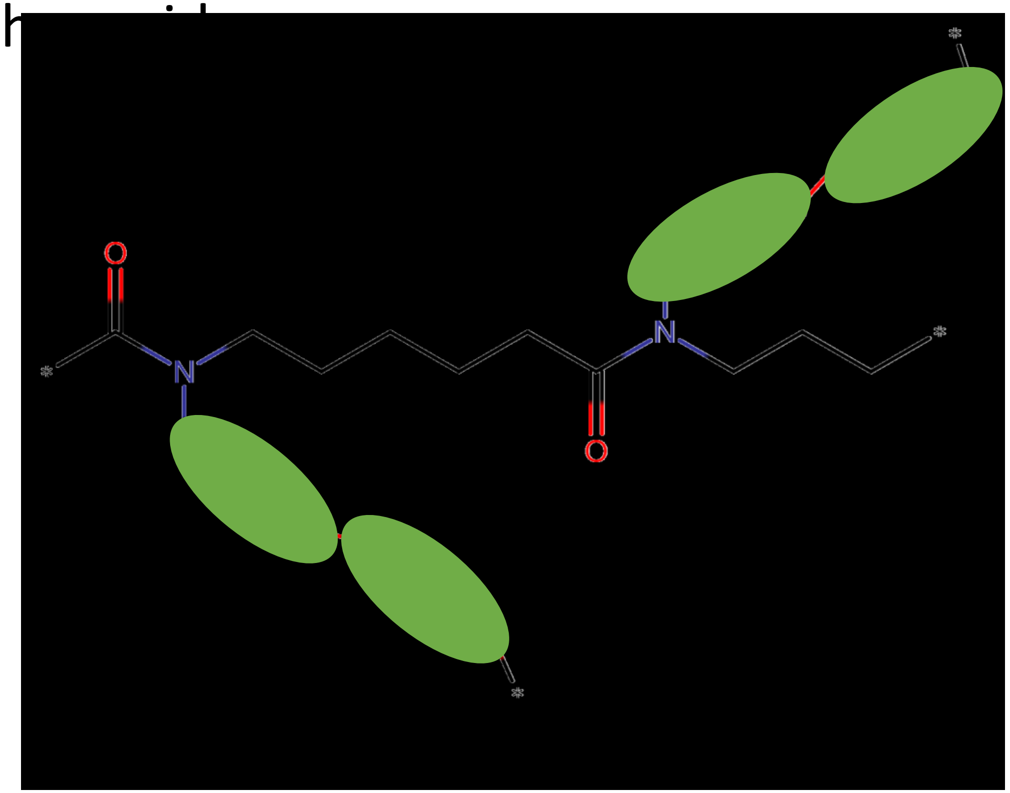
dissolving polymer A

adding monomer B and initiator I*

Grafting of oxirane chains on PA

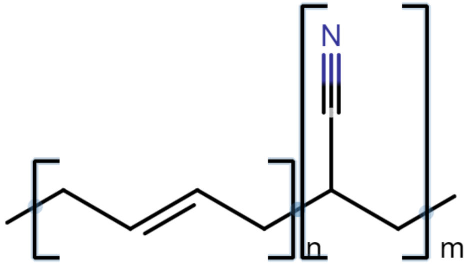
- increase in wettability and sorption properties
  - significant in the modification of about 15% of th



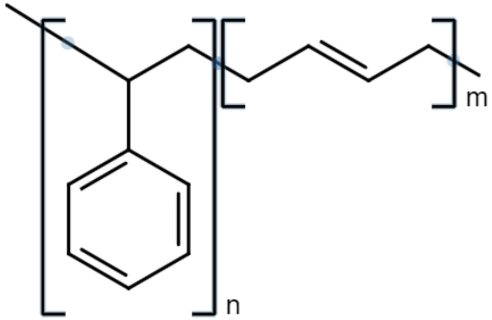


Copolymers in practice

- NBR
  - acrylonitrile butadiene (nitrile) rubber
  - non-oily in non-polar solvents (fuel hoses)



- SBS
  - styrene-butadiene-styrene (tough PS)
  - block polymer (anionic polymerization)
  - usually styrene:butadiene = 3:7
  - styrene provides hardness, butadiene flexibility and toughness
  - partially cross-linked



Copolymers in practice

- ABS
  - acrylonitrile-butadiene-styrene
  - amorphous thermoplastic material (e.g. for the production of LEGO bricks)
- VC+VAc
  - vinyl chloride + vinyl acetate
  - VAc content reduces T_m (over 25% it is already hot melt adhesives)
- SAN
  - styrene-acrylonitrile
  - styrene provides hardness, acrylonitrile chemical resistance and flexibility

Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

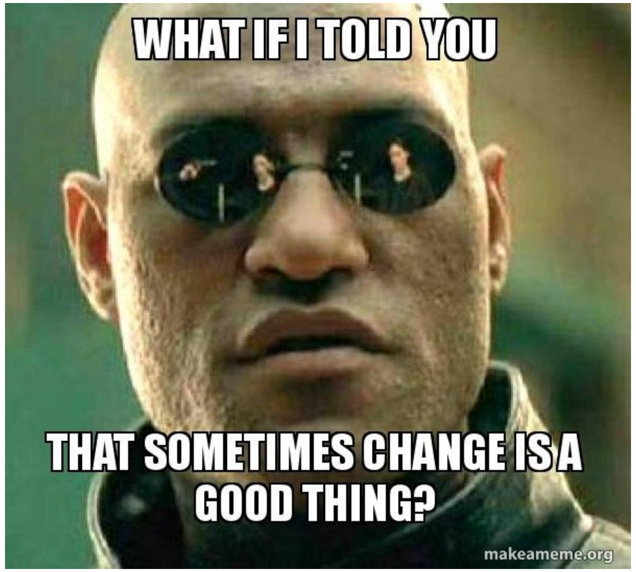
Chemical reactions of polymers

Chemical reactions of polymers

- divided according to the effect on the length of macromolecule chains
  - polymerization degree without change = polymer analog reactions
  - halogenation, esterification, hydrolysis or alcoholysis of substituents, intramolecular cross-linking...
  - can be further divided into reactions:
    - changing the original substituents
    - introducing new substituents
- change in degree of polymerization
  - increasing
    - graft
    - block copolymerization
    - networking
  - reducing
    - degradation (heat, mechanical stress, oxidative, photochemical, hydrolytic, enzymatic)
    - depolymerization

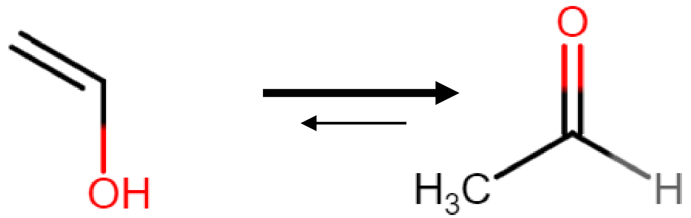
I. Polymer analogue transformations

- take place in polymers with a stable main chain
  - preferably pure carbon
- take place in solution or swollen polymer
  - easier contact of reacting substances
- better performed in a nitrogen atmosphere
  - preventing oxidative cleavage of the backbone of macromolecules

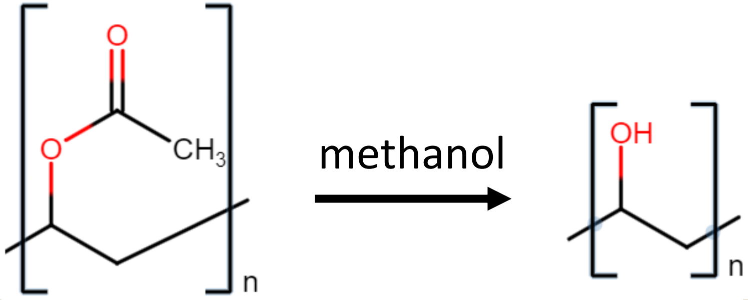


Preparation of PVA from PVAc

- cannot be prepared from PVA
    - enol form shifts to keto form (here to aldehyde)

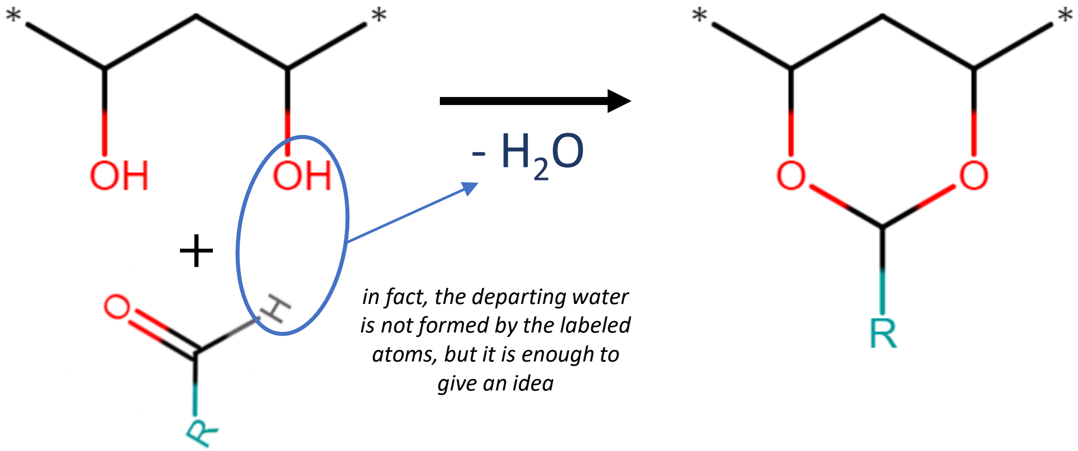


- it is prepared from polyvinyl acetate by alcoholysis
    - the amount of replaced groups describes the so-called degree of hydrolysis
        - usually between 80% and 99.9%
        - from a certain degree of hydrolysis, further increases impair water solubility



Preparation of polyvinyl acetals

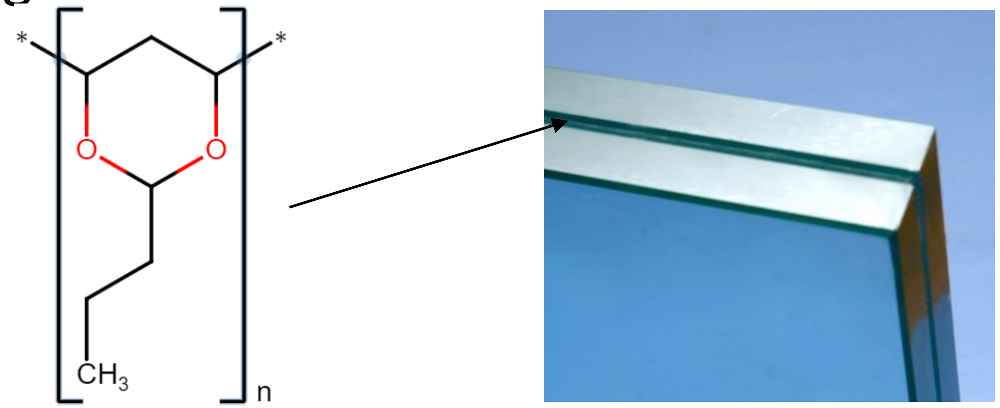
- PVF (polyvinyl formal)
- PVB (Polyvinyl Butyral)
  - it is used as glue, foil (e.g. for gluing layers of safety glass) and varnishes
- condensation of PVA in acidic medium or hydrolysis with aldehyde in acidic medium



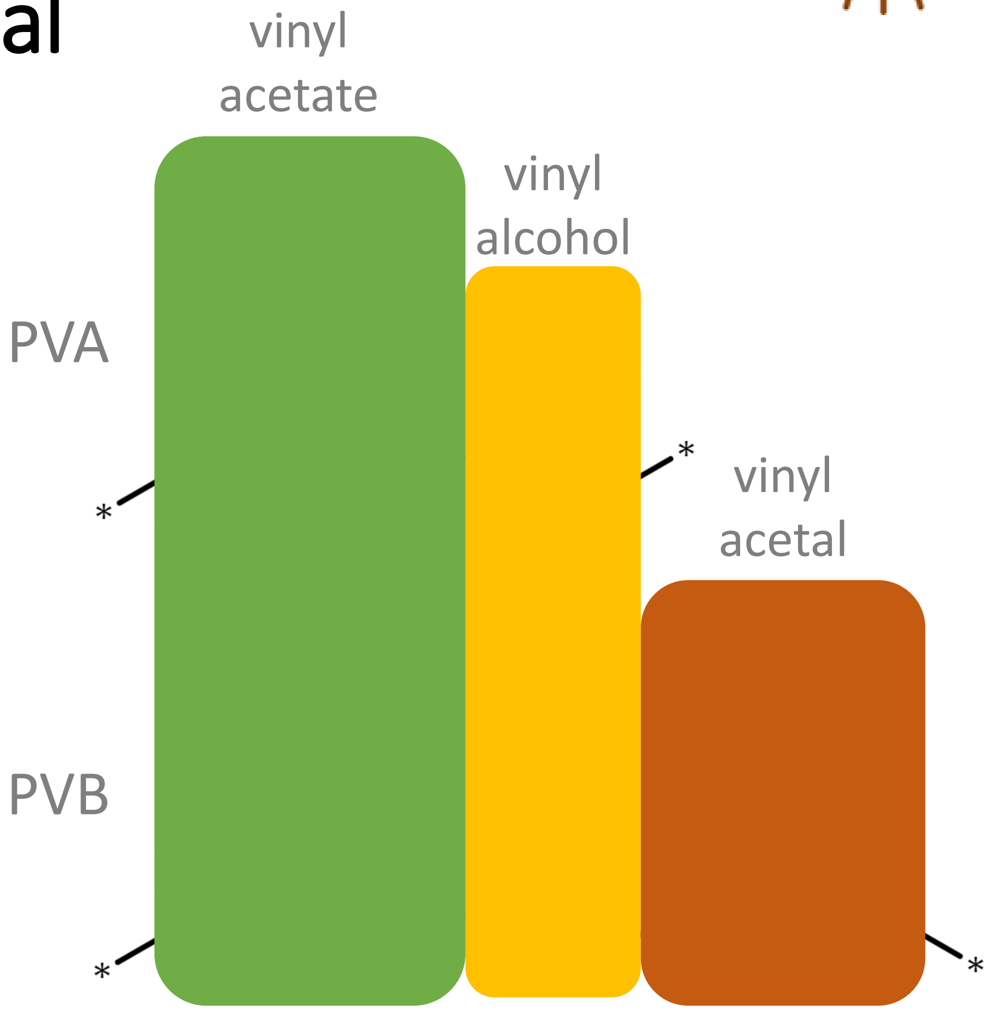
in fact, the departing water is not formed by the labeled atoms, but it is enough to give an idea

Polyvinyl acetal

- as with PVA and polyvinyl acetals, there is not always a complete conversion of the original substituents
  - of PVA there remain VAc and VA groups
  - the number of residual groups is therefore given



PVB



PVB

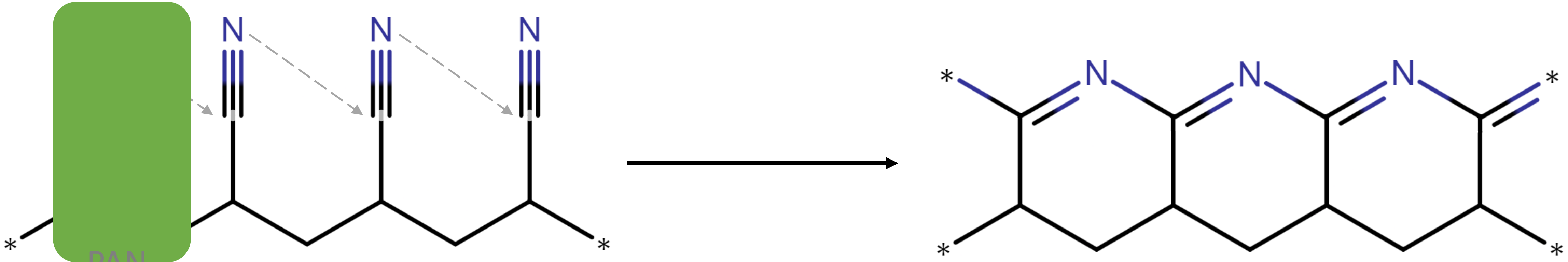
Grade	Non-volatile content (DIN 53216)	Content of polyvinyl alcohol [1]	Content of polyvinyl acetate [2]	Dynamic viscosity [3] 10 % solution in Ethanol [4]
	wt-%			mPa · s
Mowital B 14 S	≥ 97,5	[redacted]	[redacted]	9-13
Mowital B 16 H	≥ 97,5	[redacted]	[redacted]	14-20
Mowital B 20 H	≥ 97,5	[redacted]	[redacted]	20-30
Mowital B 30 T	≥ 97,5	[redacted]	[redacted]	30-55
Mowital B 30 H	≥ 97,5	[redacted]	[redacted]	35-60
Mowital B 30 HH	≥ 97,5	[redacted]	[redacted]	35-60
Mowital B 45 M	≥ 97,5	[redacted]	[redacted]	80-110
Mowital B 45 H	≥ 97,5	[redacted]	[redacted]	60-90
Mowital B 60 T	≥ 97,5	[redacted]	[redacted]	180-280
Mowital B 60 H	≥ 97,5	[redacted]	[redacted]	160-260
Mowital B 60 HH	≥ 97,5	[redacted]	[redacted]	120-280
Mowital B 75 H	≥ 97,5	[redacted]	[redacted]	60-100 [5]

[1] *Hydroxyl groups in terms of polyvinyl alcohol*

[2] *Acetyl groups in terms of polyvinyl acetate*

Preparation of cyclized PAN

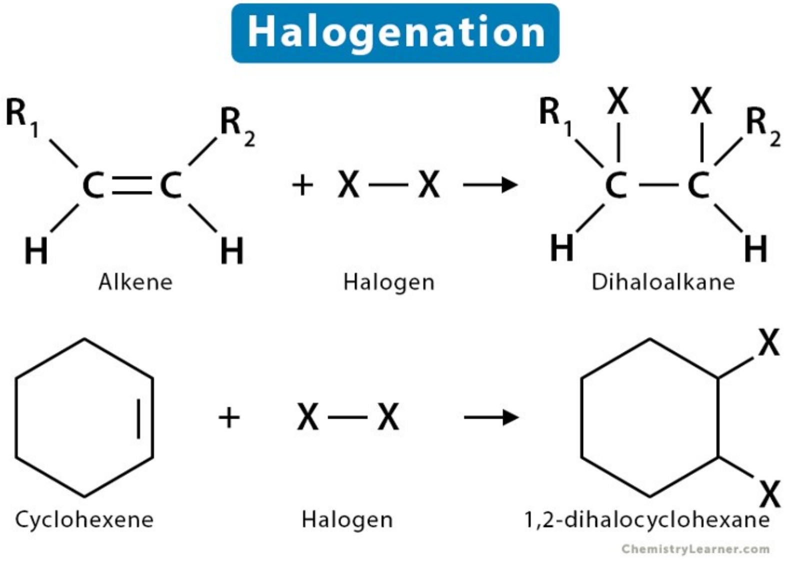
- high chain stability (heat resistance)
- conjugated double bonds (possibly conductivity) in a ladder-like arrangement
- is formed by intramolecular cross-linking of PAN
- it is one of the starting materials for the preparation of pure carbon fibers

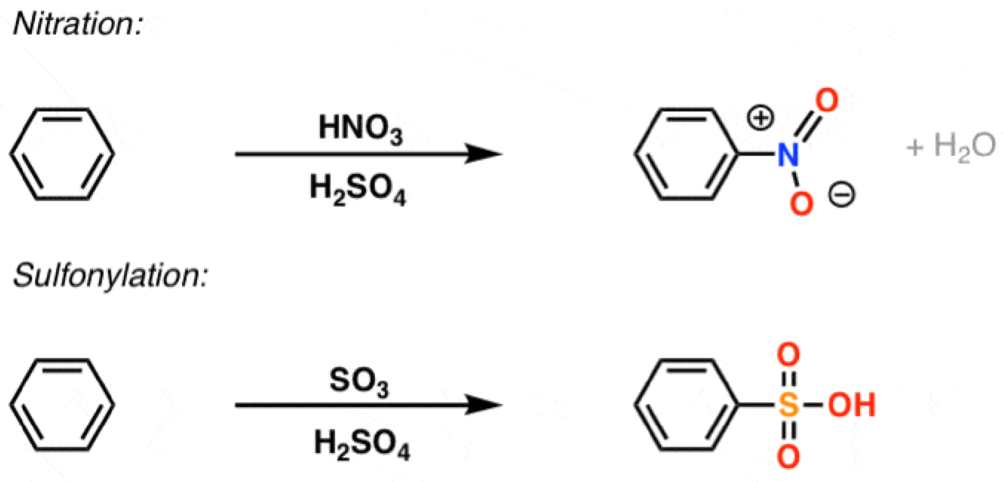


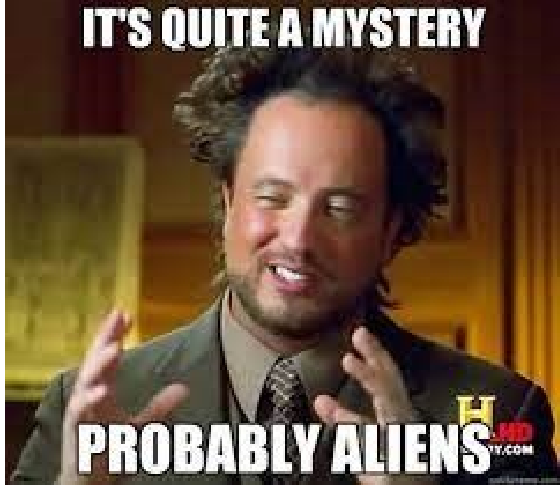
PAN

Introduction of new substituents

- halogenation, halogensulfonation, hydrogenation, nitration, sulfonation

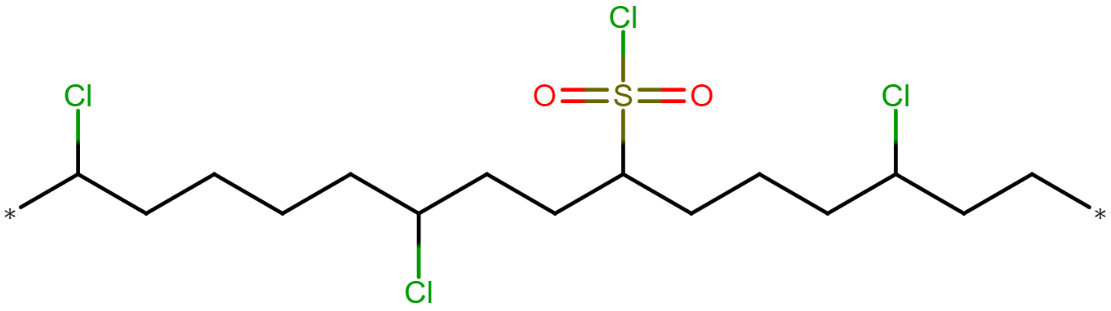






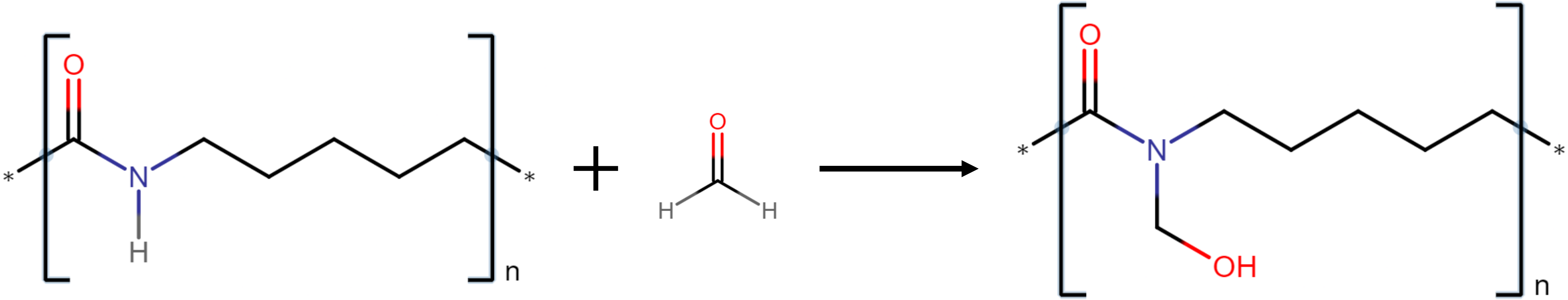
Chlorosulfonated PE

- CSM or less commonly CSPE
  - the meaning of the M at the end means saturated hydrocarbon chain (but still quite misterious symbol)
- production of synthetic rubber from PE
  - introduction of Cl_2 and SO_2 into a boiling solution of LDPE in tetrachloromethane with initiator (ABIN)
  - chlorine content approximately 25-40%
  - crosslinked with sulfur or peroxides (non-crosslinked is also used)
- does not proceed very well in the crystalline phase (hence LDPE)
  - inhomogeneous product in the case of more crystalline PE



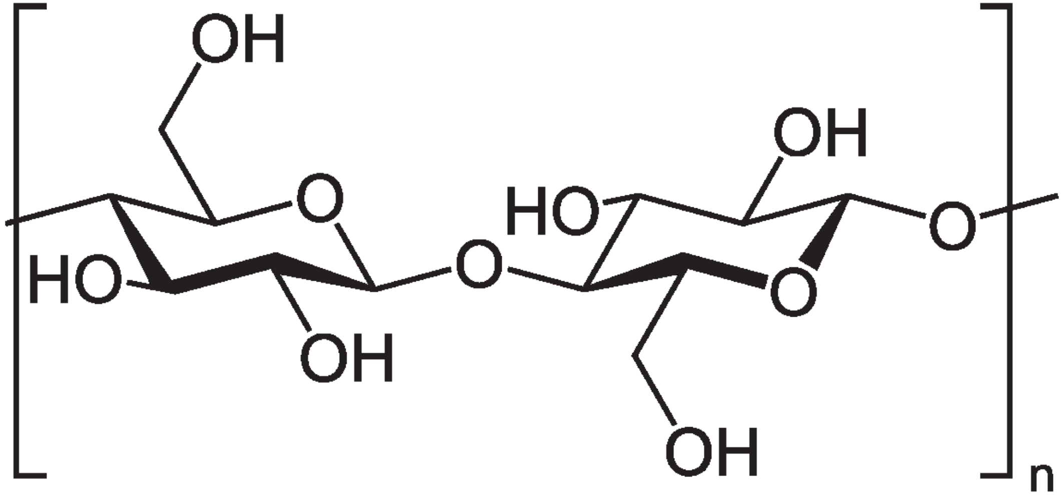
Modification of PA

- introduction of formaldehyde
  - increase in humidity



Cellulose reaction

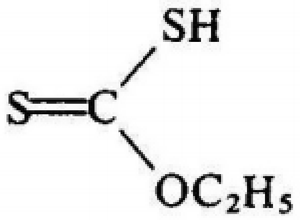
- cellulose
  - the most represented (by mass) polymer in the world
  - part of plant bodies (together with hemicelluloses and lignin)
  - a homopolysaccharide of β-D-glucopyranoses linked by a β-1,4 glycosidic (glycosidic) bond

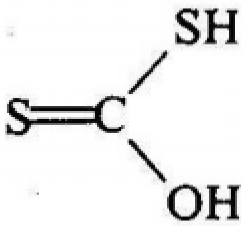


Viscose fibers and foils

- Abbreviation CV
- also referred to as regenerated cellulose
- preparation
    1. pulverized cellulose is converted to natron cellulose (sodium salt of cellulose) under the influence of NaOH solution
    2. by carbon disulfide (CS_2) it is converted to cellulose xanthogenate
    3. it is an esterification with xanthogenic acid and thiolthiocarbonic acid
    4. dissolution of xanthogenate in NaOH (formation of viscous solution → viscosity)
    5. ripening (about a week)
    6. filtration
    7. regeneration in a H_2SO_4, $ZnSO_4$ and Na_2SO_4 bath
    8. extrusion through nozzles (fibers - viscose silk) or foil casting (cellophane)

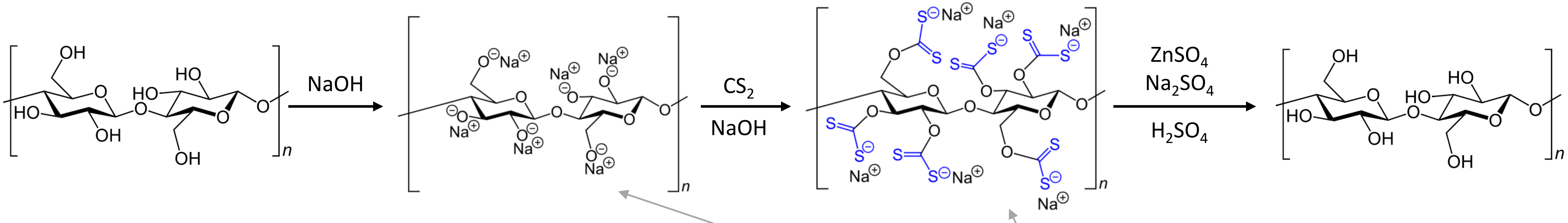
xanthogenic acid





thiolthiocarbonic acid

The formation of regenerated cellulose

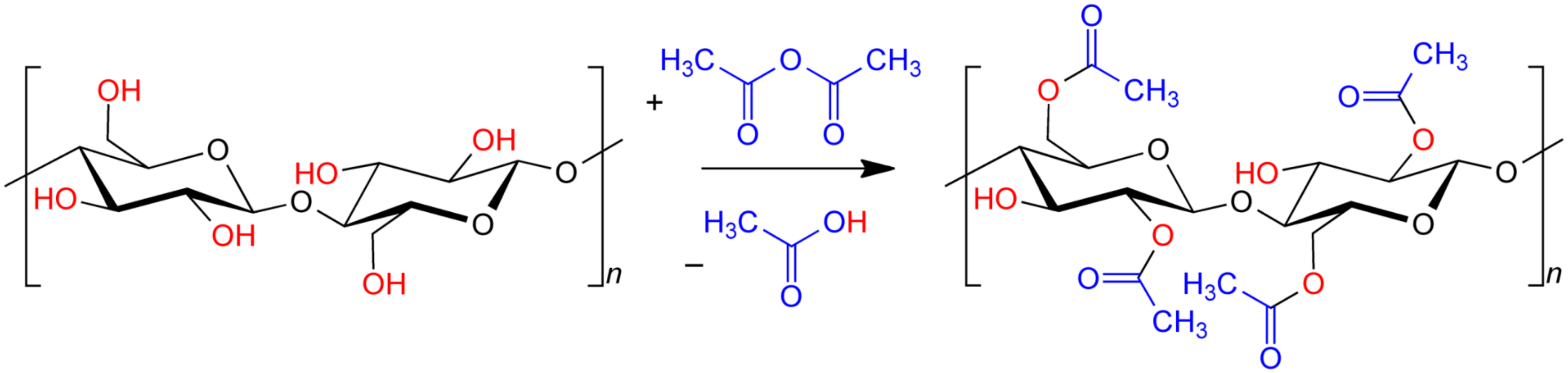


not necessarily all OH groups must react (the primary will almost certainly, the secondary may not)

1. cellulose
2. sodium cellulose
3. cellulose xanthogenate
4. viscose (xanthogenate dissolved in NaOH solution)
5. regenerated cellulose (viscose silk or cellophane)

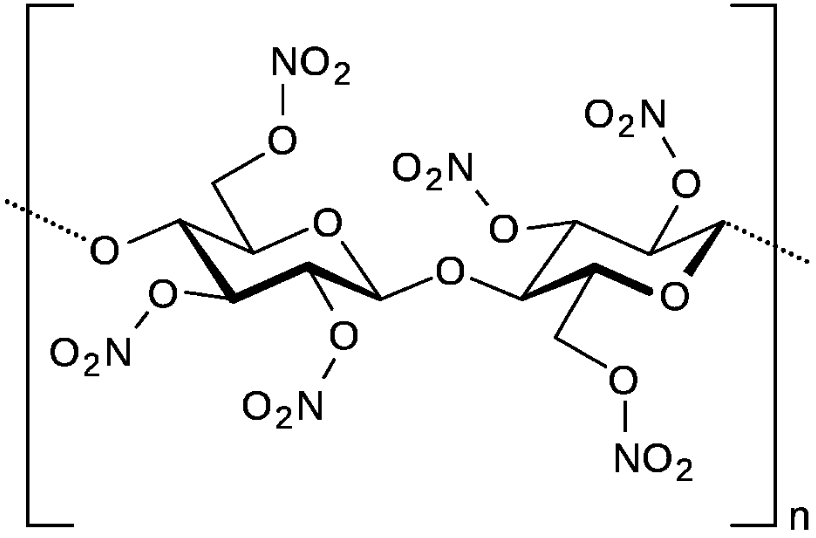
Cellulose esters

- cellulose acetate (CA)
  - introduction of acetate groups to cellulose hydroxyls
    - hardly usable when all three hydroxyls react → necessity of additional hydrolysis back to –OH
    - average number of acetates per glucopyranose unit between 2.2 – 2.9 (out of 3 total)



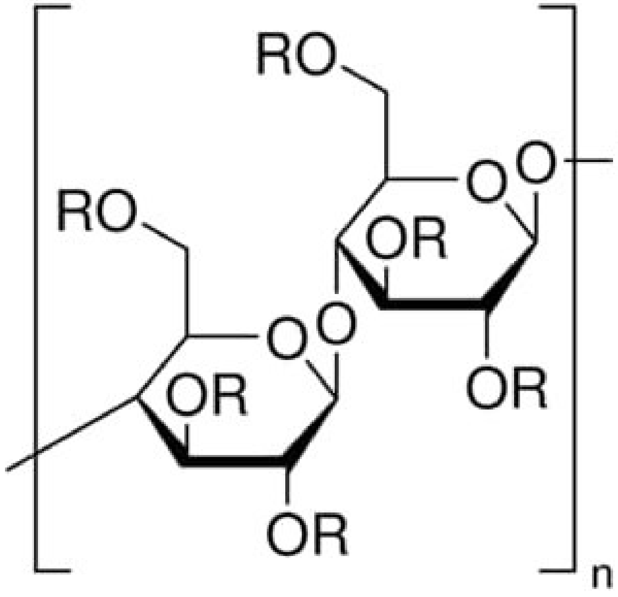
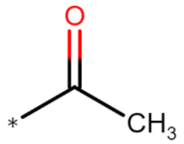
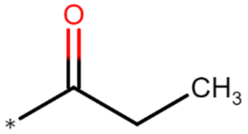
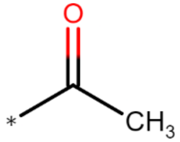
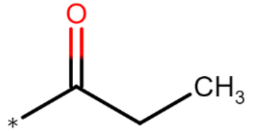
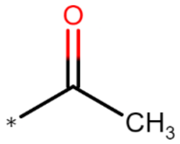
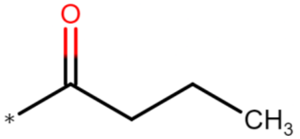
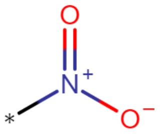
- introduction of additional ester groups
  - propionate (CP)
  - mixed esters acetopropionate (CAP), acetobutyrate (CAB)

Cellulose nitrate



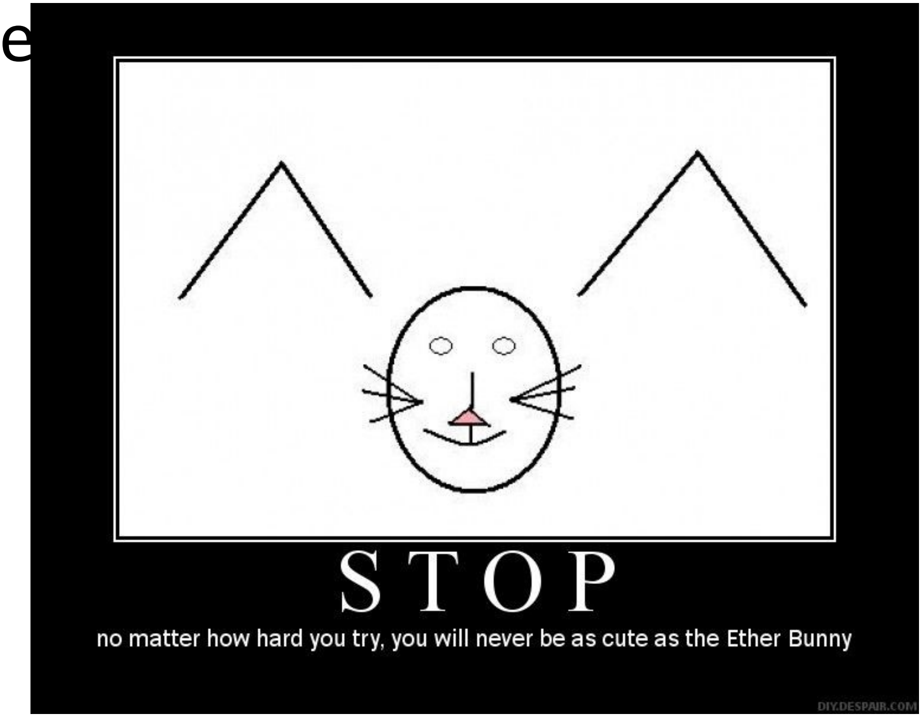
- it is another cellulose ester
- is formed by the action of HNO_3 on cellulose in the presence of another acid (most often sulfuric, less phosphoric or acetic)
  - with theoretical esterification of all 3 OH groups, the N content would be about 14.14%
    - is not produced
  - nitrates with N content 10 – 11%
    - paint materials, celluloid (after addition of camphor)
  - nitrates with an N content of 11.8 – 12.5% with resins and solvents
    - nitro lacquers
  - nitrates with N content 12 – 13.5%
    - explosives (smokeless gunpowder)
- incorrectly nitrocellulose (difference between nitro and nitrate)

Cellulose esters

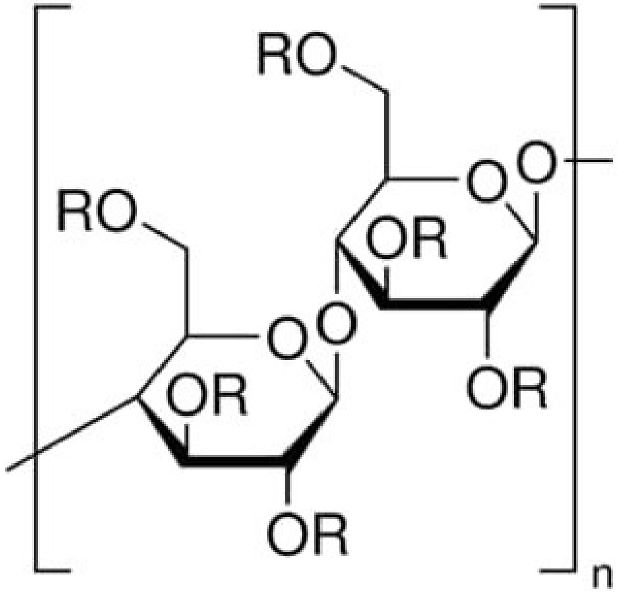
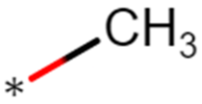
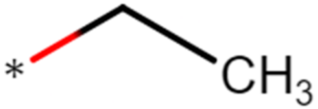
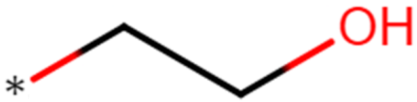
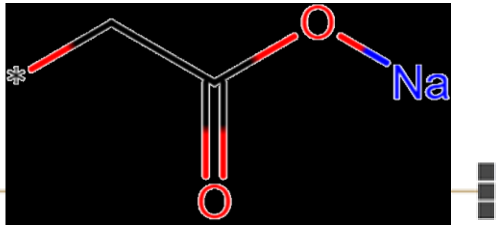
term	*abbreviation*	*general structure*	*R substituents*
cellulose	-		-H
cellulose acetate	CA		
cellulose propionate	CP		
cellulose acetopropionate	CAP		 a 
cellulose acetobutyrate	CAB		 a 
cellulose nitrate	CN		

Cellulose ethers

- for the production of adhesives and thicke
  - some soluble in water
- dependent on the degree of substitution
- examples
  - (methyl)cellulose
  - (ethyl)cellulose
  - (hydroxyethyl)cellulose
  - (carboxymethyl)cellulose

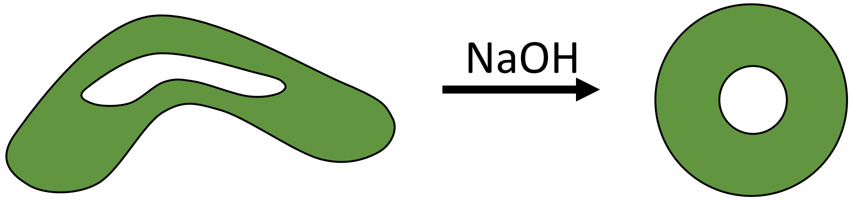


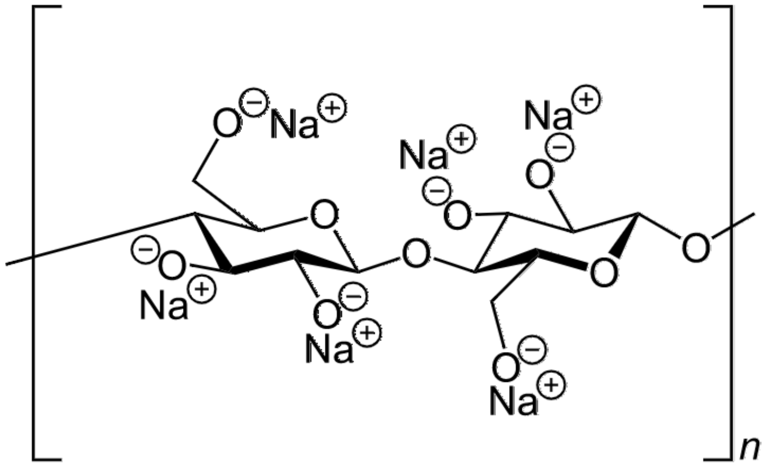
Cellulose ethers

term	*abbreviation*	*general structure*	*R substituents*
cellulose	-		-H
(methyl)cellulose	MC		
(ethyl)cellulose	EC		
(ethylhydroxy)cellulose	HEC		
(karboxymethyl)cellulose	CMC		

Mercerization of cellulose

- formation of sodium salt due to NaOH (not all OH groups need to react)
  - takes place under voltage
  - (does not apply to viscose)
  - the kidney-shaped cross-section of the fiber changes to a round one
  - improvement:
    - tensile strength
    - shine
    - digestibility
    - the quality of the sauce





II. Reactions accompanied by a change in the degree of polymerization

Reactions accompanied by a change in the degree of polymerization

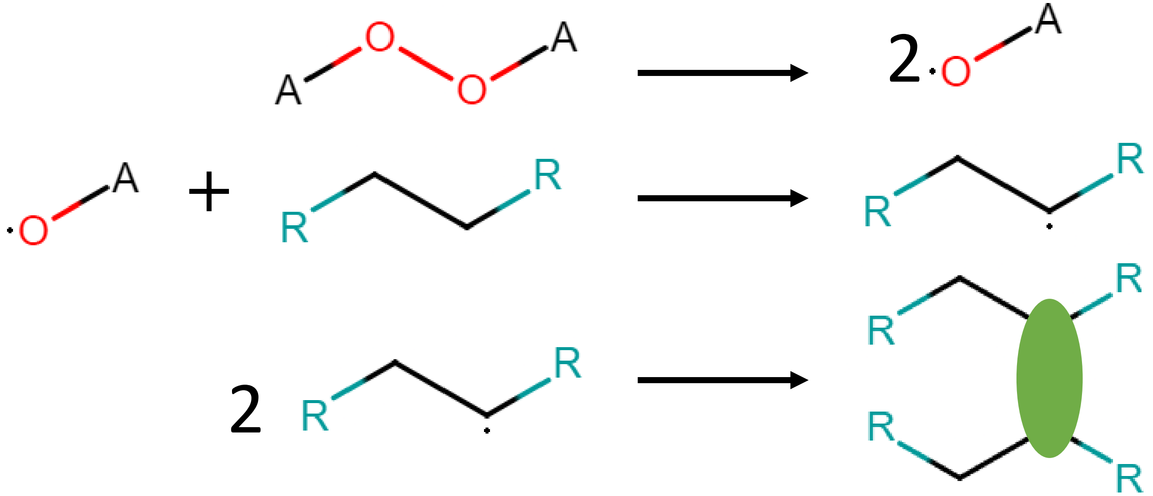
- grow
  - graft
  - linking macromolecules (block polymers)
  - for both see the previous lecture Copolymers
- networking
  - connecting polymer chains using covalent bonds to form a spatial network
  - loss of solubility and fusibility
    - they do not dissolve in the solvent, they can at most swell (swell)
  - lose thermoplasticity (become infusible)
  - resistance to elevated temperatures, chemicals, hardness increases
    - the more densely cross-linked, the worse the penetration of molecules of low mole
  - swelling and humidity decrease
  - used in:
    - rubbers
    - polyolefins
    - PES resins
    - epoxy resins
    - phenol formaldehyde resins
    - superabsorbent polymers

Crosslinking of polyolefins

- crosslinking with peroxides (at a temperature of 200 °C in a nitrogen atmosphere)
  - radical reaction
  - fission or chain branching can also occur (radicals are very reactive)
- the degree of crosslinking can be improved by introducing suitable comonomers during polymer production
  - depending on the desired network density, I can build a few multifunctional groups into the macromolecules, which I will later use for crosslinking the whole

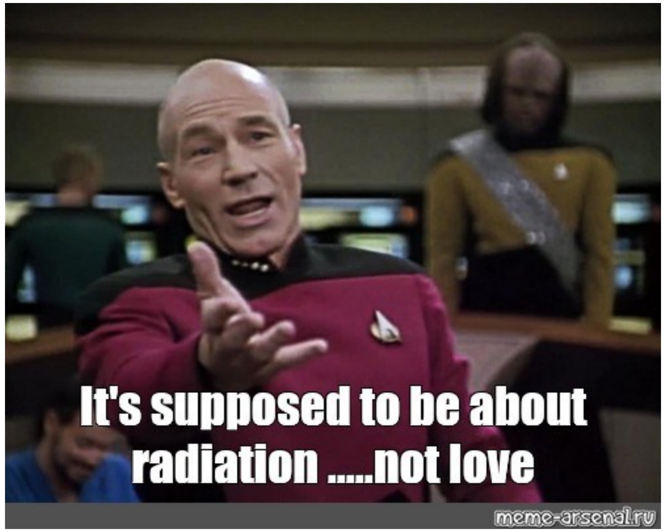
Crosslinking of polyolefins

- crosslinking with peroxides (at a temperature of 200 °C in a nitrogen atmosphere)
    - radical reaction
    - chain breaking or branching can also occur (radicals are very reactive)



Radiation cross-linking

- radical cross-linking again
- high-energy radiation ruptures molecules to form radicals, which then cross-link macromolecules with each other
    - possible problem with the penetration of radiation into the depth of the product

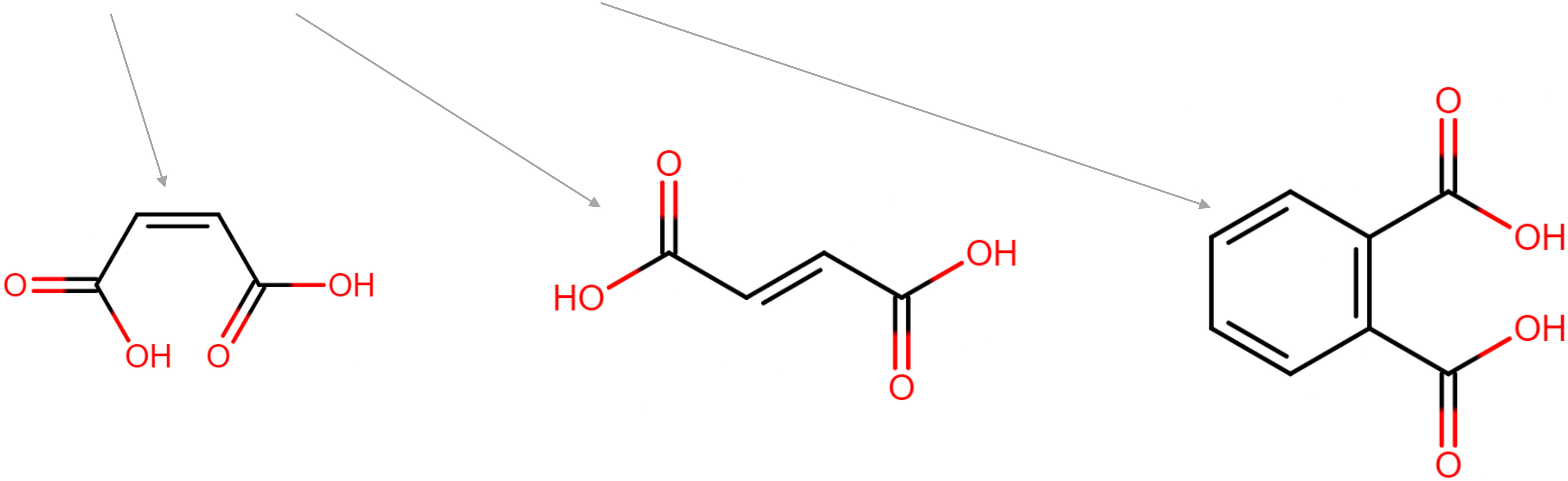


Crosslinking of unsaturated PES resins

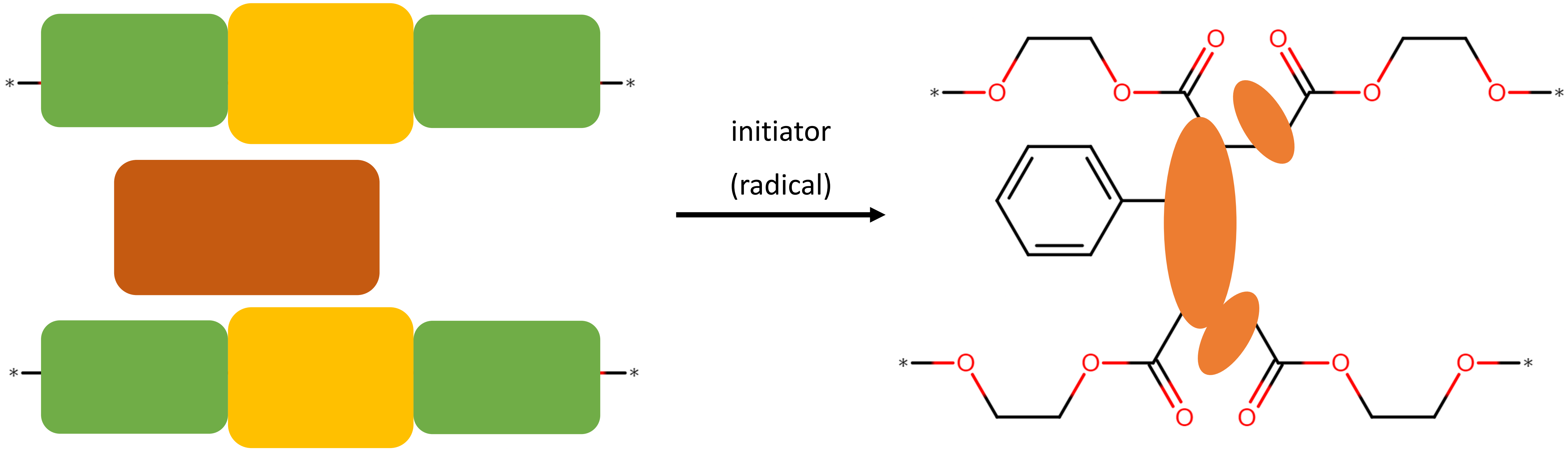
- solutions of linear unsaturated PES in monomers polymerizing by chain mechanism
  - are prepared by polycondensation of mixtures of saturated and unsaturated dicarboxylic acids (or their derivatives) with diols
    - maleic, fumaric or phthalic acid (or their anhydrides)
      - ensure the unsaturation of the resulting product
    - ethane-1,2-diol or propane-1,2-diol
  - monomers are most often styrene, less often methyl methacrylate, vinyltoluene, etc.
- the radical reaction of unsaturated PES resins with styrene creates styrene bridges (crosslinking)

Crosslinking of unsaturated PES resins

- maleic, fumaric or phthalic acid (or their anhydrides)

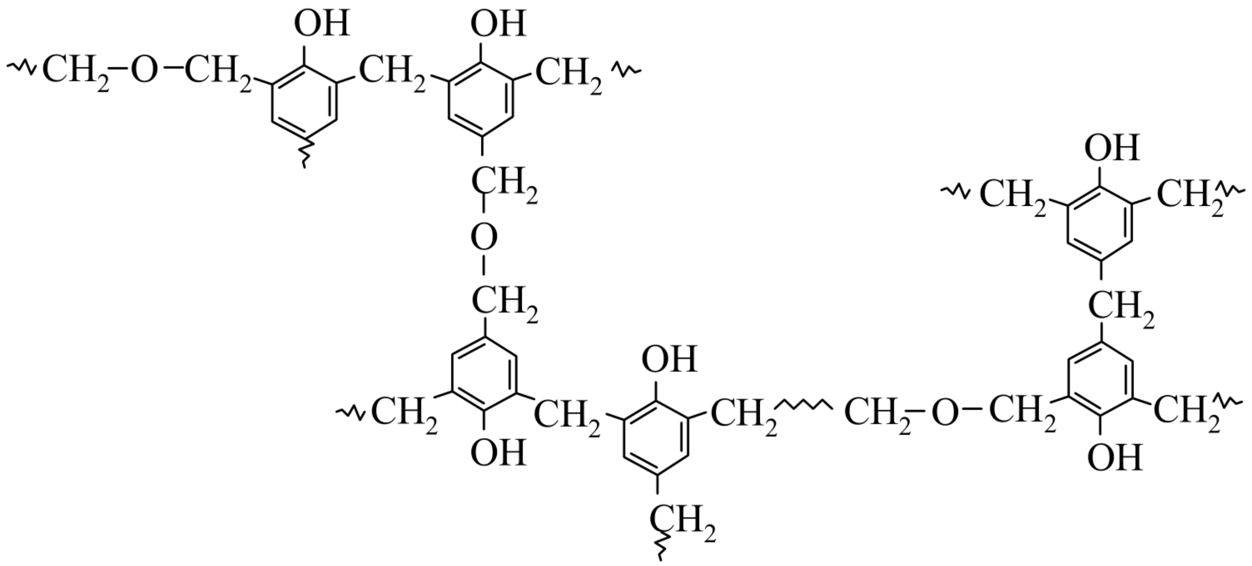


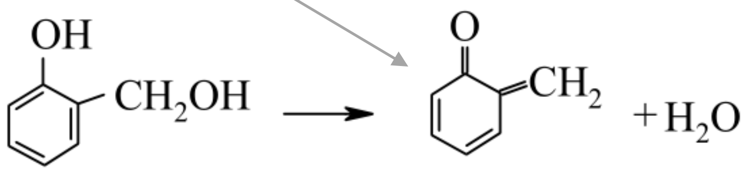
Crosslinking of unsaturated PES resins



Crosslinking of phenol-formaldehyde polymers - resins

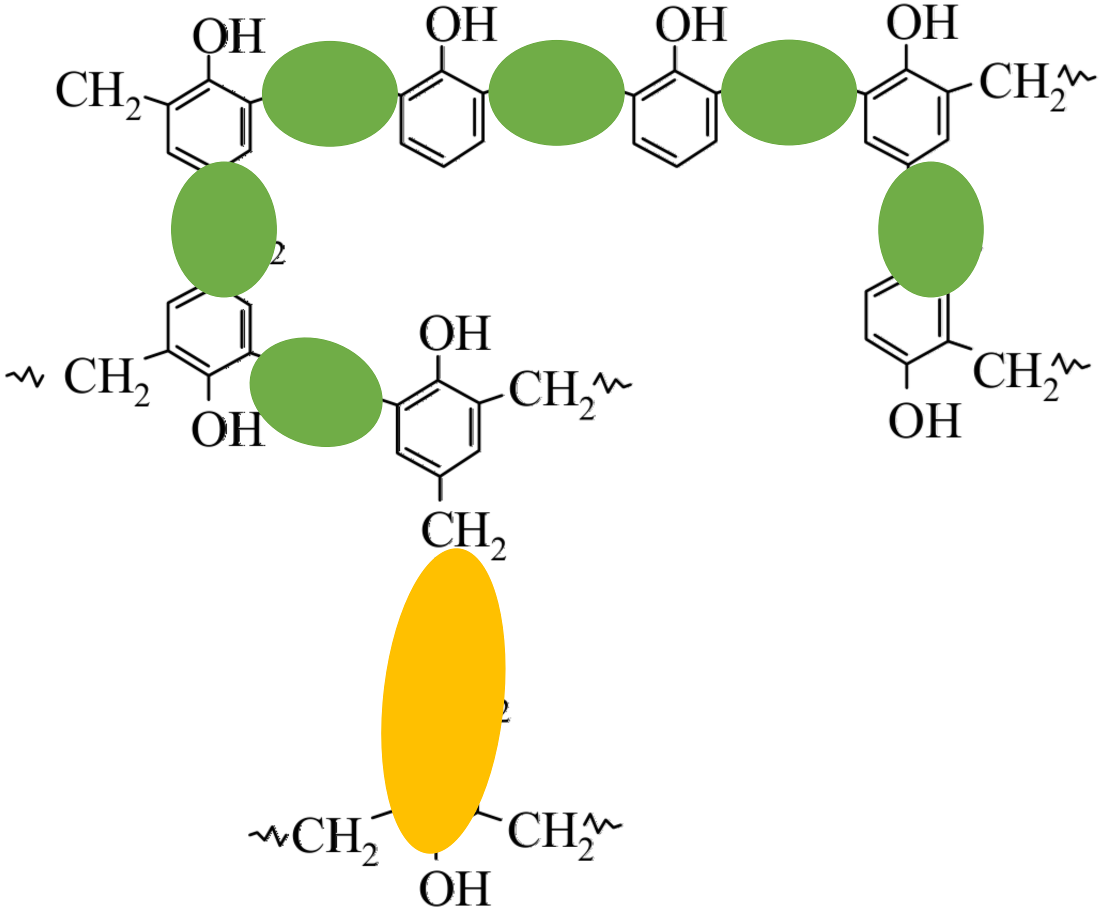
- resins are formed by cross-linking resols
  - takes place in an acidic environment at higher temperatures (180 °C)
    - methylene (-CH_2-) or methyl ether bridges (-CH_2-O-CH_2-)
    - the higher the temperature, the more methylene bridges prevail over methyl ether bridges
- brown-red coloration caused by the formation of quinone methides (their conjugated double bonds absorb visible radiation) during the thermal splitting of water from methylolphenols during cross-linking





