Macromolecular Chemistry
MC 2.1.3

Makro – „Crashkurs"

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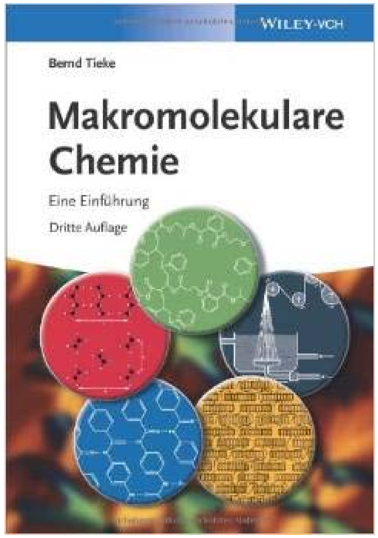
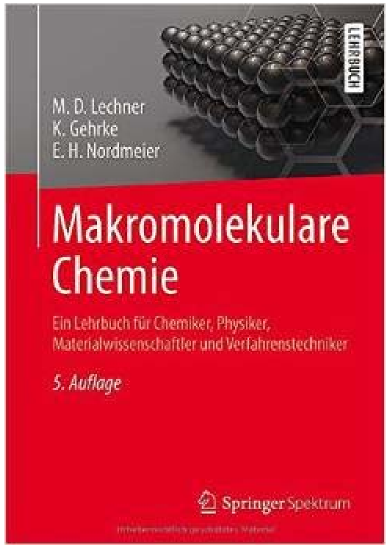
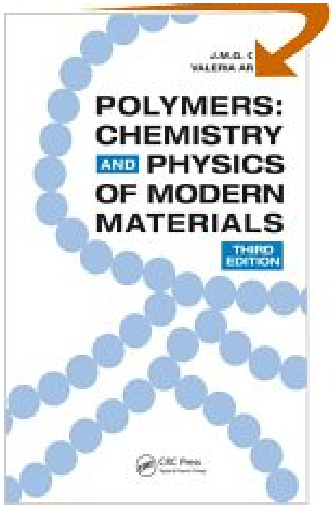
Textbooks

- Tieke, Bernd: *Makromolekulare Chemie*, Wiley-VCH (2014, 49.90 €)
- Lechner, Gehrke, Nordmeier: *Makromolekulare Chemie*, Birkhaeuser (2014, 69,99 €)
- Elias: *Makromoleküle 1-5*, Wiley-VCH (2003, > 800 €)
- Cowie: *Polymers: Chemistry and Physics of Modern Materials* CRC-Press Inc. (2011, 65,95 €)







Advantages:

- Cheap
- Good quality
- Easy to process, fast to process, *i.e.* to convert into certain forms, such as bottles or fibers (lower temperatures than needed for metals)
- Light-weight (energy-saving in cars or planes)
- Sufficient petrochemical resources (at present, more than 90% are used for energy production)
- Possibility to switch to natural resources (poly(lactic acid), soy beans, cellulose)
- Easy formulation compounding → a broad spectrum of different properties is available
- Recycling possibilities (thermal recycling, reuse)
- Tunable properties (choice of monomer, constitution, molar mass, …)