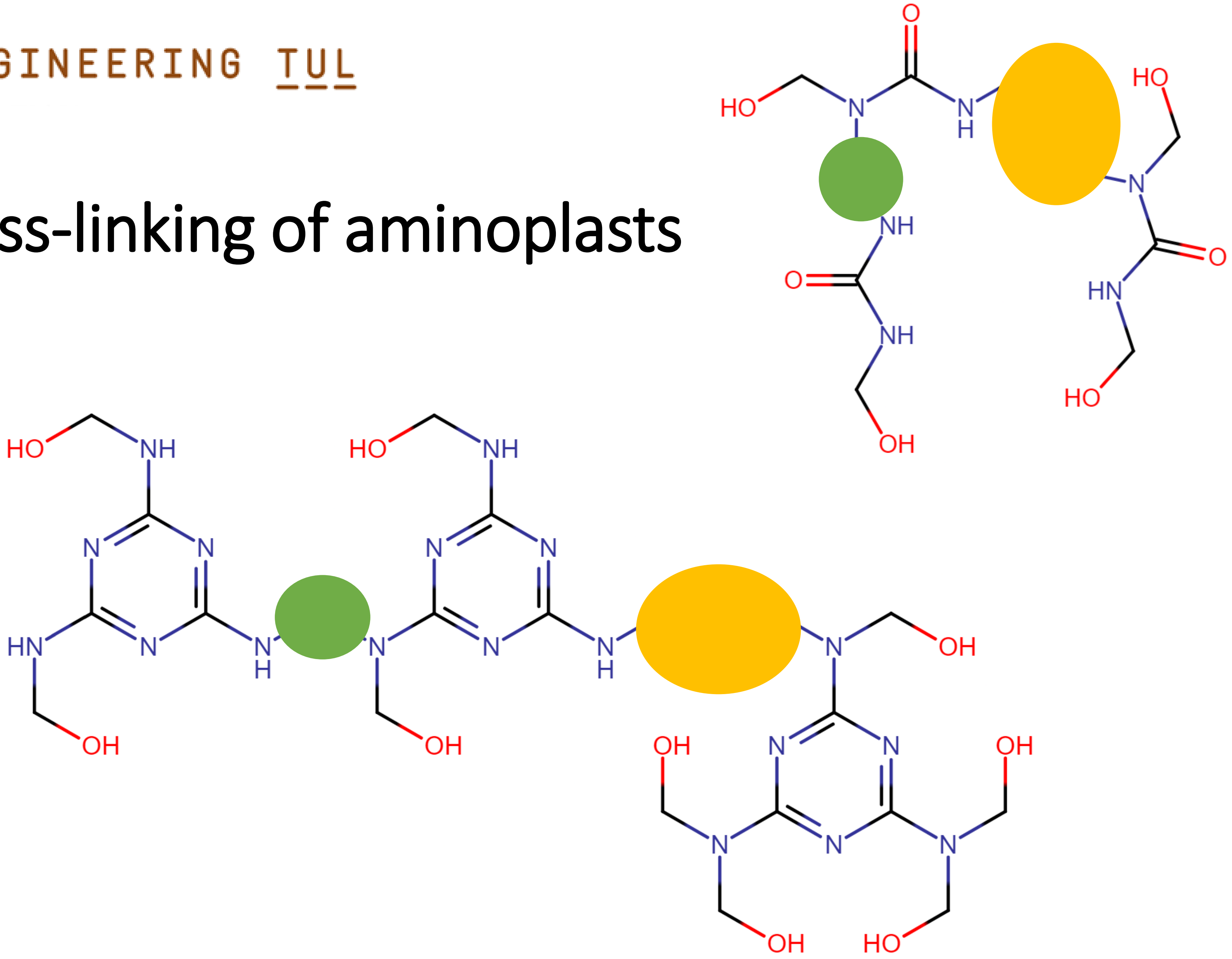
Cross-linking of phenol-formaldehyde polymers – phenol-formaldehyde resins

- cross-linking of novolacs with formaldehyde-releasing substances (e.g. hexamethylenetetramine with water) at higher temperatures (160 °C)
  - [redacted]
  - [redacted] (Ph-CH$_2$-NH-)



Cross-linking of aminoplasts

- again increased temperature and acidic environment
- again 🟩 and 🟨 bridges
- due to the high functionality of urea and melamine, a very dense network is created



Sulfur crosslinking of elastomers - vulcanization

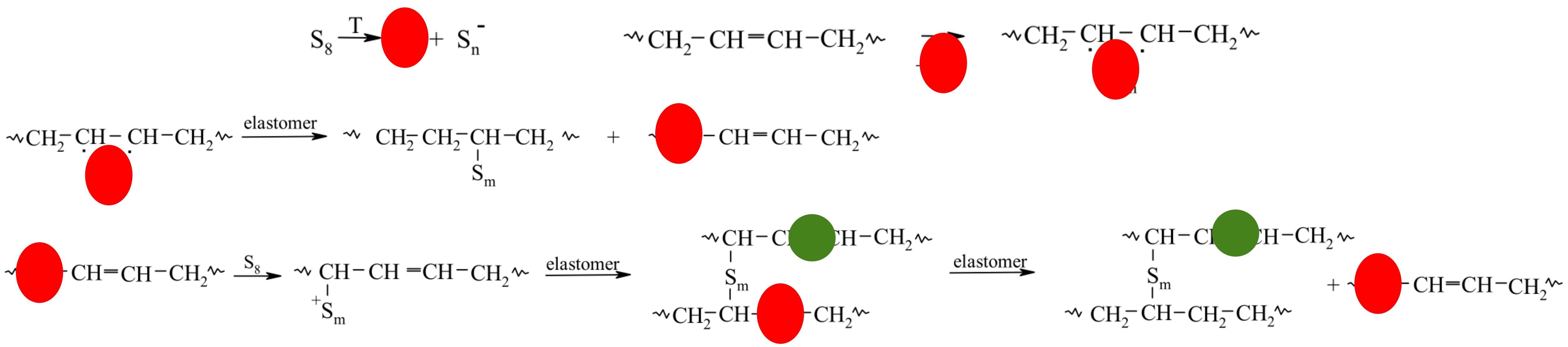
- the most common cross-linking reaction
  - action of sulfur and heat (around 140 °C)
- can be used for practically all butadiene homopolymers and copolymers
- the product of elastomer vulcanization is rubber
  - other additives are added to the final products (fillers, dyes, UV stabilizers, etc.)
- resulting properties dependent on the amount of sulfur
  - is determined in parts by weight of sulfur per hundred wt. rubber parts (phr)
    - soft rubber - up to about 4 phr
    - semi-hard – usually 12 to 25 phr
    - hard (ebonite) – 25 to 50 phr

Sulfur crosslinking of elastomers - vulcanization

- it doesn't work very well without other substances
- in this case, the sulfide bridges are quite long after vulcanization (40 to 50 sulfur atoms)
  - bridges on neighboring atoms and cyclic sulfide structures do not particularly help physically
  - therefore accelerators and activators are used
- the average number of sulfur atoms is reduced to about 1.6
  - no cyclic structures or bridges are formed on neighboring atoms
- activators
  - ZnO, stearic acid
  - accelerators
  - 2-mercaptobenzthiazole, tetraalkylthiuram disulfide, zinc salts of dialkyldithiocarbamates

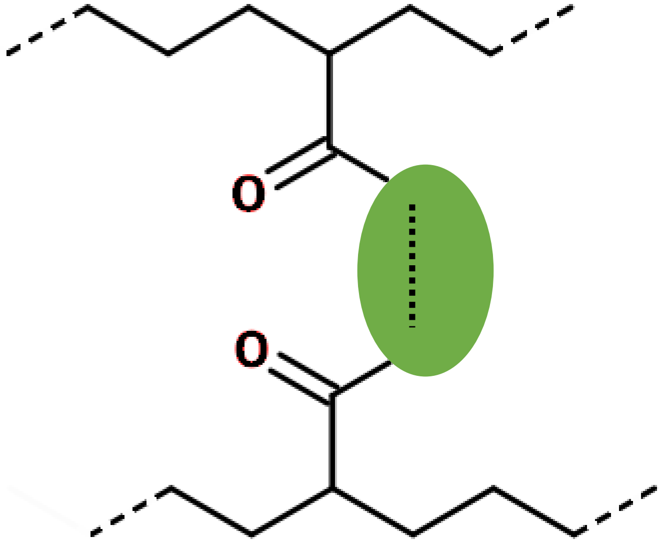
Sulfur crosslinking of elastomers - vulcanization

- probably takes place through an ionic mechanism
  - observe the positive charge to understand the reaction
  - the interesting thing is that both double elastomers do not participate in the cross-linking reaction, but only one - the other thus remains in the structure



Ionomers

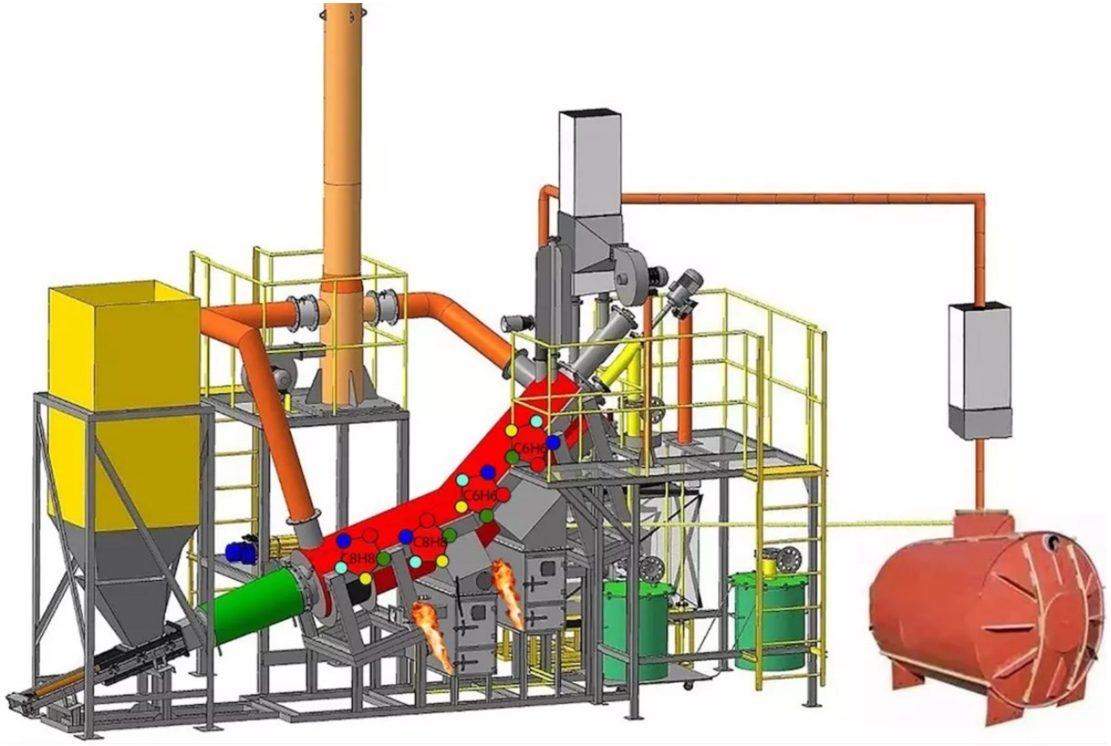
- crosslinking bonds are not covalent but ionic (or hydrogen)
- copolymer of ethene and 5-10% acrylic or methacrylic acid
  - carboxyl groups can be neutralized to form an acrylate or methacrylate salt (Na, Ca, Mg, Zn, Al, Ba)
  - it is not a static network and monovalent ions (Na) contribute to its strength
- with enough temperature I can disrupt the network without degrading the macromolecules themselves
  - can be melted and after cooling I get the network again
- physically they behave similarly to thermoplastic elastomers



Depolymerization and degradation of polymers

Depolymerization of polymers

- the opposite of polymerization reactions
  - there is a gradual splitting off of the mers from the ends of the macromolecules
  - molecular weight decreases gradually
- sometimes the monomer can be recovered in this way
  - Opus Magnum of ecologically based macromolecular chemists
  - the Czech product ERVOeco comes a little closer to that
- depolymerization is usually caused by higher temperature
  - it must not be overdone, otherwise the polymer would begin to degrade
  - sometimes it can also be started chemically (e.g. depolymerization of cellulose due to alkaline pH)
- they dopolymerize well with polymers that
  - have quaternary carbon (e.g. PMMA),
  - or can stabilize a reactive intermediate with a conjugated structure (e.g. PS)

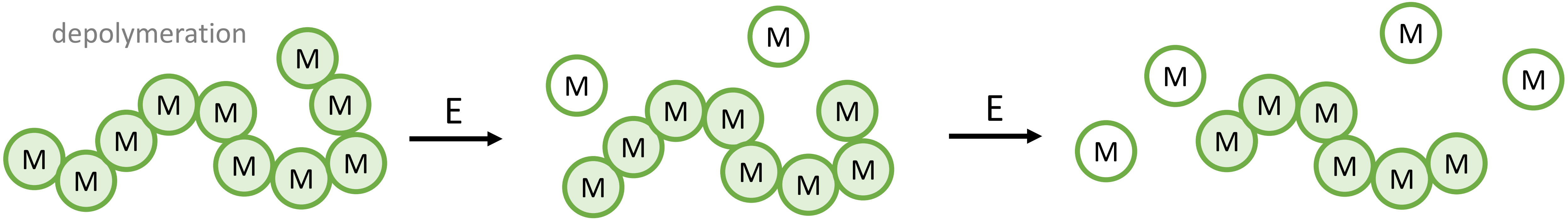


Polymer degradation

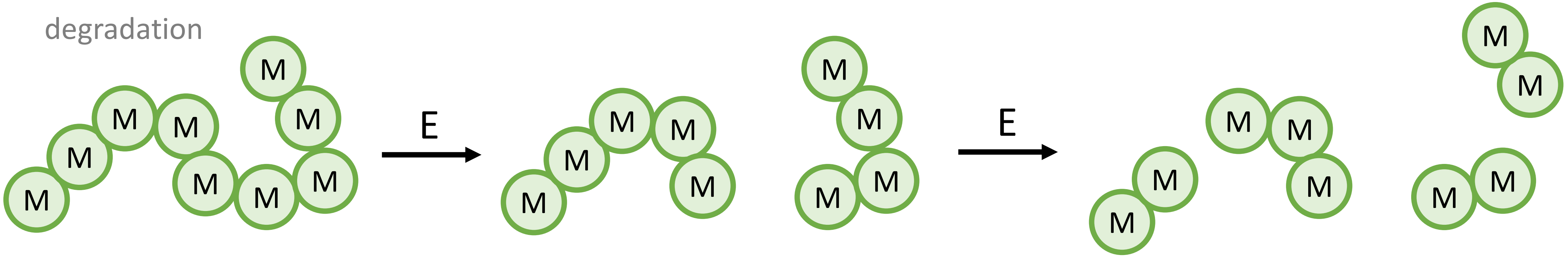
- primary bonds are split at a random location in the chain
  - occurs when the energy of the external action is greater than the strength of the bonds in the main chain
- accompanied by a deterioration of the useful properties of the polymer
  - in particular, there is a reduction in strength, a change in color, the polymer becomes more brittle,...
- occurs by:
  - heat
  - radiation (light, UV, high energy)
  - oxygen
  - water
  - enzymes
  - mechanical stress
  - most often a combination of the previous one

The principle of depolymerization and degradation

depolymeration

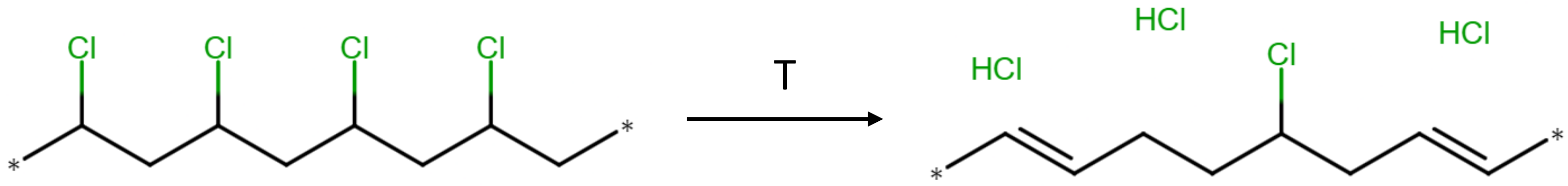


degradation



Thermal degradation in an inert atmosphere

- effective heat
  - generally pyrolysis
- first the chains are split
- subsequently sufficiently low molecular weight substances escape in the form of gases
  - stable low molecular weight substances can form liquid oily products
  - eventually the residue will char (if it has a carbon base)
  - can occur together with depolymerization (PS)
- sometimes the bonds of the substituents to the main chain are weaker than those in the main chain
  - primary cleavage of substituents then occurs



Thermooxidative degradation

- combination of heat and oxygen
  - if the temperature is high enough, it will usually burn at some stage
- initiation
  - depends on structural defects
  - the presence of benzene nuclei or double bonds (they like to absorb radiation)
  - the accelerating element of initiation are transition metal compounds
    - Fe, Mn, Ni, Cu
- bond breakage
  - most often tertiary carbons are attacked by oxygen compounds
  - hydroperoxides are formed, which break down the chains

$$R^* + O_2 \longrightarrow R\text{-}O\text{-}O^*$$

$$R\text{-}O\text{-}O^* + RH \longrightarrow R\text{-}O\text{-}O\text{-}H + R^*$$

Photooxidative degradation

- it is not necessary for the polymer to burn, even energy from the sun will suffice (even if it will go slower)
  - occurs when the radiation energy overcomes the strength of the bond
  - the rate of decay depends on the wavelength of the light and the energy of the radiation
    - less than 330 nm (i.e. UV) is required for cleavage of C–C or C–H bonds
    - in the case of double bonds, a light wavelength of 350 nm is sufficient
    - therefore, UV absorbers are added to polymers
- the rate of photochemical reactions depends on the presence of groups that absorb in the 300-350 nm region
  - aldehydes, ketones, hydroperoxides
- radiation is absorbed by groups of atoms, subsequently radicals are formed and the chain breaks down

Hydrolysis and alcoholysis

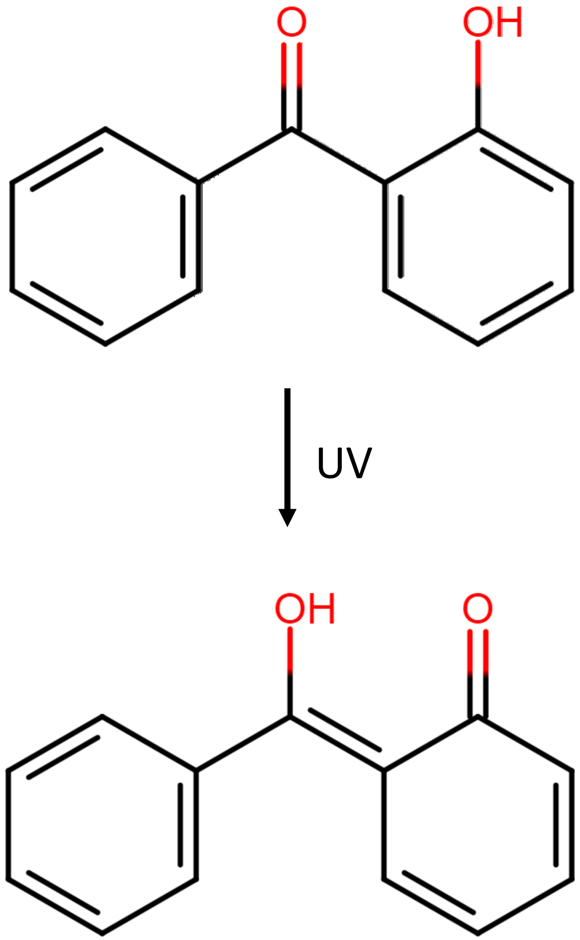
- these are reactions in which the main medium is water (or alcohol) and ions
  - thus, an –OH group is usually formed at the point of bond breaking
  - can be considered the opposite of some condensation reactions (e.g. esterification or amidification)
- polymers with heteroatoms in the chains are most often subject to hydrolysis
  - cellulose, PES, PA, PUR
- use in the processing of PET waste
  - splitting into starting substances
- application in healthcare
  - absorbable surgical sutures
    - polyglycolic acid
    - polycaprolactone

Mechanical demolition

- it is mainly used during the so-called plasticization (mastification)
  - facilitates processing
  - reduces and unifies molecular weights
- degradation occurs through mechanical action
  - while extruding the polymer from the nozzle at its sharp mouth
  - by kneading between two rollers rotating at unequal speeds
- usual for rubber compounds

Polymer stabilization

- reducing the rate and impacts of degradation
- two methods
  - absorptive
    - the stabilizer absorbs the energy or influence of the harmful effect
      - in the process they can be consumed (retarders) or can be regenerated
        - they will use the incoming energy for their own transformation, and the rest of the unused energy is no longer sufficient to degrade the polymer bonds
        - the second option is to stabilize the intermediate so well that it does not want to react further (stabilization of radicals by aromatics)
    - carbon black, UV absorbers, antioxidants etc.
  - reflexive
    - the stabilizer prevents harmful influences from coming into contact with the polymer
- coatings, foils, films



Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

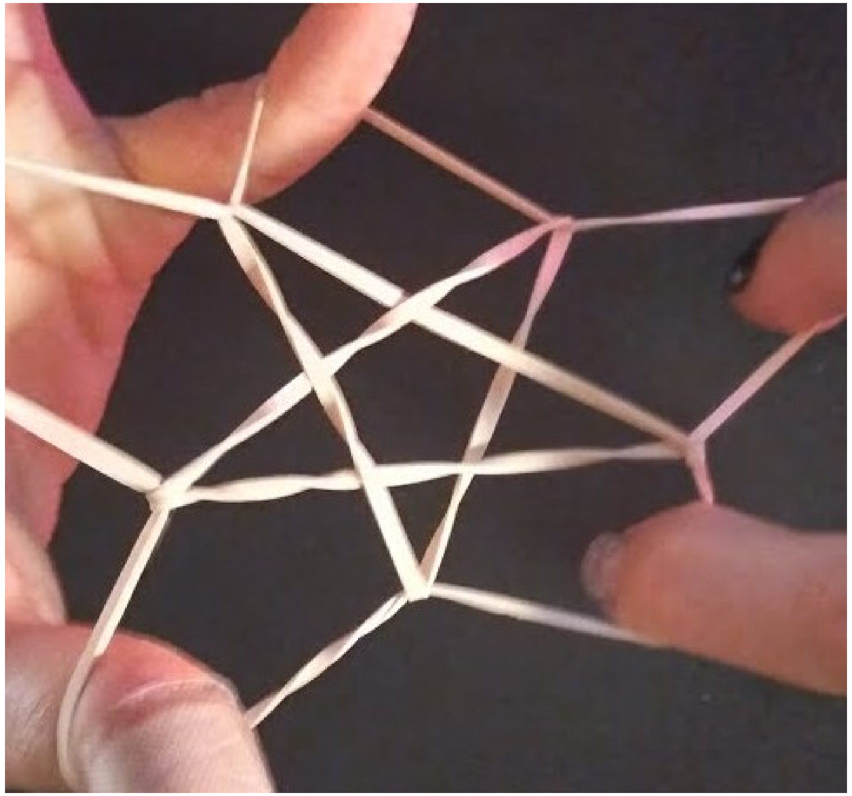
Národní plán obnovy

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Elastomers

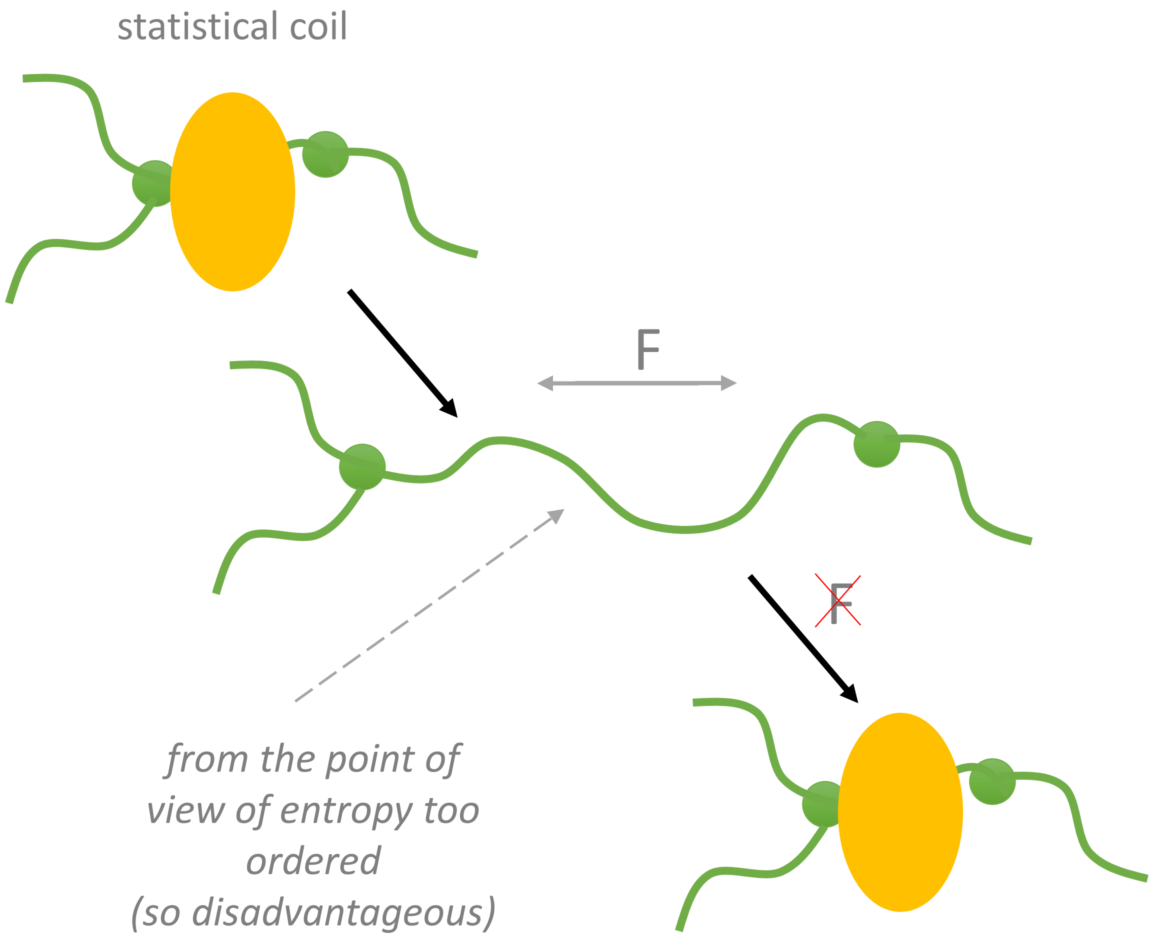
Elastomers

- definition:
  - a material which, within its application temperature, is capable of quickly, mostly reversibly deforming with a small force by at least 100% of its original length
    - its elastic limit is low at a high rate of relative deformation
  - exhibits rubbery properties usually over a wide range of temperatures
- can generally be divided into:
  - rubber
    - elasticity ensured mainly by chemical knots
  - thermoplastic elastomers
    - elasticity ensured mainly by physical knots
    - ionomers are a special kind



Rubbery elasticity

- entropy driven plot
  - between the nodes of the network (chemical or physical), the chains are coiled into the most energetically stable (poorest) form of the so-called statistical coils
  - due to the mechanical force, the coil untangles and the chains are stretched - but this is not an energetically advantageous arrangement of the chains
  - after the end of the stress, the chains want to return to the energetically advantageous arrangement of the coils and thus tangle back to approximately their original form
    - the coils will certainly not be rolled in the same way, but their size (radius of gyration) will be the same as in the initial state



from the point of view of entropy too ordered (so disadvantageous)

Knots

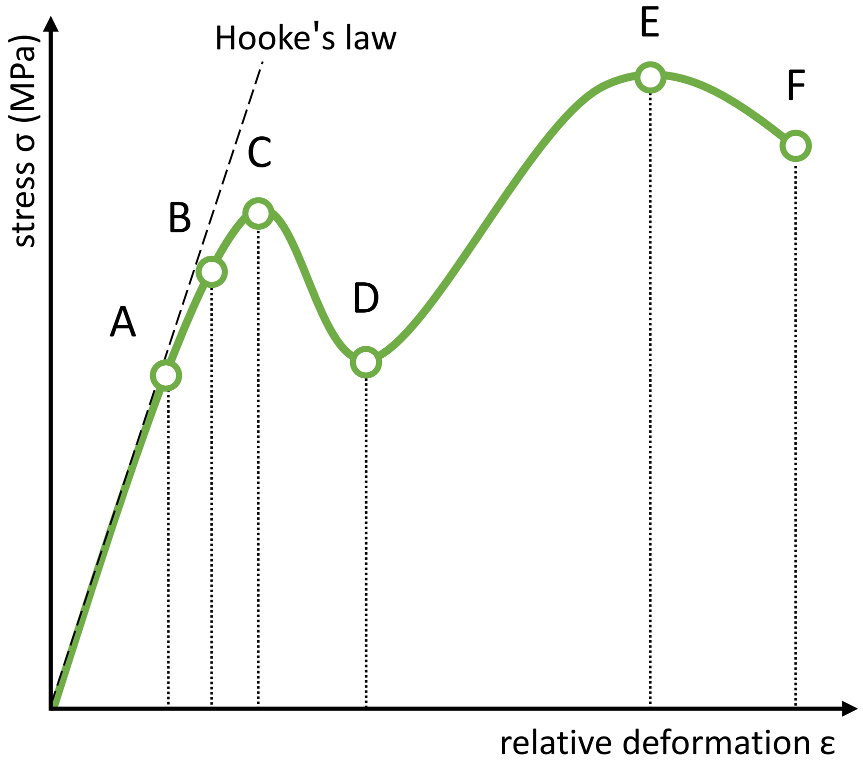
- a place in the structure of a macromolecule that firmly fixes two or more chains or parts thereof together
  - chemical knot
    - it can be a chemical bond or a binding side chain
    - the nature of cross-linking reactions
  - physical
    - really knotted strings
    - crystallites
- they support elastic behavior

Graph of deformation

- dependence of stress on the elongation of the body
  - by tension we mean the force F on the cross-section of the body S
    - therefore it has a unit of pressure
  - first reversible (elastic) deformation
  - perfectly flexible to A
  - almost perfectly flexible to B
    - then irreversible (plastic) deformation
  - finally rupture (F)
- Hooke's law

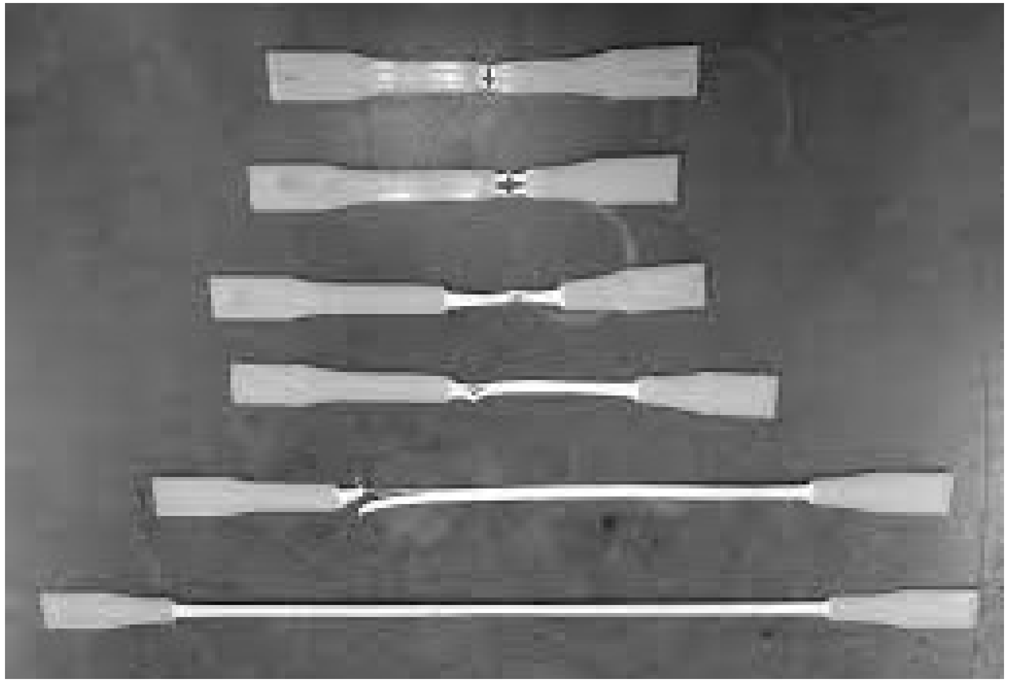
$$\sigma = E\varepsilon$$

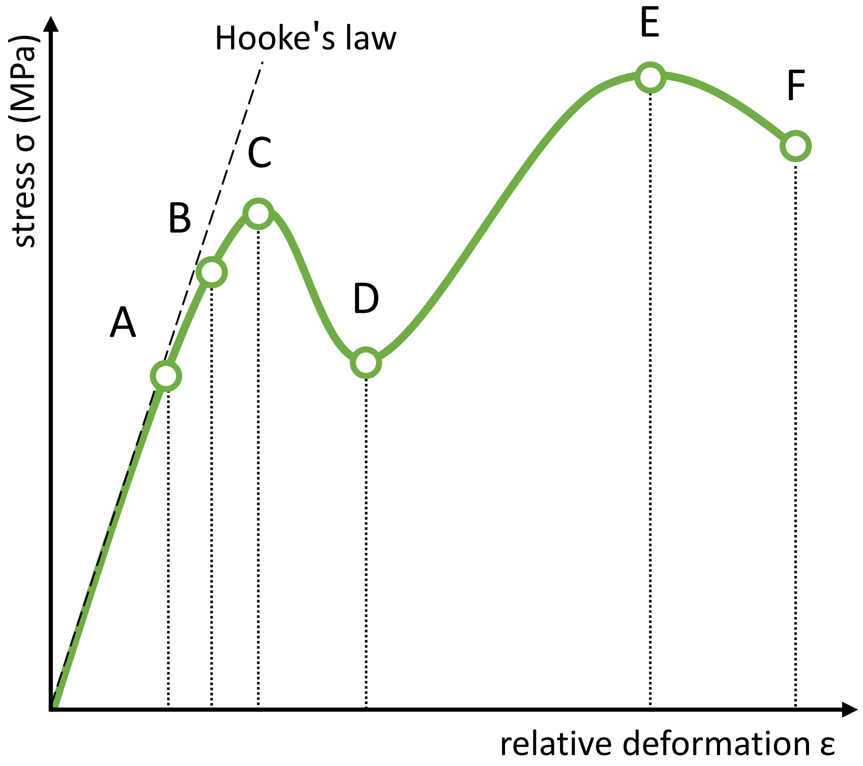
  - direct relationship between stress and strain
  - valid until A, usable until B
    - elastomers have a proportionality constant E (Young's modulus of elasticity) in the order of units to low tens



A	...	*limit of proportionality*	D	...	*lower yield point*
B	...	*elastic limit*	E	...	*strength limit*
C	...	*upper yield limit*	F	...	*breaking point*

Tensile test result

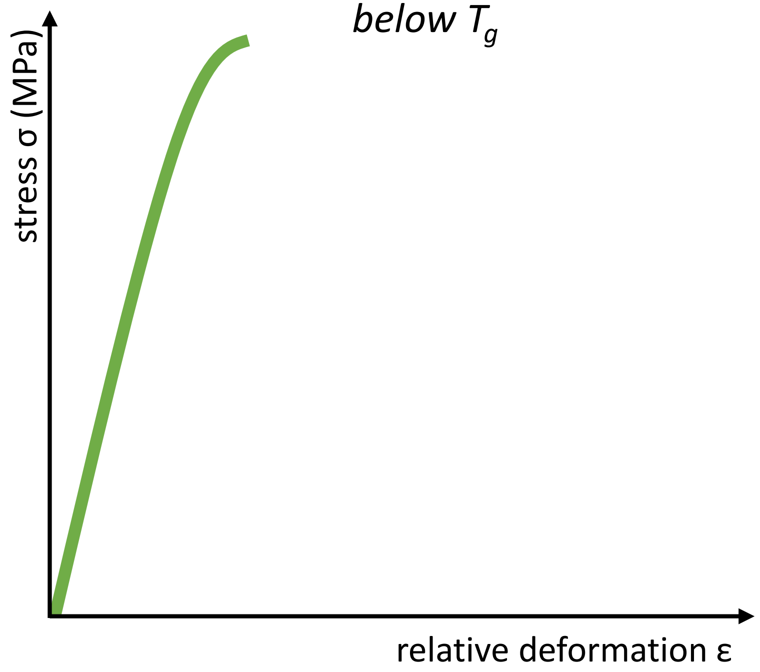




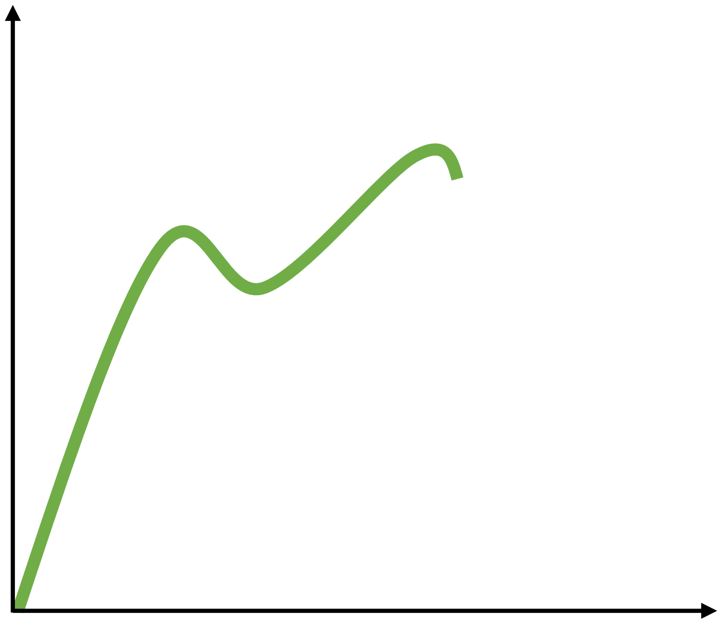
A … *limit of proportionality*
B … *elastic limit*
C … *upper yield limit*
D … *lower yield point*
E … *strength limit*
F … *breaking point*

Shapes of tensile curves

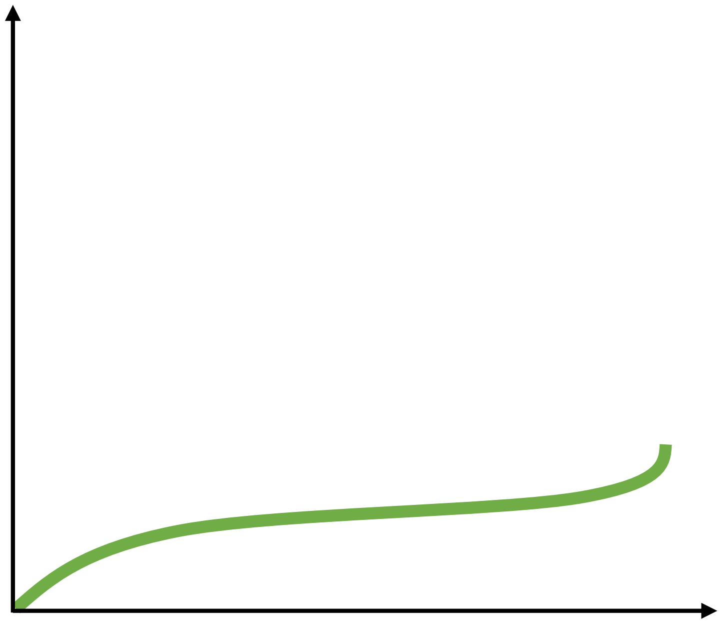
glass, ceramics, extremely crosslinked rubbers, polymers below T_g



metals, plastomers (in the rubbery region T)

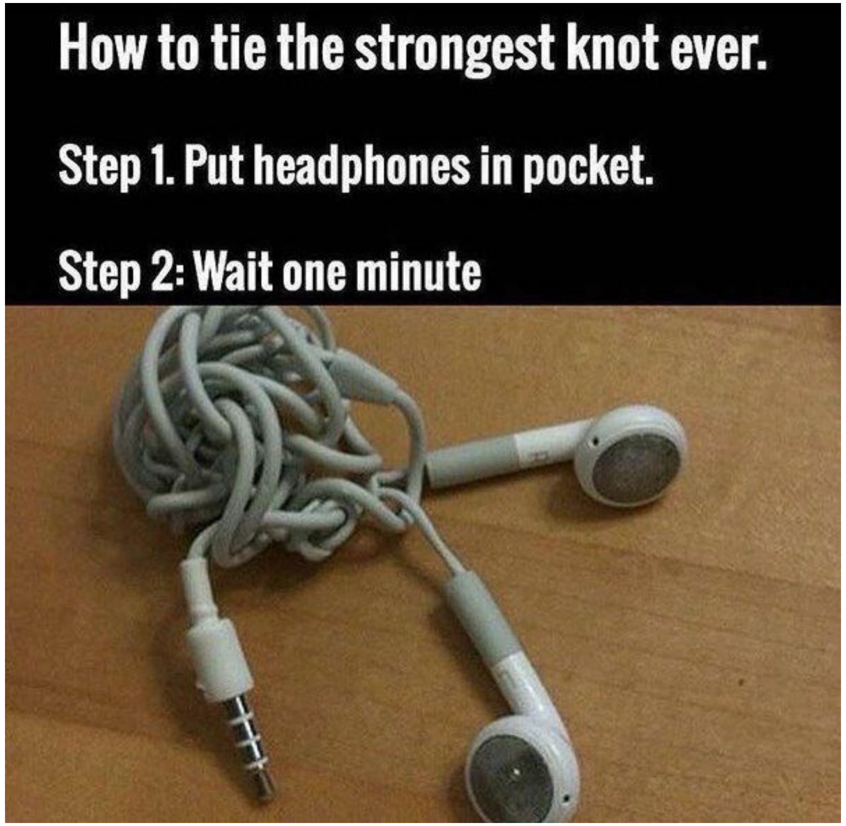


elastomers (in the rubbery region T)



Conditions of reversible deformability of elastomers

- enough nodes
  - knots can be chemical (cross-linking) or physical (actual crumples or crystallites)
- temperature in the rubbery region
  - below this temperature the elastomer behaves as a brittle material (glass region)



How to tie the strongest knot ever.

Step 1. Put headphones in pocket.

Step 2: Wait one minute

I. Rubbers

I. Rubbers

- chemically cross-linked material which, within its application temperature, is capable of quickly, mostly reversibly deforming with a small force by at least 100% of its original length
- otherwise they are called gums (from Latin gummi)
  - these are synonyms, although other claims can be found (Do not believe them!)
- it is usually made by cross-linking rubbers
  - rubbers prepared from monomers other than butadiene (or derivatives) are sometimes referred to as rubbers

Rubbers

- usually homopolymers or copolymers of butadiene derivatives
  - rubbers are created by their cross-linking
- they are substances related to terpenoids, which are formed by similar reactions from a butadiene base, but often not in the form of chains
- they usually have long strings
  - they may not exhibit elastic properties by themselves (TPE of course does - see below)
- in the undeformed state they are amorphous
- they have a wide temperature range of the rubbery region, the T_g being relatively low
- can be understood in two ways
  - polymer that can be cross-linked to form rubber (e.g. poly(cis-isoprene))
  - rubber, which is produced by cross-linking the rubber of the same name (e.g. ethylene-propylene rubber)

Selected types of rubbers

rubber name	*abbreviation*	*approximate amount (%)*	*utilization*
butadiene styrene	SBR	37	general
natural	NR (natural rubber)	32	
butadien	BR	10	
ethylene propylene ehtylene propylene diene	EPM EPDM	7	
isoprene (synthetic)	IR	3	
butyl rubber	IIR	3	
chloroprene	CR	3	oil resistant
butadiene akrylonitrile	NBR	3	
akrylic	ACM	0,5	
silicone	MQ	0,1	
polysulfide	OT	0,1	heat resistant
fluorocarbon	FPM	0,1	

Abbreviations for rubbers (in case it was unclear)

group marking	*main chain contains:*
M	saturated hydrocarbon chain only
R	unsaturated hydrocarbon chain
N	nitrogen
O	oxygen
Q	siloxane groups (-Si-O-)
T	sulphur
U	nitrogen and oxygen
Z	phosphorus and nitrogen

Cross-linking of rubbers - the creation of rubber

- rubbers themselves usually do not have very good properties
  - they tend to be sticky substances without an increased capacity for elastic deformation
  - therefore it must network
- cross-linking bridges form knots that prevent the chains from flowing one after the other and force them to regain approximately their original conformation (secured precisely by cross-linking)
  - reactive chains (usually those with double bonds) are most often cross-linked by sulfur
    - NR, BR, CR, SBR
- chains with a saturated backbone can be cross-linked, for example, by peroxides (radically) or by incorporating three or more functional comonomers into their structure during production and subsequent appropriate reaction
  - ethylene-propylene rubber (peroxide cross-linking)
  - ethylene-propylene-diene rubber (suitable reaction on the double bond, which are here only in the side chains)
- cross-linking will cause the impossibility of dissolving the given product
  - they can only swell

Recap.: Sulfur crosslinking of elastomers - vulcanization

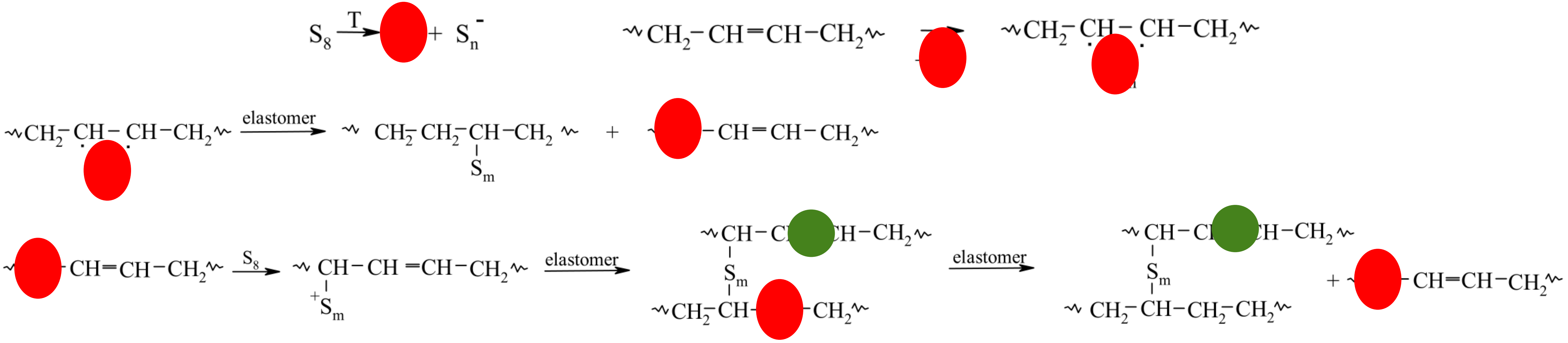
- the most common cross-linking reaction
  - action of sulfur and heat (around 140 °C)
- can be used for practically all butadiene homopolymers and copolymers
- the product of elastomer vulcanization is rubber
  - other additives are added to the final products (fillers, dyes, UV stabilizers, etc.)
- resulting properties dependent on the amount of sulfur
  - is determined in parts by weight of sulfur per hundred wt. rubber parts (phr)
    - soft rubber - up to about 4 phr
    - semi-hard – usually 12 to 25 phr
    - hard (ebonite) – 25 to 50 phr

Recap.: Sulfur crosslinking of elastomers - vulcanization

- it doesn't work very well without other substances
- in this case, the sulfide bridges are quite long after vulcanization (40 to 50 sulfur atoms)
  - bridges on neighboring atoms and cyclic sulfide structures do not particularly help physically
  - therefore accelerators and activators are used
- the average number of sulfur atoms is reduced to about 1.6
  - no cyclic structures or bridges are formed on neighboring atoms
- activators
  - ZnO, stearic acid
  - accelerators
  - 2-mercaptobenzthiazole, tetraalkylthiuram disulfide, zinc salts of dialkyldithiocarbamates

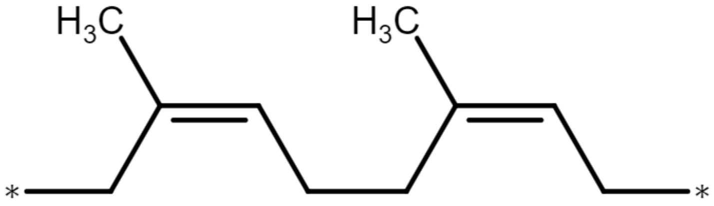
Recap.: Sulfur crosslinking of elastomers - vulcanization

- probably takes place through an ionic mechanism
  - observe the positive charge to understand the reaction
  - the interesting thing is that both double elastomers do not participate in the cross-linking reaction, but only one - the other thus remains in the structure

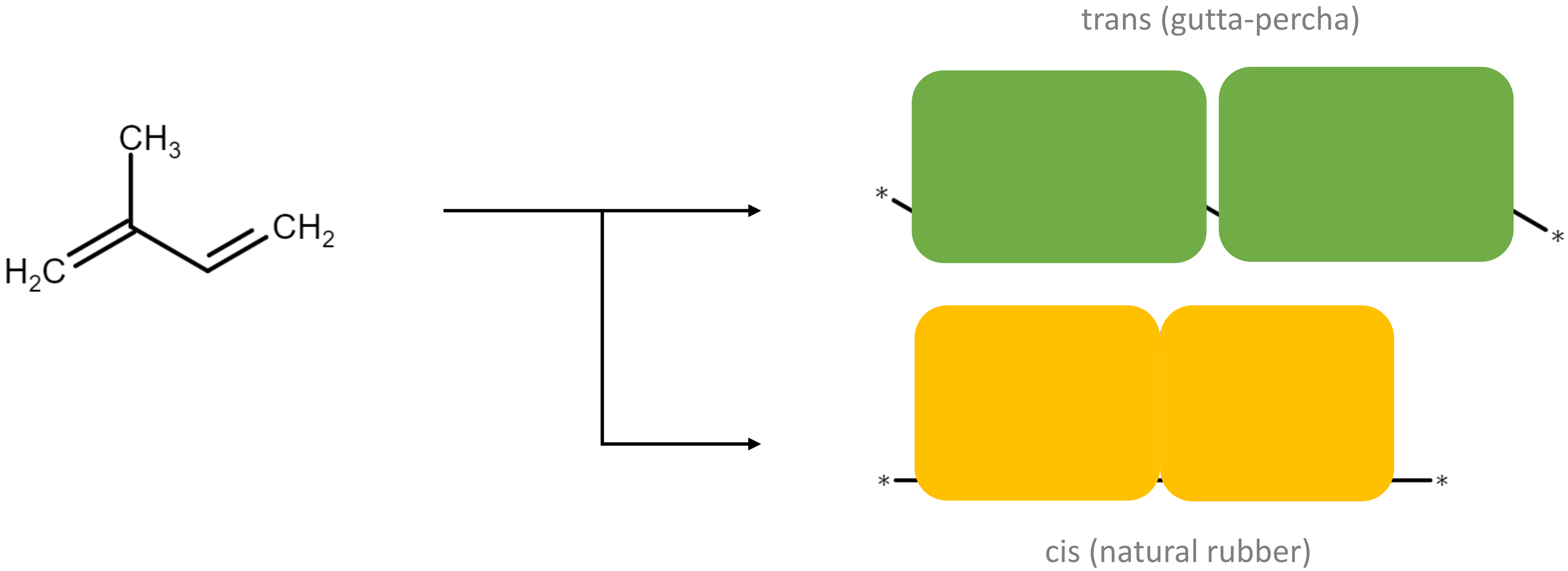


General rubbers - natural

- natural almost pure poly(cis-isoprene)
  - name perhaps from the Indian Kau-ču (weeping tree)
  - obtained from latex
    - aqueous dispersion of poly(cis-isoprene)
      - occurs in the lactiferous cells of some plants (e.g. buttercup, swallowtail, poppy, maple, rubber tree)
  - in large quantities it is obtained by cutting the bark of the Brazilian rubber tree (Hevea braziliensis)
- its cross-linking creates natural rubber (gum)



General rubbers - natural

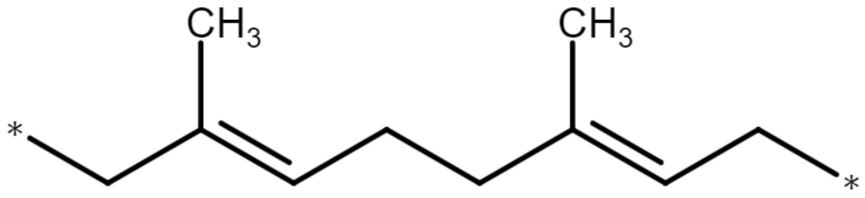


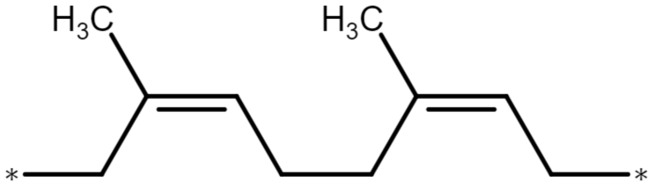
trans (gutta-percha)

cis (natural rubber)

Gutta-percha

- natural poly(trans-isoprene)
  - obtained from the latex of the Palaquium gutta tree
  - its cross-linking creates gutta-percha
    - it is not an elastomer but a rigid semi-crystalline polymer



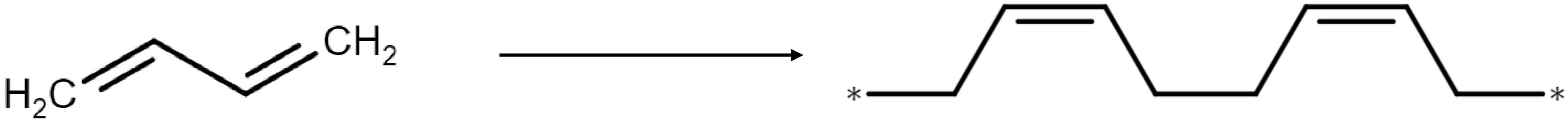


General rubbers - isoprene

- it is basically a human attempt to copy natural rubber
  - we cannot synthetically prepare poly(cis-isoprene) as pure as plants
    - plants vs. human = 99.9% vs. 98%
  - it is produced from isoprene by polyinsertion
    - industrial production is still more expensive than natural
    - depending on the purity, synthetic poly(cis-isoprene) can be mixed with natural (for a purity of around 92% from about 20%, for a purity of 96% about 50%, purer almost unlimited)

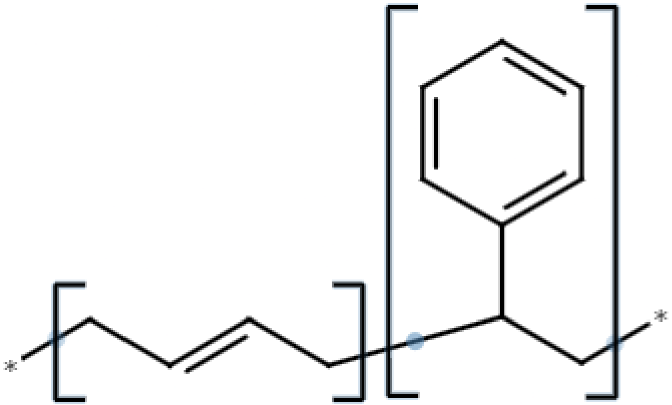
General rubbers - butadiene

- abbreviation BR
- solution Ziegler-Natta
- three different ways of binding the new monomer
    - cis-1,4 (96 to 98%)
    - trans-1,4 (1 to 3%)
    - 1,2 additions (1 to 2%)



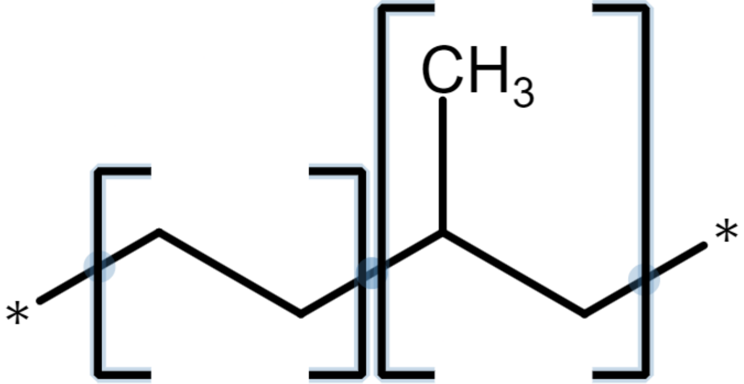
General rubbers - butadiene styrene

- abbreviation SBR
- production
  1. by radical emulsion copolymerization (decomposition of emulsifiers adds fatty or resinous acids) – statistical copolymer (rubber)
     - styrene content about 20 to 25%
  2. solution copolymerization – high styrene SBR
     - styrene content about 40 to 80%
  3. by ionic copolymerization - block copolymer (thermoplastic elastomer YSBR)



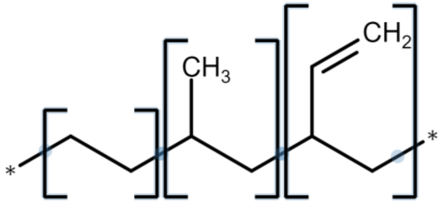
General rubbers - ethylene propylene

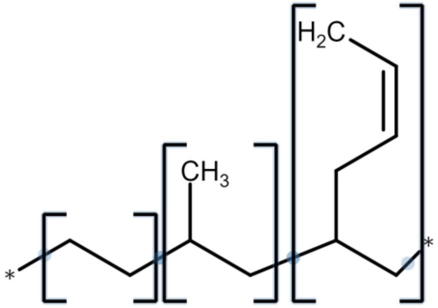
- abbreviation EPM
- bipolymer of ethylene and propylene
- Ziegler-Nattou copolymerization
- resistant to degradation, but they are saturate
- ethylene:propylene ratio about 3:1

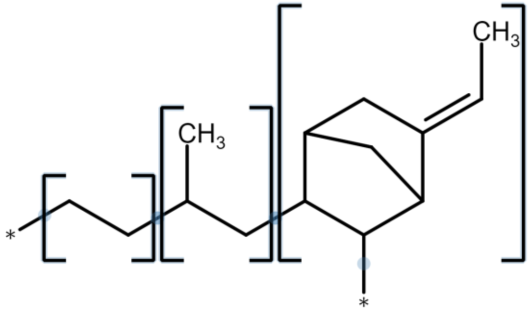


General rubbers - ethylene propylene diene

- abbreviation EPDM
- terpolymer of ethylene, propylene and some diene (for example hexa-1,4-diene)
- Ziegler-Nattou copolymerization
- resistant to degradation unless the main chain is saturated
    - only the side chains are unsaturated and serve for cross-linking
- content of diene mer around 5% (no more than 10%)

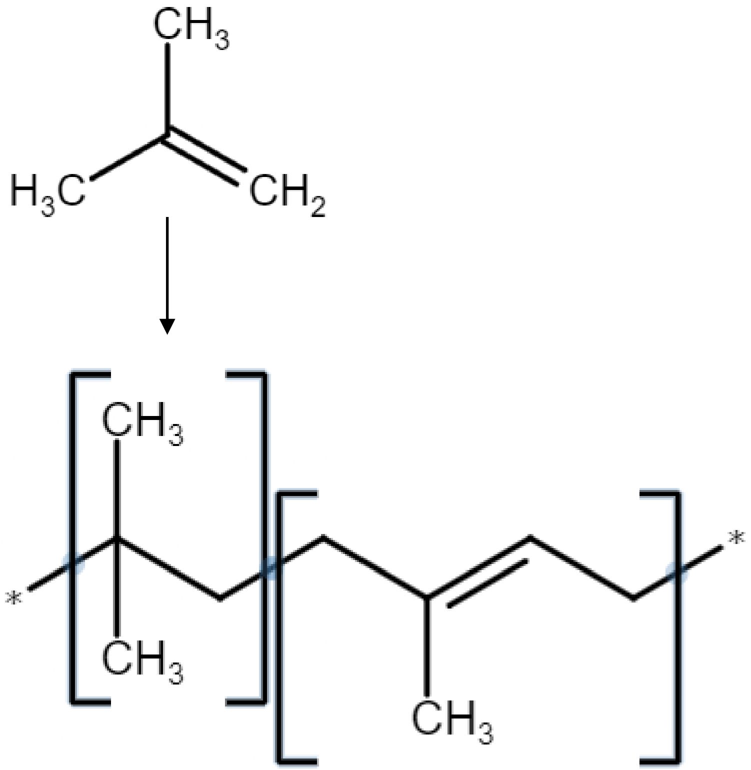


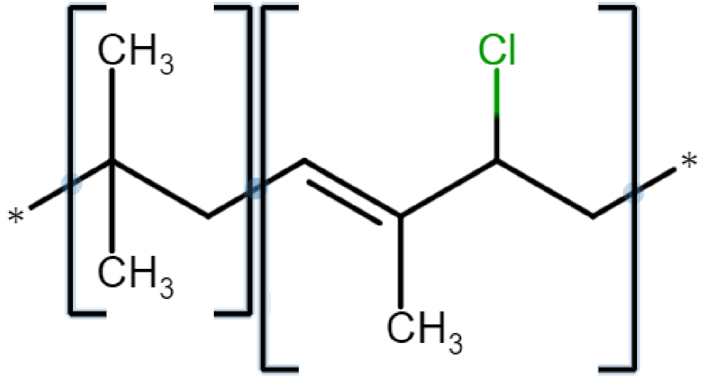


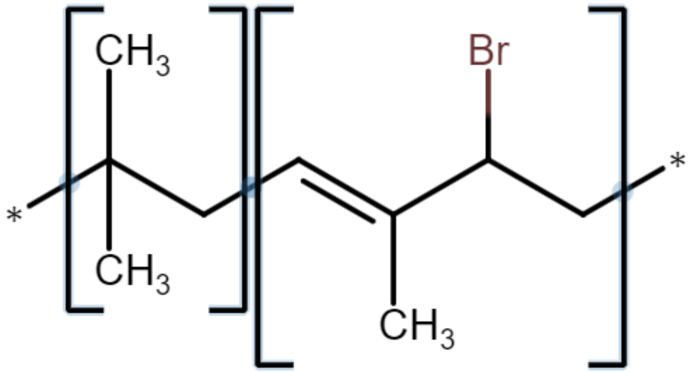


General rubbers - butyl rubber

- abbreviation IIR
- cationic copolymerization of isobutylene and isoprene
  - random copolymer
  - isoprene measures mainly in trans
- it can be chlorinated (CIIR) or brominated (BIIR)

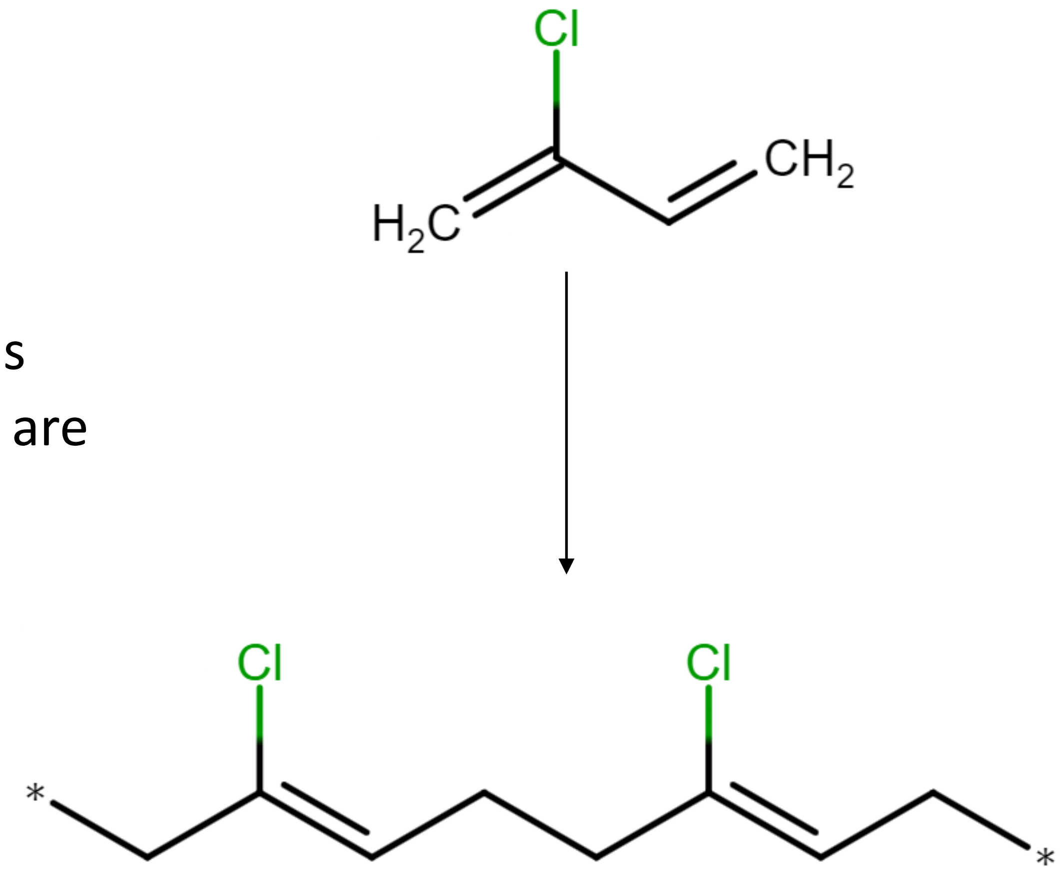






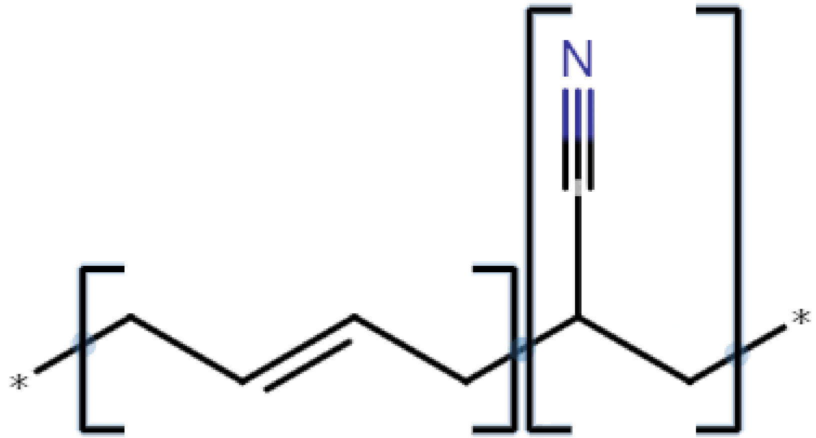
Oil-resistant rubbers - chloroprene

- polychloroprene
    - Neoprene (DuPont)
- abbreviation CR
    - about 85% is in the trans configuration
    - it has a tendency to crystallize as a result
- resistant to elevated temperatures, weather and oils
- according to the temperature during synthesis they are prepared:
    - fast crystallizing CR (10 °C)
        - little branched, solid even without vulcanization
    - medium fast crystallizing CR
    - slowly crystallizing (45 °C)
- for tubes, cables



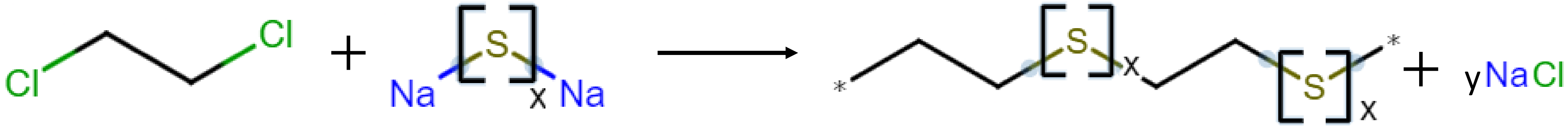
Oil-resistant rubbers - butadiene acrylonitrile

- abbreviation NBR
  - sometimes referred to as nitrile rubbers
- statistical bipolymer
- according to the content of acrylonitrile mers
  - with low content (18 to 26%)
  - with medium content (30 to 35%)
  - with a high content (40 to 50%)
- oil resistant



Oil-resistant rubbers - polysulphide

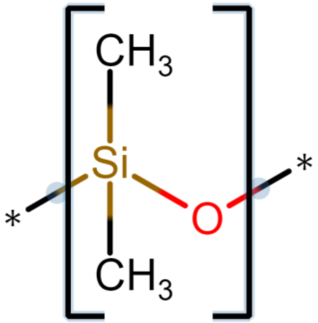
- many advantages
  - excellent oil resistance
  - partially resistant to even slightly polar solvents
  - they swell little
  - chemically resistant (do not contain double bonds) - weather resistance
  - low gas permeability
- they have only a small drawback
  - when heated it bursts with sulphur
    - if you want to play devils, definitely consider it an advantage



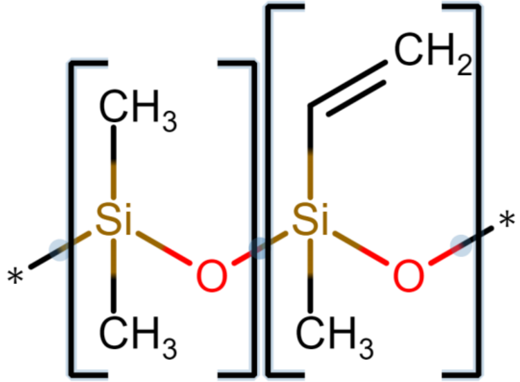
Heat-resistant rubbers - silicone

- these are linear siloxanes
- wide temperature range of the rubbery region
  - due to low chain cohesion
    - but also worse physical properties because of this
- heat resistant
- peroxides can be cross-linked, for example
- adhesive materials (insulating tapes), mastics, glues, rubbers are made from them
  - in addition to silicone polymers, the tube also contains methyltriacetosilane, which functions as a crosslinker (anionic reaction initiated by air humidity)

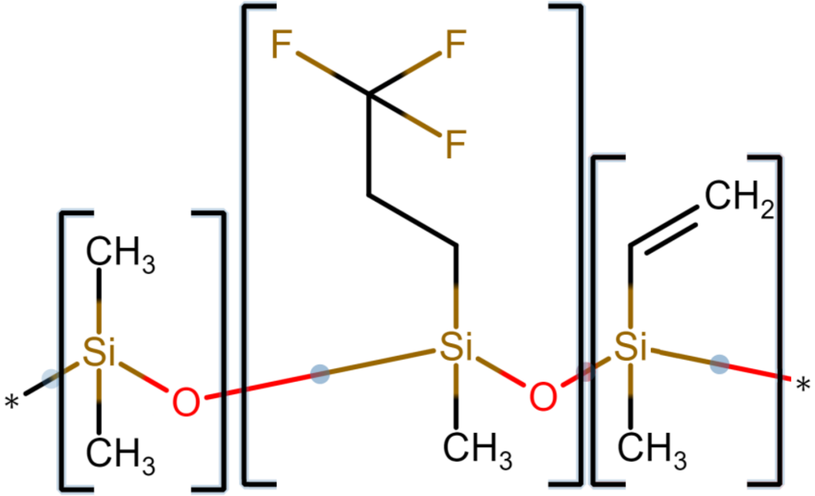
Heat-resistant rubbers - silicone



polydimethoxysiloxane
(MQ)

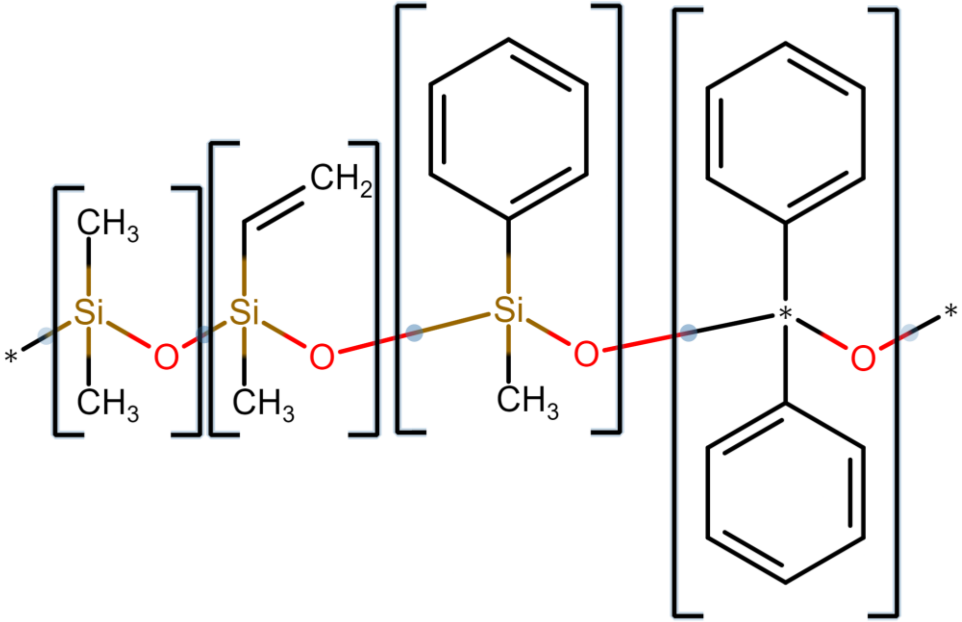


methylvinylpolysiloxane
(MVQ)



methyltrifluorpropylvinylpolysiloxane
(MPQ)

methylfenylvinylpolysiloxane
(MPVQ)

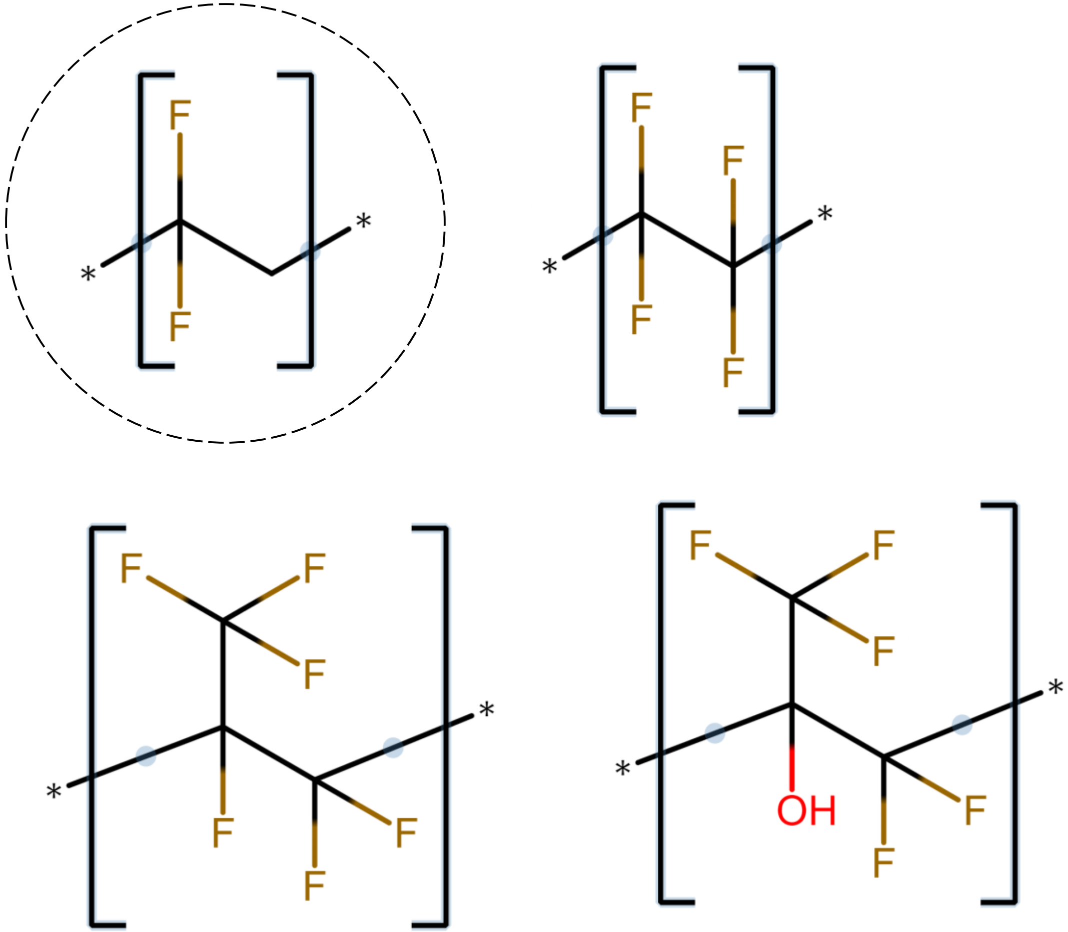


Heat-resistant rubbers - fluorocarbon

- Rambo among rubbers
  - withstands the highest temperatures among rubbers (over 200 °C)
  - rubbery area already from about -25 °C
  - resistant to oils
  - resistant to acids (concentrated sulfuric, nitric, etc.)
  - resistant vapors
  - resistant to oxidation (weathering)
- this is why they are some of the most expensive

Heat-resistant rubbers - fluorocarbon

- they are usually copolymers of vinylidene fluoride and other comonomers:
    - tetrafluoroethylene
    - hexafluoropropylene
    - hydroxypentafluoropropylene
    - etc.



Additives in rubbers

- most common isoprene or diene rubbers
  - therefore, they contain double bonds that are relatively reactive
  - are susceptible to degradation
  - it must be doped with anti-degradation substances
- rubbers with a saturated chain are usually quite stable and thus do not need anti-degradation agents
  - e.g. ethylene-propylene rubbers

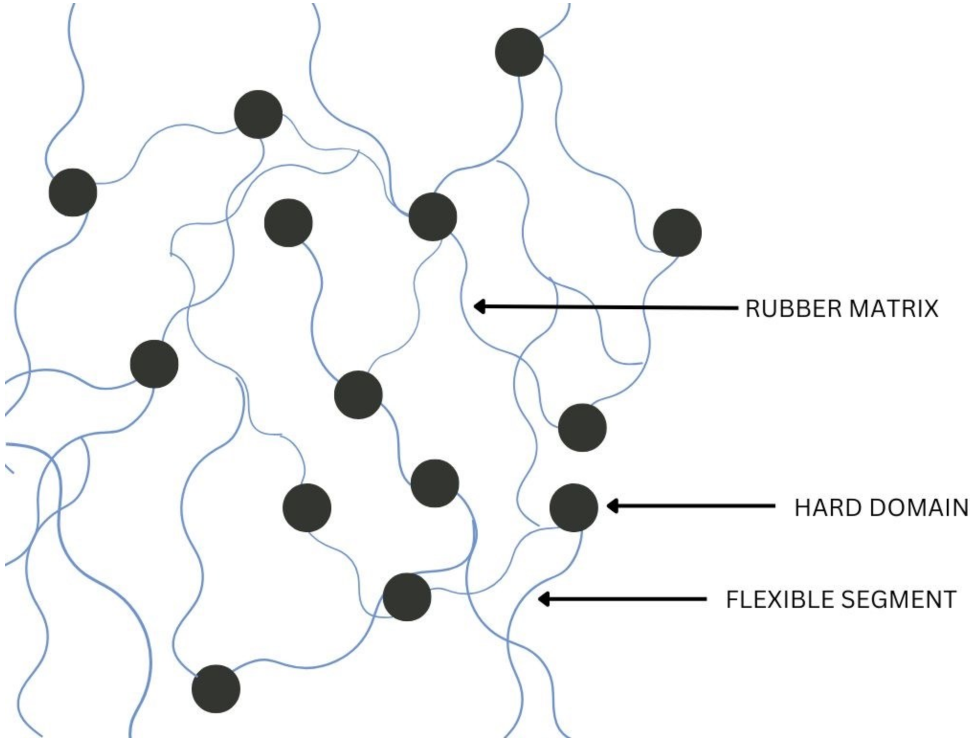
II. Termoplastické elastomery

Termoplastické elastomery

- TPE
- definition
  - general:
    - a group of chemically non-cross-linked heterogeneous substances capable of significant reversible deformation under the application of low voltage and an amorphous structure in the undeformed state
  - specific:
    - thermoplastic copolymers consisting of immiscible flexible (elastic) and rigid (rigid) segments resulting in an elastic material (like rubber) that can be recycled (like thermoplastics)
    - this is how thermoplastic elastomers are more often understood
- elasticity given by physical knots (so they are not networked) and entropy

Thermoplastic elastomers

- segments
  - flexible
    - rubbery in a wide temperature range
    - they add flexibility to the material
  - stiff
    - glassy or highly crystalline at the temperature conditions of use
    - they limit the mutual mobility of the chains and fulfill the function of nodes
    - thanks to the absence of a chemical bond, they enable the material to be recycled



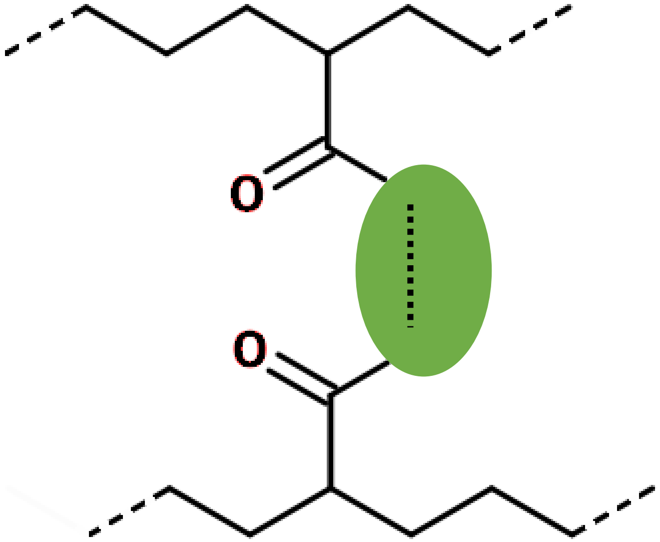
Types of thermoplastic elastomers

- blocky
  - usually by ionic (living) polymerization
- polycondensation
  - polyurethanes
  - polyetheresters
  - polyetheramides
- mixed polymers
  - mixing molten elastomers with thermoplastics
  - sometimes a sparse network is formed due to shear stress
    - at that moment they are on the borderline of thermoplastic elastomer and sparsely cross-linked rubber

group	*subgroup*	*flexible (soft) segment*	*rigid (hard) segment*	*structure*
block		-butadiene-	-styrene-	-styrene-butadiene-styrene-
		-isoprene-	-styrene-	-styrene-isoprene-styrene-
		-ethylene-propylene-	-styrene-	-styrene-ethylene-propylene-styrene-
		-ethylene-butylene-	-styrene-	-styrene-ethylene-butylene-styrene-
		-ester-	-styrene-	-styrene-estere-styrene-
		-amide-	-styrene-	-styrene-amide-styrene-
polycondensated	polyuretany	-ether- *or* -ester-	-uretane- *or* -urea-	-uretane-ether-uretane- *or* -urea-ester-urea-
	polyetherestery	-ether-	-ester-	-ester-ether-ester-
	polyetheramidy	-ether-	-amide-	-amide-ether-amide-
mixed		-elastomeric-	-thermoplastic-	

Ionomers

- crosslinking bonds are not covalent but ionic (or hydrogen)
  - it is thus in a way a rubber whose crosslinks can be relatively easily split and then restored again (something between rubber and thermoplastic rubber)
- copolymer of ethene and 5-10% acrylic or methacrylic acid
  - carboxyl groups can be neutralized to form an acrylate or methacrylate salt (Na, Ca, Mg, Zn, Al, Ba)
  - it is not a static network and monovalent ions (Na) contribute to its strength
- with enough temperature I can disrupt the network without degrading the macromolecules themselves
  - can be melted and after cooling I get the network again
- physically they behave similarly to thermoplastic elastomers



Thank you for your attention

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií NextGenerationEU

Národní plán obnovy

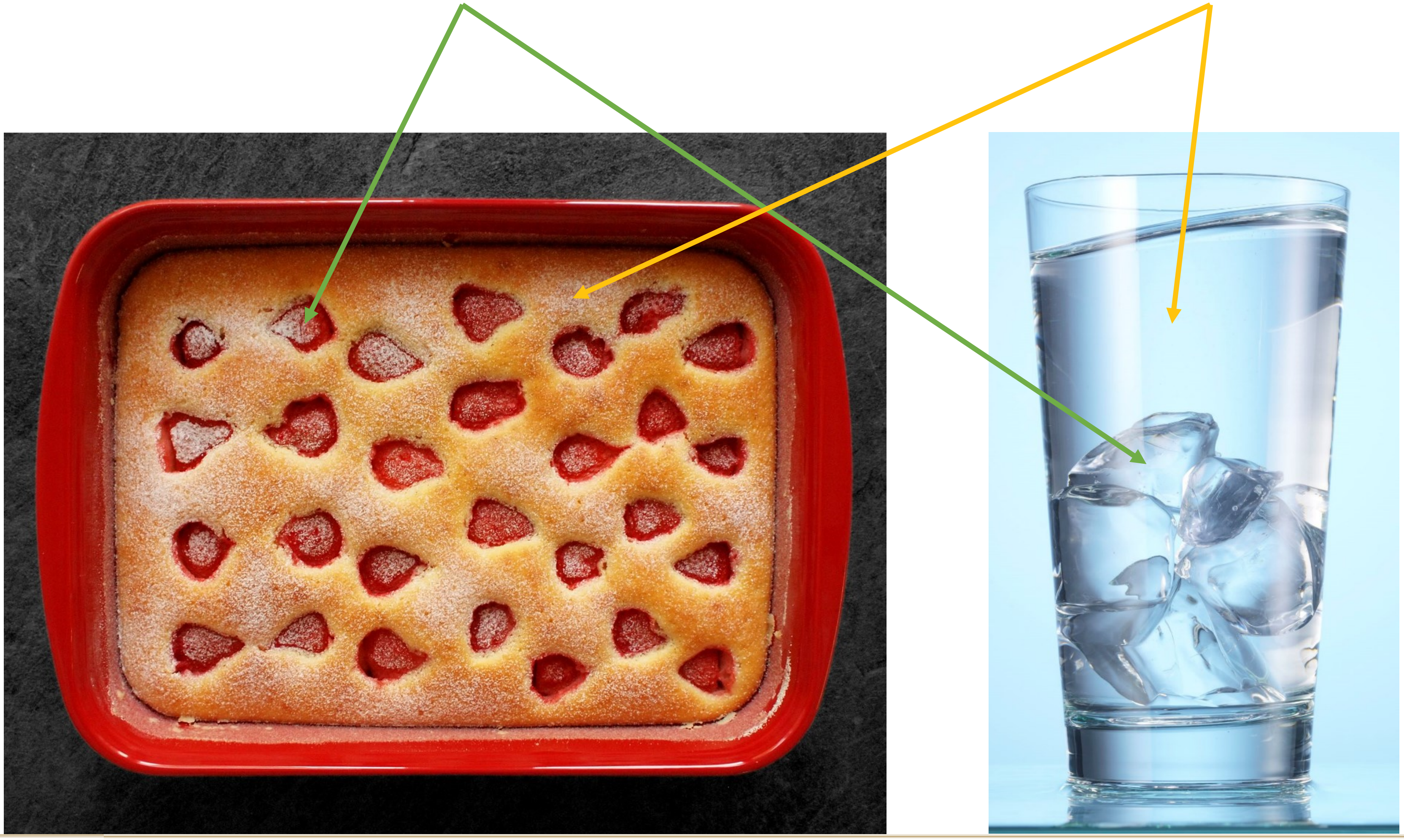
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Polymer solutions

1. Dispersions

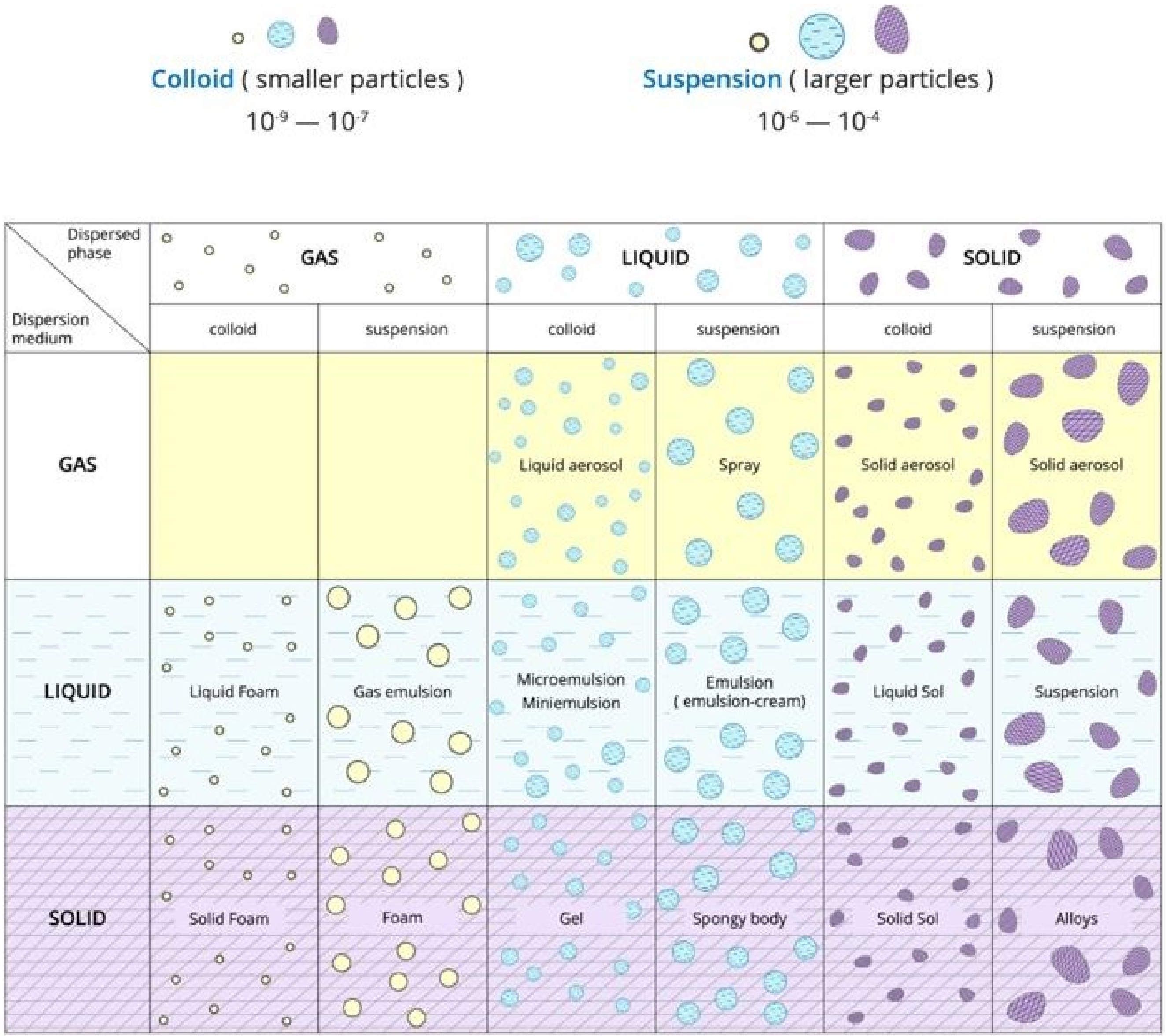
Dispersion - basic terms

- dispersion system
  - generally a mixture of at least two phases
  - the dispersion fraction dispersed in the dispersion medium
- degree of dispersion
  - describes the particle size of the dispersed phase
  - inverse of the particle size of the dispersion fraction
- the shape of the particles of the dispersion fraction
  - isometric
    - similar in all three dimensions (e.g. spherical)
  - anisometric
    - flattened (plates, lamellae), elongated (rods, fibers)
  - the shape of the molecules can change



the dispersion fraction

the dispersion medium

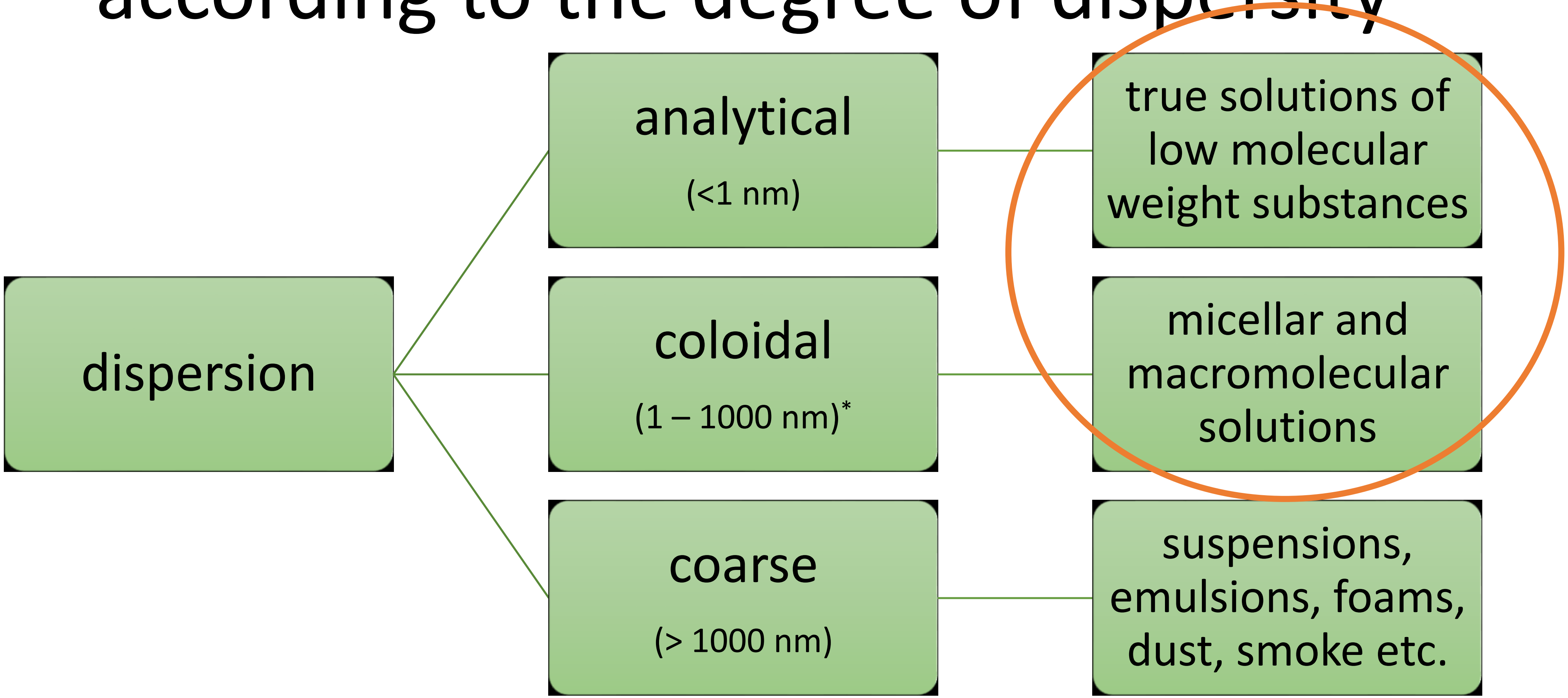


Colloid (smaller particles)
$10^{-9} — 10^{-7}$

Suspension (larger particles)
$10^{-6} — 10^{-4}$

Dispersed phase / Dispersion medium	GAS		LIQUID		SOLID	
	colloid	suspension	colloid	suspension	colloid	suspension
GAS			Liquid aerosol	Spray	Solid aerosol	Solid aerosol
LIQUID	Liquid Foam	Gas emulsion	Microemulsion Miniemulsion	Emulsion (emulsion-cream)	Liquid Sol	Suspension
SOLID	Solid Foam	Foam	Gel	Spongy body	Solid Sol	Alloys

Dispersions
according to the degree of dispersity



dispersion

analytical

(<1 nm)

coloidal

(1 – 1000 nm)*

coarse

(> 1000 nm)

true solutions of low molecular weight substances

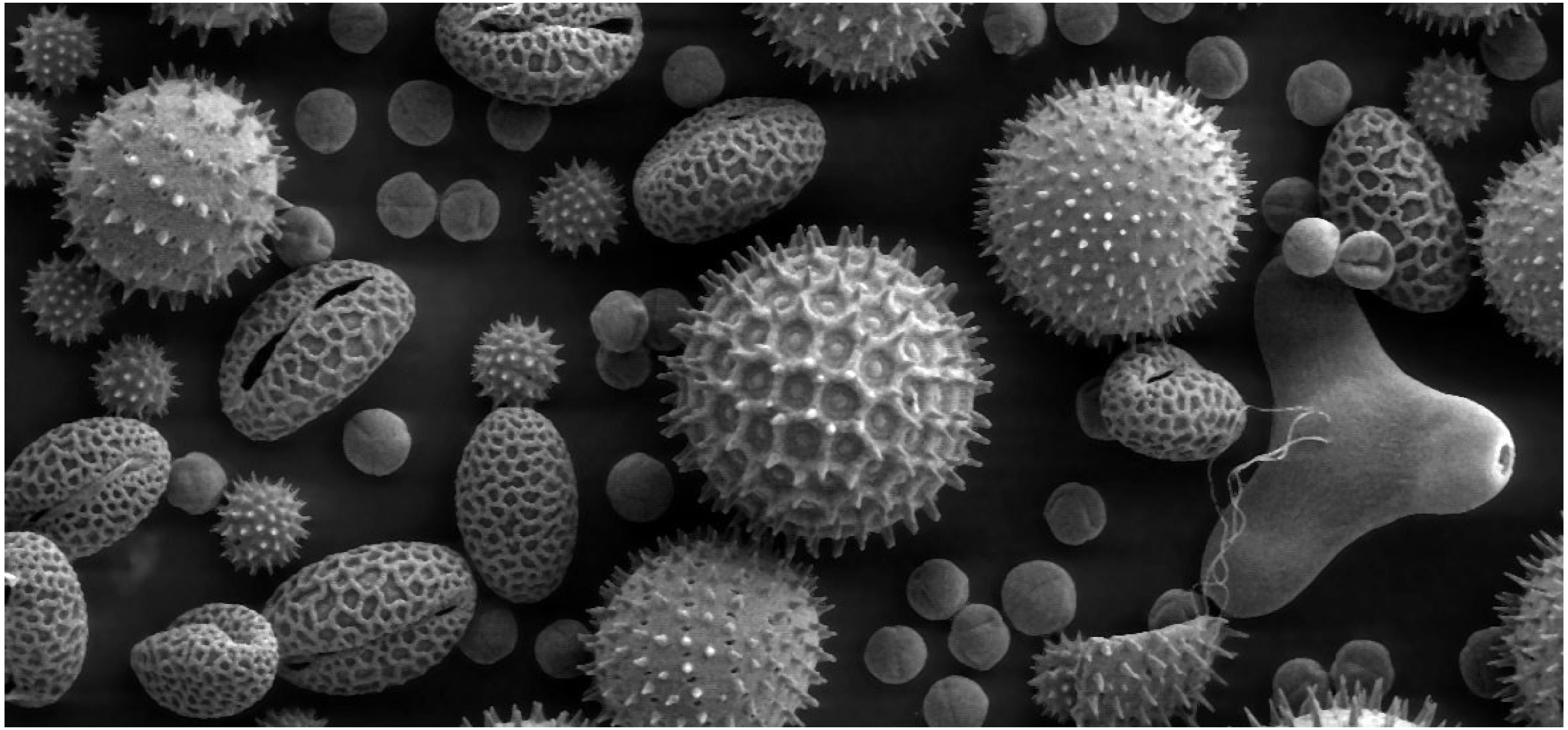
micellar and macromolecular solutions

suspensions, emulsions, foams, dust, smoke etc.

---

* není pevná hranice

2. Thermal movements of the dispersion fraction

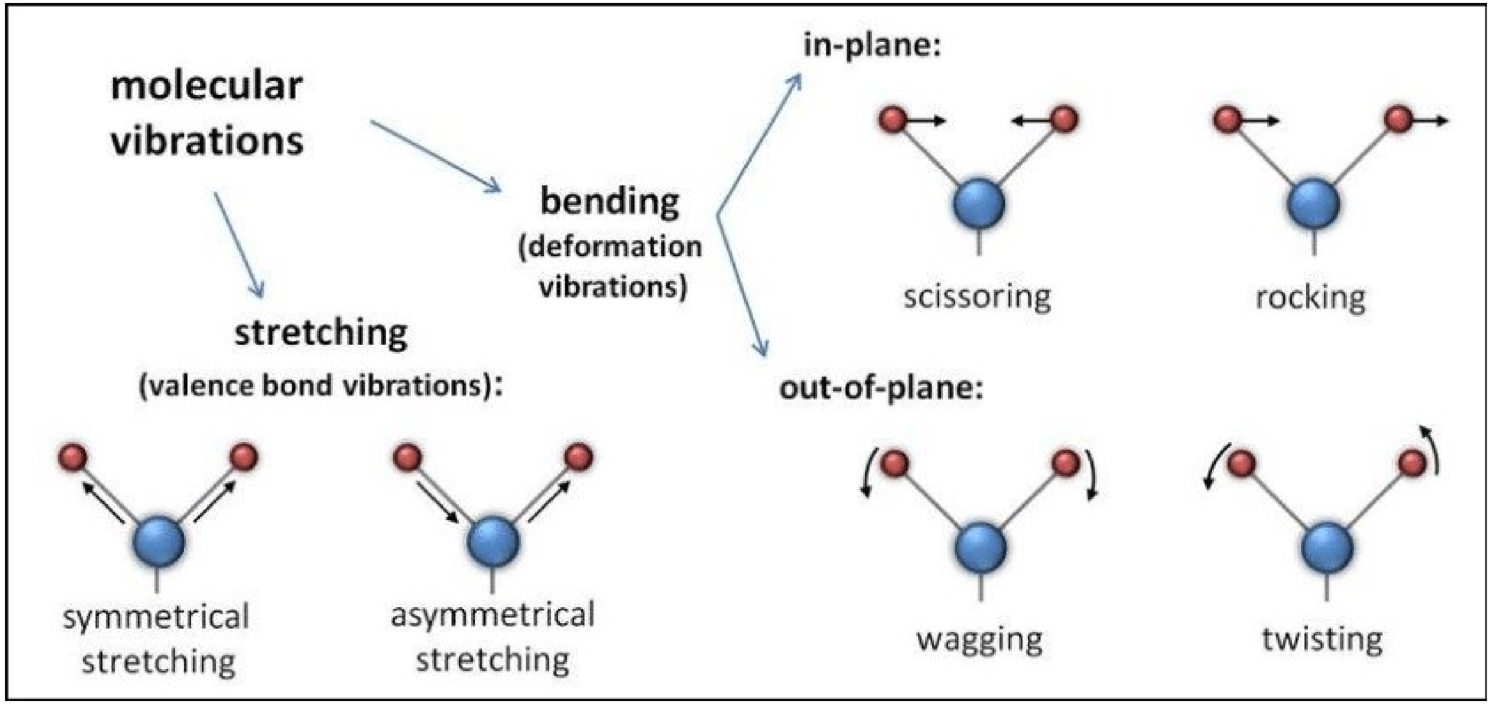


Thermal movement of the particles of the dispersion fraction

- oscillation of atomic nuclei around equilibrium positions
- accidental collision of molecules of the dispersion medium into the particles of the dispersion portion due to the influence of heat
  - due to randomness, it is necessary to investigate statistically
- types of the movements
  - vibratory
  - translational
  - rotational
  - internal (intramolecular) rotation
    - in macromolecules

Vibrational movements

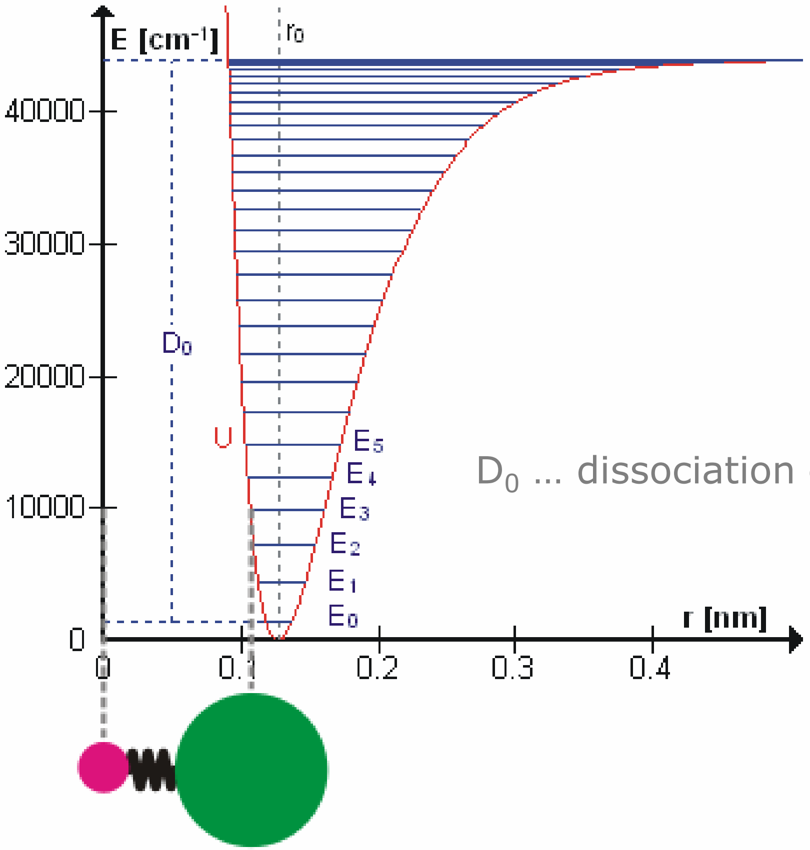
- movements of the nuclei of the atoms of the molecule relative to the center of gravity of the molecule



* visualization of vibrational movements: https://en.wikipedia.org/wiki/Molecular vibration

Vibrational motion – valence deformation

- the atoms oscillate with respect to the center of gravity of the molecule
  - in the animation, the hydrogen atom is static and the chlorine atom is moving
    - in fact, the lighter hydrogen atom vibrates more
- the higher the temperature, the greater the movement path



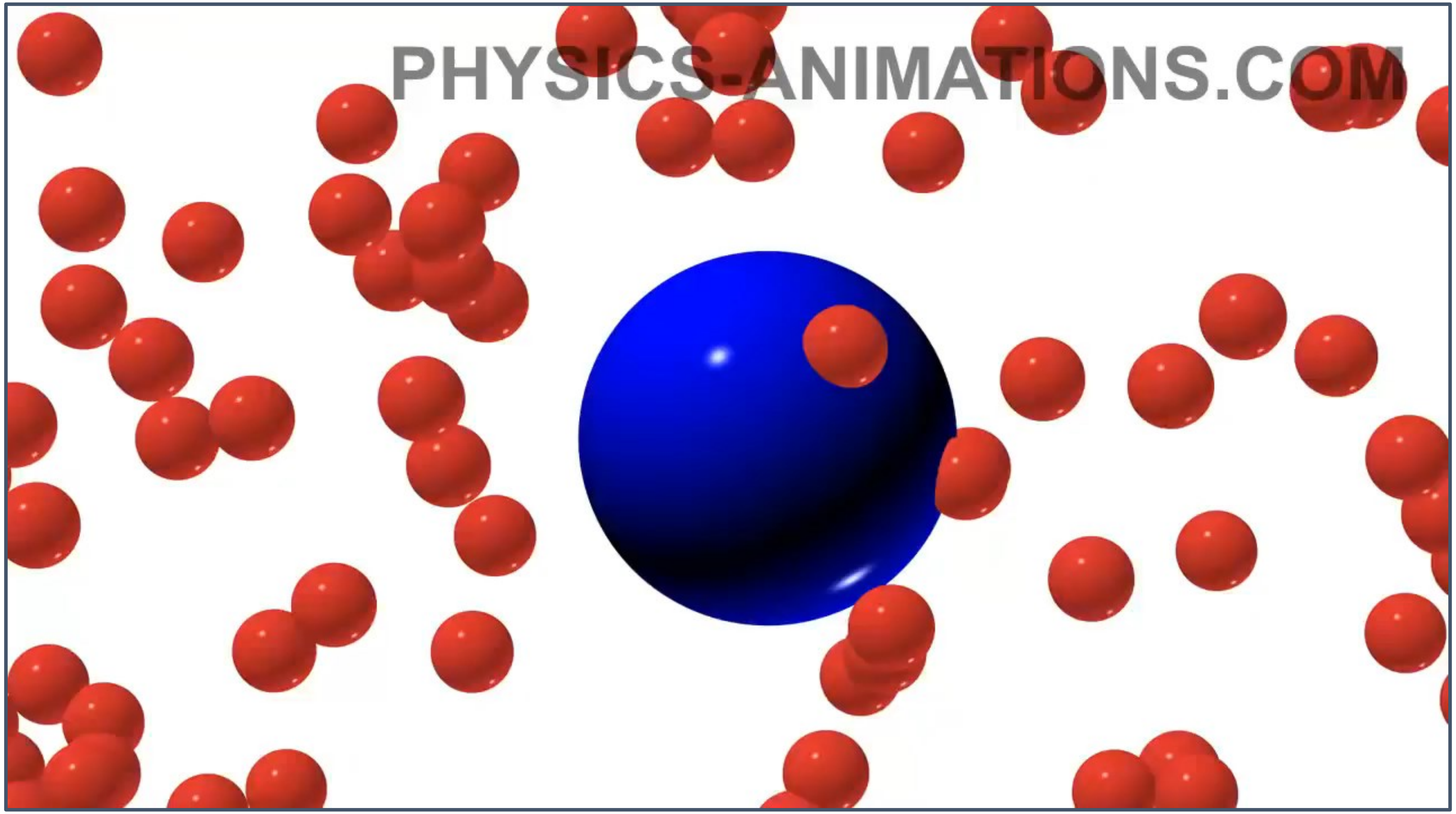
D_0 … dissociation energy

* vibrational model of HCl : https://en.wikipedia.org/wiki/File:Anharmonic_oscillator.gif

Brownian motion

- disordered movement of small particles in a liquid observed in 1827 by the botanist Robert Brown
  - pollen grains of the sculpin (Clarkia pulchella) in water
    - size of pollen grains approximately 1 μm
    - later he also tried the pollen grains of other plants
  - at first he believed that the living substance of the pollen was responsible for the movement, but after experiments with inanimate particles he disproved it himself
  - the smaller the particles he used, the more vivid the movement he observed

Brownian motion - model



* molecular model of Brownian motion: https://youtu.be/6VdMp46ZIL8

Brownian motion - fact

* real observation of Brownian motion (with extremely moving music, so you better turn off the sound for a moment): https://www.youtube.com/watch?v=R5t-oA796to

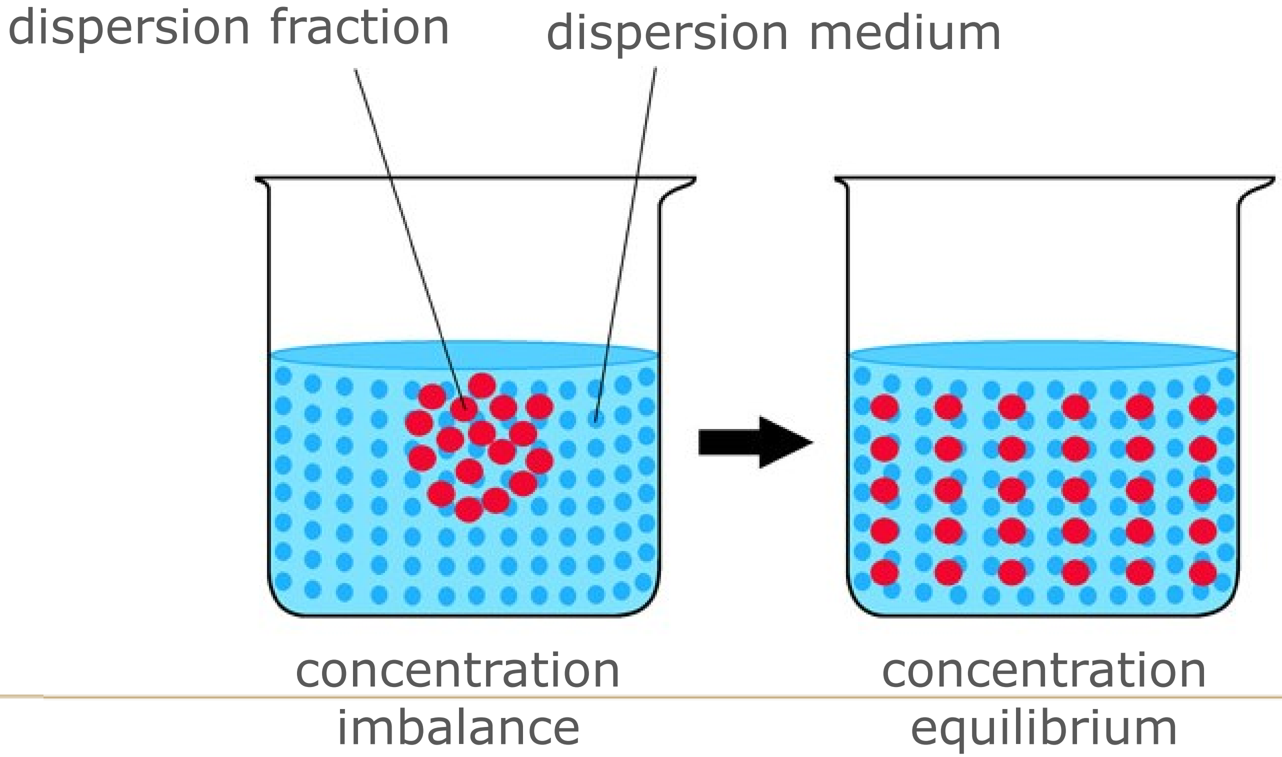
Translational thermal motion

- causes equalization of concentrations in the system (given by the concentration gradient)

- diffusion
  - the movement of particles of the dispersion fraction into an environment with a lower concentration
- osmosis
  - the movement of molecules of the dispersion medium into an environment with a higher concentration of particles of the dispersion fraction
  - through a semipermeable (semipermeable) membrane
    - it only passes the dispersion medium, it captures the dispersion part

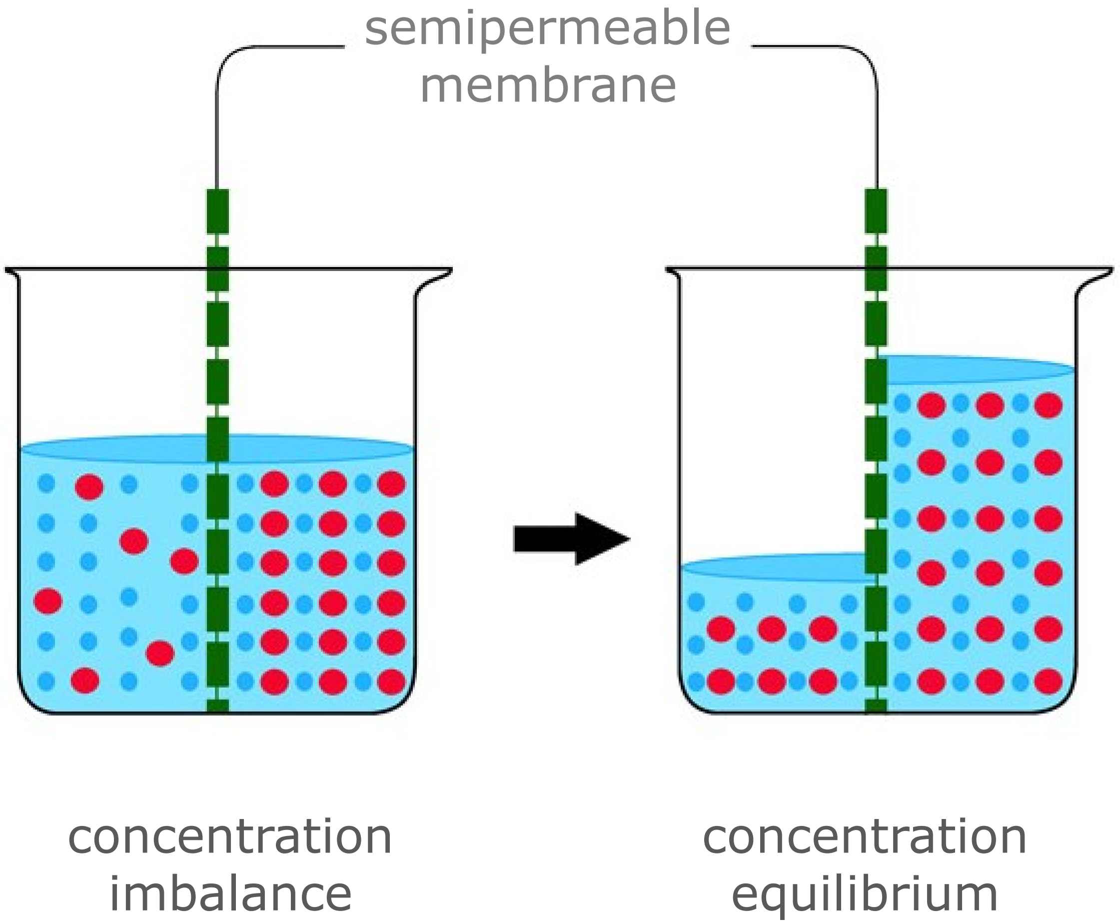
Diffusion

- the movement of particles of the dispersion fraction into an environment with a lower concentration



Osmosis

- movement of particles of the dispersion medium into an environment with a higher concentration of particles of the dispersion portion



Osmotic pressure

- osmotic pressure π:

$$\pi = -\frac{RT}{V}\ln a$$

R … relative gas constant (8.314 J·K^{-1} ·mol^{-1})

T ... thermodynamic temperature [K]

V … system volume [m^3]

and … solvent activity (describes the degree of interaction of the fluid with its environment)

- for a highly dilute solution:

$$\pi = \frac{RT}{V}n = RTc$$

n ... substance amount of solvent [mol]

c … molar concentration·[mol·dm^{-3}]

Osmometry

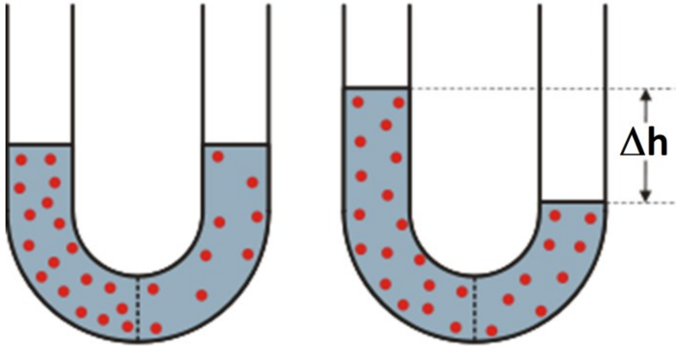
- determination of osmotic pressure π:

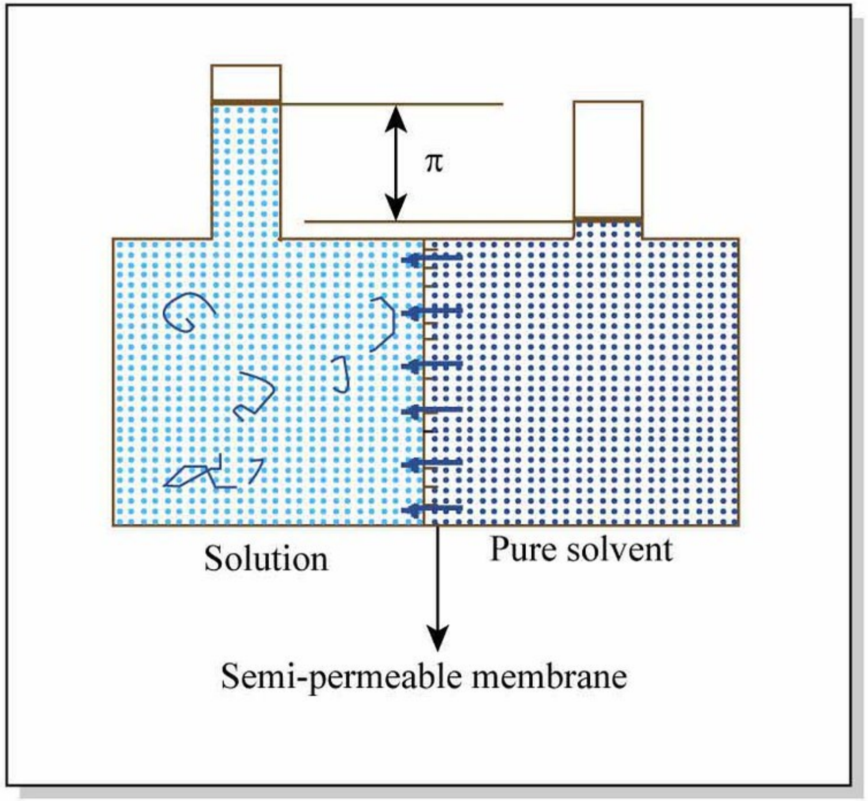
$$\pi = \rho h g$$

ρ ... solvent density

h ... the difference in the heights of the levels

g ... gravitational acceleration

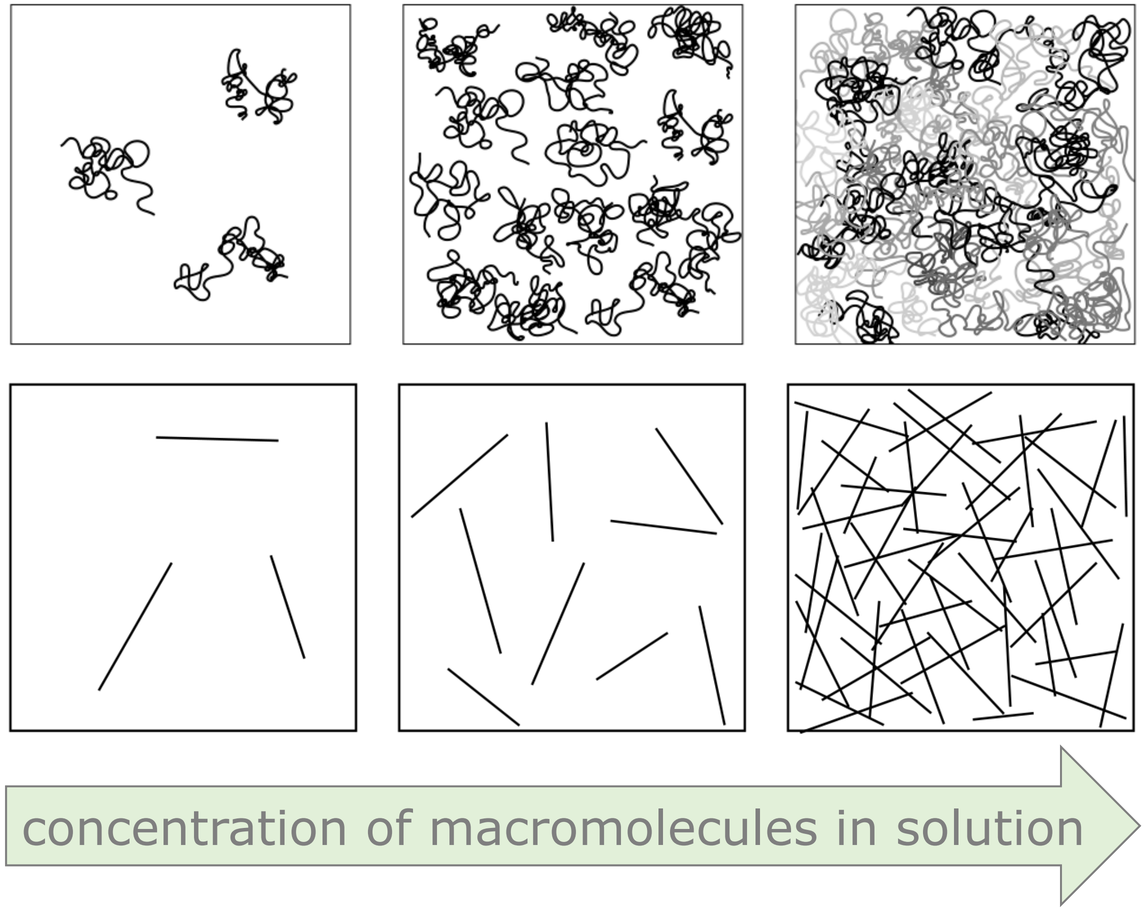




2. Solubility of polymers

Similia similibus solvuntur.

Macromolecules in solution



flexible chains

rigide chains

concentration of macromolecules in solution

Shapes of macromolecules in solution

- globules
  - tightly coiled polymer chains
  - interaction with the solvent only on the surface of the globule
  - chemical or physical bonds ensure a more permanent shape of the globule
- coil
  - not very tightly coiled polymer chains
  - polymer chains interact with other chains and with solvent molecules
- unfolded chains
  - the polymer chain interacts almost exclusively with solvent molecules (good soln.)

Basic thermodynamic quantities

- Gibbs (free) energy G
  - the basic condition for the spontaneity of the plot
  - ΔG < 0 says that the action can be spontaneous (at constant temperature and pressure)
  - as a state quantity, it considers only the initial and final state, not the progress
    - due to e.g. an energy barrier, the event may not occur spontaneously, even though ΔG < 0 applies to it

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

- enthalpy H
- transferred energy (heat) at constant pressure
  - exothermic reaction (ΔH < 0) – energy leaves the system
  - endothermic reaction (ΔH > 0) – energy enriches the system

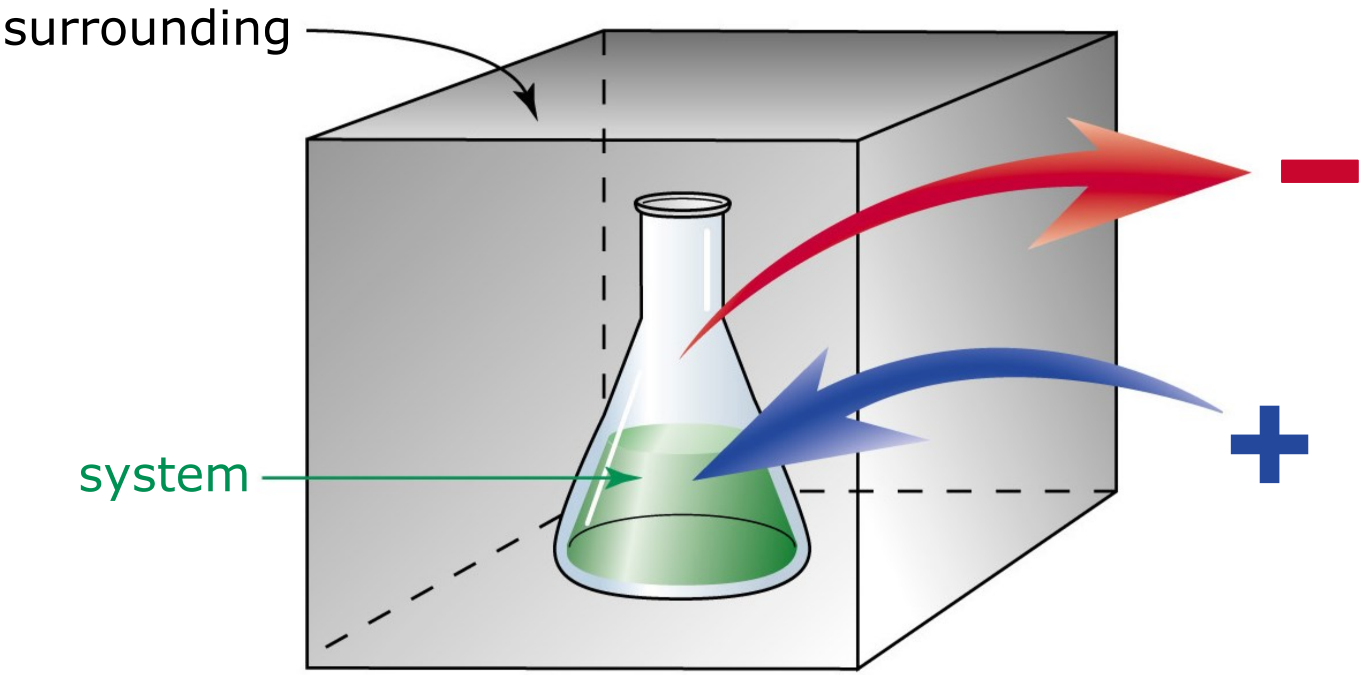
$$\Delta H = \Delta U + p\Delta V$$

- entropy S
  - degree of system disorder (the larger, the more disordered)
  - for mixing it must practically always increase (i.e. be positive)
    - thus, the change in Gybbs energy during mixing is mainly influenced by the change in enthalpy

Gibbs free energy

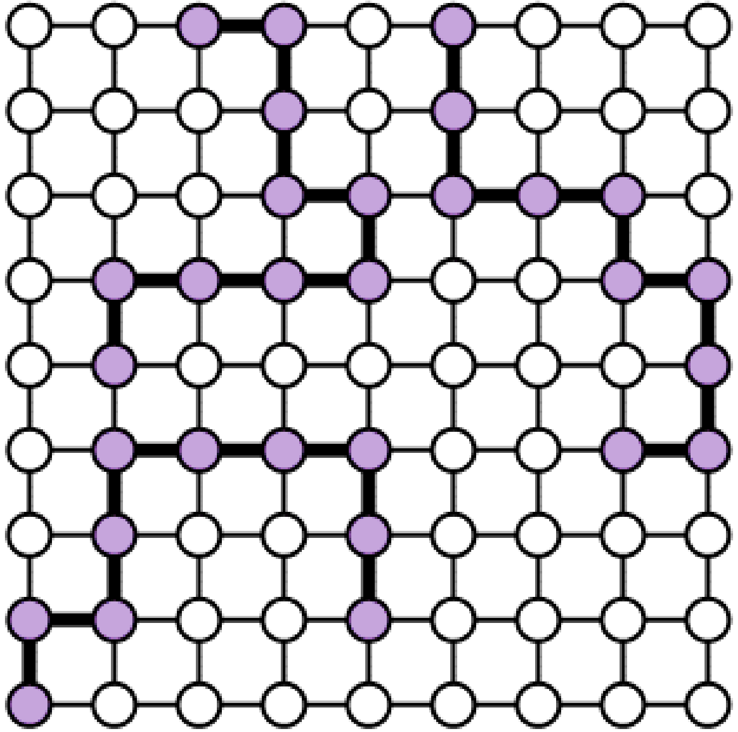
- the possibility of self-mixing of the solvent assumes ΔG < 0

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



Solvent lattice model

- a two-dimensional mixture of two components at grid nodes
  - does not contain blank spaces
  - each node is occupied by exactly one segment
  - after mixing, the total volume does not change
  - the volume of one segment of solvent equal to the volume of one molecule* of solvent
- coordination number of
  - the number of interactions of one segment with others
  - z = 4 in our case
- segment interaction
  - their total number does not change, only the "links" between them
- types of mutual interactions of segments in a two-dimensional grid
  - polymer-polymer
  - polymer-solvent
  - solvent-solvent



---

* in the case of the lattice model, the term segment will be used for the volume unit in the lattice, whether it is a polymer or a solvent

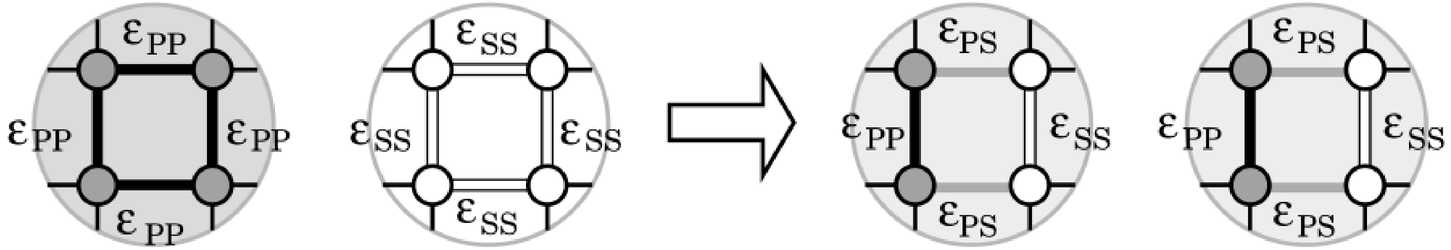
Enthalpy of a two-component mixture

- the change in enthalpy of mixing ΔH_m corresponds to the energy change $\Delta\varepsilon$ of all new bonds (their total number is l) polymer-solvent

$$\Delta \boldsymbol{H_m} \cong \Delta \boldsymbol{\varepsilon} \cdot \boldsymbol{l}$$

- bond energy change $\Delta\varepsilon$ upon mixing
  - given by the sum of changes in polymer-polymer (ε_{pp}), polymer-solvent (ε_{pr}) and solvent-solvent (ε_{rr}) interaction energies
  - if 1 ε_{pp} and 1 ε_{rr} disappear, 2 ε_{pr} bonds can be formed by mixing

$$\Delta\varepsilon = 2\varepsilon_{pr} - \varepsilon_{pp} - \varepsilon_{rr}$$



$\varepsilon_{PP} = \varepsilon_{pp}$ $\quad\varepsilon_{SS} = \varepsilon_{rr}$ $\quad\varepsilon_{PS} = \varepsilon_{pr}$

Enthalpy of mixing

- the total number of polymer-solvent interactions l is given by:
  - the probability of the occurrence of a solvent in the vicinity of a given polymer segment
    - it is represented by the solvent volume fraction φ_r (small phi)

$$\varphi_r = \frac{V_r}{V_{celk}}$$

  - by the coordination number z (number of neighbors of each segment)
  - by the number of polymer segments N_p
    - the number of N_p segments can be calculated using Avogadro's constant N_A and the molar amount of polymer segments n_p

$$N_p = N_A \cdot n_p$$

- so overal:

$$l = \varphi_r \cdot z \cdot N_A \cdot n_p$$

- the change in enthalpy of mixing ΔH corresponds to the energy change Δε of all new polymer-solvent bonds

$$\Delta H \cong \Delta\varepsilon \cdot l$$

- then:

$$\Delta H \cong \frac{1}{2}\Delta\varepsilon \cdot \varphi_r \cdot z \cdot N_A \cdot n_p$$

Hildebrand-Scott solubility parameter

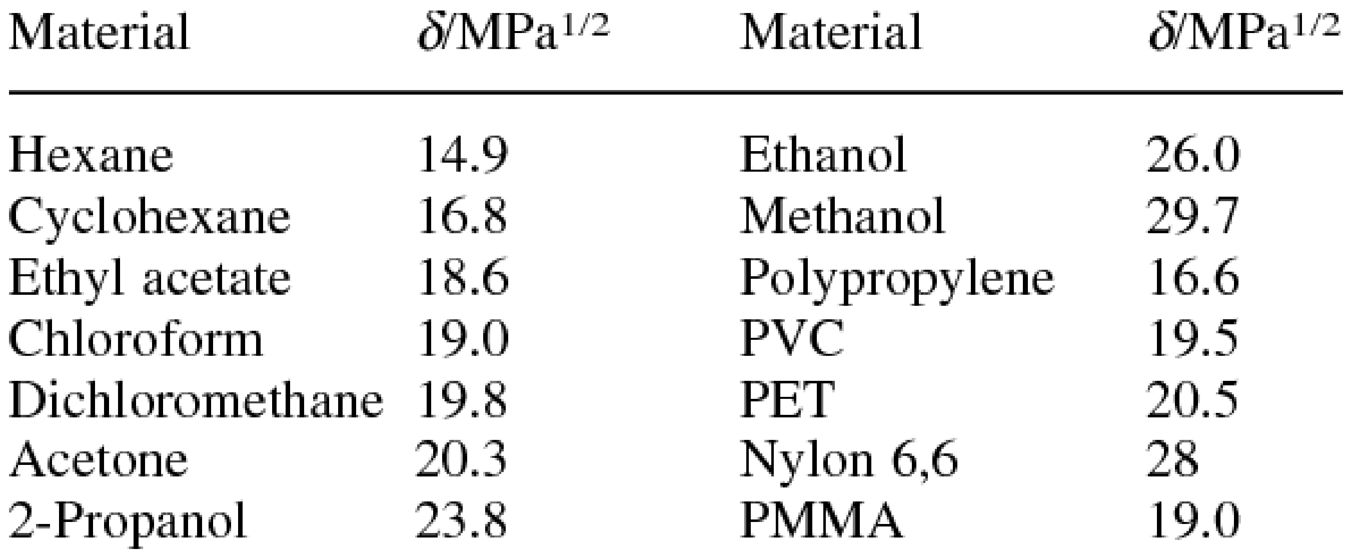
- is denoted by δ (small delta)
- sometimes also called the total solubility parameter

$$\delta = \sqrt{CED} = \sqrt{\frac{\Delta_v H_m - p\Delta V}{V_m}}$$

  - where CED is the **cohesive energy density**, $\Delta_v H_m$ is the molar vapor enthalpy change, p is the pressure, ΔV is the volume change, and V_m is the molar volume
- CED
  - describes the mutual cohesion of the molecules of the given substance, or the total energy of its secondary bonds (therefore we do not consider gases)
  - defined as the internal vapor energy U_v of a unit volume of liquid V_m
  - increases with the polarity of the substance

Hildebrand-Scott solubility parameter

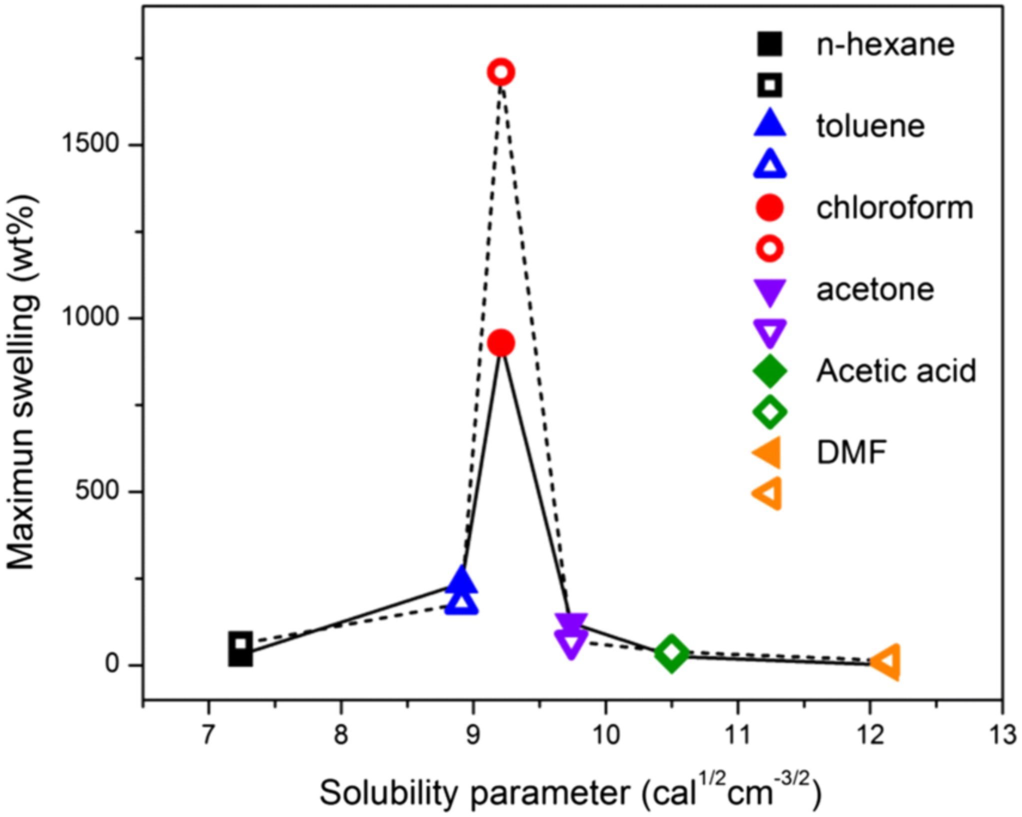
- substances with similar δ tend to be miscible
- for a mixture of several substances, the resulting δ is equal to the weighted (according to their volumes) average of the parameters of the mixed substances



Material	δ/MPa$^{1/2}$	Material	δ/MPa$^{1/2}$
Hexane	14.9	Ethanol	26.0
Cyclohexane	16.8	Methanol	29.7
Ethyl acetate	18.6	Polypropylene	16.6
Chloroform	19.0	PVC	19.5
Dichloromethane	19.8	PET	20.5
Acetone	20.3	Nylon 6,6	28
2-Propanol	23.8	PMMA	19.0

Determination of δ of polymers

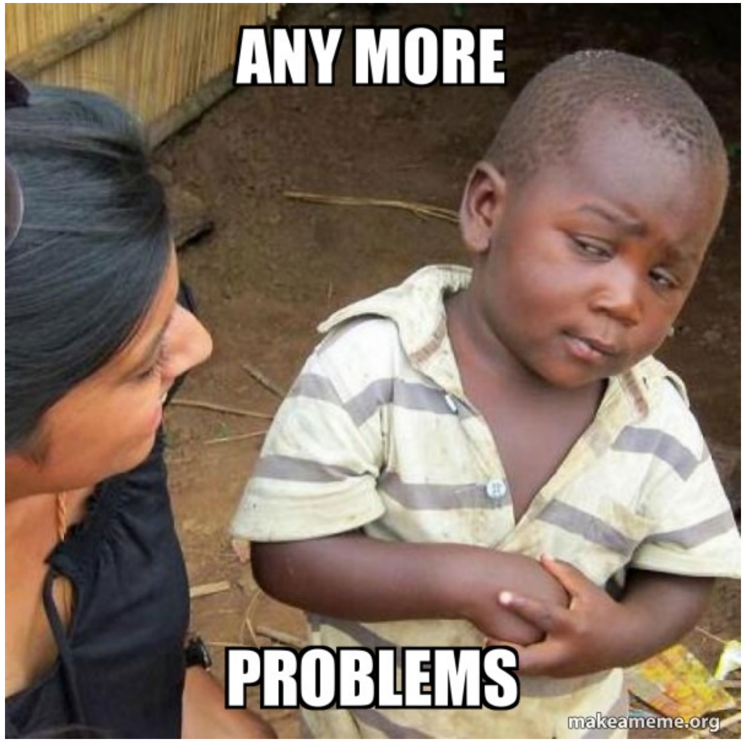
- I am not able to evaporate polymers without their decomposition
  - it is not possible to determine CED by the usual method
- non-solvent precipitation
  - dissolve the polymer in the right solvent and titrate with the non-solvent
  - at the moment of precipitation, we determine the δ of the polymer
- swelling in solvent
  - we soak the cross-linked polymer in solvents of different δ values
  - in which it swells the most, we assign such a δ to the polymer



Disadvantages of the Hildebrand parameter

- for some substances, discrepancies appeared between the theoretical (calculated) value of the Hildebrand solubility parameters and the experimentally determined value
- The Hildebrand parameter describes the contribution of all secondary bonds
  - it would be more appropriate to consider individual contributions separately
  - three contributors
    - dispersion forces
    - polar forces
    - hydrogen bonds

↓ growth of bond strength



Hansen parameters

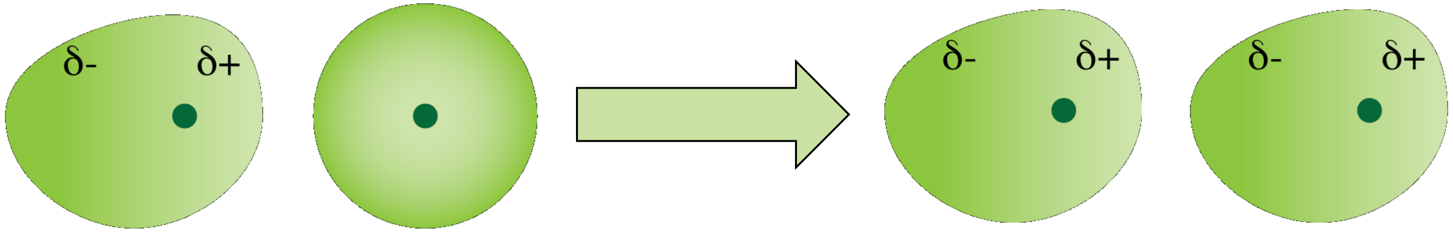
- splitting the Hildebrand (total) solubility parameter δ into three **partial solubility parameters**:
  - dispersion forces δ_d
  - polar forces δ_p
  - hydrogen bonds δ_h

$$\delta = \sqrt{{\delta_d}^2 + {\delta_p}^2 + {\delta_h}^2}$$

  - unit is $\sqrt{MPa}$
- ionic interactions are not considered
- they are determined experimentally and by calculation

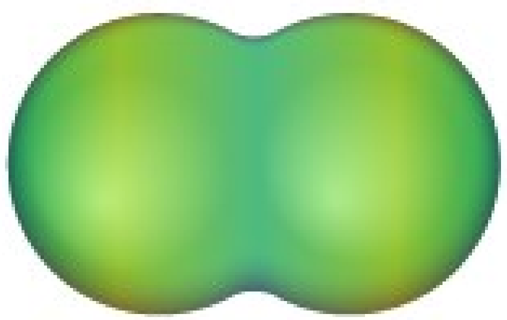
Dispersion (London) forces

- generally the weakest of the physical forces
  - they decrease with the 6th power of the distance (so they act over a short distance)
- temporary weak dipoles
  - they arise due to short-term random changes in the electron density in the atomic shell
    - a consequence of the imaginary movement of electrons in the shell
  - they can induce a similar change in neighboring atoms
- their number increases with the size of the surface of the molecule
  - straightened chains therefore a greater number than coiled

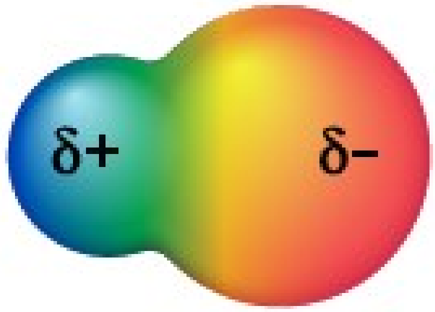


Polar interactions

- permanent dipoles
  - they arise due to a permanent imbalance of the electron density distribution in the molecule
  - a consequence of the different electronegativities of the atoms in the molecule



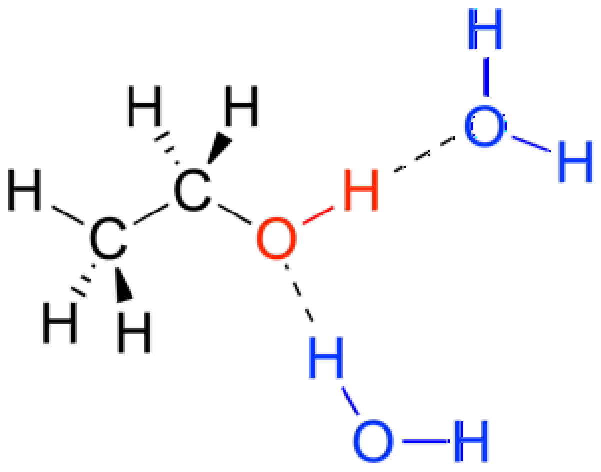
non-polar molecule
(does not form a
permanent dipole)



polar molecule
(forms a permanent
dipole)

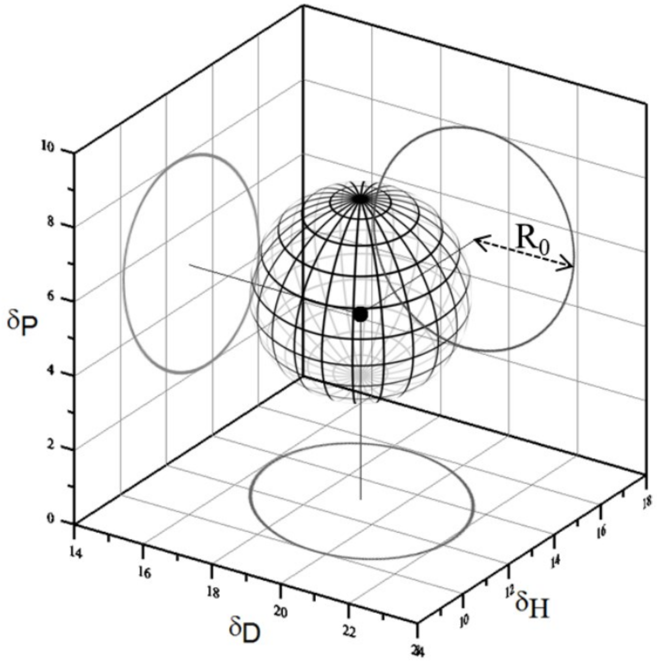
Hydrogen bridges

- the strongest of physical forces
  - basically a special case of polar interaction
- permanent dipole
  - hydrogen bonded to a very electronegative element (F, O, N)
    - hydrogen bond strength given by the structure
  - the hydrogen electron is attracted to the more electronegative atom so much that the hydrogen nucleus (proton) is practically exposed
  - allows interaction with a neighboring dipole to form a "proton bridge"



Solubility ball

- plotting Hansen's parameters in a three-dimensional graph
  - unfortunately, the dispersion forces are so small that the ball usually does not come out
    - the dispersion forces parameter δ^d is therefore multiplied by 2
- the center of the sphere corresponds to the parameters of the solute
- for each substance there is the largest radius R^0 of the solubility sphere, for which it is valid that if the solvent lies in the solubility sphere, it dissolves the given substance
  - we call R^0 the interaction radius



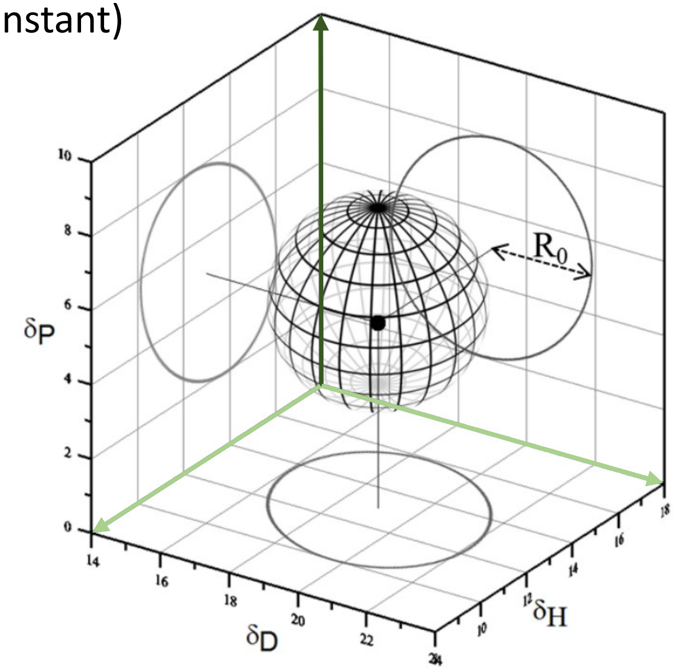
$$V^2 = (2\Delta\delta_d)^2 + \Delta{\delta_p}^2 + \Delta{\delta_h}^2$$

$$V = \sqrt{4\left(\delta_{dr} - \delta_{dp}\right)^2 + \left(\delta_{pr} - \delta_{pp}\right)^2 + \left(\delta_{hr} - \delta_{hp}\right)^2}$$

V ... is the distance of the solvent position from the center of the sphere

2D graphs of Hansen parameters

- plotting two Hansen parameters in a two-dimensional graph
  - rectangular projection of the 3D graph into one of the planes given by the coordinate axes (one parameter constant)



δ_H

δ_P

δ_D

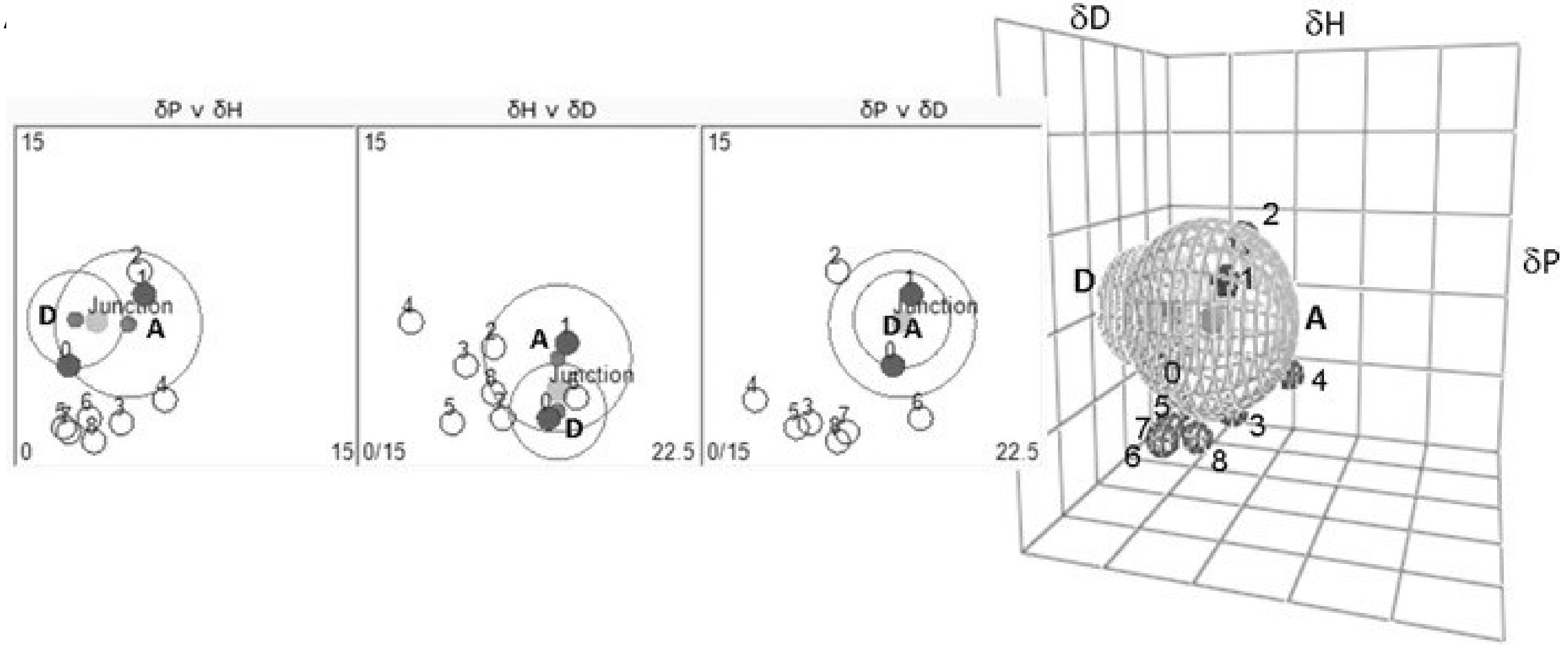
δ_D

δ_P

δ_H

2D graphs of Hansen parameters

- plotting two Hansen parameters in a two-dimensional graph
  - rectangular projection of the 3D graph into one of the planes given by the coordinate axes (one parameter constant)



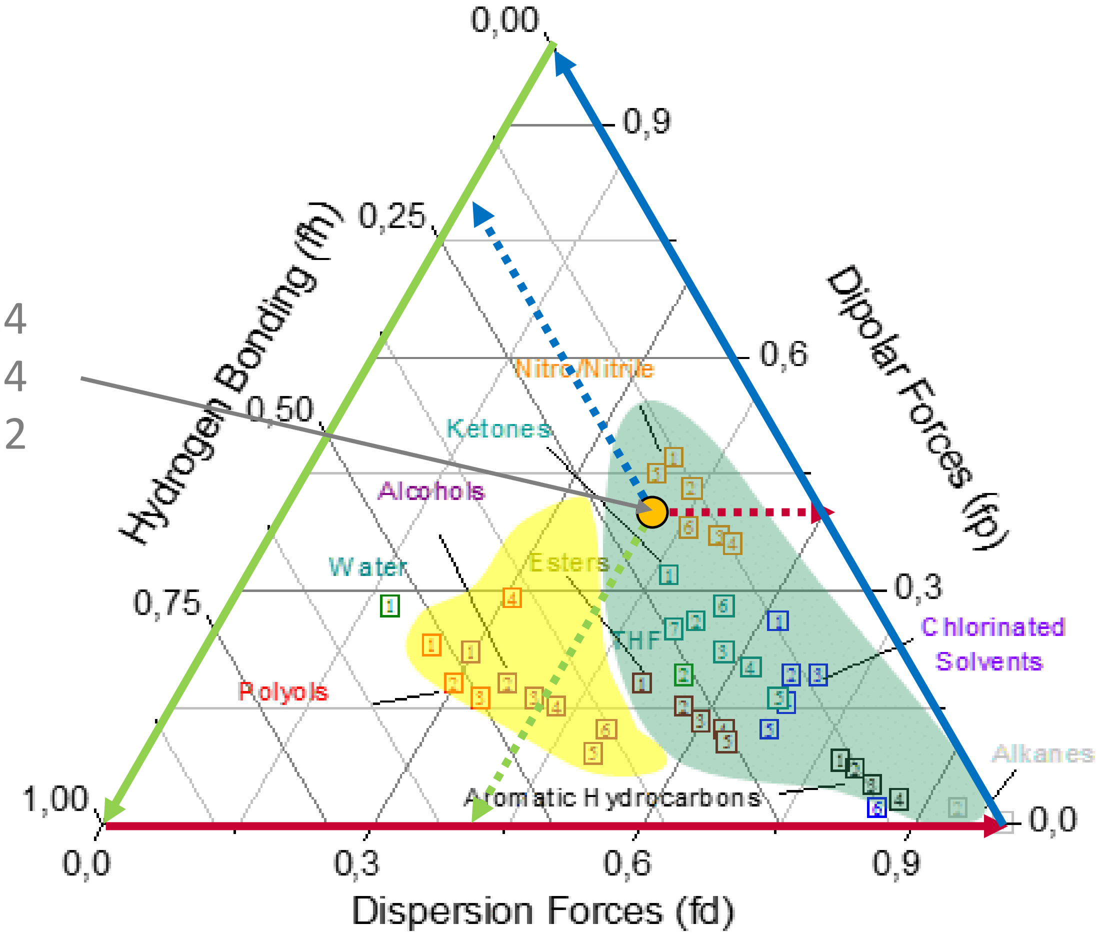
Teas (triangle) charts

- the solubility sphere is difficult to work with in a two-dimensional display
- practice often uses triangular charts
    - individual parameters are relativized

$f_i = \dfrac{\delta_i}{\delta_d + \delta_p + \delta_h}$	$f_d = \dfrac{\delta_d}{\delta}$	$f_p = \dfrac{\delta_p}{\delta}$	$f_h = \dfrac{\delta_h}{\delta}$

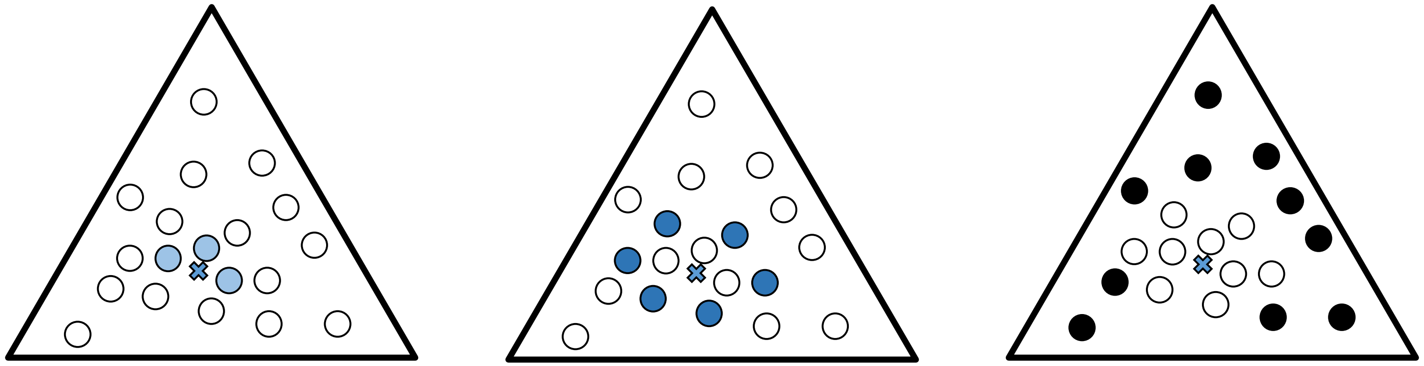
- the graphs describe only the mutual proportion of individual solubility parameters
    - it appears as if all fouling substances have the same absolute value of the Hildebrand parameter
    - they are not completely accurate, but they are usually sufficient for practice

Teas (triangle) charts



f_D = 0,4
f_P = 0,4
f_H = 0,2

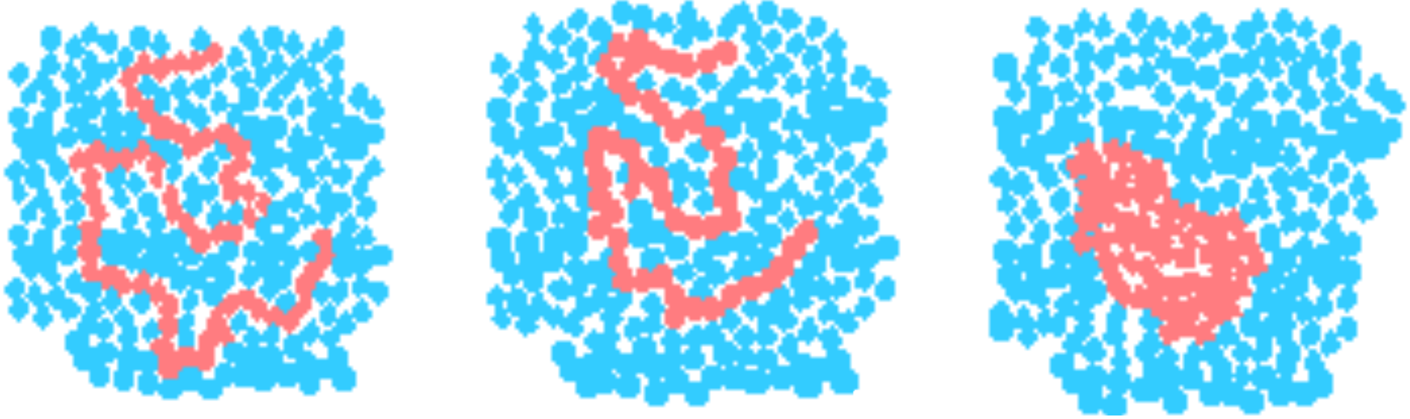
Good and bad solvents



ideal solvents

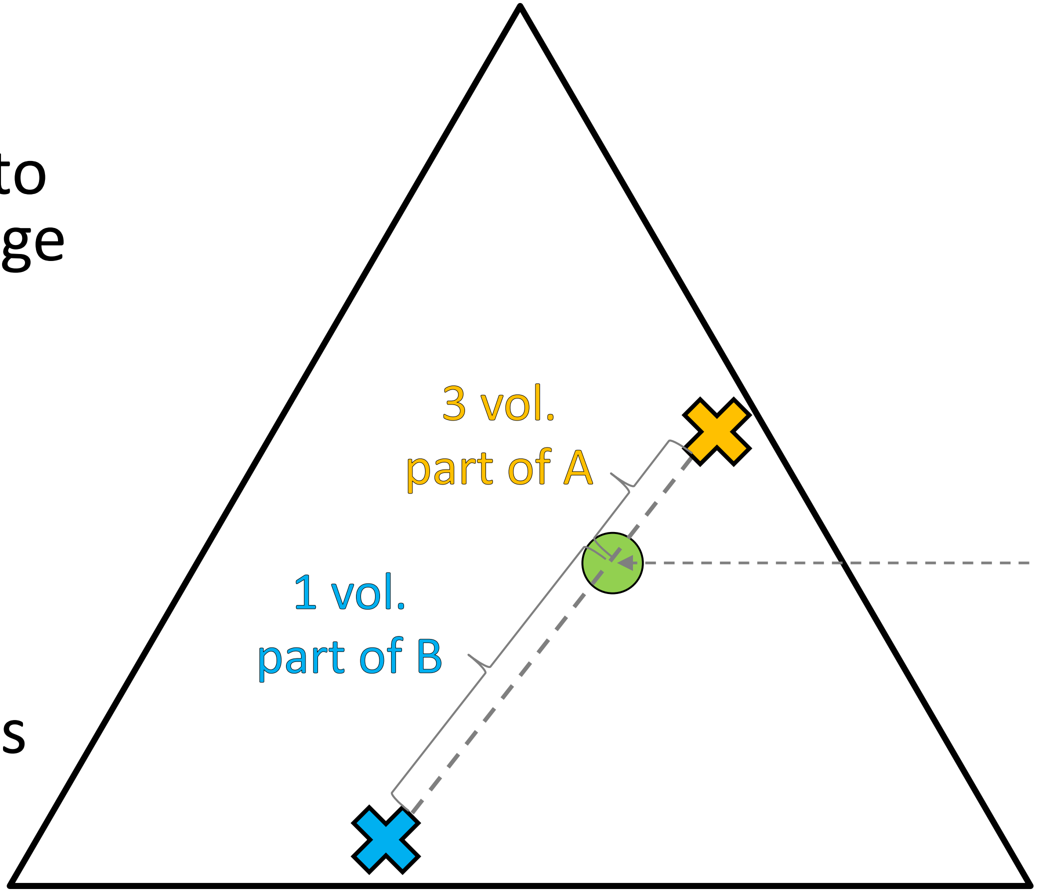
good solvents

bad solvents



Teas (triangle) charts

- for the mixture it is again true that the resulting f is equal to the weighted average of the relative parameters of the mixed substances
- in this way, a good solvent can be prepared from several bad solvents (so-called cosolvency)



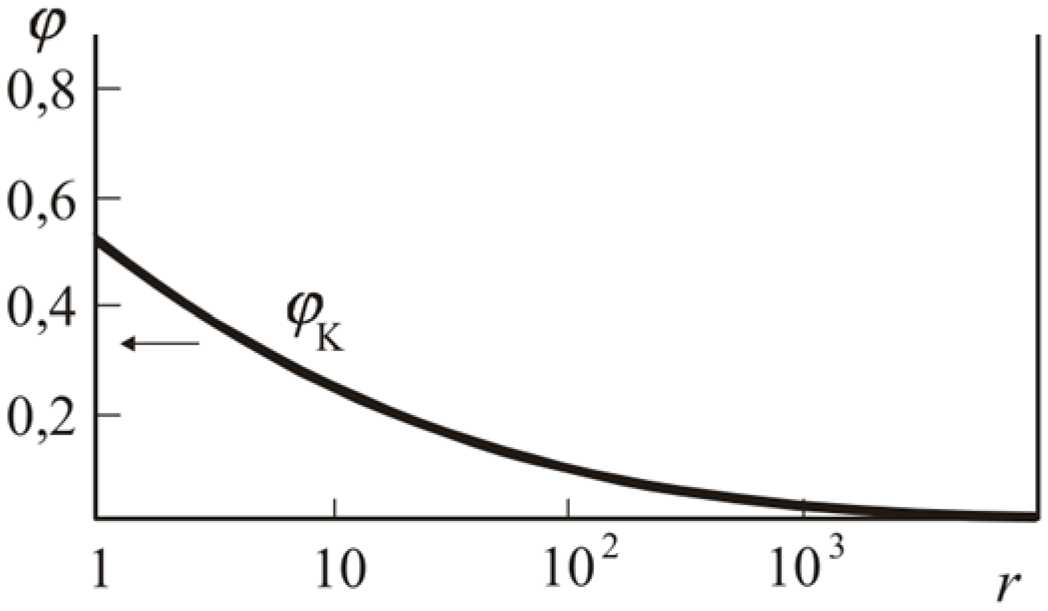
we want to dissolve this, but we only have the not-so-suitable solvents A and B

Solubility of polymers

- we consider a binary polymer-solvent mixture
    - In this case, the polymer is monodisperse (polydisperse systems are understandably more complicated)
- different for amorphous and semi-crystalline polymer
- dependent on solvent, polymer, temperature, pressure, etc.

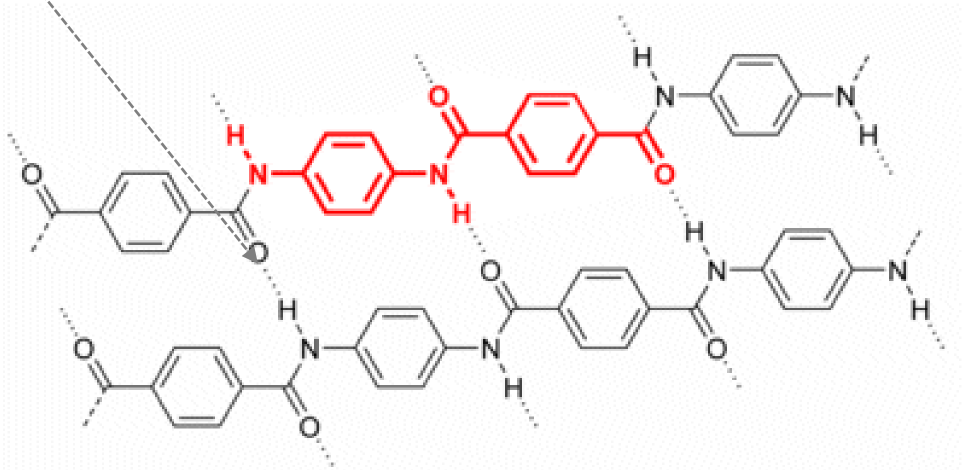
Effect of molar mass on solubility

- the critical concentration decreases with increasing molar mass
  - r = the volume fraction of the macromolecule segment to the unit volume of the solvent (these segments do not generally correspond to monomeric units)



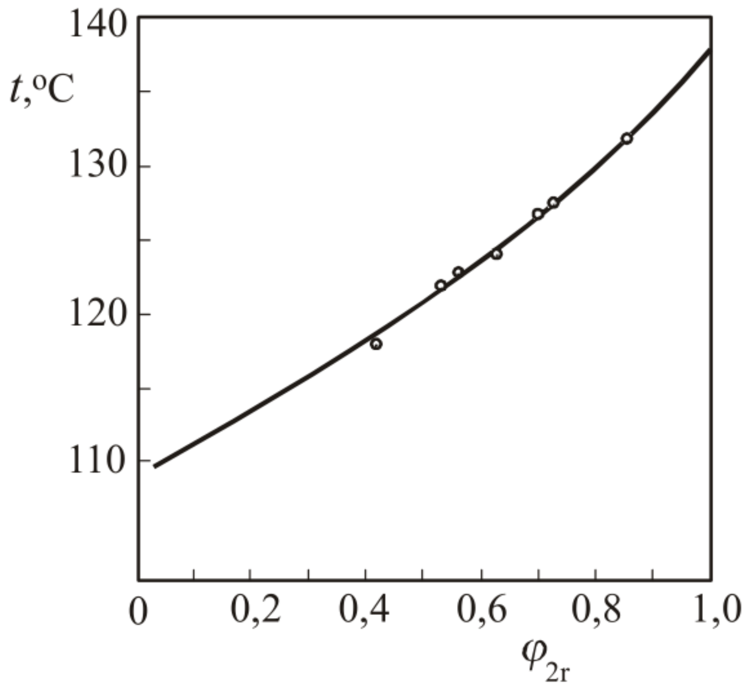
Dissolution of semicrystalline polymers

- crystalline parts less soluble
  - the solvent must overcome the physical bonds between the macromolecular chains



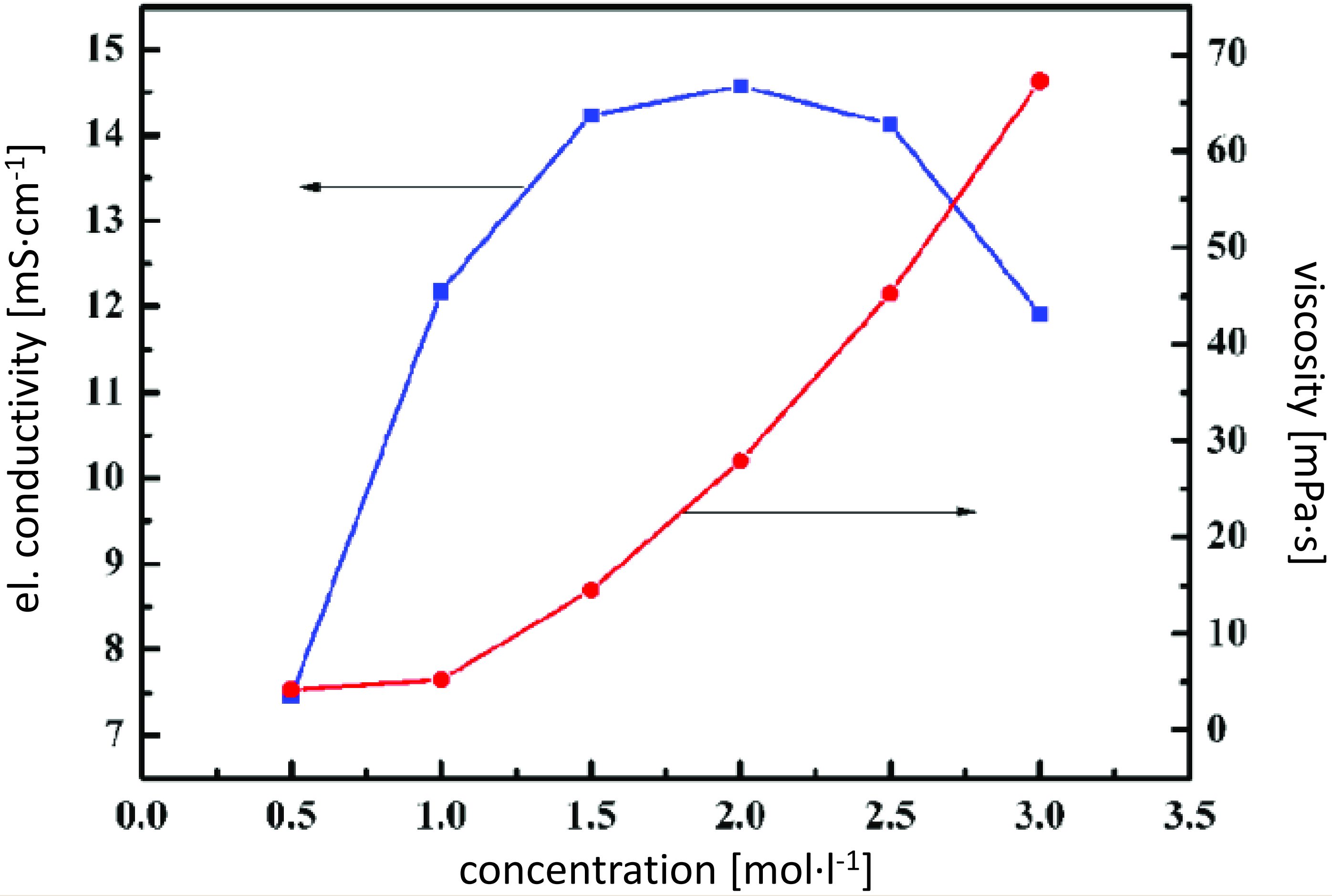
Dissolution of semicrystalline polymers

- can be conceptually divided into two parts
  - crystallite dissolution
    - The Gibbs energy due to the disappearance of crystallites (below their melting temperature) increases and must be compensated (reduced) by the Gibbs energy of mixing
      - however, it needs a significant excess of solvent and a sufficient temperature
    - semicrystalline polymers can thus be of limited solubility
  - dissolution of the amorphous polymer

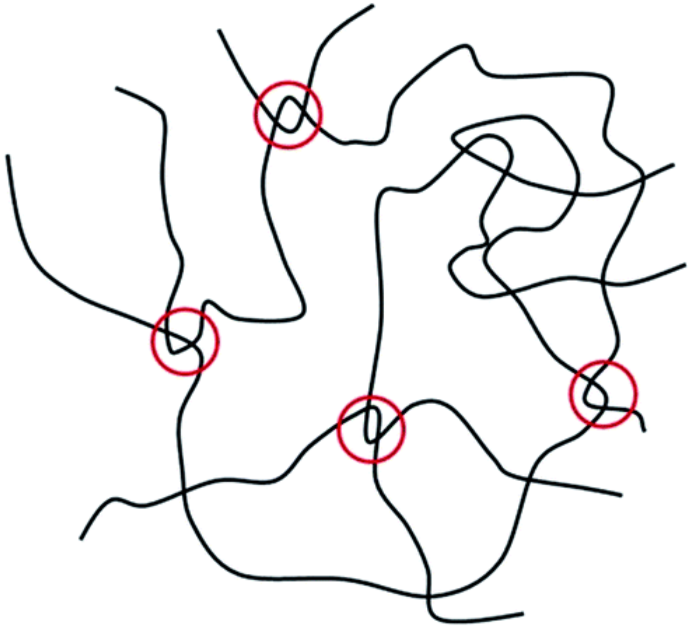


solubility of semicrystalline PE depending on temperature (φ_{2r} is the maximum soluble volume fraction of the polymer in the solution)

Conductivity of the polymer solution

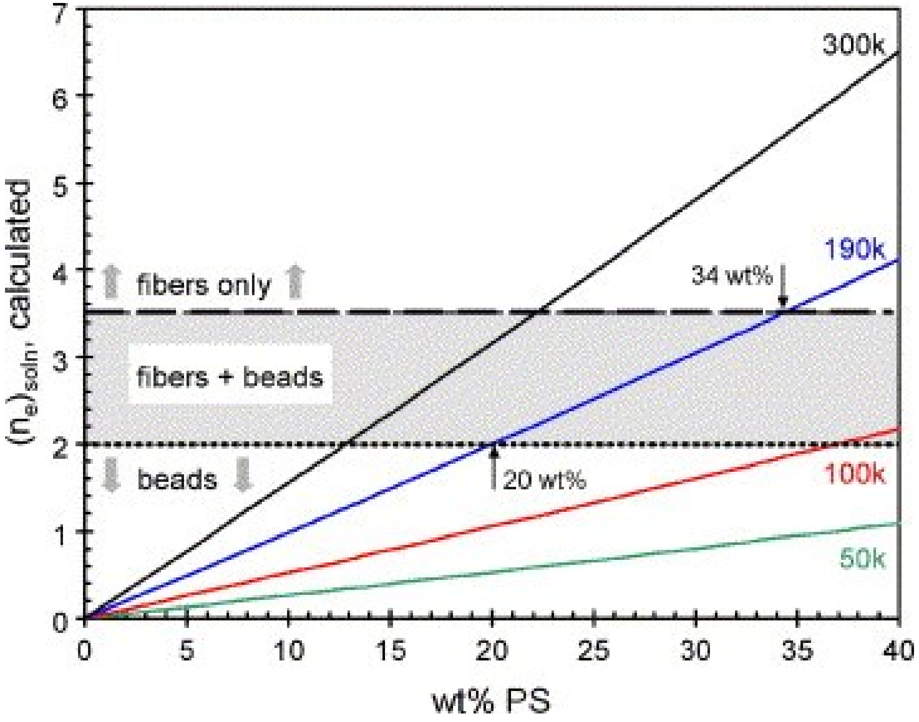


Entanglements

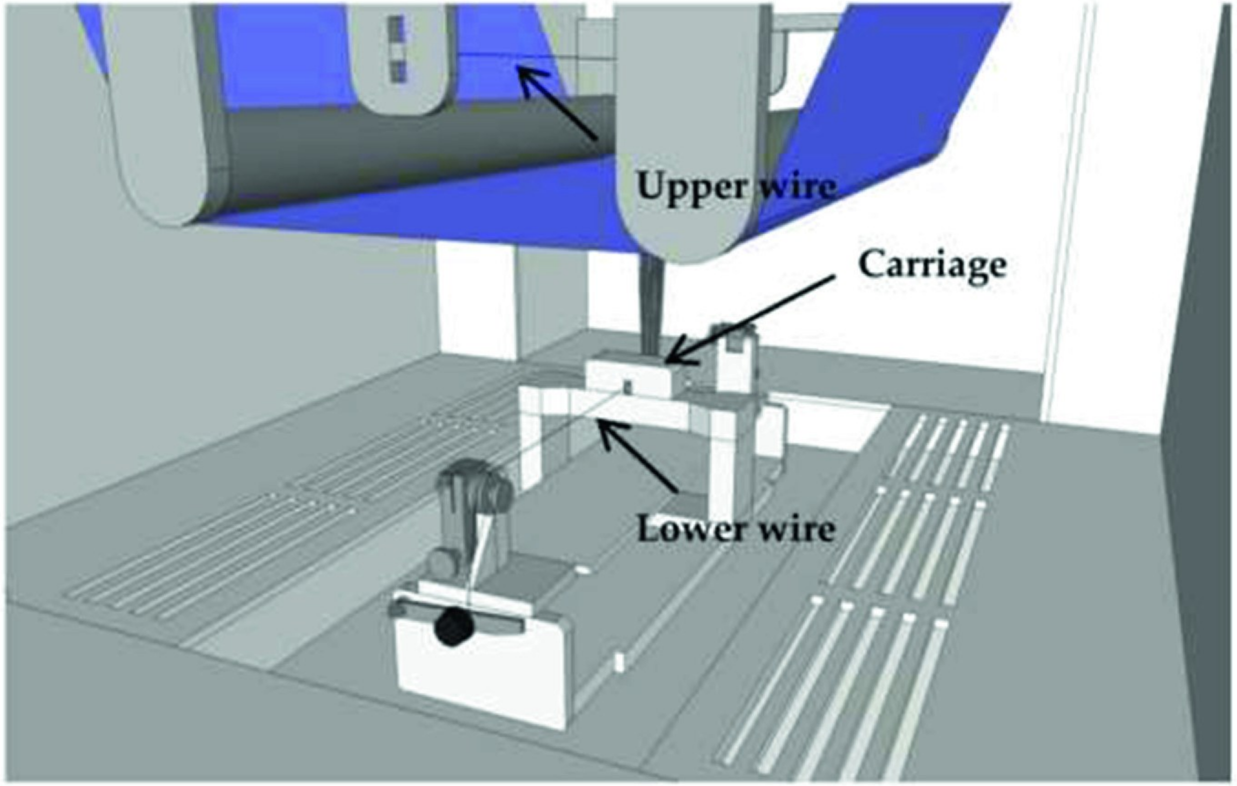


physical entanglements (knots)

cohesive entanglements



4. Polymer solutions for electrospinning



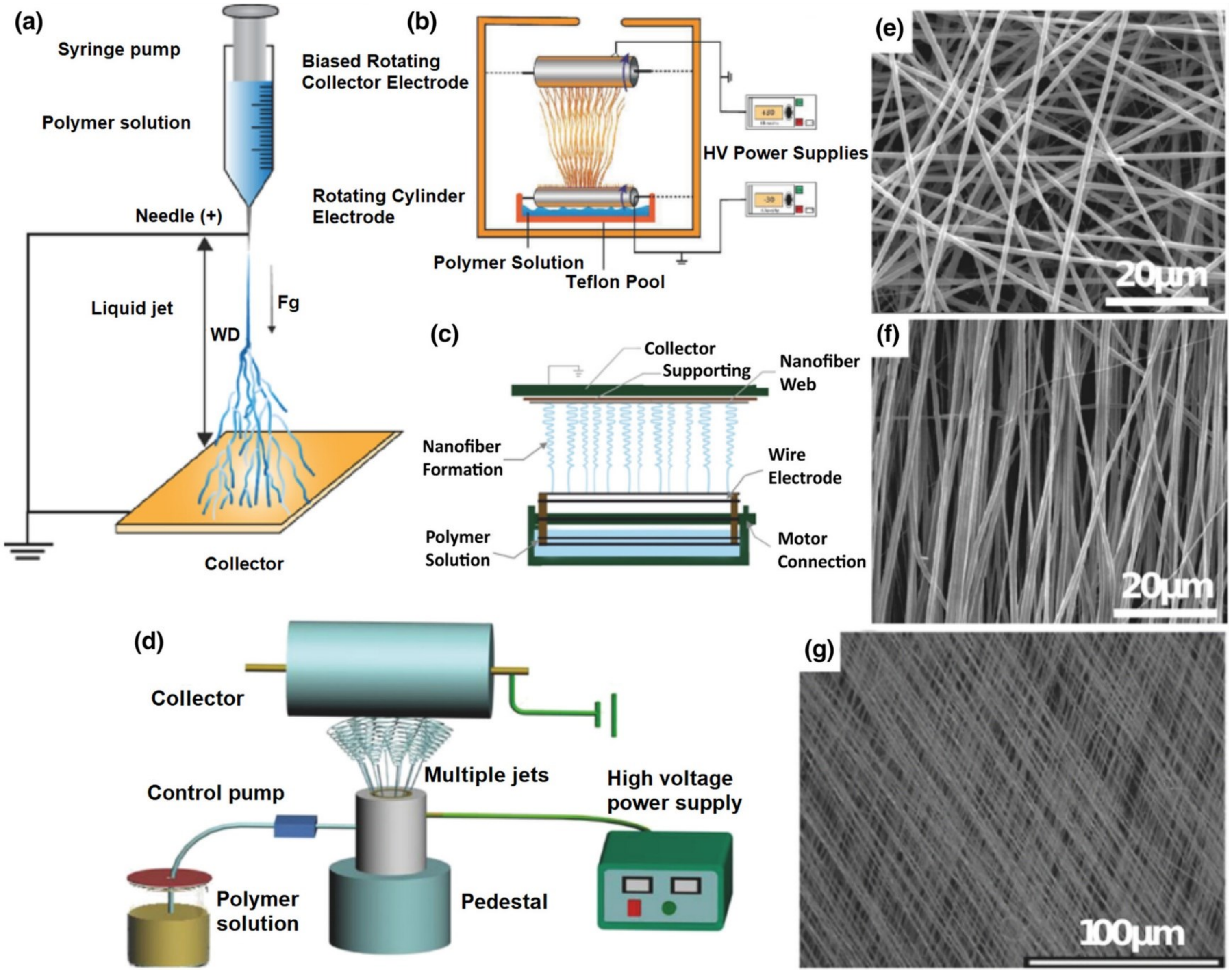
Electric spinning

- polymer solution or melt
- direct current (DC) or alternating voltage (AC)
  - combinations also possible (e.g. DC + centrifugal)
- needle, rod, roller, disc, string, other

- elongation and orientation of macromolecules (from solution or melt) induced by strong el. field

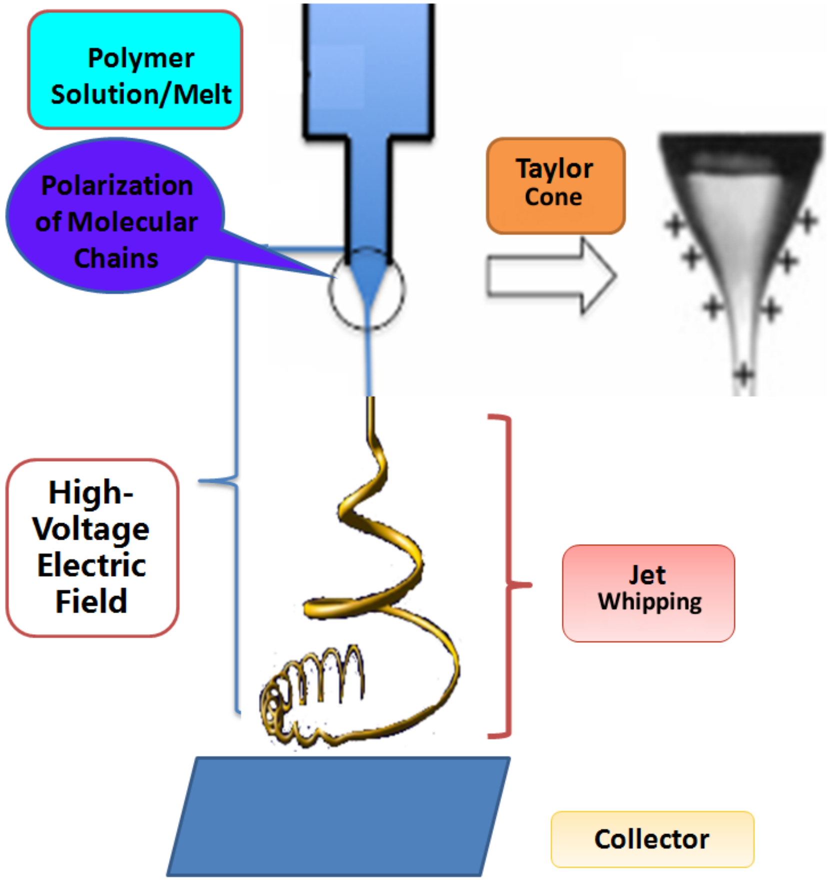
Process parameters of spinning

- electrode
- collector
- electric field strength
- temperature
- humidity
- the duration of the electric field
- solution flow rate


(a)
Syringe pump
Polymer solution
Needle (+)
Liquid jet
WD
Fg
Collector
(b)
Biased Rotating
Collector Electrode
HV Power Supplies
Rotating Cylinder
Electrode
Polymer Solution
Teflon Pool
(c)
Collector
Supporting
Nanofiber
Web
Nanofiber
Formation
Wire
Electrode
Polymer
Solution
Motor
Connection
(d)
Collector
Multiple jets
Control pump
High voltage
power supply
Polymer
solution
Pedestal
(e)
20μm
(f)
20μm
(g)
100μm

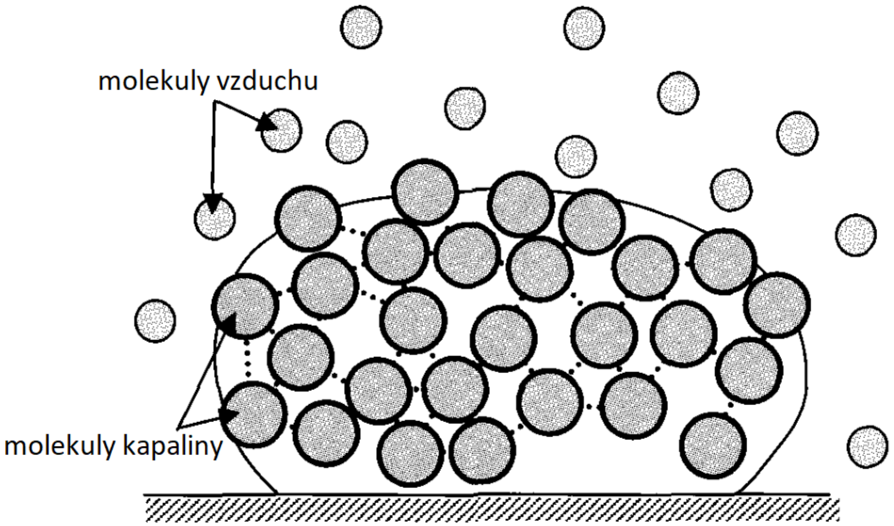
Electrospinning system parameters

- polymer
  - molecular weight
  - concentration
- solvents
  - permittivity
  - volatility
  - surface tension
  - electric conductivity
- viscosity



Surface tension of solvents

- the molecules of the liquid have a higher affinity to each other than to the molecules of the surrounding gas
  - surface tension where liquid and gas molecule meet
- acts against the electric voltage
  - preventing the formation of a cone
  - excessive surface tension → does not thread, spray or drip defects on the threads

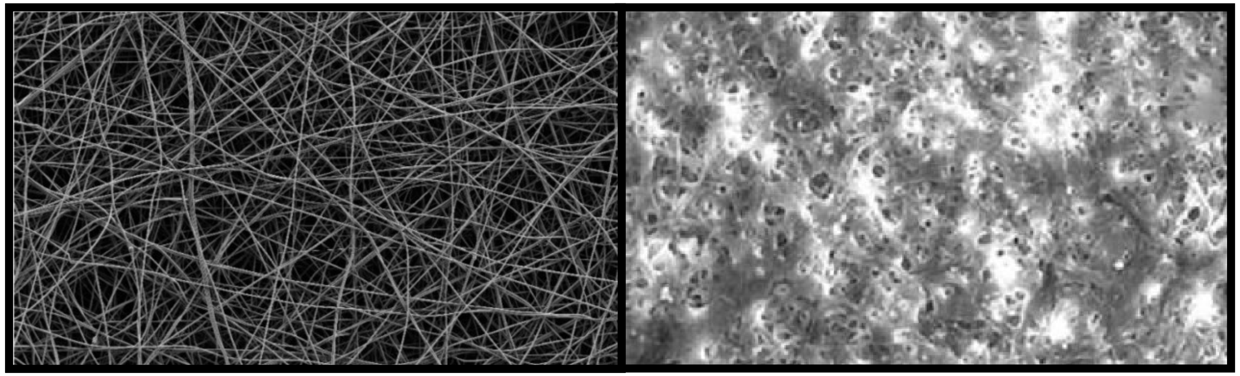


Permittivity of solvents

- measure of resistance to polarization of the dielectric
  - ε (small epsilon)
  - units of F·m^{-1}
- generally the higher the better
  - more uniform charge distribution on the surface of the solution
  - higher productivity, lower fiber diameters

Volatility of solvents

- evaporation rates (under given conditions)
- ideally, all solvent should evaporate before depositing on the collector
  - otherwise there is a risk of reverse dissolution
  - too much volatility causes the fibers to solidify before reaching nanoscale

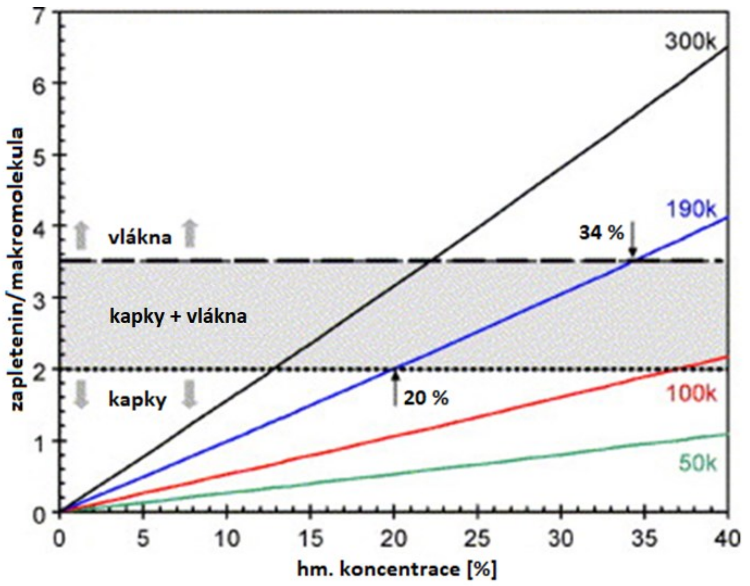


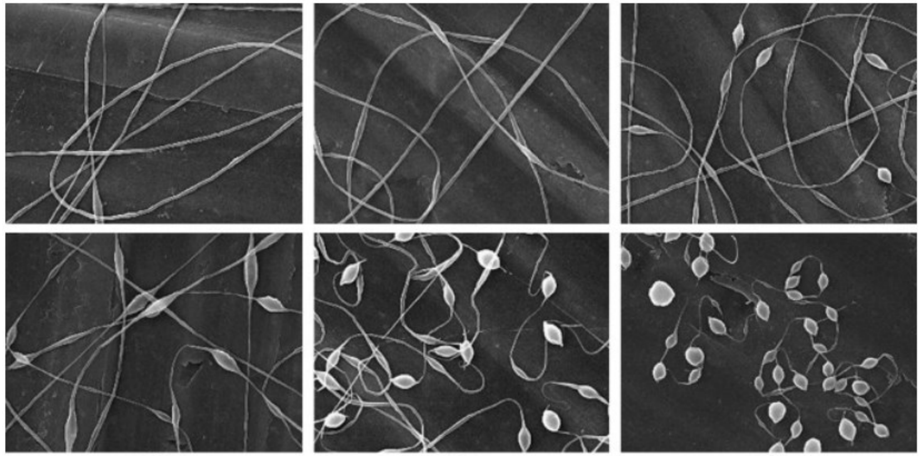
standard fibers

back dissolved fibers

Zapleteniny

- předpoklad dobrého zvlákňování
  - přechod mezi sprejováním a zvlákňováním
- závislé na rozpouštědlech, polymeru, molární hmotnosti, koncentraci





Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

MŠMT
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Polymer melts

Polymer melts

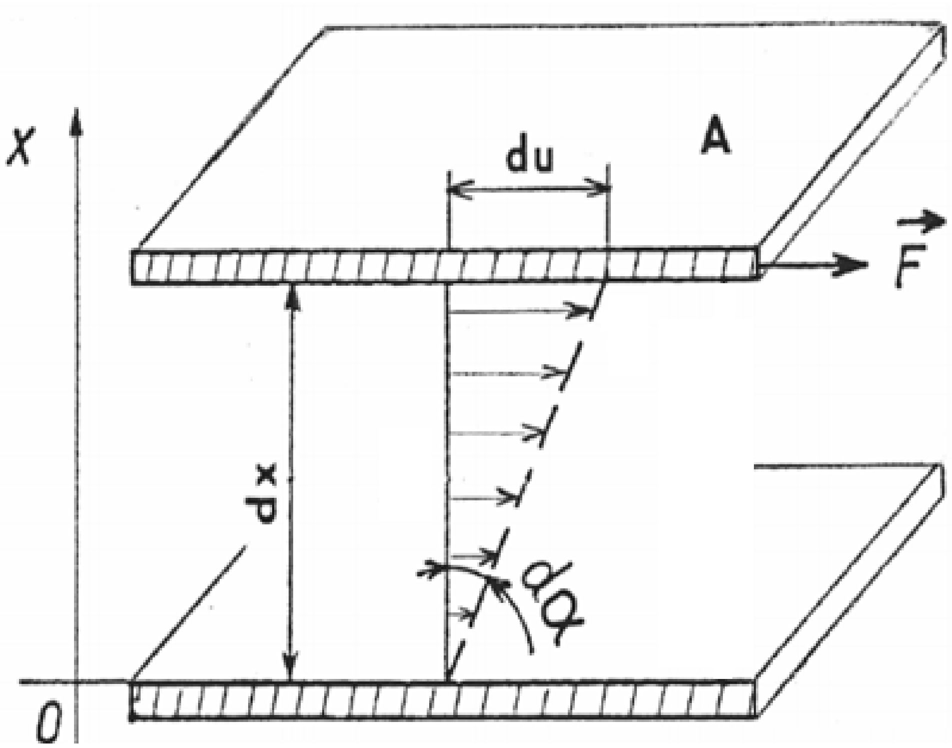
- polymer in liquid state
  - only non-crosslinked polymers with $T_{degradation}$ higher than T_f
    - more densely cross-linked rubbers cannot be melted
    - PAN is not cross-linked, but degrades before it melts (has $T_{degradation} < T_f$)
- above the flow temperature T_f
  - intermolecular secondary bonds disappeared due to thermal motions
  - macromolecules slide and flow over each other

Flow properties of polymer melts

- creep resistance (viscosity) of polymer melts dependent on many factors:
  - temperature
  - molecular weight
  - molecular weight distribution
  - additives
  - creep rate
  - creep time
- are generally referred to as non-Newtonian fluids (more generally fluids)

Viscosity model

- the investigated fluid is closed between the static pad and the upper plate of surface A moving due to the force F
- the fluid moves together with the upper plate
- we divide the fluid into imaginary layers (flow channels)
  - the layer closest to the static substrate practically does not move
  - the layer closest to the top plate moves the most



Newton's law of viscosity

- flow properties are expressed by the so-called shear (tangential) stress σ (small sigma)
  - sometimes also marked τ (small tau)
  - its negative value is often given because it acts against the direction of the force F

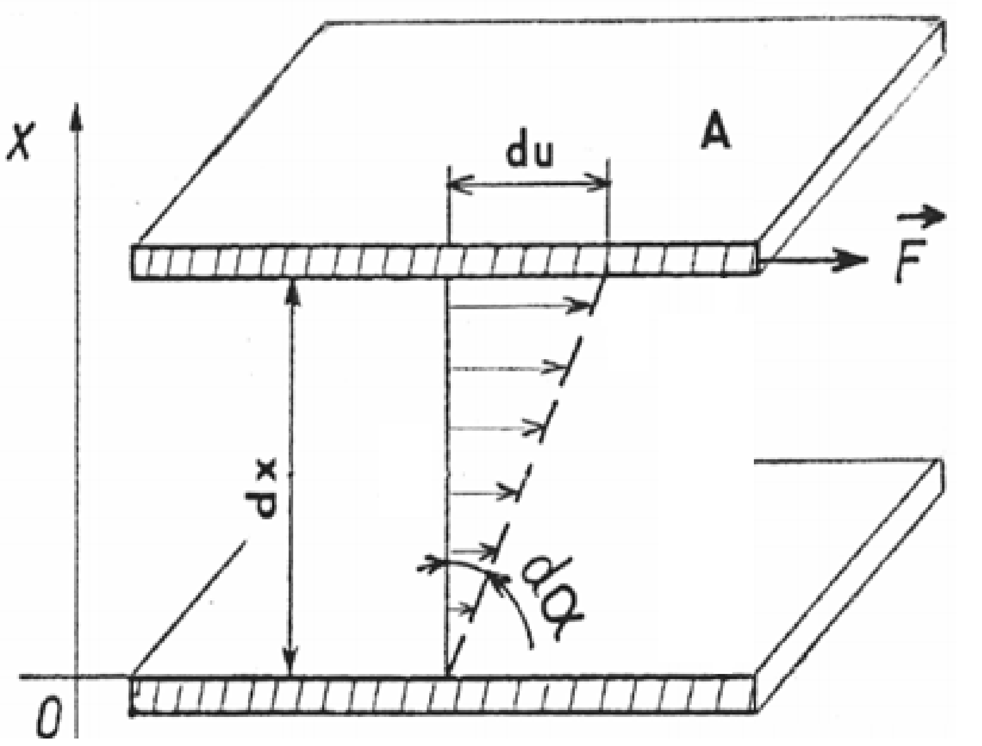
$$\sigma = \frac{F}{A} = \eta\dot{\gamma}$$

σ … shear stress [Pa]
F … force acting on the top plate [N]
A … plate area [m^2]
η … dynamic viscosity [Pa·s^{-1}]
$\dot{\gamma}$ … velocity gradient (shear velocity gradient) [s^{-1}]

$$\dot{\gamma} = \frac{d\gamma}{dt}$$

$$\gamma = \frac{du}{dx} = \operatorname{tg}\alpha$$

γ … rate of shear deformation (describes the relative displacement of the layers, therefore dimensionless)
t … time [s]



Attention!

- some texts consider the value described in the figure by the number du differently:
  - displacement of parallel surfaces
    - dimension is [m] and then:

$$\gamma = \frac{du}{dx}$$

  - shift speed change
    - dimension is [m·s^{-1}] and then:

$$\dot{\gamma} = \frac{du}{dt}$$

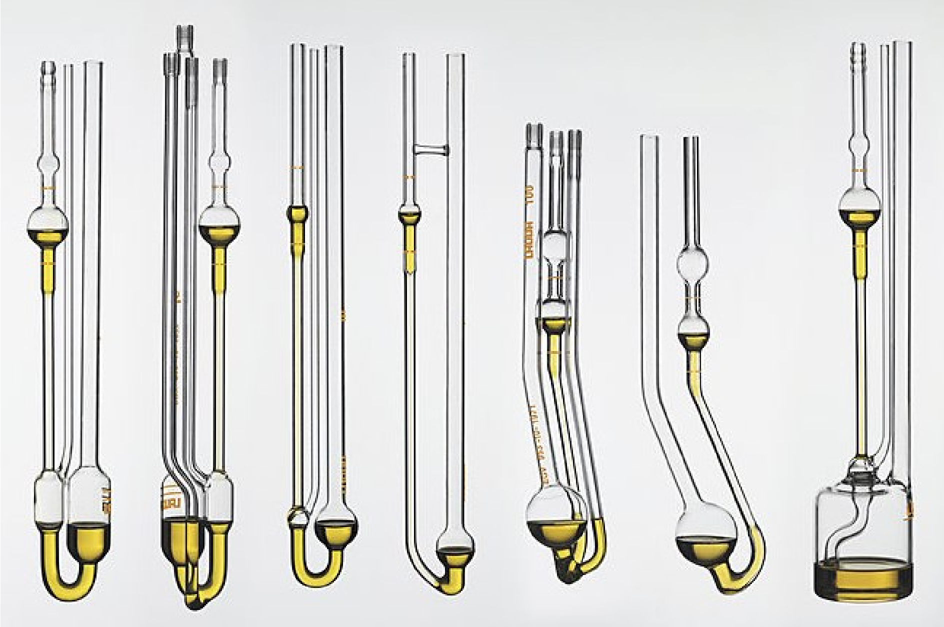
- therefore, in some texts, Newton's law appears in one of the following forms:

$$\sigma = \eta\dot{\gamma} \qquad \sigma = \eta\gamma \qquad \tau = \eta\dot{\gamma} \qquad \tau = \eta\gamma$$

$$\sigma = -\eta\dot{\gamma} \qquad \sigma = -\eta\gamma \qquad \tau = -\eta\dot{\gamma} \qquad \tau = -\eta\gamma$$

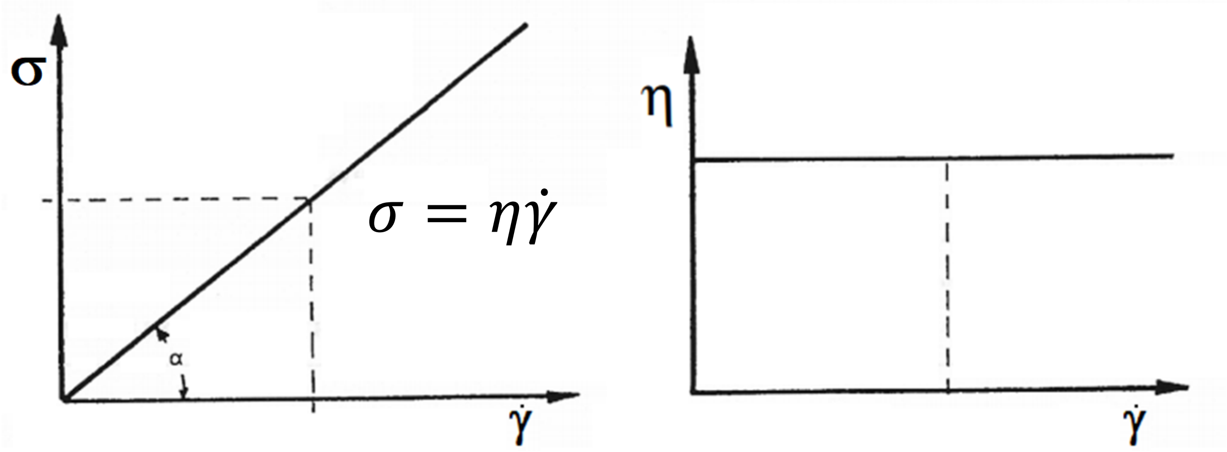
Viscosity

- describes the degree of internal friction of the liquid and thus the resistance to creep
  - it is the cohesive forces between the streamlines that slow down the flow
- generally depends on
  - temperature
  - concentration and molecular size
- different types of viscosities*
  - dynamic
  - kinematic
  - relative
  - reduced



Newtonian fluids

- they behave according to Newton's law
  - the strain rate is directly proportional to the shear stress
  - viscosity is a proportionality constant
    - it does not change with strain rate, shear stress, or its duration
    - is temperature dependent



$$\sigma = \eta\dot{\gamma}$$

Non-Newtonian fluids

- eg polymer solutions and polymer melts
- viscosity is not constant
- they generally behave according to an equation strikingly similar to Newton's equation

$$\sigma = \eta_z \dot{\gamma}$$

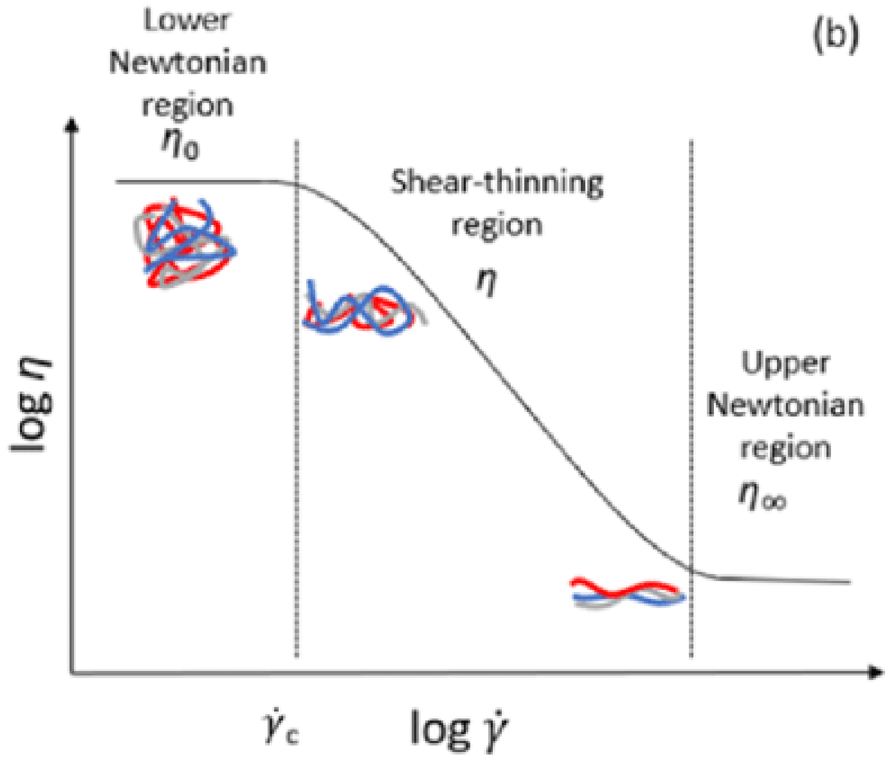
- however, instead of the dynamic viscosity η, it uses the apparent viscosity η_z (sometimes also η_a)
  - this is dependent on temperature (just like Newtonian fluids)
  - further dependent on the rate of deformation, the shear stress or the time of its action

Apparent viscosity η_z

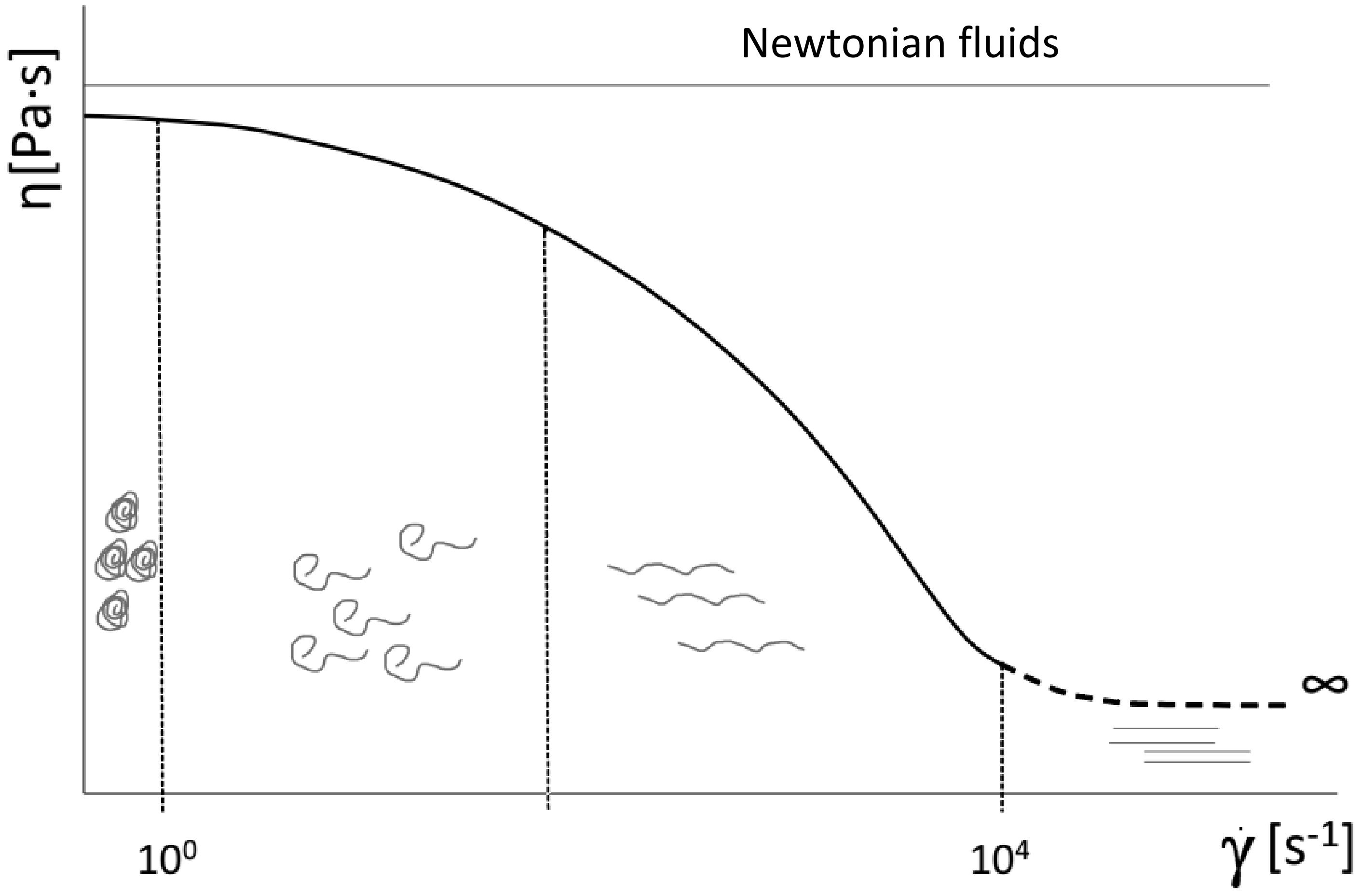
- temperature dependent a
  - shear rates
    - pseudoplastic liquids
    - dilatant liquids
  - during shear stress
    - thixotropic liquids
    - reopex liquids
  - shows a flow limit
    - Bingham liquids

Pseudoplastic liquids

- the apparent viscosity decreases rapidly with increasing tangential stress
  - the more I strain, the better it flows
- reduction of viscosity caused by the orientation of anisometric particles in the direction of movement of the liquid
- e.g. usual polymer solutions and their melts
  - generally applies to dispersions with an anisometric dispersion fraction
- technologically usually advantageous

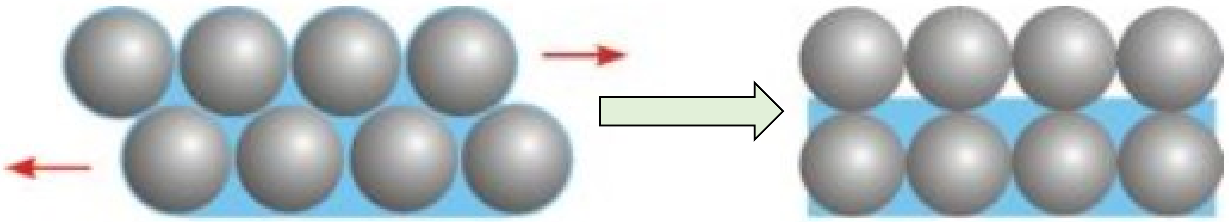


Pseudoplastic liquids



Dilatant liquids

- the apparent viscosity increases rapidly with increasing tangential stress
    - the more I strain, the worse it flows
- in a concentrated suspension at rest, the particles are surrounded by a small layer of liquid (which acts as a lubricant and thus allows flow) and occupy the smallest possible volume (they fit together as best as possible)
    - however, during shear stress, the particles move from their ideal position, increase their volume, and the liquid is no longer sufficient to wet them
    - if the rate of shear stress is too high, it is not enough for the liquid to reach all the particles and this will significantly increase the internal friction in the liquid (i.e. viscosity)
- observed for concentrated suspensions (e.g. polymer suspensions, concretes, etc.)
- technologically disadvantageous



Thixotropic and rheopex liquids

- thixotropic liquid
  - the apparent viscosity decreases with the duration of the shear stress
  - the longer I strain, the better it flows
  - a reason similar to that of pseudoplastic liquids, but the arrangement of anisometric particles occurs with a considerable delay
  - technologically advantageous
    - especially for mixing or painting
- reopex liquids
  - the apparent viscosity increases with the duration of shear stress
  - the longer I strain, the worse it flows
  - the reason is similar to that of dilatant liquids, but dilation occurs with a significant delay
  - technologically disadvantageous

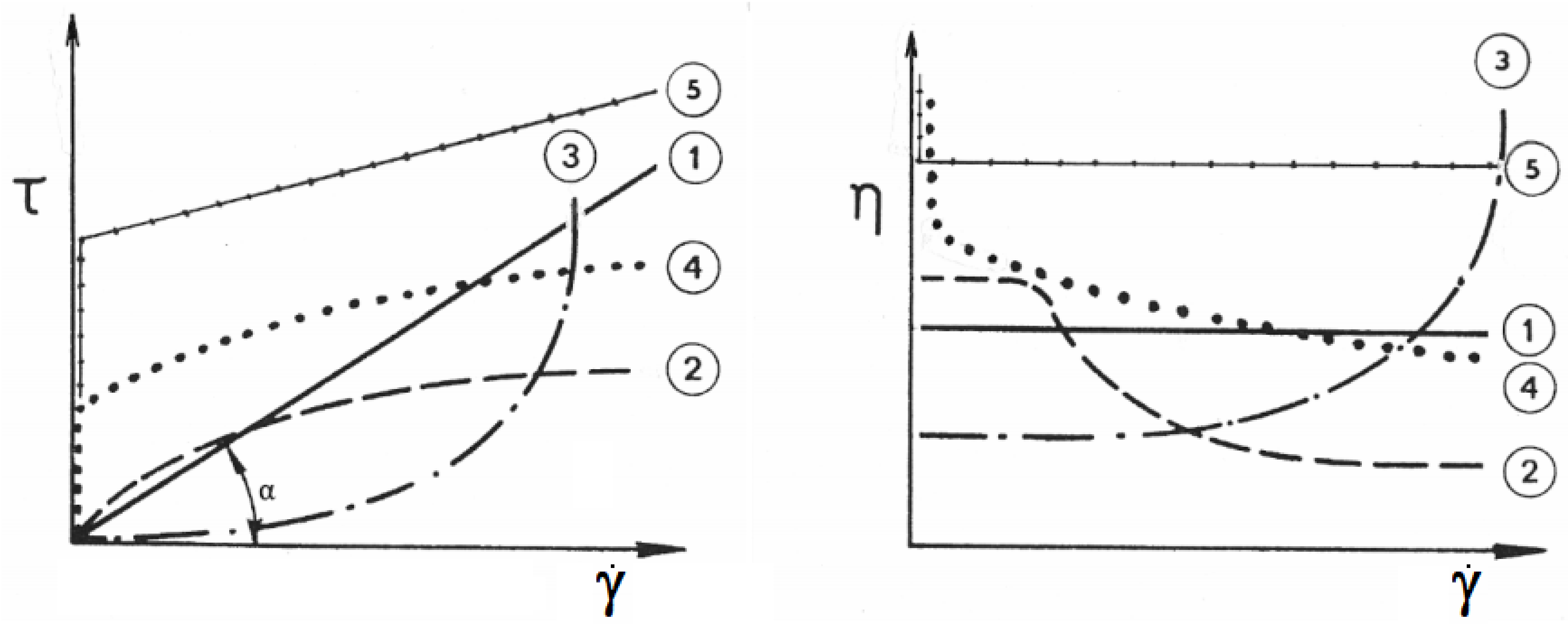
Bingham liquids

- they show significant flow properties only after exceeding the so-called (dynamic) flow (or yield) limit σt
  - they may behave Newtonian or non-Newtonian when the **flow limit** is exceeded

$$\sigma - \sigma_t = \eta\dot{\gamma}$$
$$\sigma - \sigma_t = \eta_z\dot{\gamma}$$

- **the flow limit** represents the stress that is needed to overcome the attractive forces between the dispersed particles
- usually mushy or pasty suspensions or gels (chalk, toothpaste, lime)

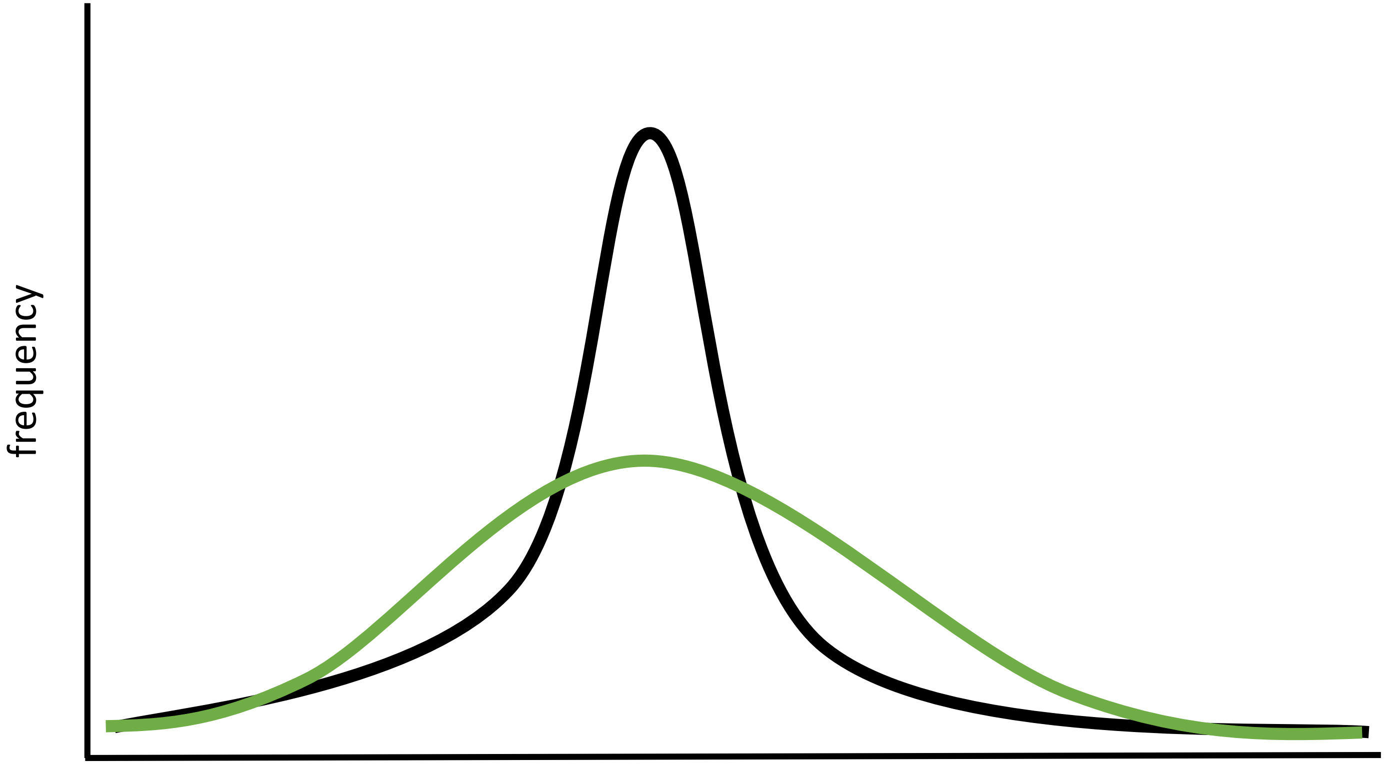
Newtonian and non-Newtonian fluids



1 – Newtonian, 2 – pseudoplastic, 3 – dilatant, 4 – Bingham non-Newtonian, 5 – Bingham Newtonian

Effect of molecular weight distribution

- the wider the distribution, the earlier non-Newtonian behavior appears

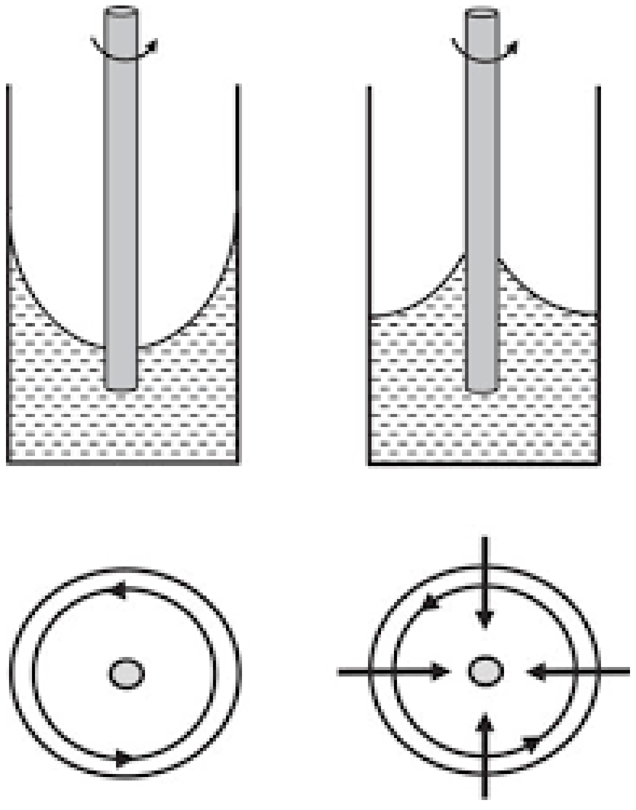


Siphon effect

- during pouring, the melt or solution pulls itself from one container to another even after e.g. water would not be able to flow
- given by physical nodes and secondary bonds between chains
  - requires a sufficiently high molecular weight

Weissenberg phenomenon

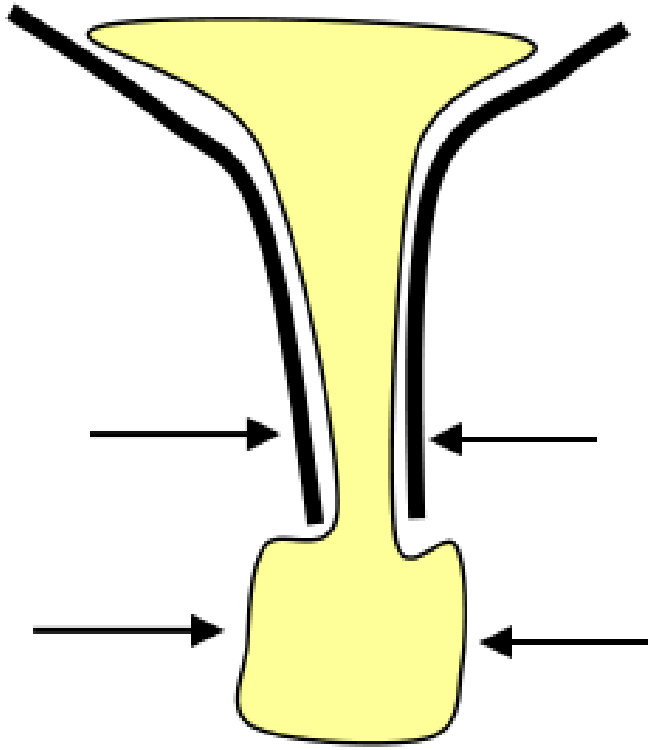
- pushing a non-Newtonian fluid towards a rotating body
    - manifestation of the elasticity of liquids
    - generation of stress perpendicular to the surface of the rotating body
- it can be simply imagined that long macromolecules wind up on a rotating body and pull others



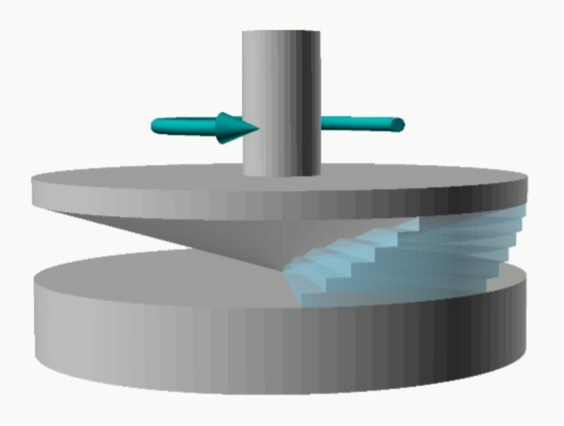
newtonské *nenewtonské*

Increase in profile behind the nozzle

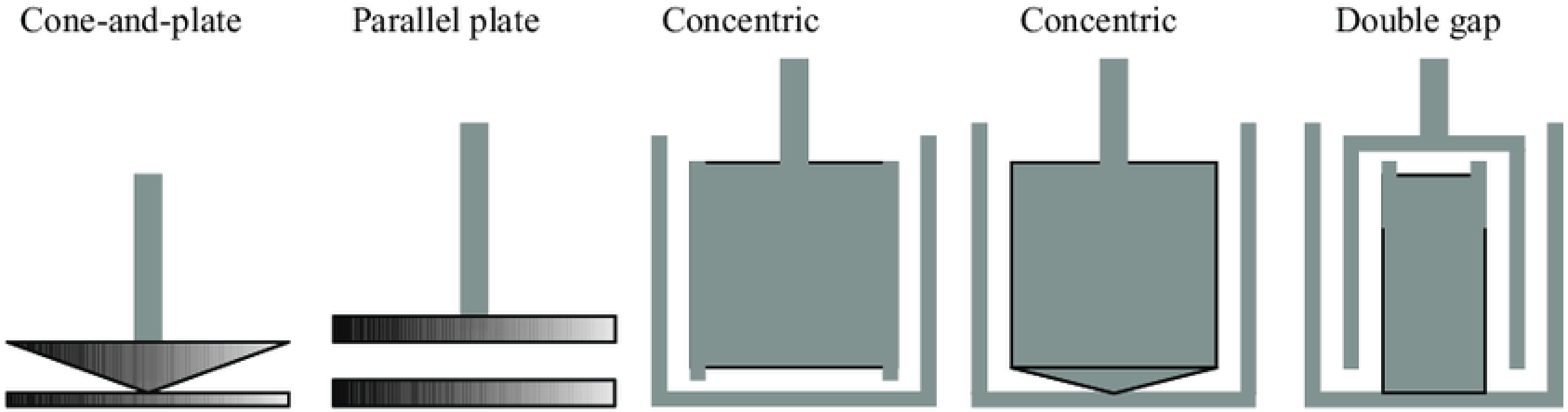
- tension is released, when the melt "springs" in free space
- it limits production speed



Rotational viscometry / rheology



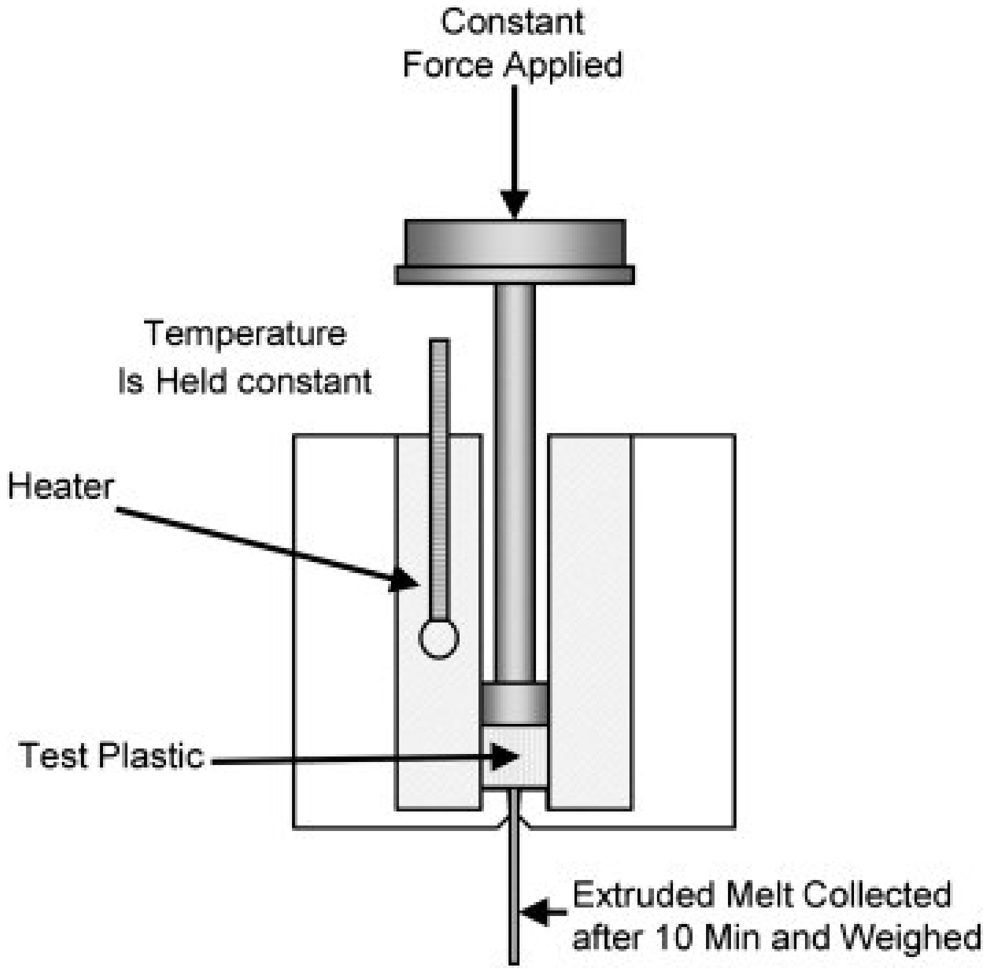
- relative method
- the torsional stress sensor senses the force, proportional to the resistance exerted by the examined fluid
- many geometric arrangements of measuring instruments:



Melt flow index

- melt flow rate (MFR)
- an important parameter for mass production
- it describes the real behavior of the melt without having to investigate the chemical-physical parameters in a complicated way
- important e.g. for meltblown or spunlace technology
- corresponds to the amount (weight, volume) of polymer melt at a defined temperature flowing through a defined nozzle at a defined pressure for a period of 10 minutes
  - units therefore g/(10 min) or ml/(10 min)
- is measured with an extrusion plastometer

Scheme of the extrusion plastometer



Processing of polymer melts

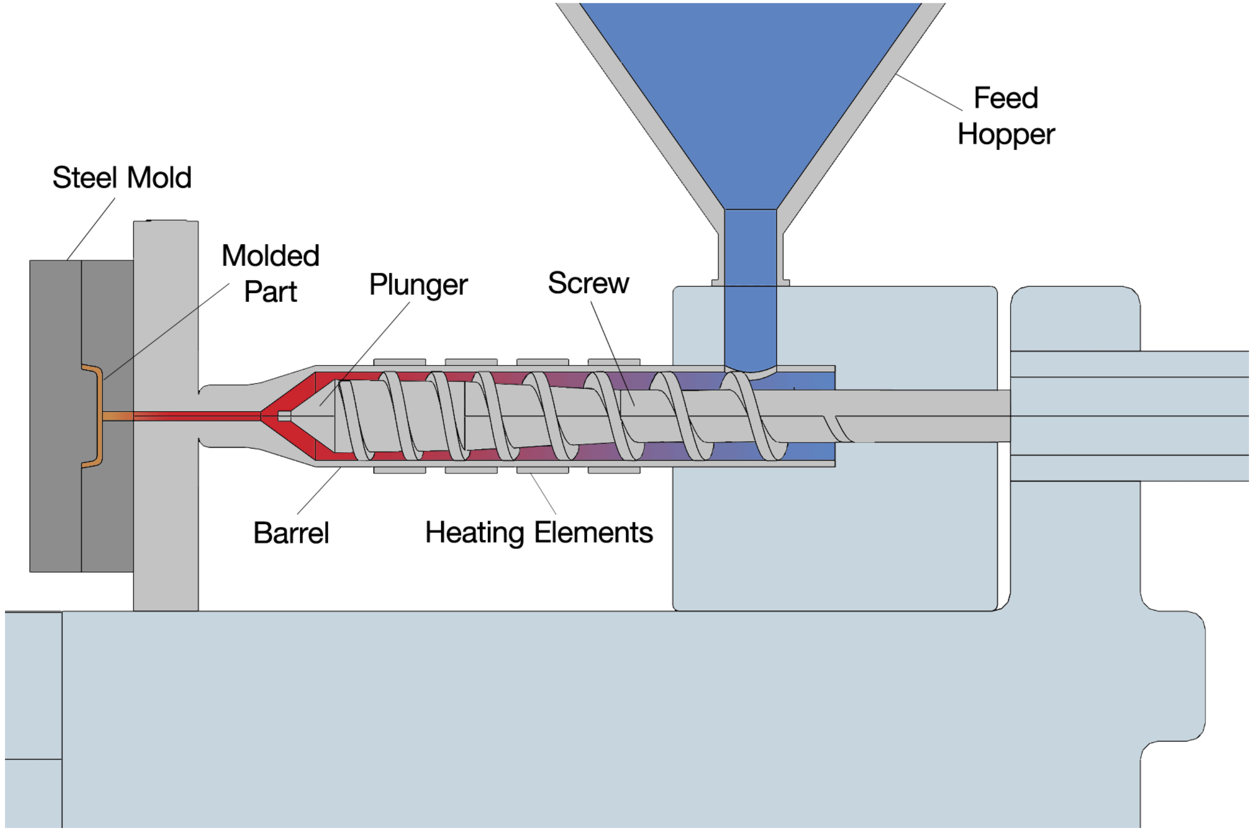
- compared to solutions, melts have a fundamental:
  - advantage – these are cleaner polymers (no solvent, etc.)
  - disadvantage - I have to heat it up a lot, which is expensive
- processing methods
  - extrusion
  - injection
  - blowing
  - thermal-vacuum forming of foils
  - calendering
  - pressing
  - fiber production

Injection molding

1. a granulate of polymer or polymers is poured into the hopper
2. the auger transports the granulate to the compression zone, where it is wetted and the heating elements heat and melt it
3. further, the screw conveys the melt to the extrusion head
4. the result depends on further processing
    - injection
    - indebtedness
    - cooling and back granulation
    - etc.

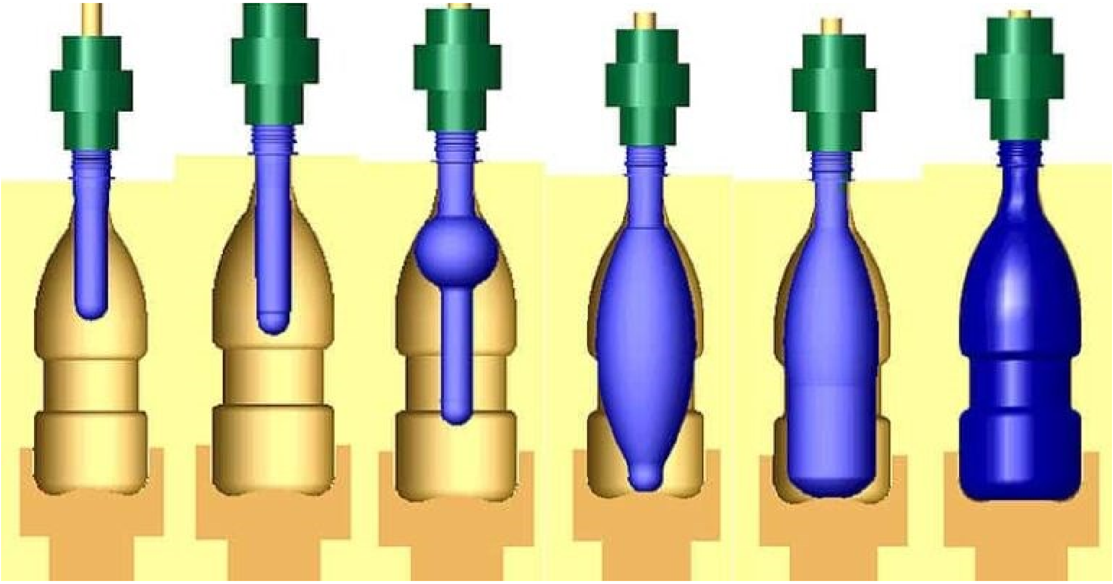
Injection molding

- first identical to extrusion, but the extrusion head leads through a narrow neck into t



Injection Blow Molding

- classic: production of hollow products
- extrusion blow molding: film production
  - the blown bubble is pressed between the rollers onto the foil



Thank you for your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

MŠMT
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Additives in polymers

Additives in polymers

- they modify the properties of the polymer product
- together with macromolecules they form polymer mixtures
- their amount in the polymer is given in unit phr
  - phr (weight parts per hundred of rubber)
- in total, it is possible to add more than 100 phr (but it depends on the polymer)
- types of ingredients
  - processing
  - antidegradants
  - mesh
  - affecting other physical properties
  - strange

Additives in polymers

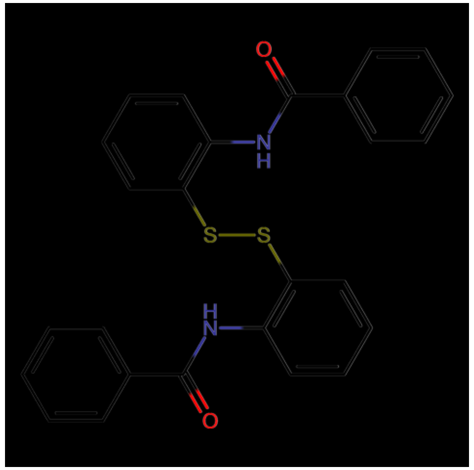
- processing
  - processing plasticizers
  - lubricants
  - separators
  - plasticizers
  - auxiliary ingredients
  - thermal stabilizers
- antidegradants
  - light antidegradants
  - antioxidants
  - antiozonants
- cross-linking
  - crosslinking agents
    - sulfur and its derivatives
    - peroxides
    - energy-rich radiation
  - activators
    - vulcanization activators
    - peroxide activators
  - accelerators
    - vulcanization accelerators
    - curing accelerators
- others
  - fillers
  - reinforcement
  - puffing additives
  - optical brighteners
  - plasticizers
- special
  - antistatic
  - adhesives
  - flame retardants
  - abrasives
  - explosives and fuels

Processing additives

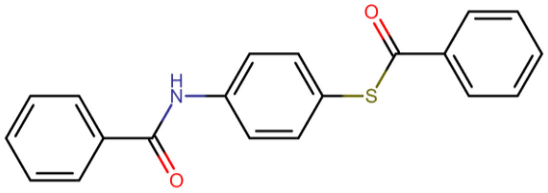
- are added to facilitate the processing of the polymer
  - their primary purpose is therefore not to influence the resulting properties of the product, but they still do so to a certain extent
- types:
  - processing plasticizers
  - lubricants
  - separators
  - plasticizers
  - thermal stabilizers
  - other processing ingredients

Processing plasticizers

- used in the plasticization (kneading) of rubbers (but sometimes also with thermoplastics)
  - a process in which the macromolecules of the rubber are mechanically torn apart and re-linked
  - unification of molecular weights
  - preparation of rubber compounds
- otherwise also peptizers
  - they facilitate kneading
  - they stabilize the radicals formed
  - accelerate plasticization
- also when recycling rubber into so-called regenerated material
  - it is about tearing the original cross-linked macromolecules so that the result is reprocessable and vulcanizable
  - moss. the properties of the regenerate are always lower than those of the original macromolecules (molecular weights are lower)
- around 0.05 phr are added for plasticization, up to about 4 phr for regeneration



Peptazine BAFD



Peptazine BFT

Lubricants

- internal lubricants
  - rather soluble in the polymer
  - reduce melt viscosity and friction (easier processing)
- external lubricants
  - rather insoluble in the polymer
  - forms a separation layer on the surface of the polymer
    - the polymer then does not stick to surrounding products or equipment
    - protects the polymer from weathering
    - unifies the look
- the lubricant is never internal only or internal only
- types of lubricants according to chemical composition
  - liquid or solid alkanes (paraffinic oils and paraffins)
  - fatty acids, their salts (calcium), esters or amides
  - waxes (natural and synthetic)
  - heavy alcohols (more than 30 carbons)
  - polyhydric alcohols
- combination of the previous ones
- dosage usually from 0.5 to 3 phr

Separators

- forms a layer preventing the product from sticking to the device
- coatings or spraying of mold surfaces
  - must withstand high temperatures
  - silicone oils, PTFE dispersion
  - they are difficult to remove and limit subsequent surface treatment of the product (e.g. dyeing [ideally green])
- separation foil
  - easier separation from the product
  - cellophane, PVA

Other processing additives (rubber)

- reduce the viscosity of the rubber mixture during mixing (with fillers, etc.)
  - they increase the possible processing speed of the mixture without degradation of macromolecules due to shear stresses
  - they reduce frictional heat during mixing of the mixture
- two kinds
  - fatty acids and their salts (Ca^{2+}, Zn^{2+})
  - resin
- dosage up to 10 phr

Plasticizers

- they reduce the T_g of the product
  - they get between the macromolecules and artificially create a space that allows the segmental movements of the macromolecules
  - the plasticizer must therefore be a solvent of the given polymer (so that it can penetrate between the macromolecules and distance them from each other)
- usually organic substances
  - they should not leak out of the product, but phthalates in PVC, for example, do not do this very well (they cause a distinctive smell of new linen)
- types
  - non-polar plasticizers
    - for non-polar and slightly polar polymers
    - oils, tars
  - polar plasticizers
    - for polar polymers
    - phthalates, adipates, sebacates of higher alcohols
  - macromolecular
    - they do not volatilize, but have lower efficiency
    - PEG, PES, resin

voda jako (těkavé) změkčovadlo bavlny

Thermal stabilizers

- prevent or at least limit the thermal degradation of macromolecules during processing (mainly for PVC)
- two main tasks
  - prevent the splitting off of low molecular weight substances from the polymer (e.g. HCl)
  - they prevent the formation of colored structures
- two kinds
  - inorganic or organic salts and their suitable mixtures
    - some salt mixtures increase the stabilization effect (synergy), while others reduce it
  - organic substances (epoxides, esters)
- dosage around 0.5 to 5 phr

Antidegradants

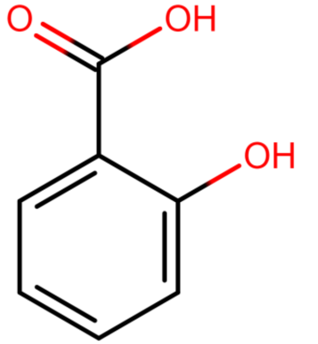
Antidegradants

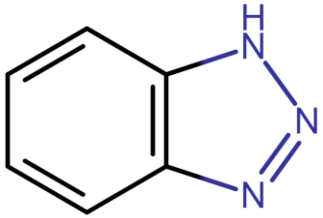
- protects the polymer from environmental influences (air oxygen, sunlight)
- types
  - light stabilizers
  - antioxidants
  - antiozonants
- dosage between 1 and 3 phr

Light stabilizers

- usually UV stabilizers
  - UV is energetically rich enough to break chemical bonds
  - visible radiation does not matter so much
- properties
  - they absorb UV radiation and convert it into energy-poor radiation that does not damage the polymer as much
  - they do not decompose themselves due to UV (they only act as catalysts)
  - do not react with the polymer (even during UV catalysis)
- examples
  - hydroxy (-OH) or alkoxy (-OR) derivatives of benzophenone
  - salicylic acid derivatives
  - benzotriazole derivatives
  - sterically shielded amines (HALS = hindered amine light stabilizer)
  - inorganic salts TiO_2 and ZnO or carbon black


benzofenone


salicylic acid

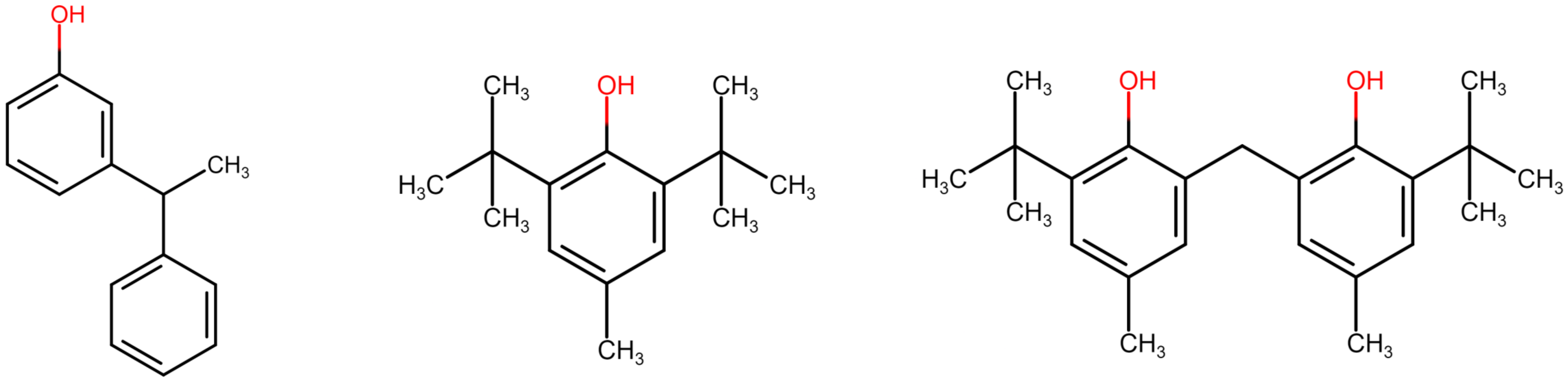

benzotriazole

Antioxidants

- they limit the action of atmospheric oxygen
- reactions of the polymer with oxygen usually take place slowly, but when heated or exposed to radiation they are greatly accelerated
- particularly susceptible to unsaturated structures
- under the influence of oxygen, radicals and cross-linking occur, which results in brittleness of the product
  - the O2 molecule binds to the structure to form hydroperoxide –OOH, when the peroxide bond is then homolytically split to form radicals
  - radicals cause chain reactions (reaction products further react with the polymer)
- mechanism of inhibition of chain reactions
  - preventing the formation of a radical
  - breaking the chain reaction

Antioxidants

- antioxidants do not always act as catalysts and reactions with oxygen or its reaction products may result in altered
  - these products may be colorless or colored (which is undesirable)
- non-dyes include phenol and cresol derivatives:



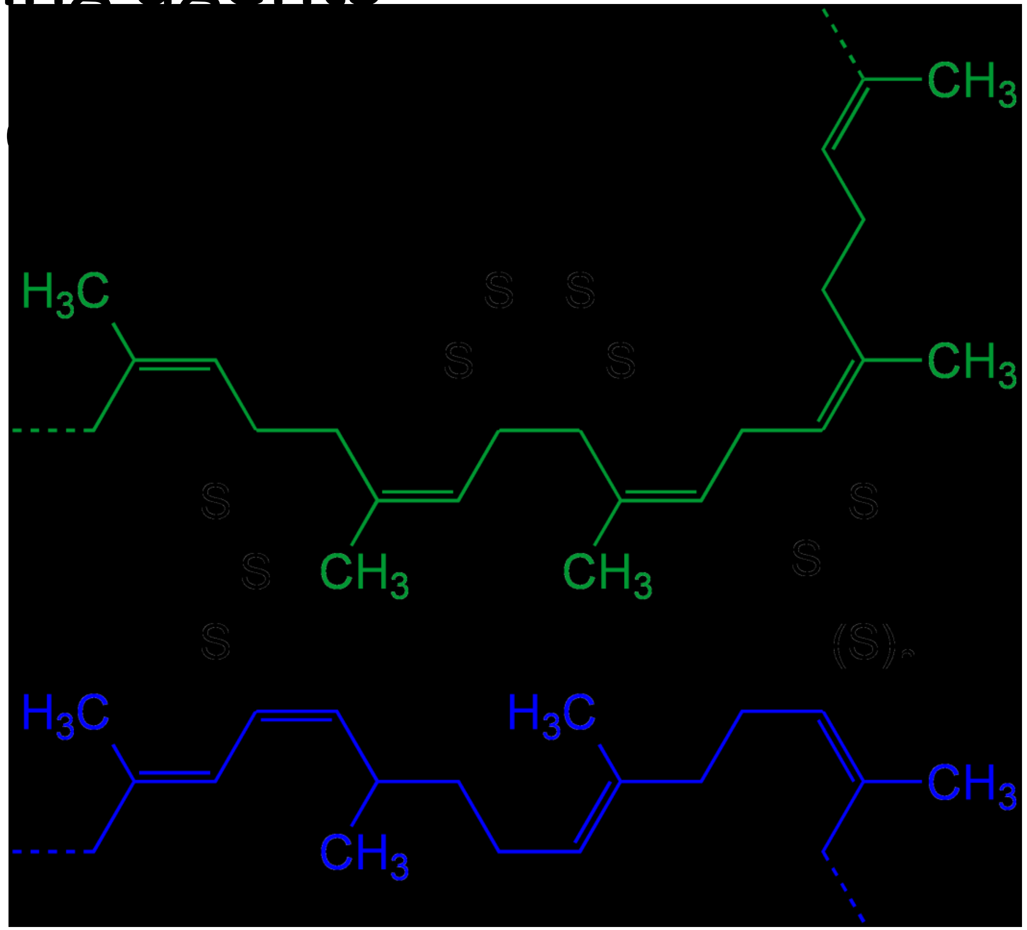
Antiozonants

- ozone reacts readily with double bonds in rubber
  - a hard inelastic layer is formed on the surface of the rubber
  - due to fragility, this layer cracks, resulting in a fresh surface
  - the new surface is exposed to new ozone and finally there is a total loss of the useful properties of the rubber
- they only work on the surface of the product (where there is ozone)
- as well as antioxidants can color the polymer after reaction
  - the most effective, but coloring, are p-phenylenediamine derivatives
- waxes or paraffins are also used (they form a barrier against ozone)
- saturated rubbers are not very susceptible to ozone

Cross-linking agents

Cross-linking agents

- are added to crosslink polymers an
- types:
  - crosslinkers (crosslinking agents)
  - crosslinking activators
  - crosslinking accelerators

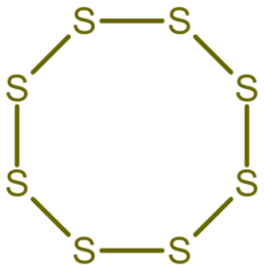


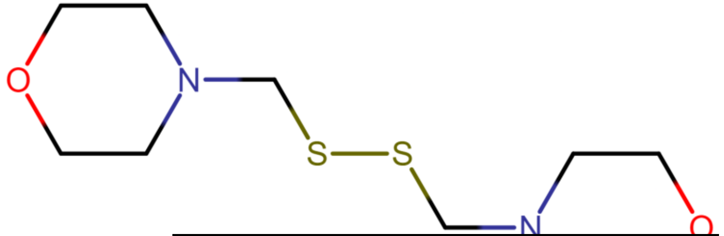
Crosslinkers (crosslinking agents)

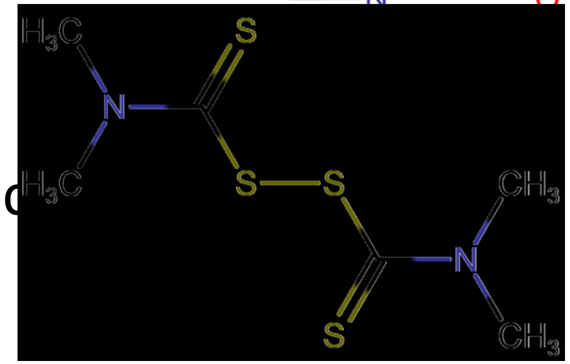
- the aim is to create a product that is stronger, harder or more stable in shape and heat
- different designations according to the material we mesh
  - vulcanizing agents (cross-linking rubbers)
  - hardeners (cross-linking reactoplasts)
  - thermoplastics can also be crosslinked, but their crosslinkers do not have a special designation
- crosslinking of thermoplastics
  - organic peroxides
  - high-energy radiation (obviously not an additive)
    - γ radiation (cobalt emitters)
    - electron beams
    - UV

Crosslinkers - vulcanizing agents

- rubber cross-linking agents (vulcanization takes place at higher temperatures)
- the most common is sulfur
  - for unsaturated rubbers
  - two kinds
    - crystalline (eight-membered rings)
    - polymeric (long chains)
      - at elevated temperature, the chains split and the rubber cross-links
    - organic disulfides or polysulfides (so-called sulfur donors)
- sulfur dosing
  - soft rubber from 0.5 to 4 phr
  - hard rubber 35 to 50 phr
- sometimes an addition of 0.5 phr Se or Te to increase heat resistanc
  - dosing of sulfur donors
    - up to 4 phr



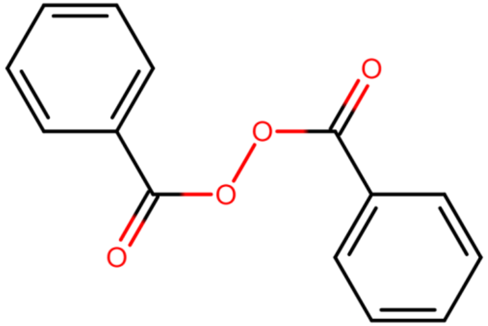


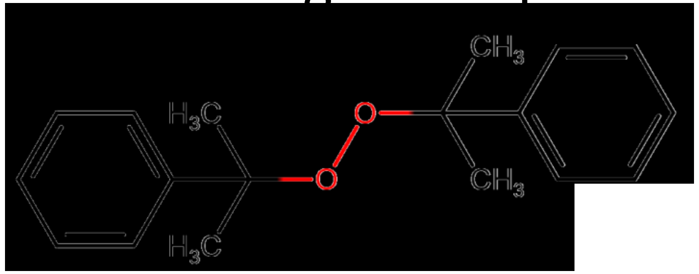


Crosslinkers – (vulcanizing) agents

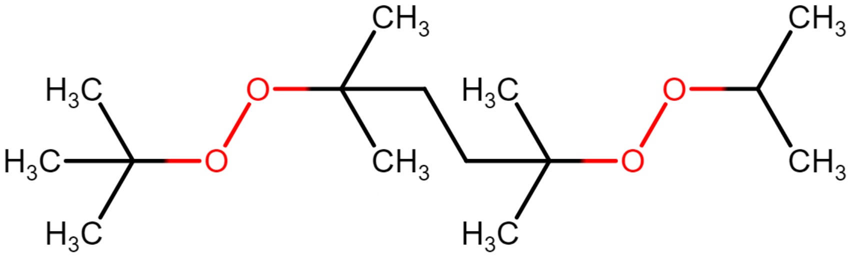
- organic peroxides
    - can cross-link saturated (as well as unsaturated) rubbers
    - dosage in phr units (but in diluted form)
    - dangerous spontaneous combustion and explosion

dibenzoyl peroxide

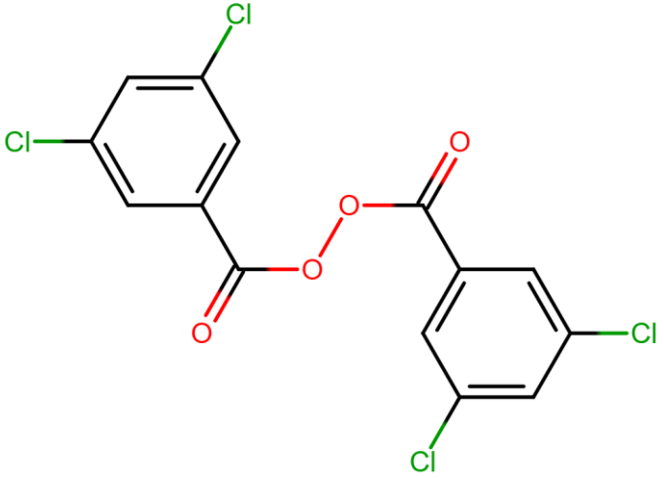




dicumyl peroxide



2,5-dimethyl-2,5-di(t-butylperoxy)hexane

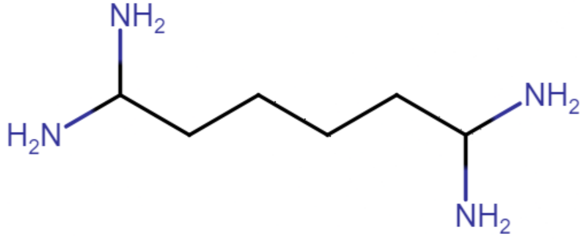


2,4-dichlordibenzoyl peroxide

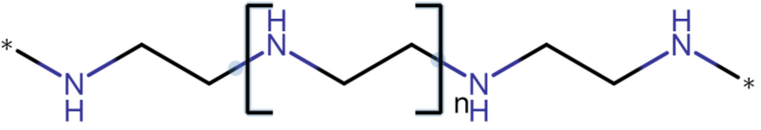
Síťovadla – vytvrzovací činidla

- cross-linking reactoplasts
- acid
  - harden aminoplasts and resols (phenoplasts)
  - acid condensation of methylol groups
    - resins are thus created from resols
- nitrogenous substances
  - hexamethylenetetramine
  - hardens novolacs (acids do not work on them)
  - condensation with the release of ammonia (NH_3) and the formation of methylene bridges
    - polyamines
    - polyaminoamides
- thiols and thioacids (sulphur-containing substances)
- peroxides (see previous)
- dosage
  - depending on the reagent used
  - usually up to 10 phr

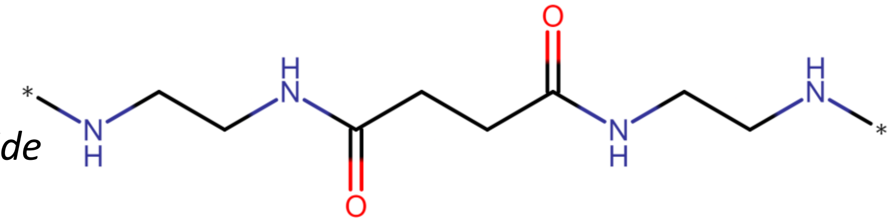
hexamethylentetraamine



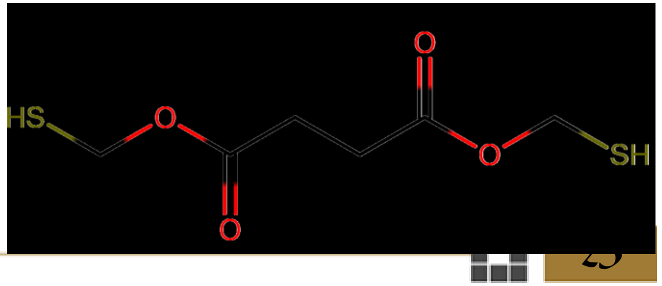
polyamine



polyaminamide



dithiol(ester)



Crosslinking activators

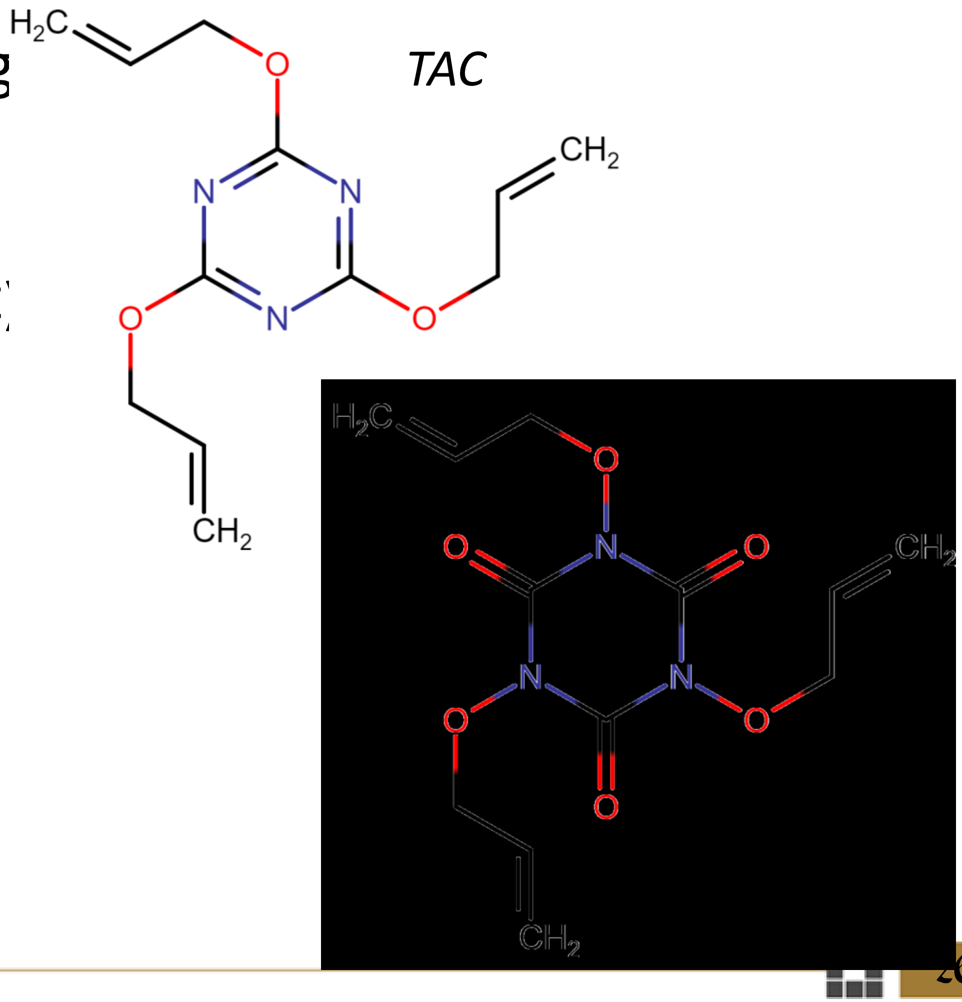
- catalyze cross-linking reactions (reduce their activation energy)
  - more homogeneous cross-linking
  - more effective cross-linking (need to add less cross-linking agent)
- they are divided according to crosslinking agents
  - vulcanization activators
  - peroxide activators
  - sensitizers (activators of radiation cross-linking)

Vulcanization activator

- inorganic oxides dissolved in fatty acids
  - acid (0.5 to 3 phr) is used to dissolve the oxide in the rubber
    - stearic (18 carbons), lauric (12 carbons), 2-ethylcapronic (2+6 carbons)
  - ZnO
    - dosage about 3 phr
  - CdO
    - it is limited due to health problems
  - PbO
    - it has one advantage – it activates well
    - it has many disadvantages
      - poisonous
      - expensive
      - black rubber during vulcanization (formation of PbS)

Peroxide activators

- multifunctional molecules, partially stabilizing radicals
  - sometimes they are crosslinkers and activators in one
  - triallyl cyanurane (TAC), triallyl isocyanurane (TAIC
  - dicarboxylic acid esters
  - methacrylate derivatives
- increase networking efficiency by up to 20%
  - after the breakdown of peroxides, the radicals preferentially react with the activator, which subsequently cross-links
- sometimes they also serve as stiffeners
- dosing up to 5 phr



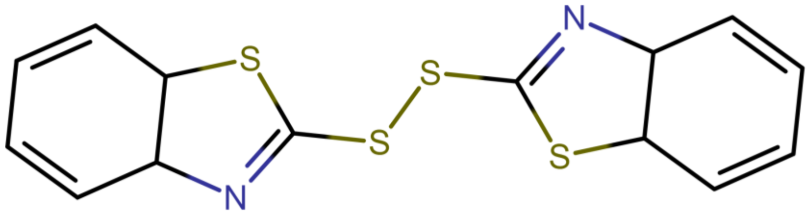
Sensitizing activators

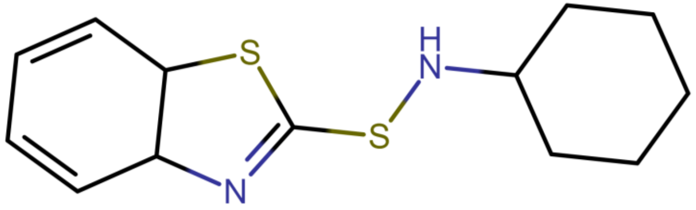
- radiation activators
- again dicarboxylic acid esters or structures with conjugated systems capable of stabilizing radicals
- they work similarly to peroxide activators, but their main goal is to prevent degradation reactions of macromolecules due to radiation

Networking accelerators

- speed up cross-linking reactions (from hours to minutes)
  - they reduce the amount of crosslinker needed
  - they reduce the necessary vulcanization temperature
  - enabled continuous vulcanization (the product goes along the line and is continuously vulcanized, so I do not stop production)
- sulfur vulcanization accelerators
  - discovered at the beginning of the 20th century
  - today mainly mercaptobenzothiazole derivatives
  - dosage according to the intended result
    - accelerator:sulfur ratios tend to be:
      - 1:5 to 1:2 for so-called conventional vulcanization
      - 1:1 for semi-effective vulcanization
      - 5:1 and more for effective vulcanization
    - the total amount of sulfur is not more than 2.5 phr

bis(2-benzothiazolyl)disulfide



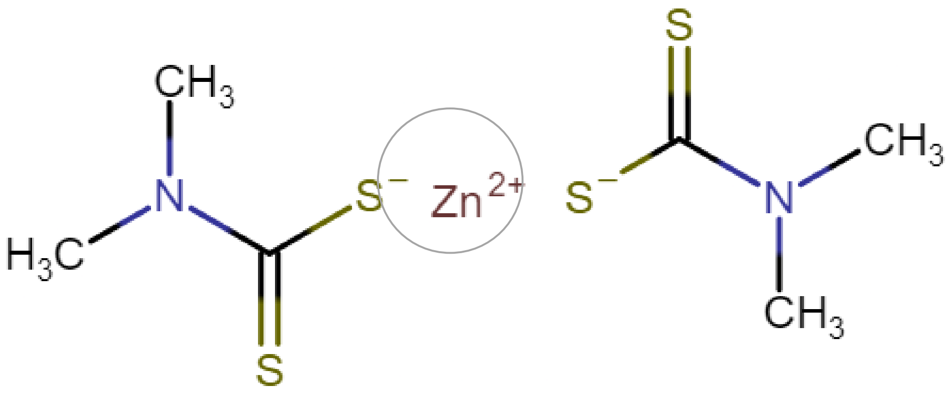


sulfenamide accelerator

Networking accelerators

- sulfur vulcanization accelerators
  - sulfur donor accelerators
    - they can also be used alone (without the addition of sulfur = so-called sulfur-free vulcanization), so they are both an accelerator and a crosslinker at the same time
  - ultraaccelerators
    - reduce vulcanization temperatures (warm water or even room temperature is enough)
    - generally zinc or sodium salts of more complex organic substances
      - used mainly for cross-linking latexes
        - these contain so much water that if they cross-linked at 100 °C, the product would be damaged by evaporation
        - laboratory gloves, balloons, etc.
  - dosage up to 1.5 phr

types of vulcanization accelerators according to speed
slow
fast
very fast
ultrafast



Curing accelerators

- different substances depending on the cured reactoplast
  - metal salts of organic acids for curing silicone resins
    - Co, Pb, Zn
  - amines for curing polyester resins or epoxy resins

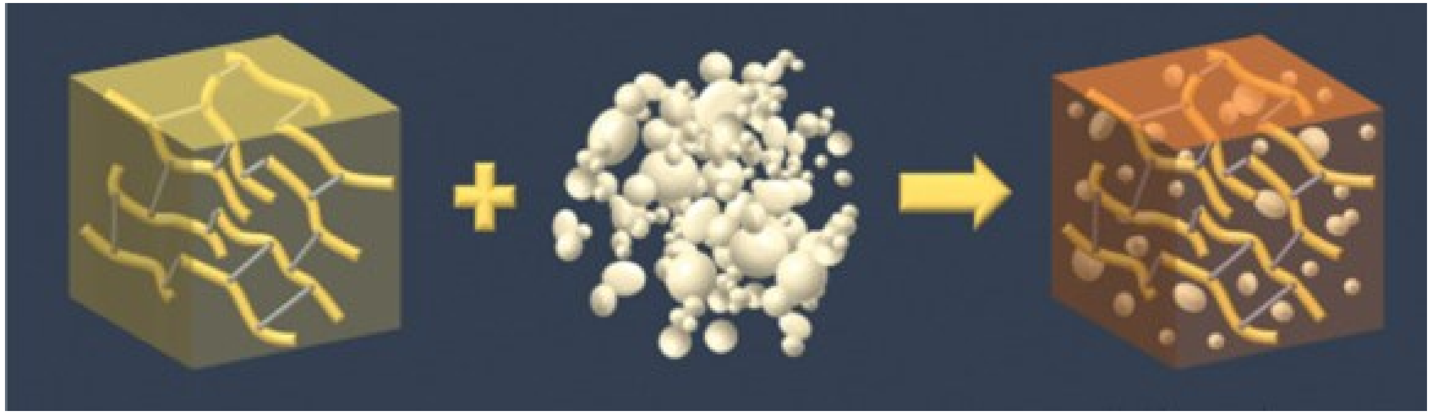
Other additives

Other additives

- affects all sorts of properties
- types:
    - fillers
    - reinforcements
    - puffed up
    - pigments
    - optical brighteners
    - plasticizers
        - they belong to processing additives, but since they also affect the final properties, they can also be included here

Fillers

- solids in the form of powder or fibers (length in units of mm)
- they influence



  - price
  - density
  - strength
  - abrasion resistance
  - toughness
  - resistance to higher temperatures, aging
  - appearance
- all sorts of dosages

Fillers - carbon black

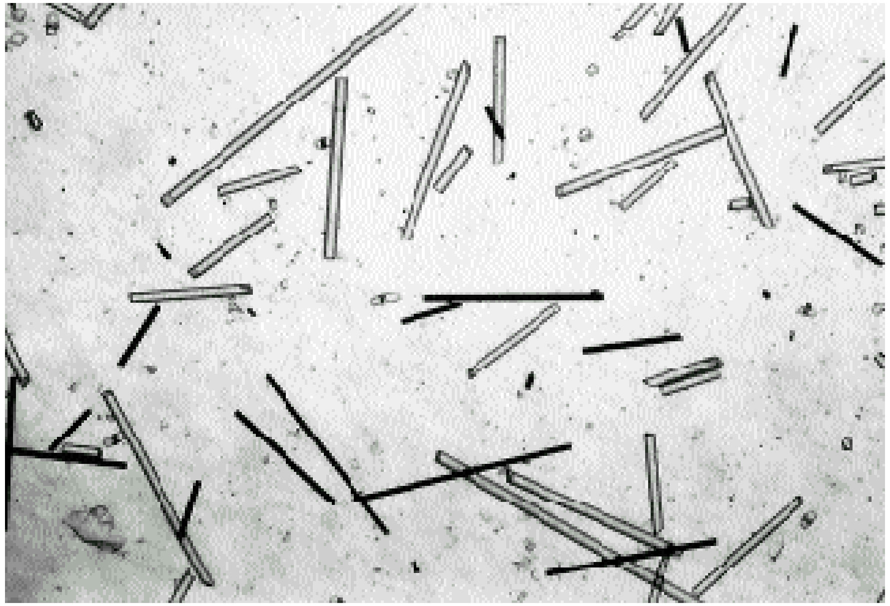
- most often in the rubber industry
- Ingredients
  - H … 0.3 – 0.6%
  - About ... 0.1 - 3.5%
  - C … 96 – 99%
  - the composition is determined by the type of carbon black, which is classified according to several aspects (production method, surface area, etc.)
- they are obtained as industrial waste (burning residues)
- rubbers improve
  - strength
  - rigidity
  - abrasion resistance
  - possibly electrical conductivity + antistatic effects
- impair workability (the polymer mixture is more viscous)
- dosage according to the product up to about 50 phr

Light fillers

- all other rubber fillers other than carbon black
- usually inorganic substances
  - SiO_2
  - $CaSiO_3$
  - hydrated aluminum sulfite (kaolin)
  - $CaCO_3$ (chalk or limestone)
  - barite ($BaSO_4$) – together with $PbSO_4$ act as shielding substances for high-energy radiation
  - $MgSiO_3$ (talc)
  - glass fibers
- also organic
  - cellulose (wood meal, fruit shell meal)
  - protein flours (soy, casein)

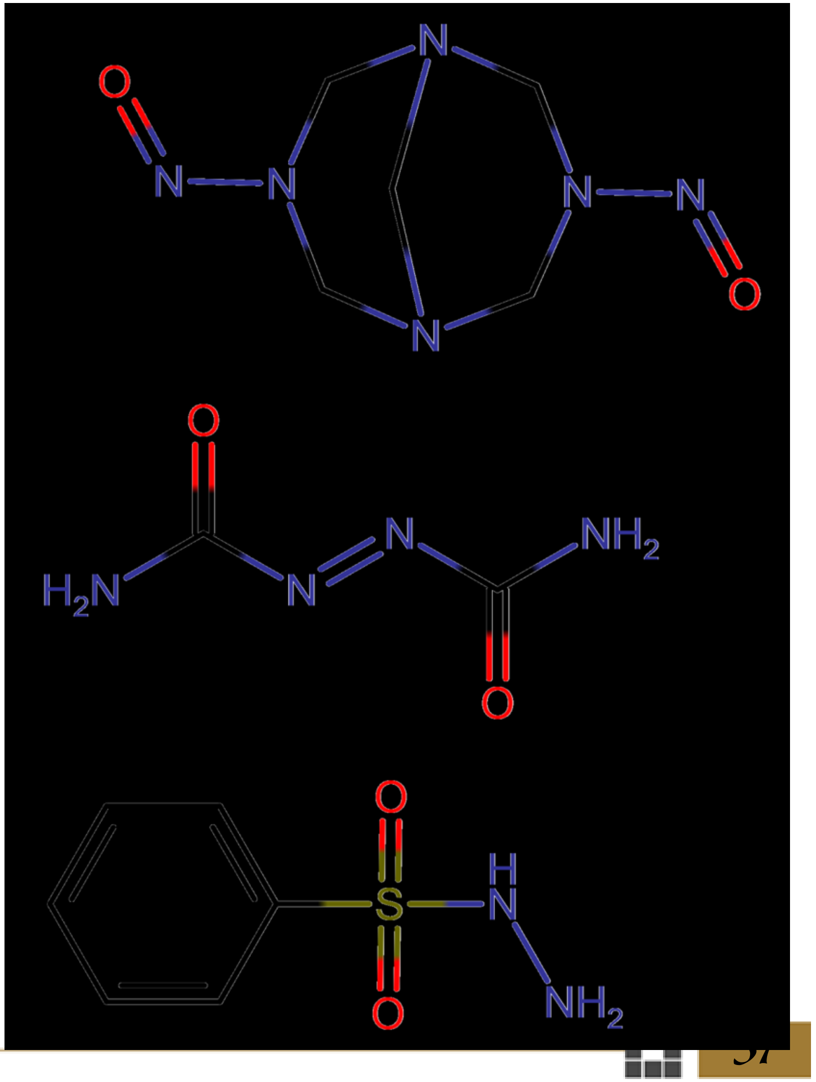
Stiffeners

- most often with reactive plastics and thermoplastics
- especially fibers
  - cellulose fibers
  - PE
  - PA
  - glass
  - metal (in combination with rubber, the so-called rubber bands)
- they improve the mechanical properties of the product
- they often lighten the overall structure



Puffing agents

- they make the product lighter and cheaper
- substances added to the polymer mixture that decompose due to the formation of gases at a higher temperature (e.g. during molding).
    - most commonly CO_2 or N_2
    - they form open and closed pores in the material
    - they basically act like baking powder or yeast (but they create CO_2 in a different way) in the dough
- formerly inorganic salts (ammonium or sodium)
- today organic blowing agents
    - usually nitrogenous substances
    - pentane works for PS (when cooking PS with pentane inside, it starts to evaporate and puffs up the final product)
- dosage from 1 to 5 phr

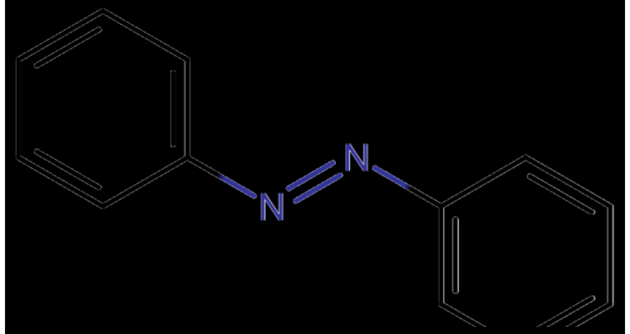


Pigments

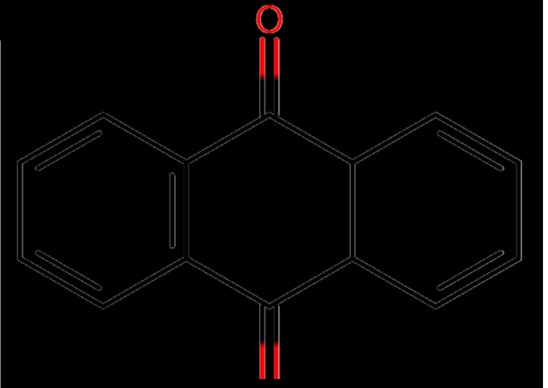
- colored particles (powders) insoluble in the carrier (polymer)
  - inorganic
  - organic
  - metal (bronze)
- inorganic
  - chalk, gypsum, graphite
  - zinc white (ZnO), titanium white (TiO_2), $ZnSO_4$, $BaSO_4$, lemon yellow ($Fe_xAl_ySi_zO_m$), red (Fe_2O_3), synthetic ultramarine (silicate complex), carbon black
  - cheap, good stability, poor coverage and discolouration

Pigments

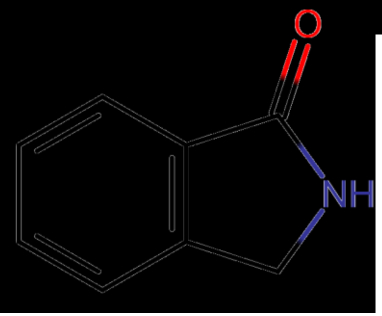
- organic
    - together with white base (TiO2)
    - dosage 0.5 to 2 phr color pigment, up to 10 phr whiteness
    - chelates of organic substances with metals
        - yellow – Cd (not so much these days), Ni
        - blue - copper
        - red – iron
        - green - copper, iron



azobenzene



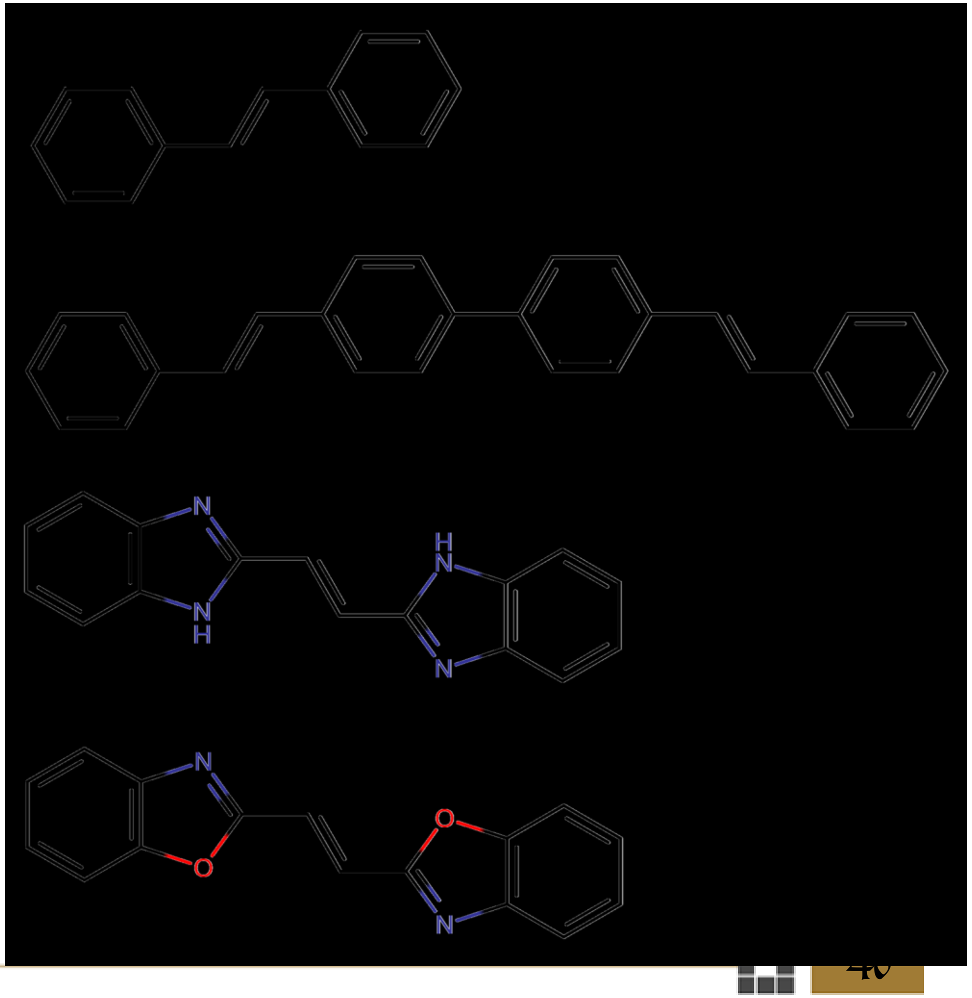
anthraquinone



isoindolidone

Optical brighteners

- they absorb wave radiation at the limit of visible light and emit UV and fluorescence back at higher wavelengths
    - simplified – incident radiation slightly below 400 nm is used to emit visible radiation around 450 nm
    - the whole appears brighter and more colorful
    - they are used a lot in the paper industry
    - may not be compatible with other radiation-absorbing substances (light stabilizers, ZnO, TiO_2)
- usually a system with at least 4 conjugated double bonds - stilbene derivatives
- dosage 0.01 to 0.001 phr



Special additives

Special additives

- they are only added to polymers with special uses
- types:
  - antistatic
  - adhesives
  - reducing flammability
  - abrasives
  - explosives and fuels

Antistatic agents

- Antistatic agents helping to remove the charge from the surface of the polymer product
- the charge accumulates on the surface, e.g. when rubbing or unwinding foils, because most polymers are poor current conductors
  - problems with attachment to the device and everything possible in the vicinity
  - in extreme cases, there may be a spark jump that can cause a fire
- antistatic agents increase conductivity, thus the accumulated charge is able to be removed
  - carbon black or a lot of polar organic matter works well
- dosage from 0.1 to 2 phr
  - it usually does not need to be added to rubbers, because there is conductive carbon black (as a filler)

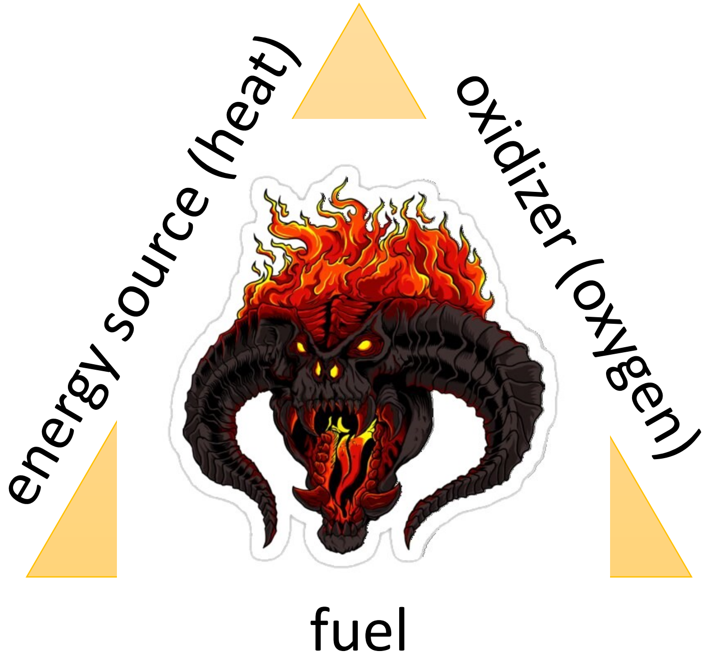
Adhesives

- they improve the adhesion between the polymer and other substances (especially reinforcement)
  - important for textiles, laminates, tires, conveyor belts, etc.
- depending on the type of polymer-adhesive, different substances are used
  - usually organometallic complexes or resins
- dosage in units of phr

Flame retardants – Hoření polymerů

- generally flammable with a low degree of fire safety
  - in other words, it burns well, quickly and easily
- the limiting factor in the use of polymers
- combustion research
  - mechanism
  - reducing flammability

- fire triangle
  - the relationship of the main factors of combustion
  - removing only one means preventing burning



General course of combustion

1. initiation heat with oxygen will start the thermo-oxidation reaction of the polymer
2. the result is oxidation of the polymer
   - release of heat of reaction (further heats the system)
   - formation of by-products
3. an increase in temperature results in thermal decomposition of the oxidized polymer
   - the formation of volatile flammable substances that further oxidize and add additional heat
   - formation of solid products that may or may not further support combustion

Classification of materials according to flammability

- Non-flammable products
  - A1 ... products made of ceramics, glass, metal, concrete, thermal insulation board made of mineral fibers
  - A2 … plasterboard or plasterboard
- Flammable products
  - B … contact insulation system with combustible thermal insulation (e.g. expanded polystyrene), vinyl floors, cement chipboards
  - C ... thermal insulation board made of phenolic foam
  - D ... construction wood, wood-based boards
  - E ... thermal insulation board made of polyurethane or expanded polystyrene (with flame retardants)
  - F ... products for which the class has not been determined

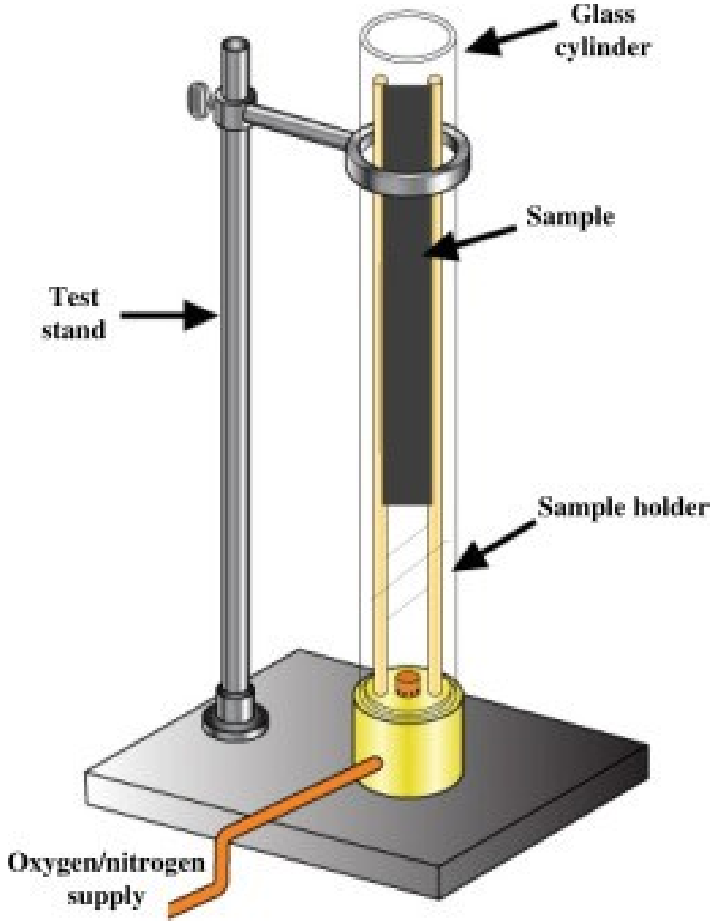
- significant material values:
  - flash point (FP = the lowest temperature at which a substance ignites and goes out again when approached by a flame
  - flame ignition temperature (FIT) = the lowest temperature at which a substance spontaneously ignites
- PE, PP and PMMA are very flammable
- there are few non-flammable polymers
  - PTFE or FEP (copolymer of tetrafluoroethylene and hexafluoropropylene), polyimides, silicones
- those containing halides (PVC) or highly cross-linked tend to be self-extinguishing

Influence of flammability

- flammability is affected by:
  - structure of monomers
  - branching (reduces)
  - by cross-linking (reduces)
  - additives
    - some may promote combustion (e.g. volatile organic solvents)
    - some may reduce or at least not support (e.g. inorganic fillers, flame retardants)
  - the size of the polymer surface
    - the fibers will burn much more easily than the whole body
  - barrier from decomposition products
    - charred residues can form a layer that is poorly permeable to oxygen and prevent further combustion

Limiting oxygen index

- LOIestimation of the material's flammability relative to the oxygen content in the air
  - defined as the representation of oxygen in the atmosphere consisting of only oxygen and nitrogen, necessary to burn through exactly 50% of the sample
  - the higher the number a given material has, the more durable it is
- it is tested by igniting a sample in a tube through which a mixture of oxygen and nitrogen of known composition is blown



polymer	*abbreviation*	*CU formula*	*elemental composition (wt. %)*					*LOI 20 °C (%)*
			H	*C*	*N*	*O*	*halogen*	
polyethylene	PE	$[C_2H_4]$	85,7	14,3	-	-	-	17,5 – 18,5
polypropylene	PP	$[C_3H_6]$	85,7	14,3	-	-	-	18,0 – 19,0
polymethyl-metacrykate	PMMA	$[C_5H_8O_2]$	60,6	8,0	-	32,0	-	17,3
polyvinylchloride	PVC	$[C_2H_3Cl]$	38,4	4,8	-	-	56,8	30,0 – 45,0
butadien rubber	BR	$[C_4H_6]$	88,9	11,1	-	-	-	17,5 – 18,5
phenoplasts	PF	$[C_7H_7]$	78,5	6,5		15,0	-	28,0 – 35,0
polyurethane	PUR	$[C_{12}H_{22}N_2O_4]$	55,8	8,5	11,2	24,8	-	19,0 – 20,0
polystyrene	PS	$[C_8H_8]$	92,3	7,7	-	-	-	18,0 – 20,0
polytetrafluor-ethene	PTFE	$[C_2F_4]$	24,0	-	-	-	76,0	95,0 – 98,0

CU … constitutional unite

Flame retardants

- substances (or parts of macromolecules) with the task of slowing down or completely preventing the burning of the material
- principles of flame retardancy
  - endothermic reaction
    - the excess heat is used for a reaction that does not support combustion
  - formation of non-flammable gases
    - they dilute the air and thus reduce the relative amount of oxygen
  - dehydration
    - excess heat is used to split and evaporate water, which further dilutes the air and reduces the relative amount of oxygen
  - melting
    - excess heat is used to melt the material, which can also form an oxygen-impermeable barrier
  - deactivation of free radicals
    - the resulting free radicals are deactivated by other substances and thus help to slow down the thermal-chemical decomposition of the substance (e.g. they deactivate HCl or HBr)

Flame retardants

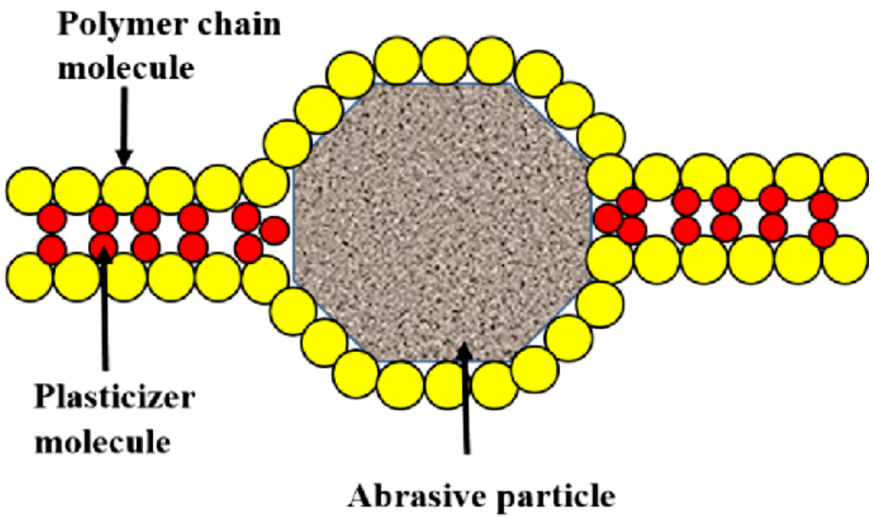
- inorganic compounds
  - $Al_2O_3xH_2O$, $Zn(BO_2)_2$, NH_4Cl, $(NH_4)_3PO_4$, Sb_2O_3
- organic compounds with halides
  - chlorinated (CFR = Chlorinated Fire Retardants) or brominated (BFR)
    - they work on the principle of capturing HO· or H· radicals produced by combustion, which further support combustion with the help of hydrogen halide HX – which itself is produced by the thermal decomposition of the retarder
    - I can either add it as an additive to the polymer or as a comonomer in the production of the copolymer
  - bromine is more commonly used (and more effective)
  - chloroparaffin, hexachlorobenzene, tetrabromobisphenol A, tetrabromophthalic anhydride etc.
- organic compounds with phosphorus
  - a combination of flame retardant and plasticizer
  - triscresyl phosphate
  - organic halogenated phosphorus compounds

LOI after adding a retardant

polymer	*LOI*	*LOI after the addition*
PES	21 %	28 %
viscose	17 – 19 %	30 %
cotton	18 – 20 %	31 – 32 %
wool	24 – 25 %	33 %

Abrasives

- hard abrasive particles in a polymer matrix
- the polymer here serves only as a binder
    - most often hard rubber (in addition to abrasives, there is also a meshing agent, etc.)



Explosives and fuels

- polymer mixture with explosive = plastic explosive
- usually rubbers or thermoplastic rubbers
- the fuel can be e.g. gasoline
  - solid fuels can also be produced in this way

Thank you for
your attention

TECHNICKÁ UNIVERZITA V LIBERCI

Nové možnosti rozvoje vzdělávání na Technické univerzitě v Liberci

Specifický cíl A2: Rozvoj v oblasti distanční výuky, online výuky a blended learning

NPO_TUL_MSMT-16598/2022

Inovace stávajících nebo tvorba nových metodických a elektronických studijních materiálů v ČJ nebo AJ

Ing. Pavel Holec

Financováno Evropskou unií
NextGenerationEU

Národní plán obnovy

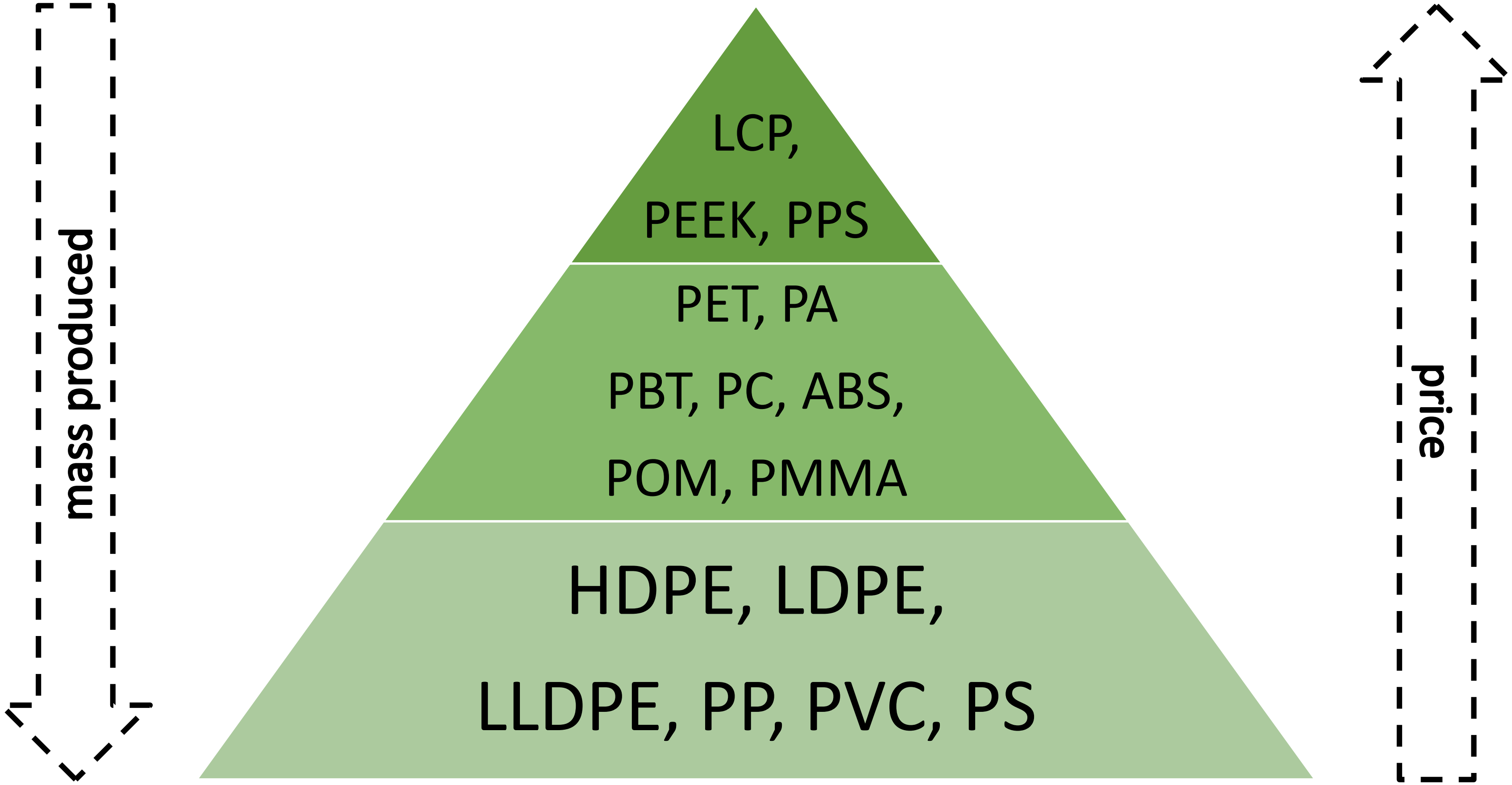
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Special polymers

Production of special polymers

- large tonnage
  - most of the volume/mass of the polymers produced
  - PE, PP, PS, PVC, PES, PA
- special
  - electrotechnics
  - cosmonautics
  - medicine
  - the military
- today the focus of polymer research
- significant price difference between regular and specialty polymer

Production of special polymers



mass produced

LCP,

PEEK, PPS

PET, PA

PBT, PC, ABS,

POM, PMMA

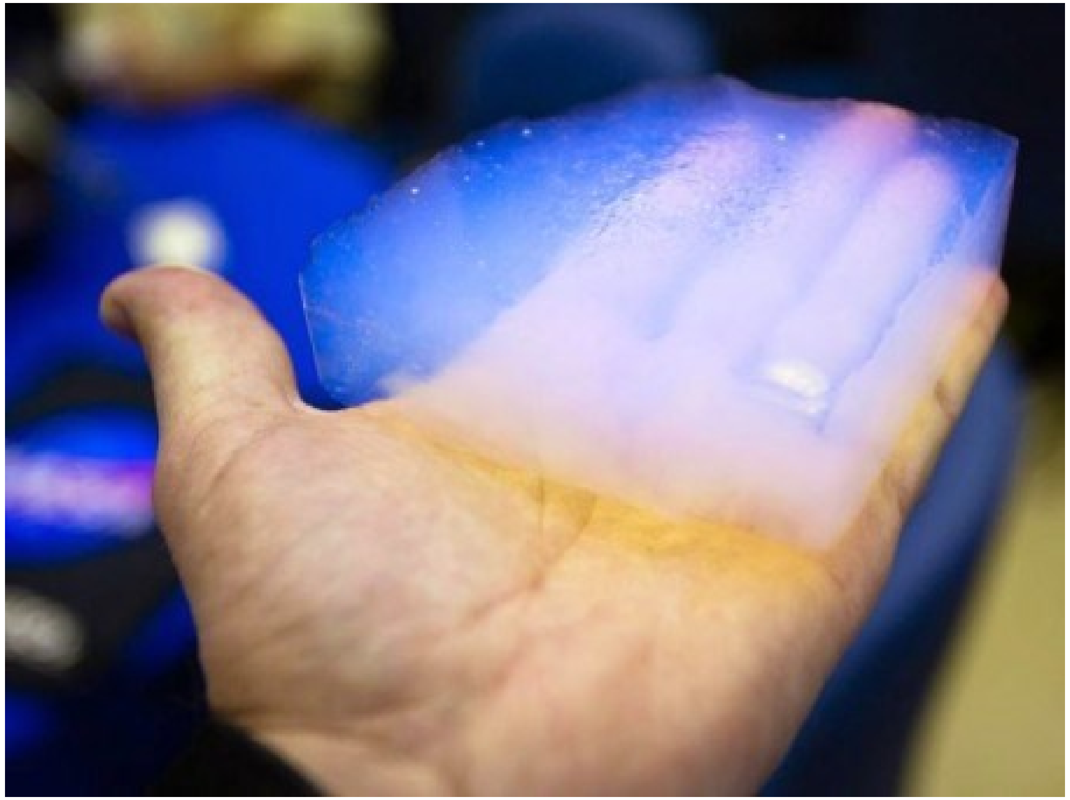
HDPE, LDPE,

LLDPE, PP, PVC, PS

price

Special polymers

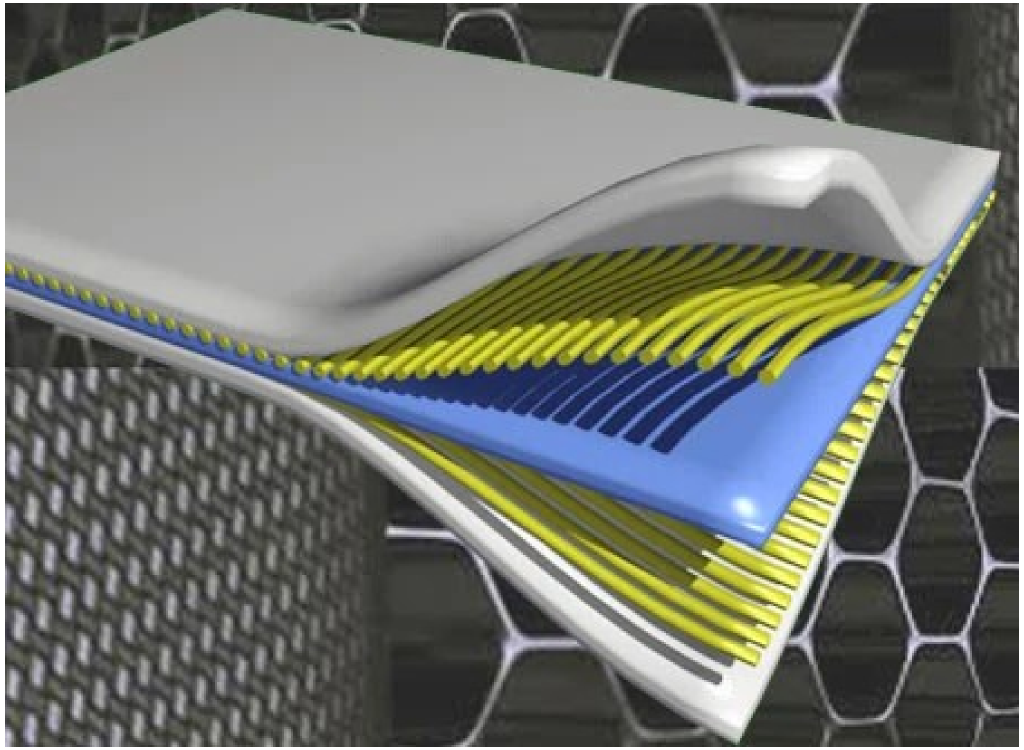
- resistant to higher temperatures
- super absorbent
- liquid crystals
- electrically conductive
- photosensitive polymers
- ion exchangers
- self-healing
- polymers in medicine



Polymers resistant to higher temperatures

Examples of heat-resistant polymers

- usually in fiberglass composite



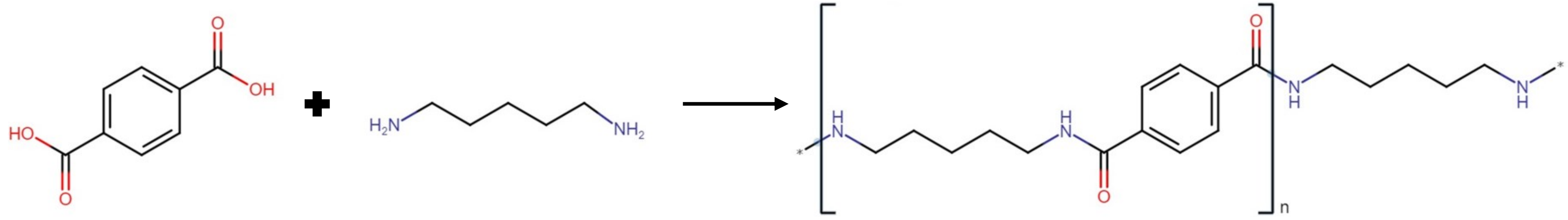
- polyphthalamide (PPA)
    - T_g up to 127 °C, T_m up to 310 °C
    - a relatively inexpensive temperature-resistant variation on PA6 or PA66
- aromatic polyamides (aramids)
    - Nomex – T_m around 350 °C, use up to 220 °C
    - Kevlar – T_m around 330 °C, use up to 200 °C
- polyetherimide (PEI)
    - long-term stable up to 170 °C
- polyimides (PI)
    - long-term stable up to 260 °C

Polyphthalamide and polyaramids

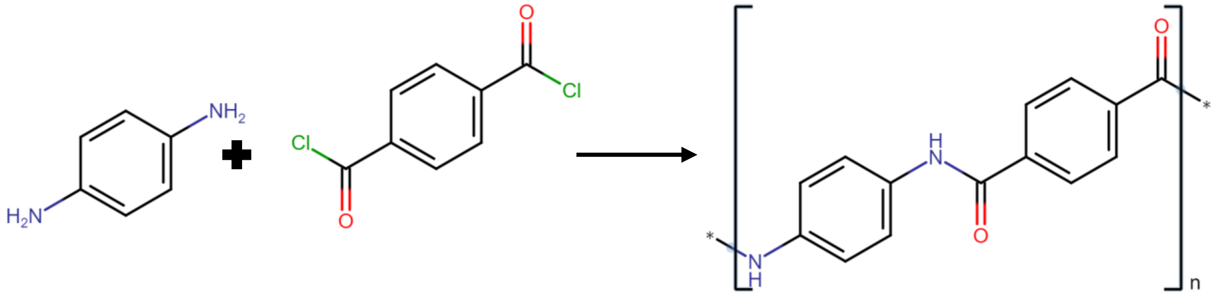
terephthalic acid

pentane-1,5-diamine

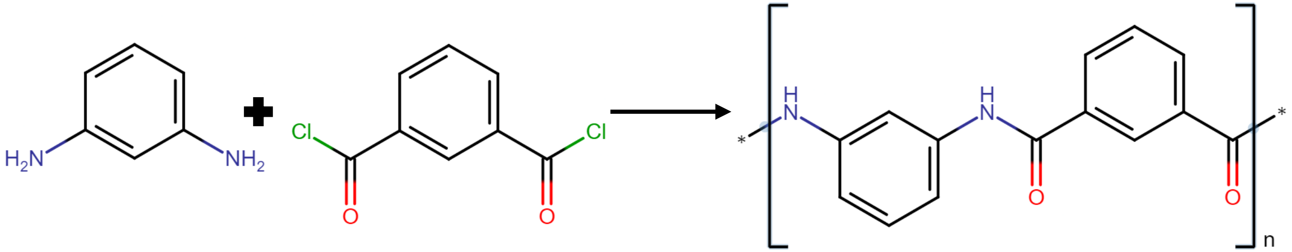
building block of polyphthalamide (NILON 6T)



Nylon 5T



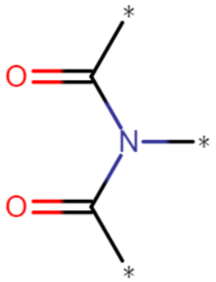
Kevlar



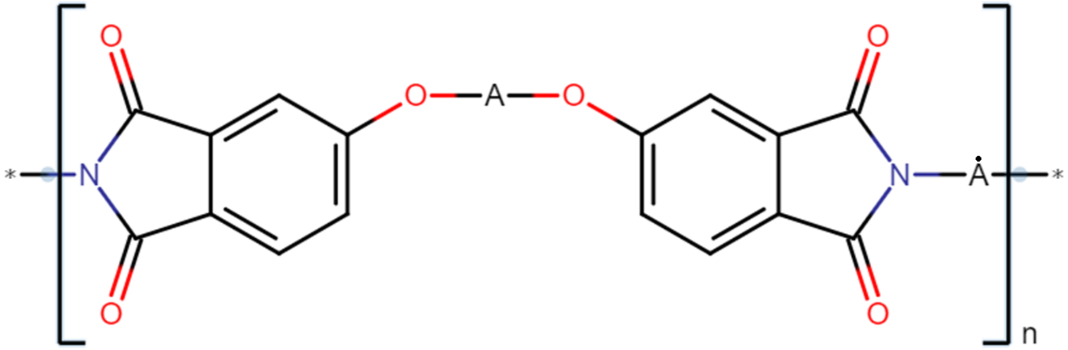
Nomex

Polyetherimide and polyimide

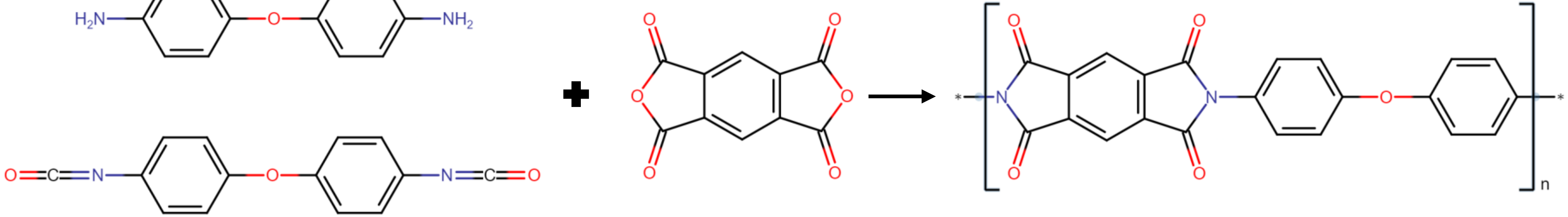
amide of two carboxylic acids



imides in general



PEI



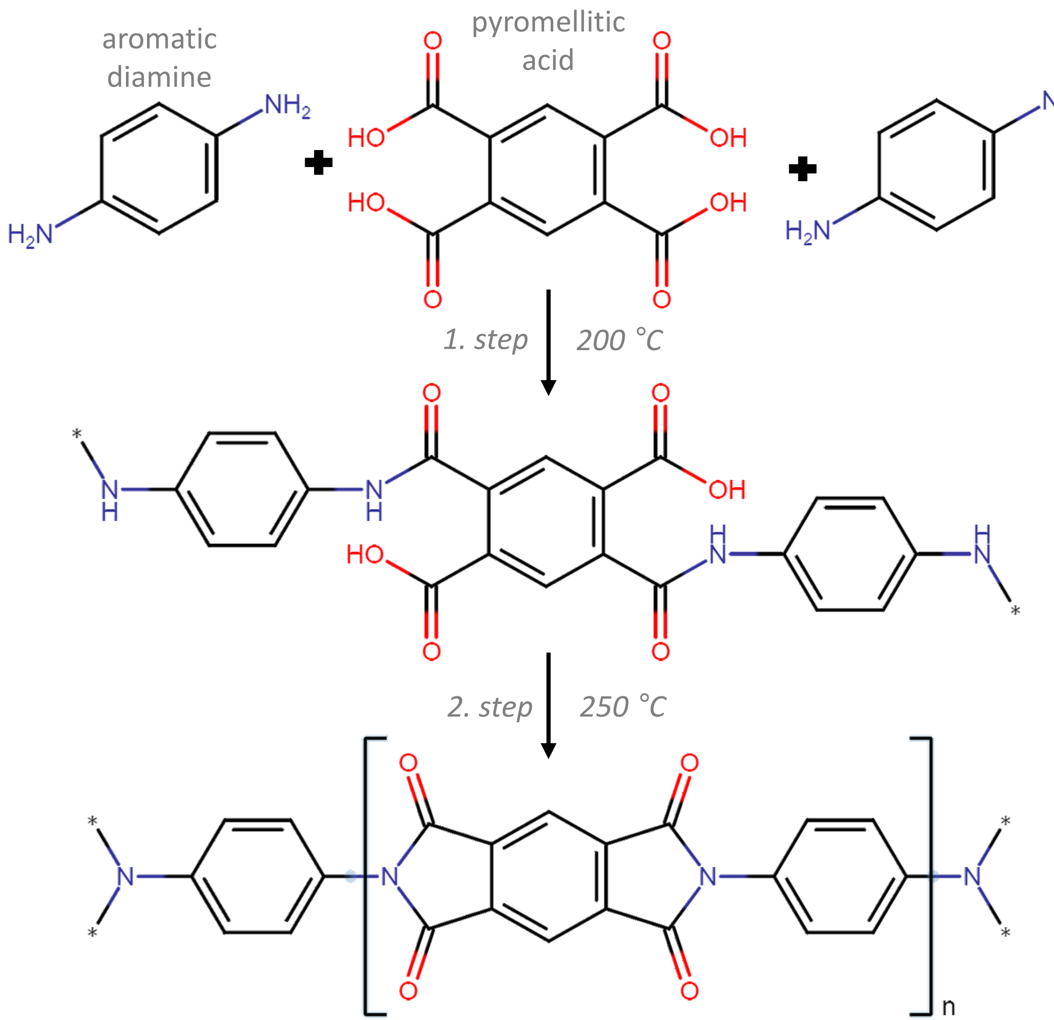
4,4'-diaminodiphenyletheroxydaniline

diphenylether-4,4'-diisocyanate

pyromellitic acid dianhydride

PEI

Preparation of polyimides

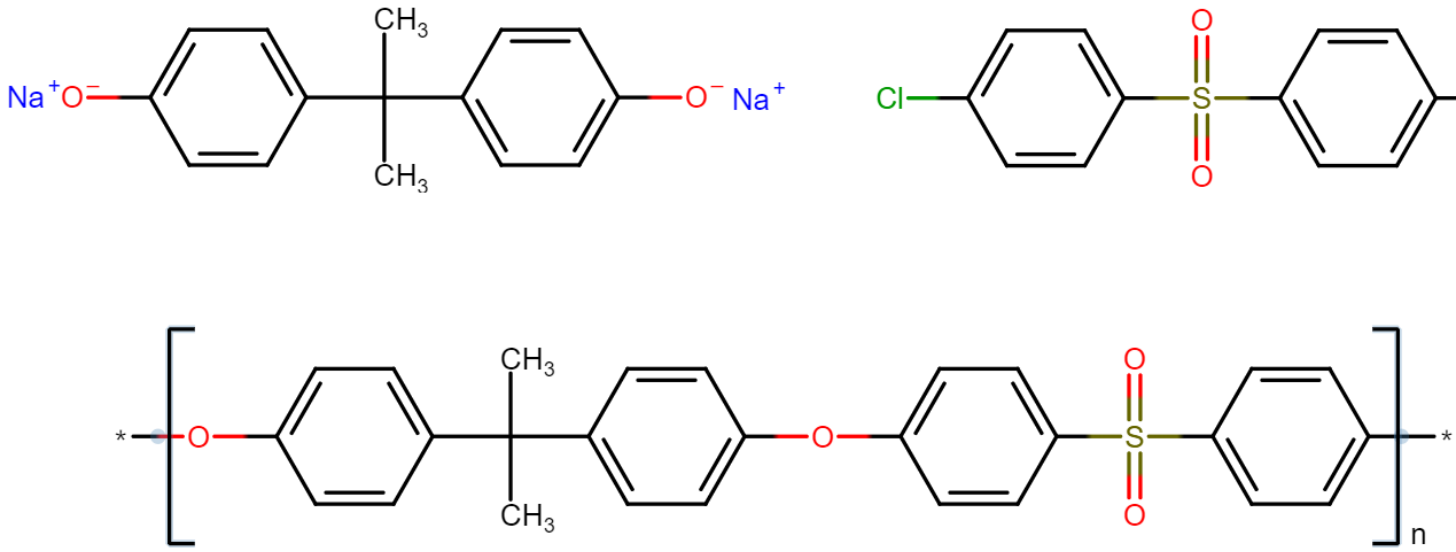


PI

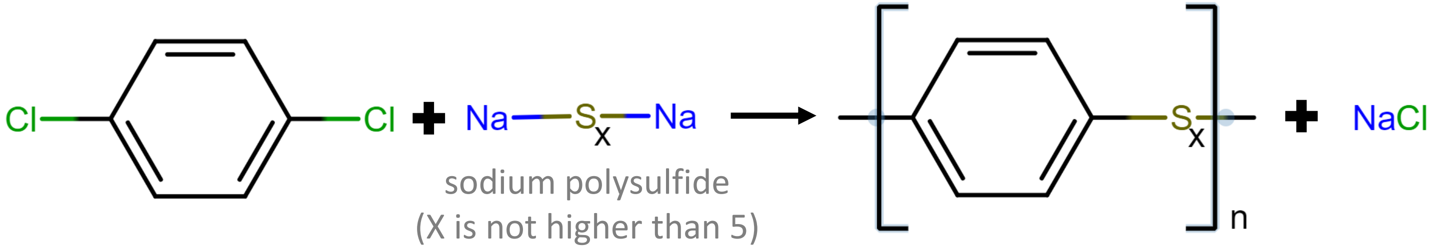
Examples of heat-resistant polymers

- polysulfones (PSUs)
  - T_g up to 250 °C
  - good mechanical properties, chemically resistant
- polyphenylene sulfide (PPS)
  - T_m around 290 °C
  - easy processing of the melt (good flow properties)
- polyether ether ketone (PEEK)
  - T_g up to 145 °C, T_m up to 335 °C
  - good mechanical properties, dimensional stability at higher temperatures, bioinert
- polybenzimidazole (PBI)
  - T_g around 430 °C, short-term withstand over 700 °C
  - the highest temperature resistance of commercially produced polymers
  - mechanically very resistant

Polysulfones and polyphenylene sulfide



PSU



PPS

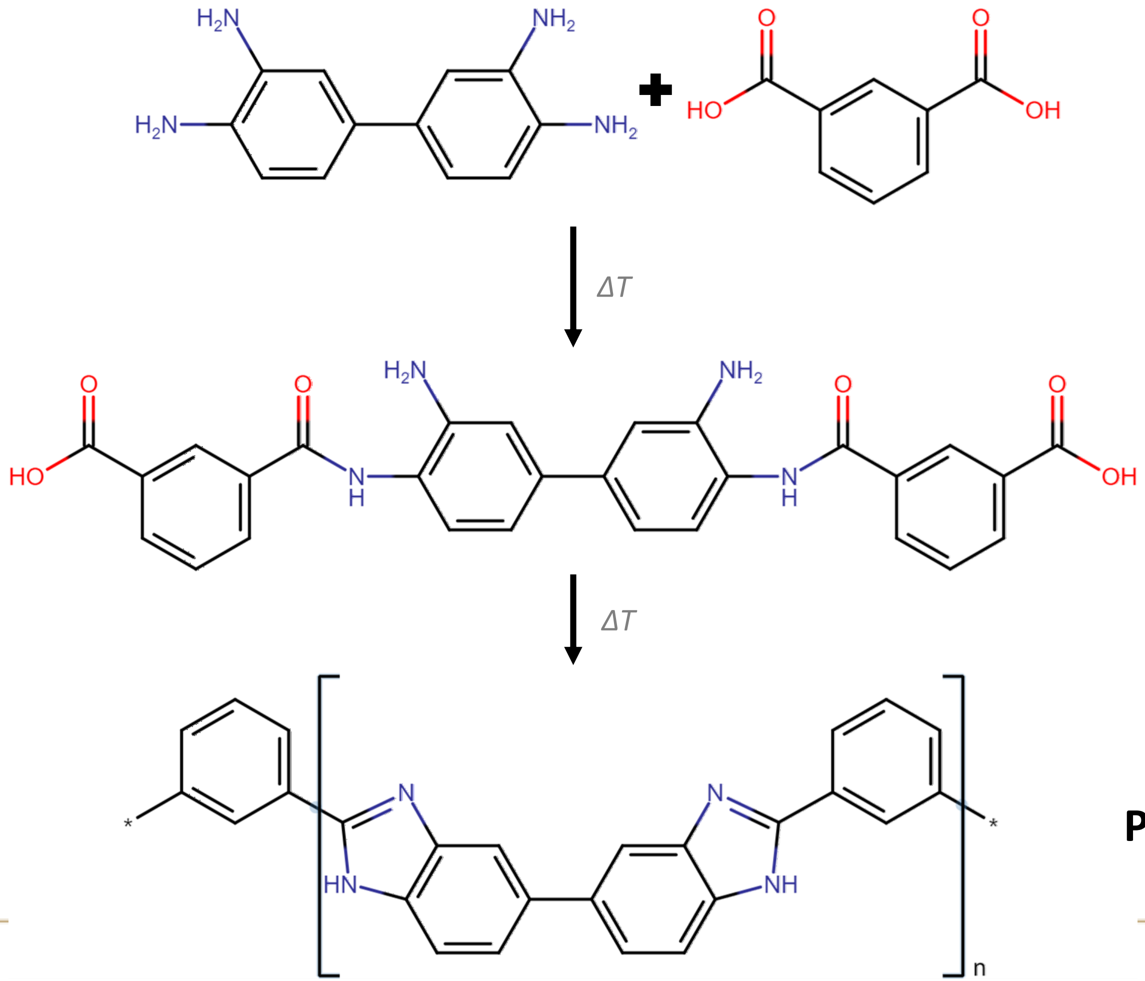
Polyetherketone

	T_g [°C]	T_m [°C]
PEK	163	361
PEEK	144	344
PEKK	154	358
PEEKK	165	391

Polybenzimidazole

3,3',4,4'-tetraamin biphenyl

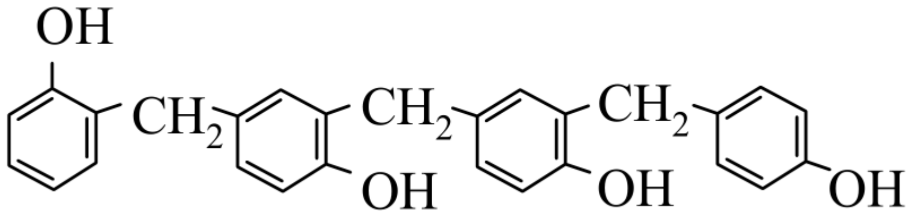
isophthalic acid

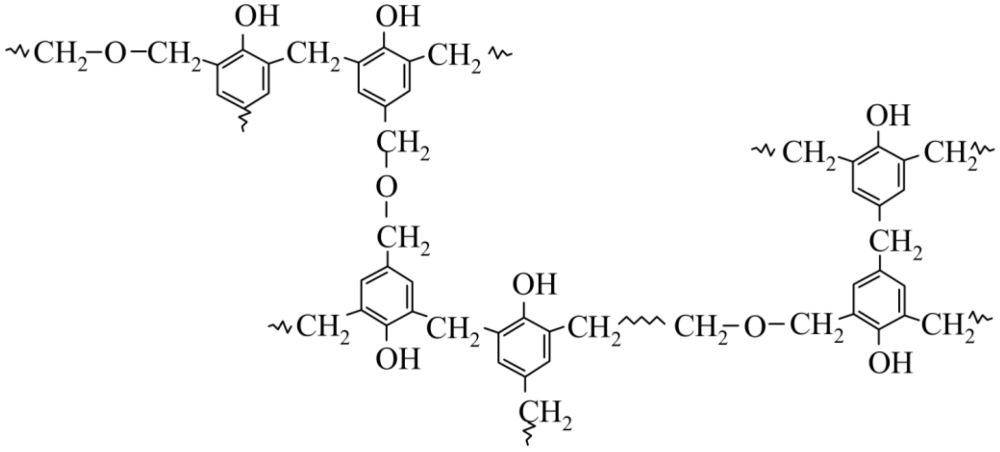


PBI

Novoloid (Kynol)

- from melt-spun phenol-formaldehyde "resin" subsequently cross-linked to the maximum extent possible
  - probably from slightly cross-linked novolacs = phenoplasts resulting from the reaction of phenol with formaldehyde, where there is an excess of phenol
- the result is a three-dimensional amorphous network
- further infusible, heat-resistant, but basically flammable
  - relatively chemically resistant, but does not benefit from conc. H2SO4 or conc. HNO_3
  - LOI 30 – 34 (PVC has 30 – 45, PTFE up to 98)
- classified as novoloids, which are at least 85% cross-linked novolacs
  - Kynol is the only representative so far 😂
- very well described from commercial perspective:
  - withstands up to 2500 °C for at least 12 s
  - can withstand 200 – 250 °C for a long time in an oxygen-free atmosphere
  - long-lasting up to 150 °C in air

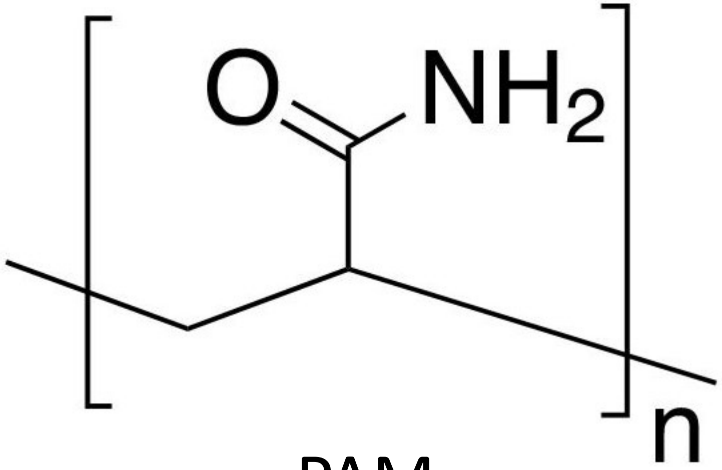




Super absorbent polymers

Super absorbent polymers (SAP)

- polymers capable of binding more than 300 times their weight (in a dry state) of distilled water
- they replace older cellulose sorbents (pulp, cotton)
- two ways of sorption
  - to polar groups (-OH, -O-, -CO-NH_2)
    - older SAPs from derivatives of cellulose, starch, gelatin (gummy bears), PVA, PEO or PAM (polyacrylamide)
    - they sorb less, but are not as sensitive to liquid composition
  - per ionic charge
    - today mainly slightly cross-linked polyacrylic acid
    - they absorb a lot, but are sensitive to the composition of the liquid



PAM

Sorptive capacity

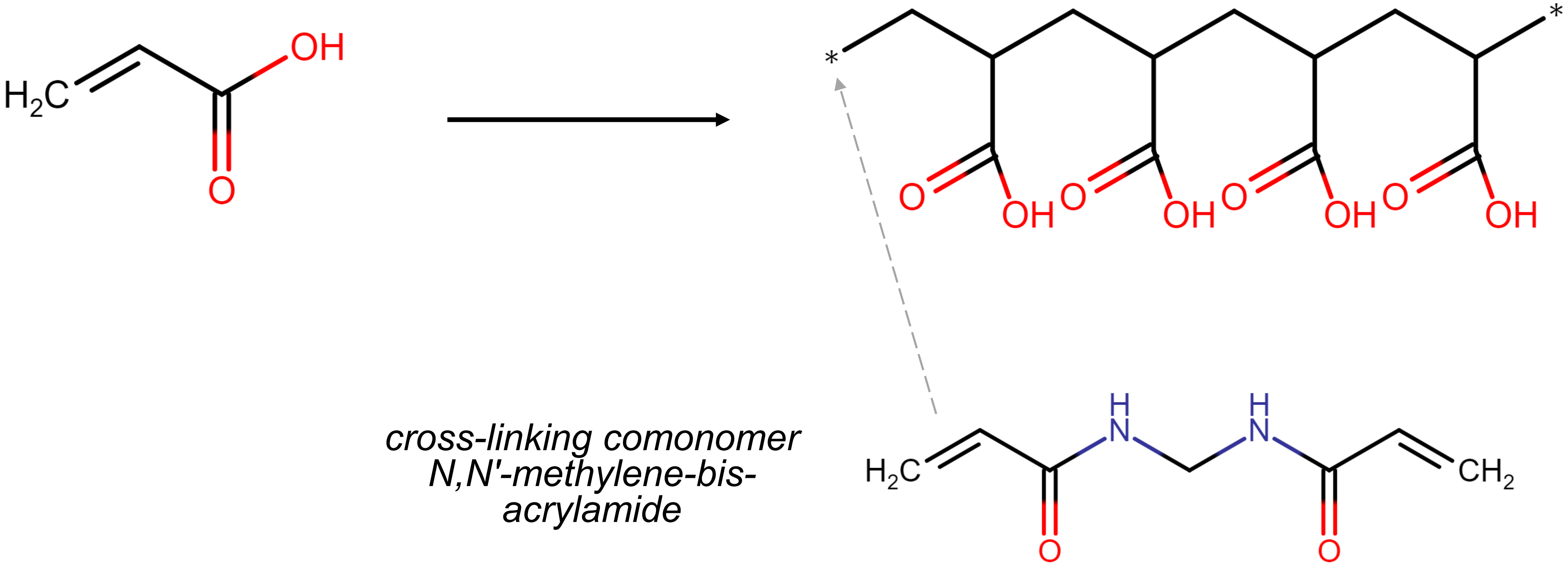
- dry SAP (sorbing by ion mechanism)
  - distilled water ... up to 300 times the weight
  - physiological solution (0.9% NaCl) ... up to 50 times
- ions in water reduce the sorption capacity
- pressure on the SAP reduces the sorption capacity
  - like wringing a wet rag

- swelling creates a hydrogel (substance made up mainly of water, which, however, retains certain mechanical properties, shape, etc.)

Polyacrylic acid (PAA)

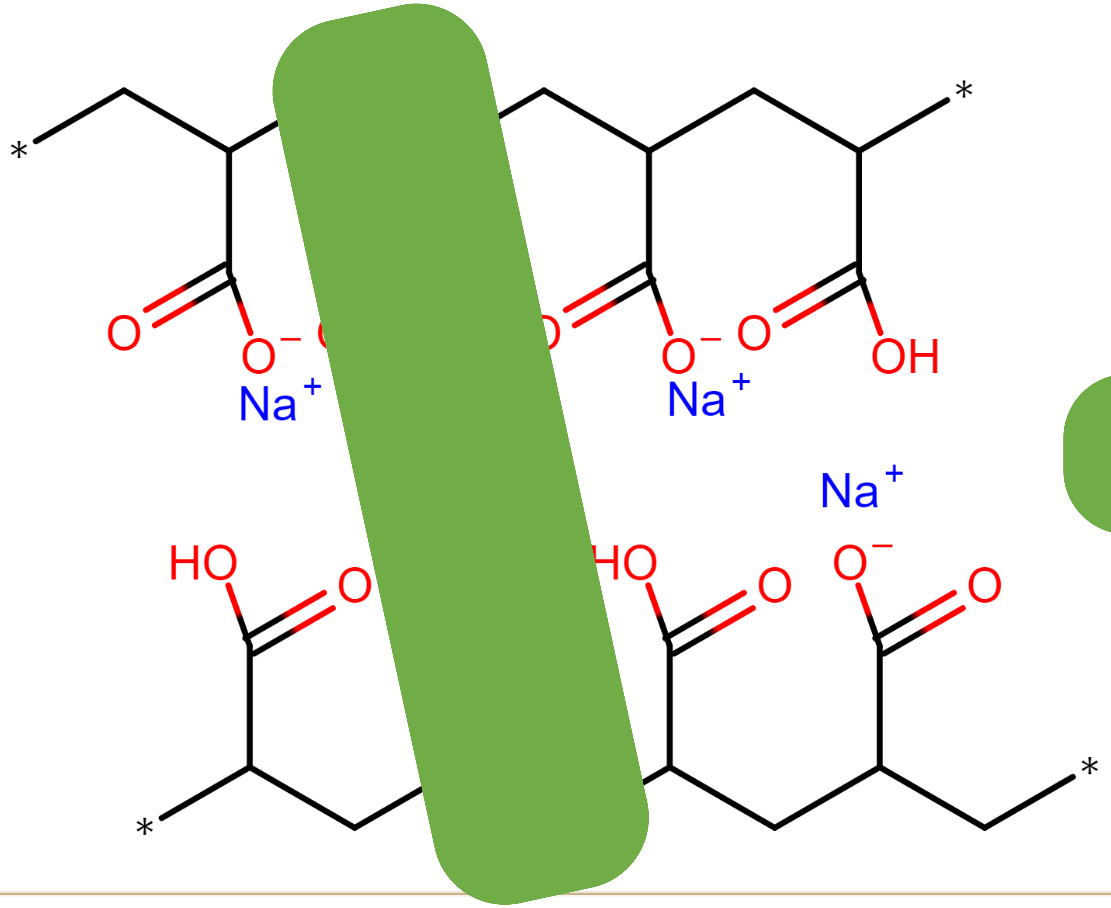
- it is not a homopolymer, but a copolymer of acrylic acid and a cross-linking monomer (N,N'-methylene-bis-acrylamide)
- a high molecular weight polymer is to be obtained
  - otherwise, the insufficiently cross-linked part could wash out
  - the mass of PAA that can be extracted in this way is usually 5 to 20% by weight
- production process:
  1. copolymerization of acrylic acid with a cross-linking comonomer
  2. neutralization by NaOH
  3. replacing part of the -COOH groups with its sodium salts –COONa
  4. at the same time, the pH value of the prepared SAP is thus adjusted
  5. drying and grinding
  6. surface finishes
  7. additional surface cross-linking of the ground particles so that, during water sorption, the surface of the particles does not swell quickly and the formation of a gel-like cluster, which is also poorly permeable to water

A simplified scheme of the polymerization of acrylic acid



cross-linking comonomer N,N'-methylene-bis-acrylamide

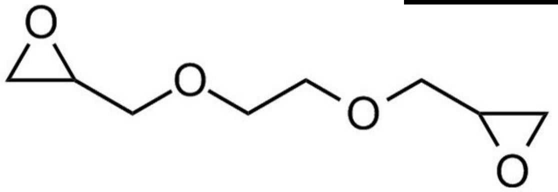
Cross-linked and partially neutralized PAA



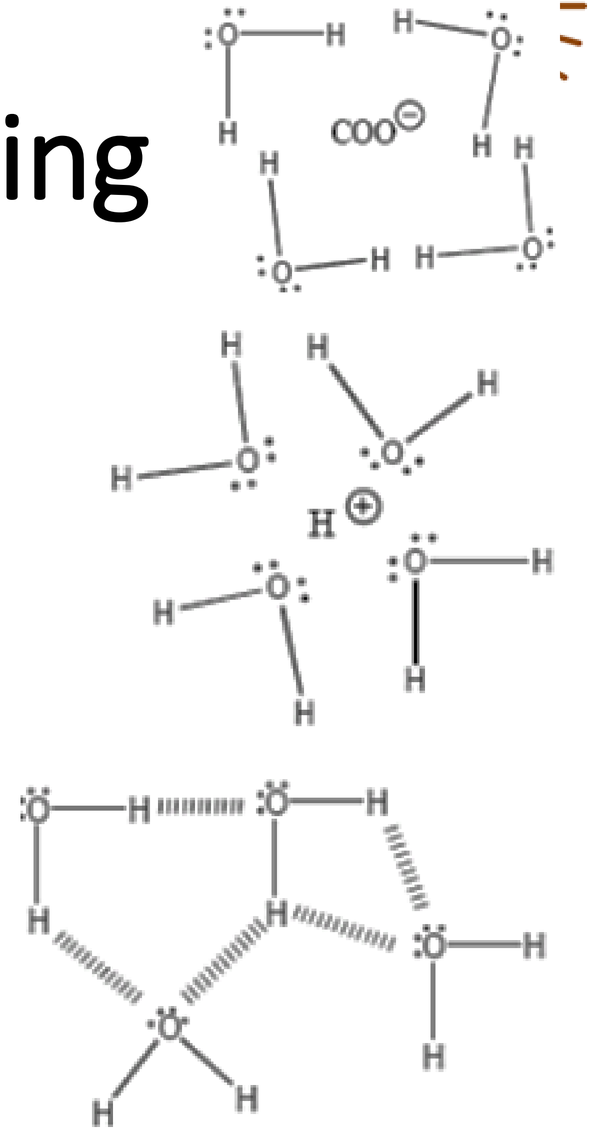
cross-linking comonomer N,N'-methylene-bis-acrylamide

PAA cross-linking

- provides:
  - insolubility of the resulting product
  - mechanical properties of the resulting hydrogel
  - reduces the amount of extractable components (linking macromolecules increases the average molecular weight)
- the more cross-linked the PAA, the stronger the hydrogel [redacted] sorb
  - PAA then cannot swell as much
- cross-linking comonomers
  - N,N'-methylene-bis-acrylamide
  - trimethylolpropane triacrylate (TMPTA)
- crosslinking of PAA homopolymer
  - ethylene glycol diglycidyl ether (EGDGE)
    - reacts with ready-made PAA macromolecules

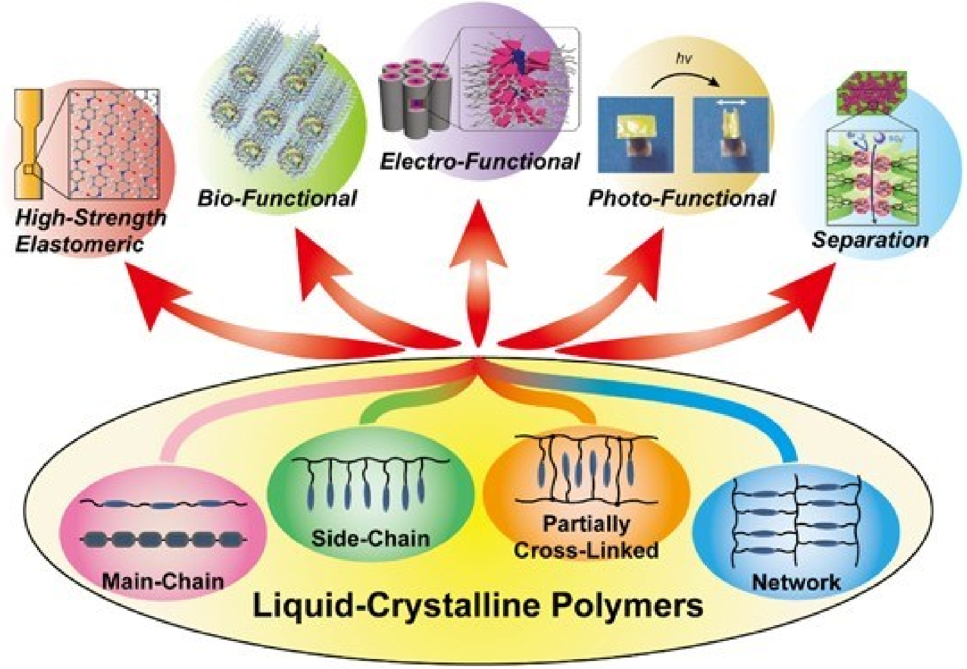


Water sorption and PAA swelling



- water with secondary bonds binds to charged or partially charged parts of macromolecules and to ions trapped inside the network
- the difference of osmotic pressures inside the PAA and in the sorbed liquid
  - cations inside the PAA network (e.g. Na+) are practically not washed out, because they are held by a large number of partially negatively charged parts of the macromolecules
- segments of chains of the same charge that come too close repel each other
  - thus helping the hydrogel to expand

Polymer liquid crystals



Liquid crystals

- 1888 – discovery of liquid crystals (F. Reintzer)
- the liquid-crystalline phase in polymeric substances was described by Paul John Flory (1954 onwards)
- the first liquid-crystalline polyester on the market in 1972
  - Ekkcel I-200

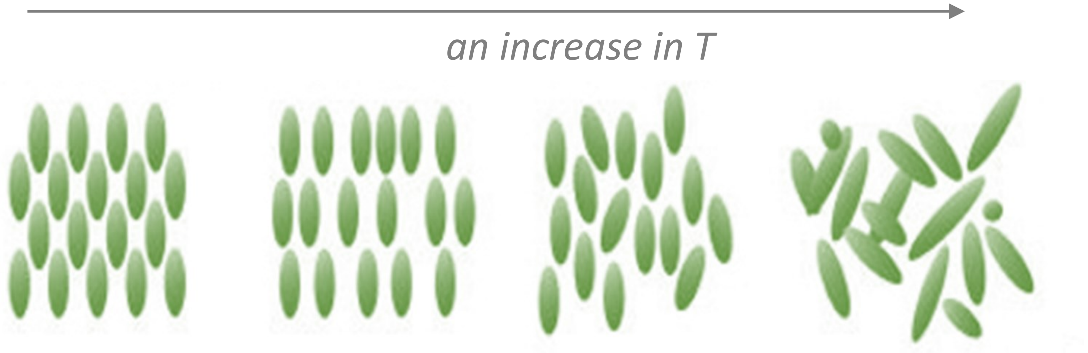
- significantly anisotropic molecules that can change their orientation in space under the influence of a force field
- transition between isotropic and anisotropic matter

Liquid crystals

- formed by mesogens
  - a molecule or part thereof, responsible for liquid-crystalline behavior
  - rod-shaped or disc-shaped (one or two dimensions significantly different)
- creates oriented structures in the external force field
  - after orientation, they show different optical, electrical and magnetic properties, density, etc.
- types:
  - lyotropic liquid crystals
    - molecules with mesogens dissolved in a foreign liquid phase
  - thermotropic liquid crystals
    - molecules with mesogens acting in the mass above the melting temperature
  - smectic phase (highly symmetric even at long distances)
  - nematic phase (less symmetric and rather at shorter distances)

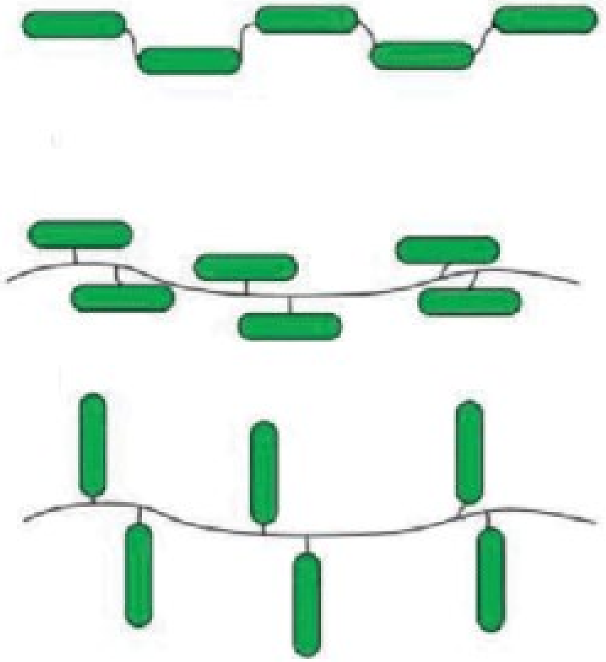
solid ↔ smectic ↔ *nematic* ↔ liquid

an increase in T

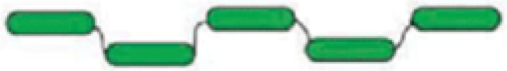


Polymer liquid crystals (LCP)

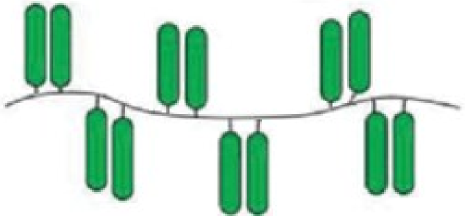
- mesogens as a repeating part of a macromolecule
- thermotropic
  - only works above T_g
- a combination of rigid (rods or disks) and flexible segments
  - on the main chain
    - chain-like
  - off the main chain
    - orthogonal
    - ridge-like



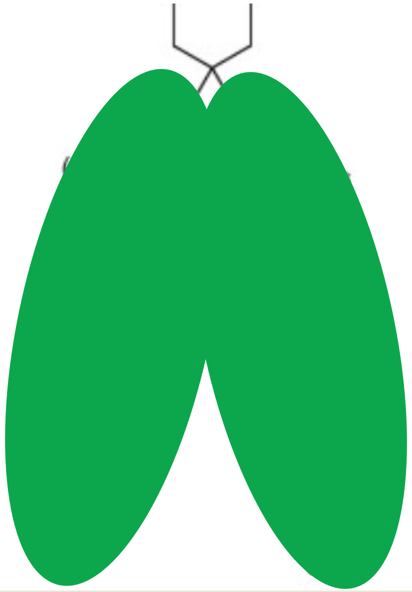
Polymer liquid crystals (LCP)



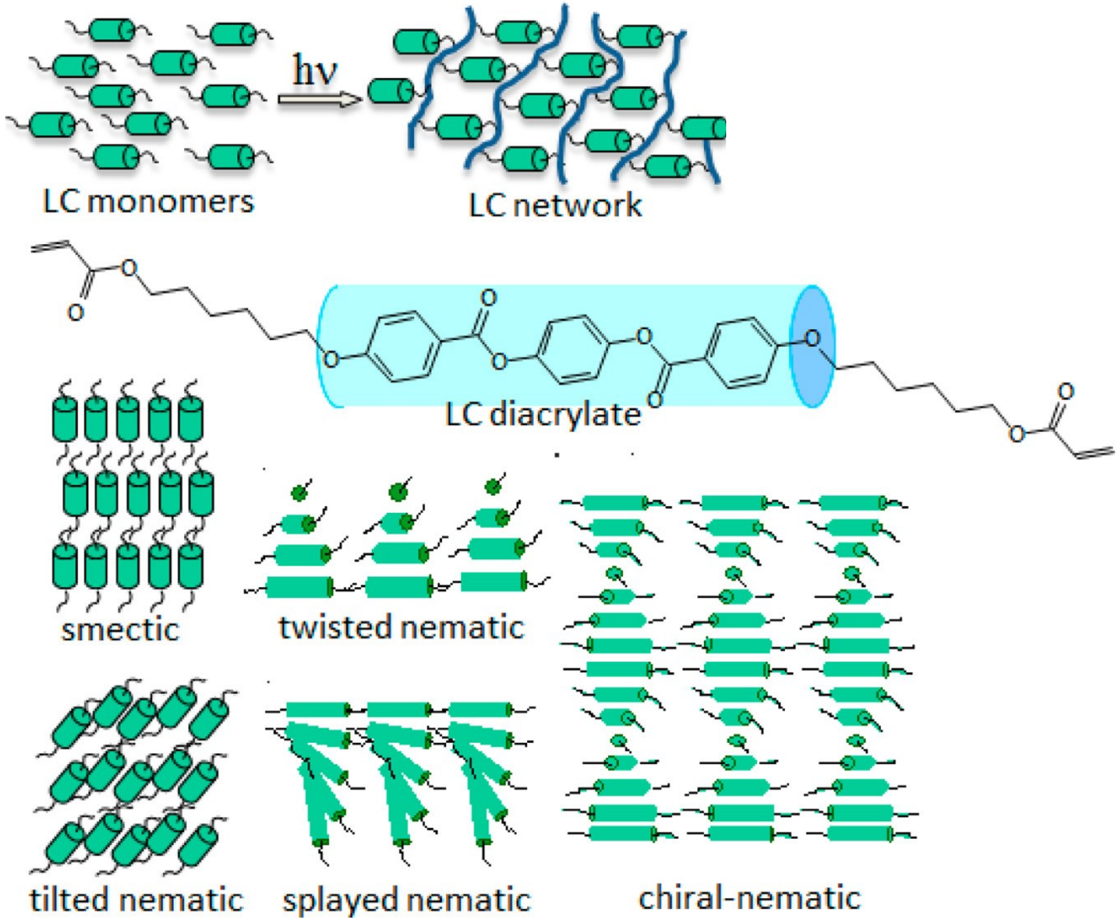
chain-like LCP
(main chain mesogens)



orthogonal LCP
(mesogens off the main chain)

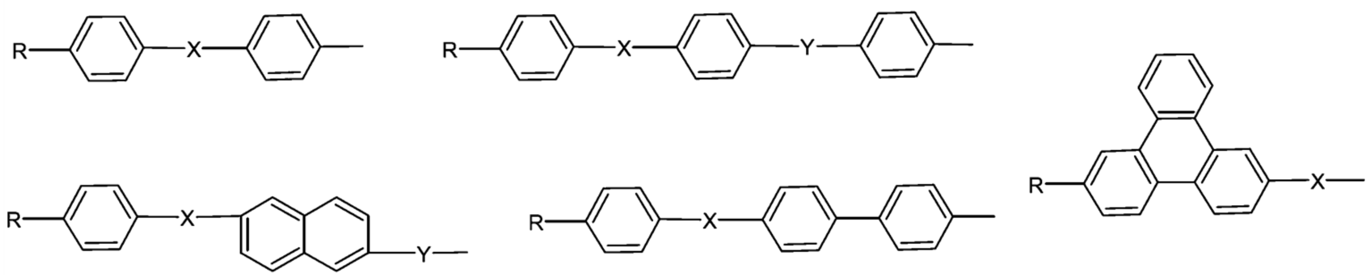


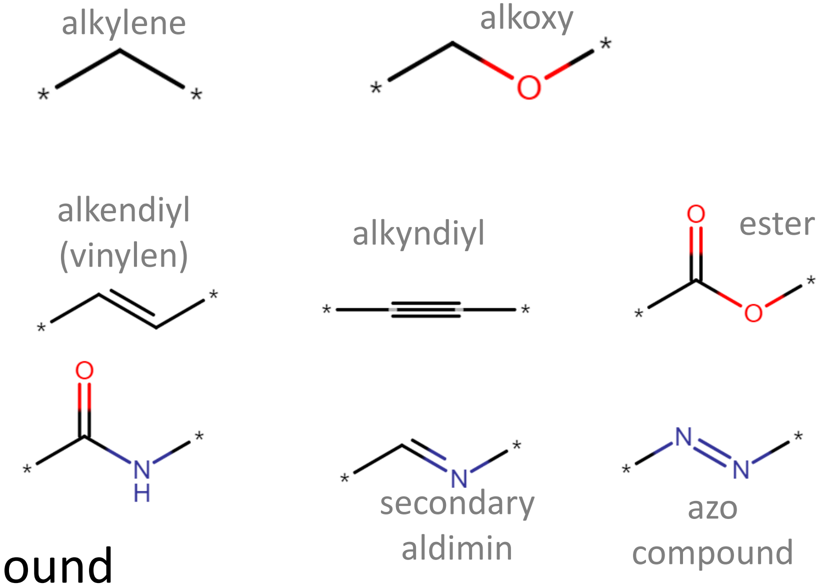
Polymer liquid crystals (LCP)



Examples of mesogens

- only works above T_g



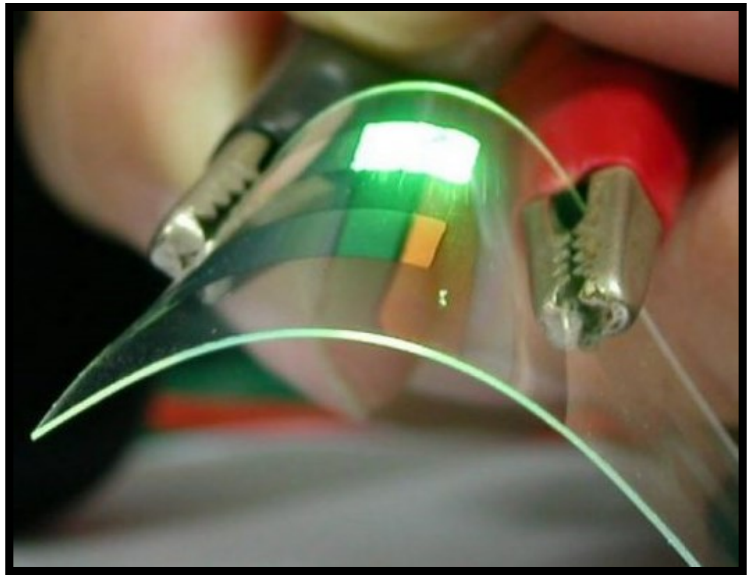


- R … flexible group
- X and Y … inflexible groups
  - alkene, alkyne, ester, amide, secondary (ald)imine, azo compound

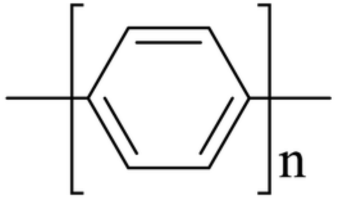
Electroconductive polymers

Electroconductive polymers

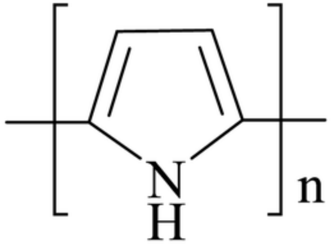
- polymers are usually insulators
- increasing the conductivity of the polymer
  - polymer with conjugated e- in the main chain
    - conjugated chain → movable π e-
    - representatives
      - polyacetylene (ie polyethylene)
        - conductivity comparable to metals
        - it burns in the air
      - polyaniline
      - polyphenylene-vinylene
        - pure aromatic backbone
      - poly(p-phenylene)
      - polythiophene
      - polypyrrole
  - redox doping (supplied e-)



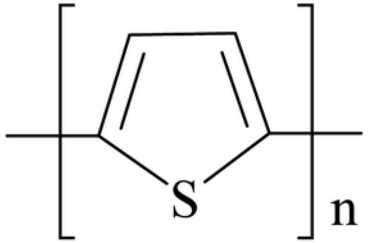
Electroconductive polymers



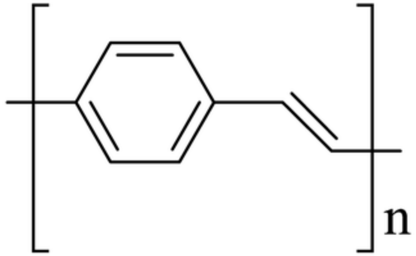
poly(p-phenylene)



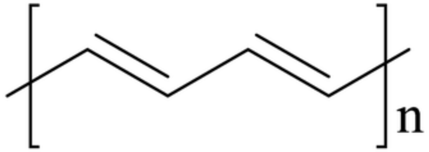
Polypyrrol



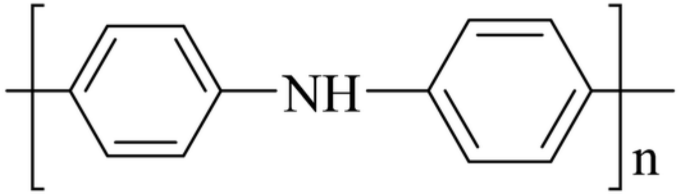
Polythiophene



poly(p-phynylene vinylene)

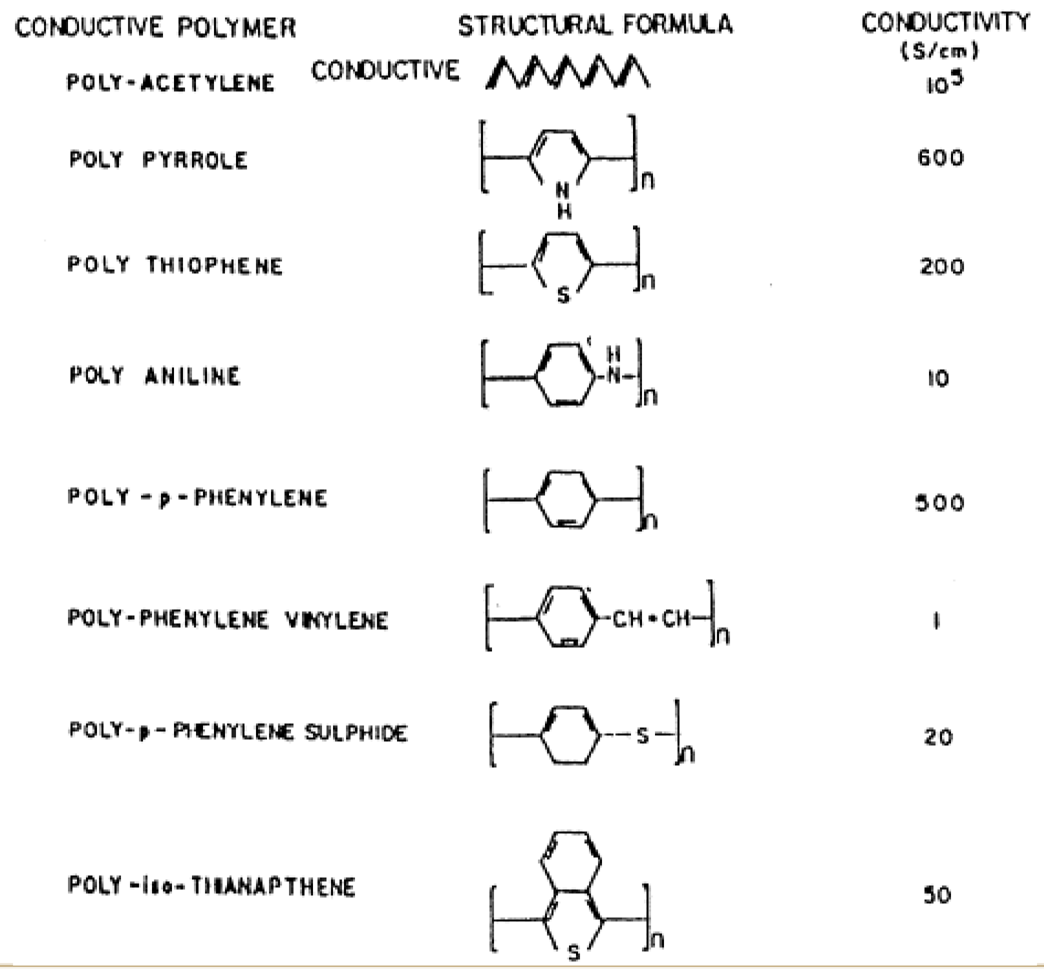


Polyacetylyne



Polyaniline

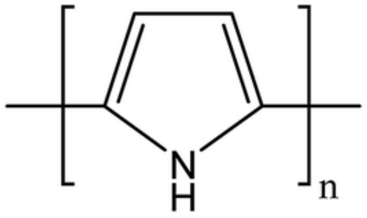
Electroconductive polymers



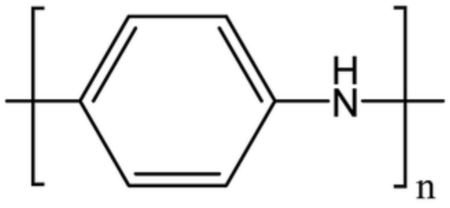
CONDUCTIVE POLYMER	STRUCTURAL FORMULA	CONDUCTIVITY (S/cm)
POLY-ACETYLENE	CONDUCTIVE	10^5
POLY PYRROLE	NH	600
POLY THIOPHENE	S	200
POLY ANILINE	-NH-	10
POLY-p-PHENYLENE		500
POLY-PHENYLENE VINYLENE	-CH=CH-	1
POLY-p-PHENYLENE SULPHIDE	-S-	20
POLY-iso-THIANAPTHENE	S	50

Use of electroconductive polymers

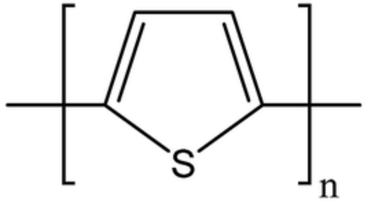
- anti-corrosion protection of metals
- accumulators
    - many times lighter than the existing one
- electrochromic devices
    - the electrically conductive polymer can have a different color in its original and doped state
    - information storage
- gas separation
    - oxygen-nitrogen, methane-CO2
    - with repeated doping of polyaniline, pores of a defined size will be formed



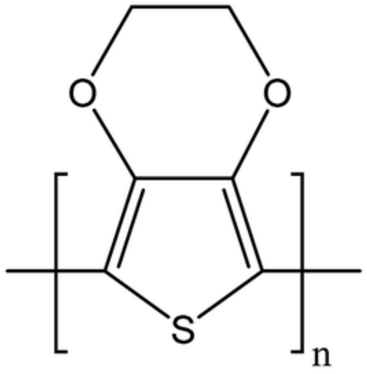
PPy



PAni

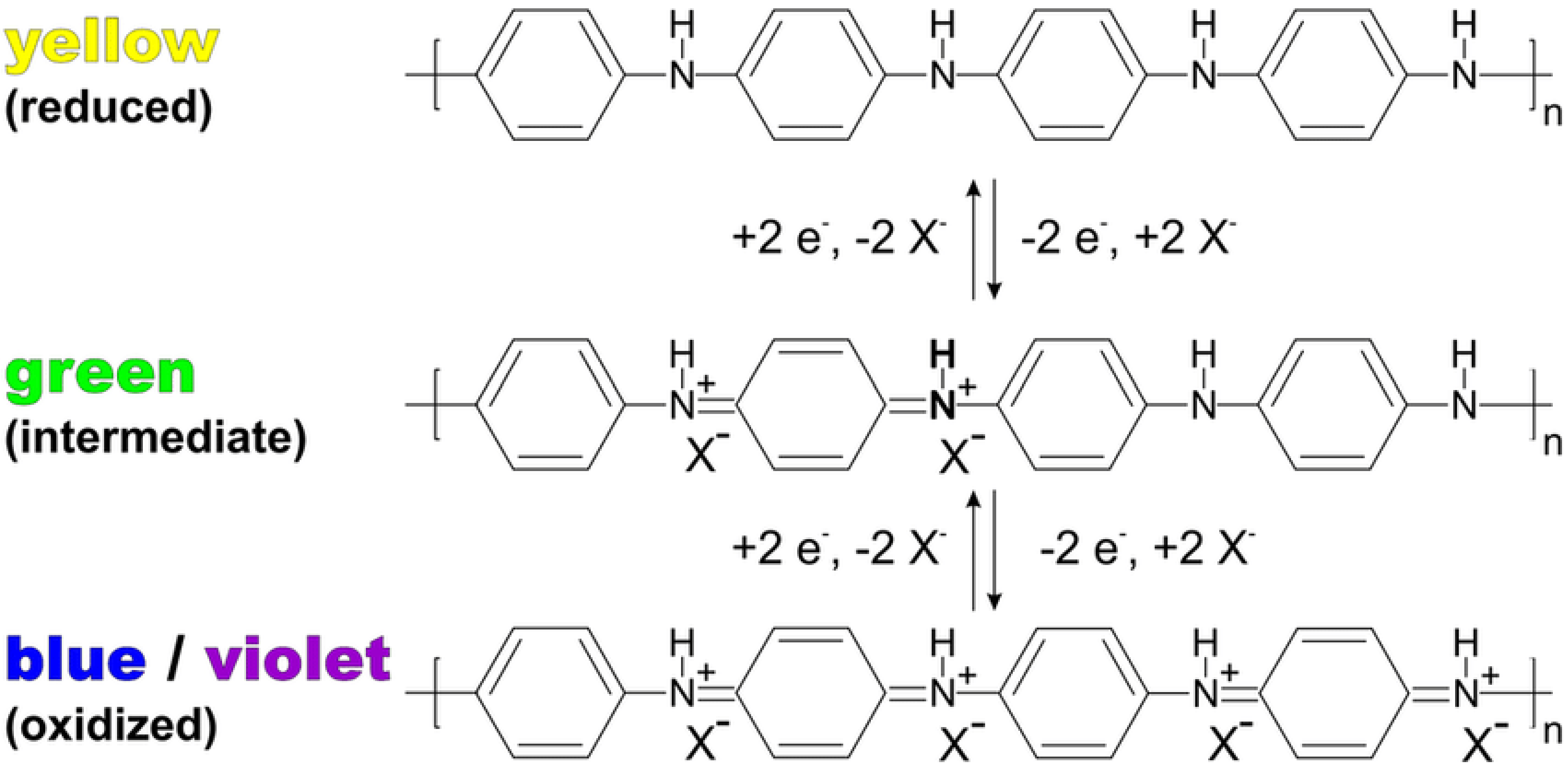


PTh



PEDOT

Redox color changes of polyaniline

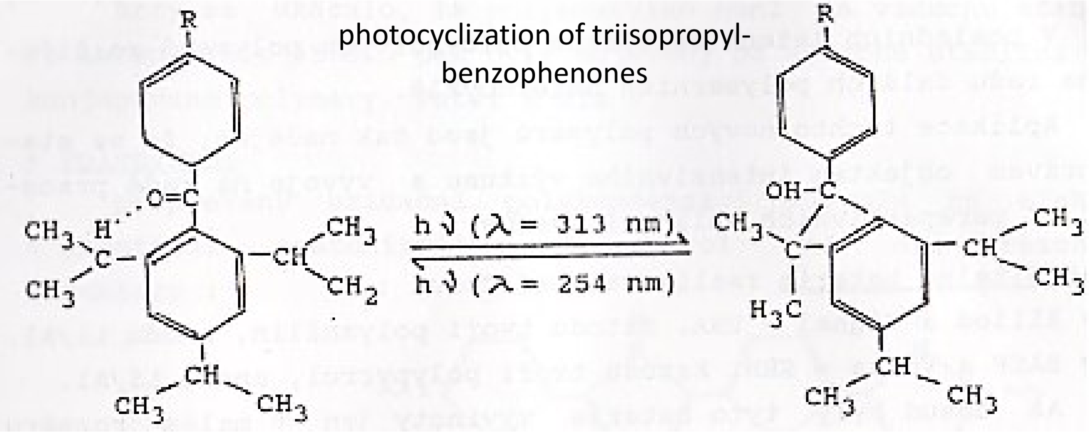


Photosensitive polymers

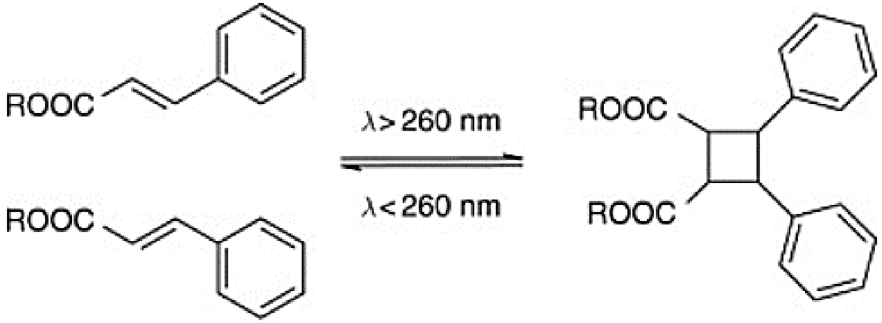
Photosensitive polymers

- not to be confused with photopolymers
  - synthetic resins cured by (usually UV) radiation
- changes the structure under the action of light
  - returnable
  - irreversibly
- classic photography – photosensitive substances applied in emulsion (defined particle size)
  - they allow for virtually infinite magnification
    - to the size of the molecules – "What more would you like to see? Quarks?"
  - change in structure → change in optical density
    - optical data storage
  - medicine

Photosensitive polymers



photocyclization of triisopropyl-benzophenones



Polymer ion exchangers

Polymer ion exchangers (ionex)

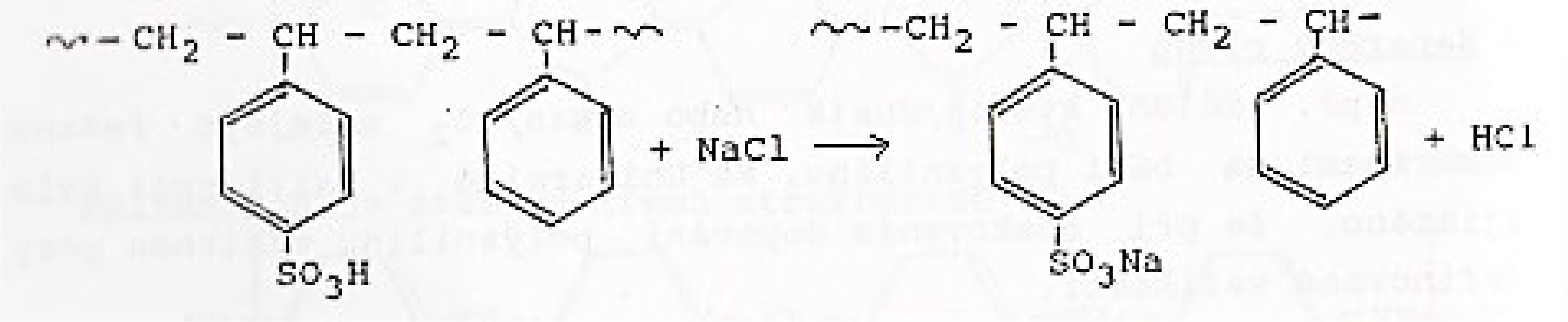
- acidic or basic functional groups on a suitable polymer support
- water softening
  - originally for steam boilers
  - water demineralization
  - extraction of precious metals from very dilute solutions
- accumulators

Ion exchangers (cathexes)

- cathexes

$$-RK_1 + K_2^+ \leftrightarrow -RK_2 + K_1^+$$

  - e.g. PS porous copolymer with divinylbenzene (crosslinker) + functional group (sulphonic -SO_3H)

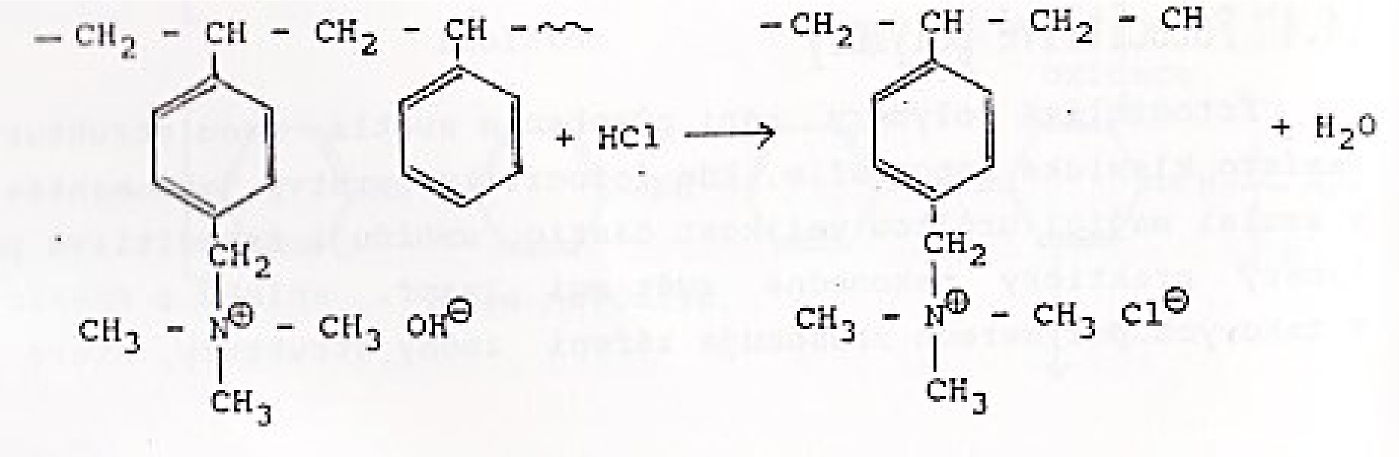


Ion exchangers (annexes)

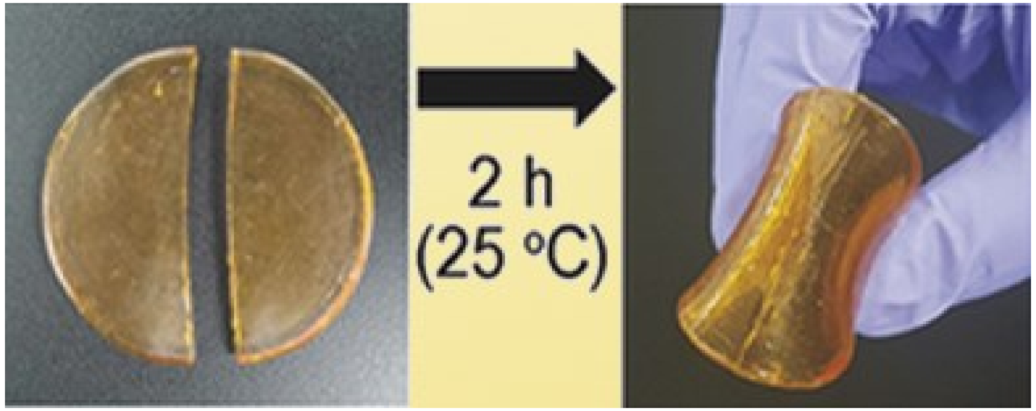
- annexes

$$-RA_1 + A_2^- \leftrightarrow -RA_2 + A_1^-$$

  - e.g. PS porous copolymer with divinylbenzene (crosslinker) + functional group (quaternary ammonium salt)



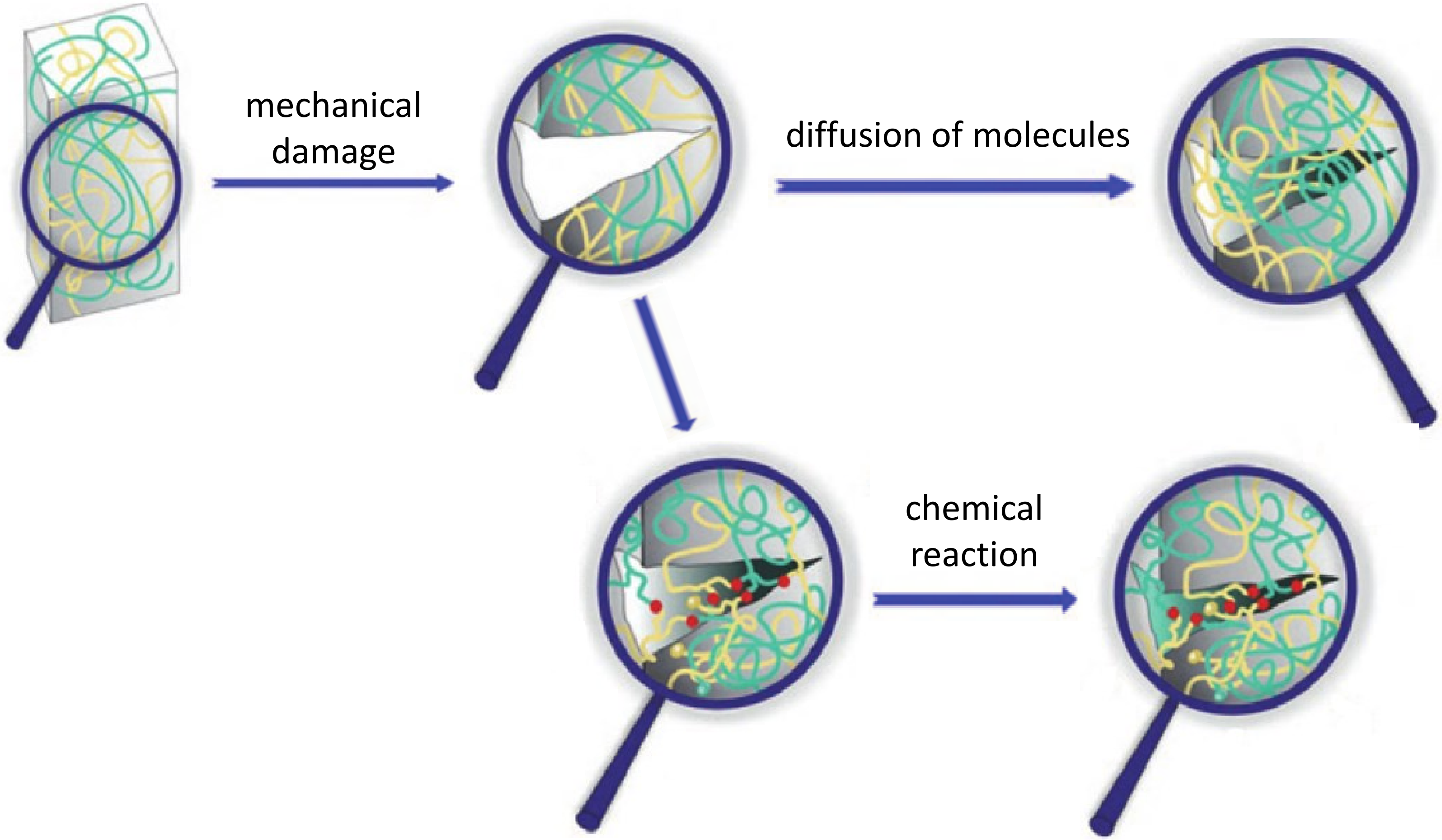
Self-healing polymers



Self-healing polymers

- they convert the mechanical energy into that which allows the broken chain to be linked with other chains
  - physically
    - diffusion of macromolecules to a new surface
    - entanglement of macromolecules into a physical network
  - physico-chemical
    - diffusion of macromolecules to a new surface
    - the formation of a covalent or supramolecular network
      - reversible or irreversible

Surface bonding methods

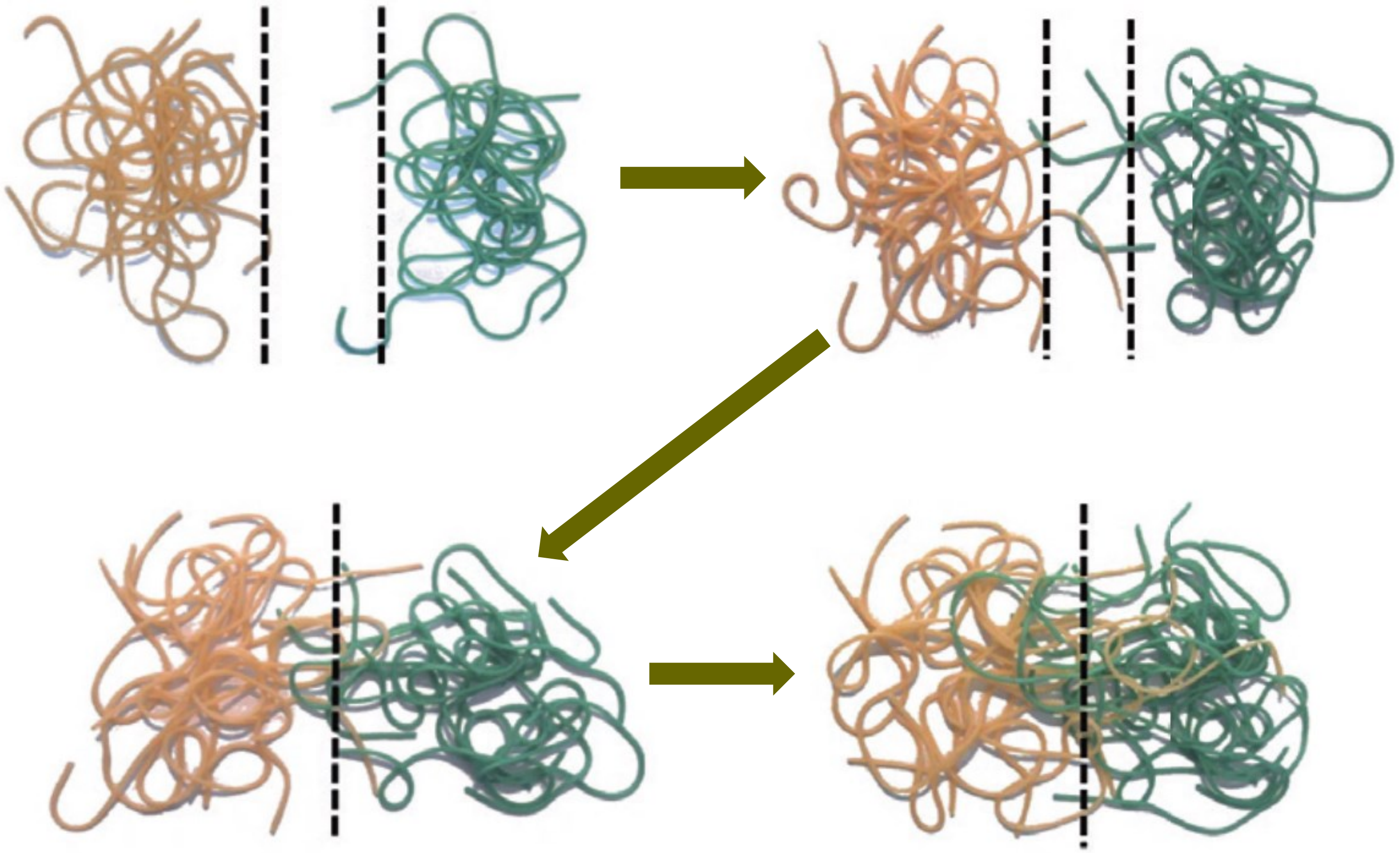


mechanical damage

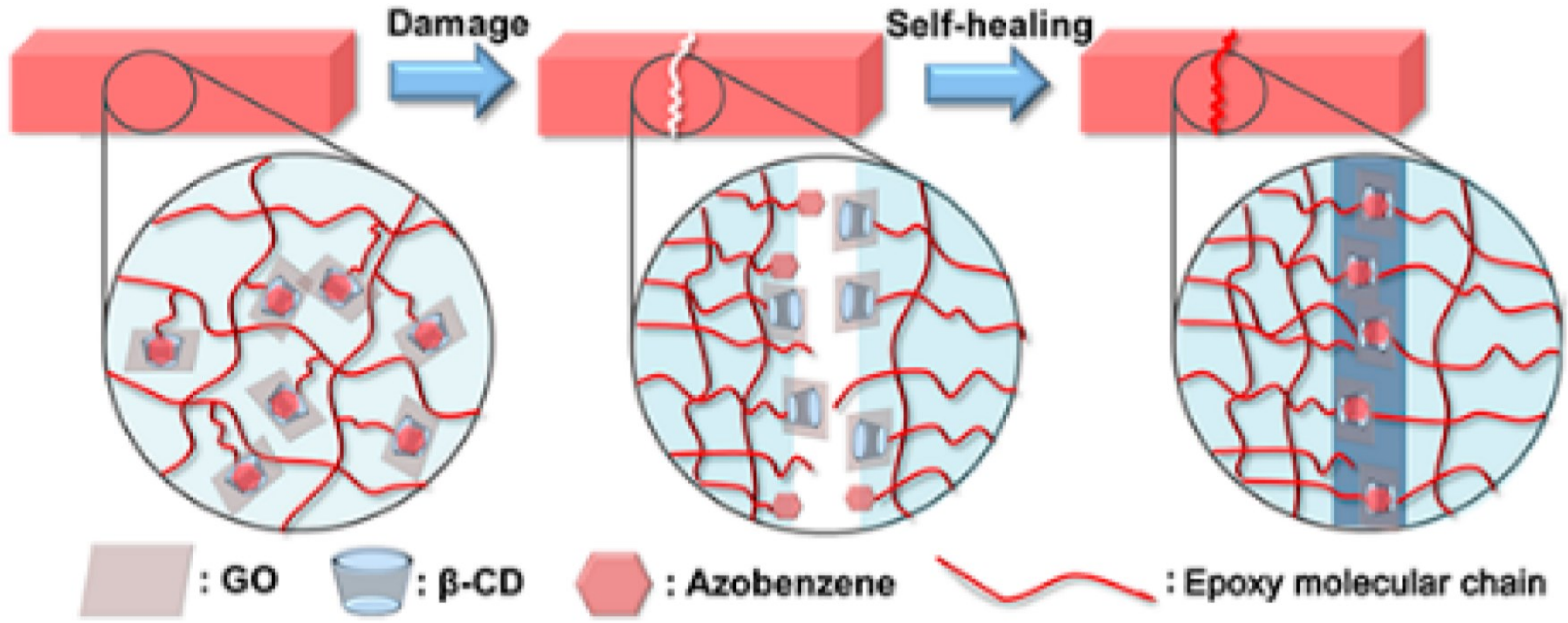
diffusion of molecules

chemical reaction

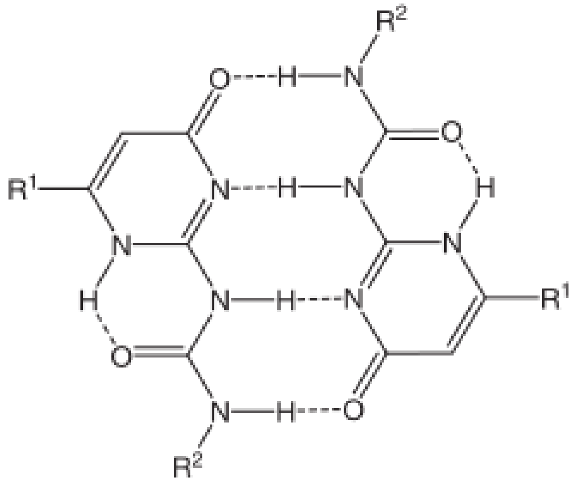
Physical bonding of surfaces

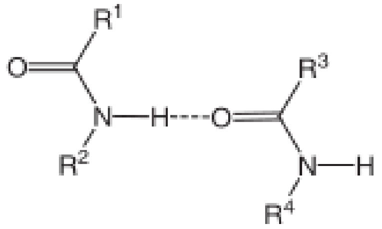


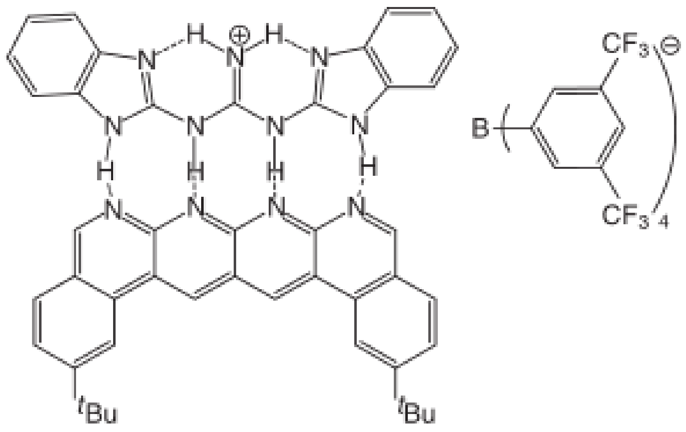
Physico-chemical bonding (irreversible)

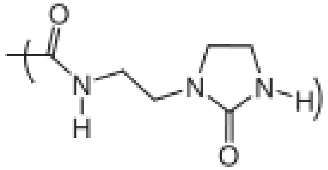


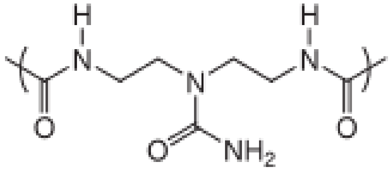
Examples of reversible cross-linking

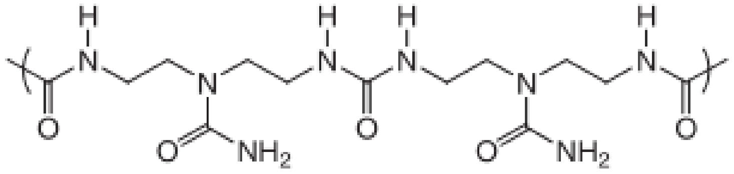








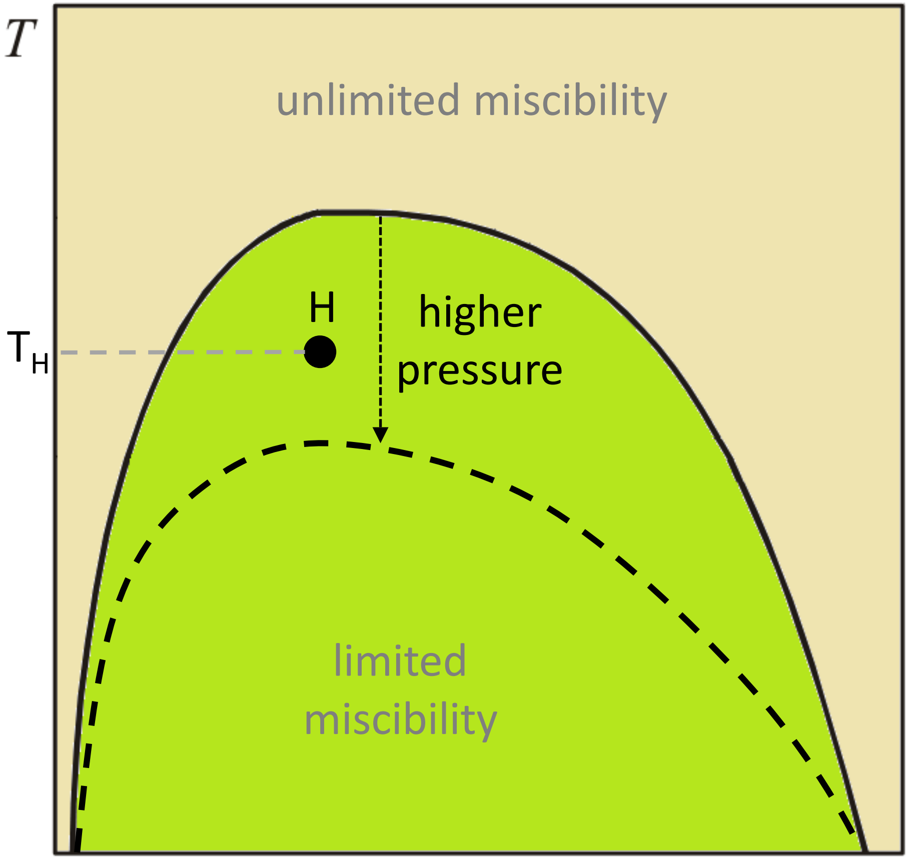




Ostatní

Baropolymers

- polymers that respond to pressure by melting at normal temperatures
  - non-crosslinked block polymers
- the possibility of recycling without the need for heating
  - does not reduce the average degree of polymerization by thermal degradation
  - can be repeated many times (not just 2-3 times)
- given by the change in phase equilibrium
  - phase of block A and phase of block B can be separated a a given pressure and temperature (I have 2 phases)
  - by reducing the pressure, the curve can be lowered and the point will reversibly reach the region of unlimited miscibility
  - after re-reducing the pressure back solidification



Polymers in medicine

Biocompatible polymers

- must meet the characteristics given by law
- must not cause side reactions in the body (e.g. allergies)
  - they should be inert in the body environment
  - few residues (according to the tables)
- UHMWPE, PP, PA6 (threads), PEEK, PTFE, PVDF

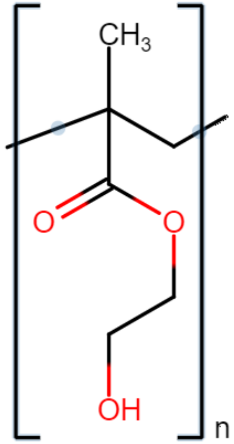
Biodegradable polymers

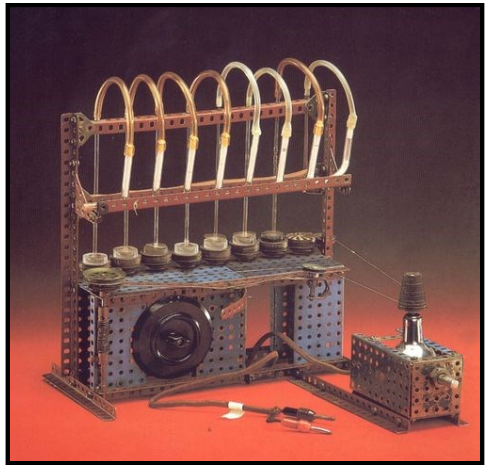
- must meet the characteristics given by law
- they degrade in the body environment without side effects
  - degradation is known in advance, "controlled"
- degradation time of the polymer in the body
  - applicability
  - the time during which the material retains its mechanical property
  - complete resorption
  - the time it takes for the body to break down the material so much that it is not noticeable
- diferentiation by origin
  - natural
    - chitosan, collagen, hyaluronic acid (mainly bacterially formed, formerly from animal bodies), alginates
    - now on the decline (badly modified, difficult repeatability of production)
  - synthetic
    - polycaprolactone, polylactic acid, polyglycolic acid, polylactic/polyglycolic acid copolymers (various proportions), polydioxanone, bacterial biodegradable polymers (hydroxybutyrates, hydroxyvalerates, hydroxysuccinates), polyurethanes

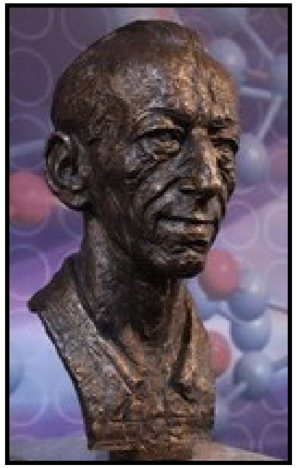
Example:

- contact lenses
    - poly(hydroxyethyl) methacrylate (HEMA)
    - gel structure (relatively tolerable for the eye)
        - Otto Wichterle
        - MERCURY
        - disadvantageously patented

- protective packaging of medicines
- polymeric drug carriers
- prosthetics







Thank you for your attention

Merry Christmas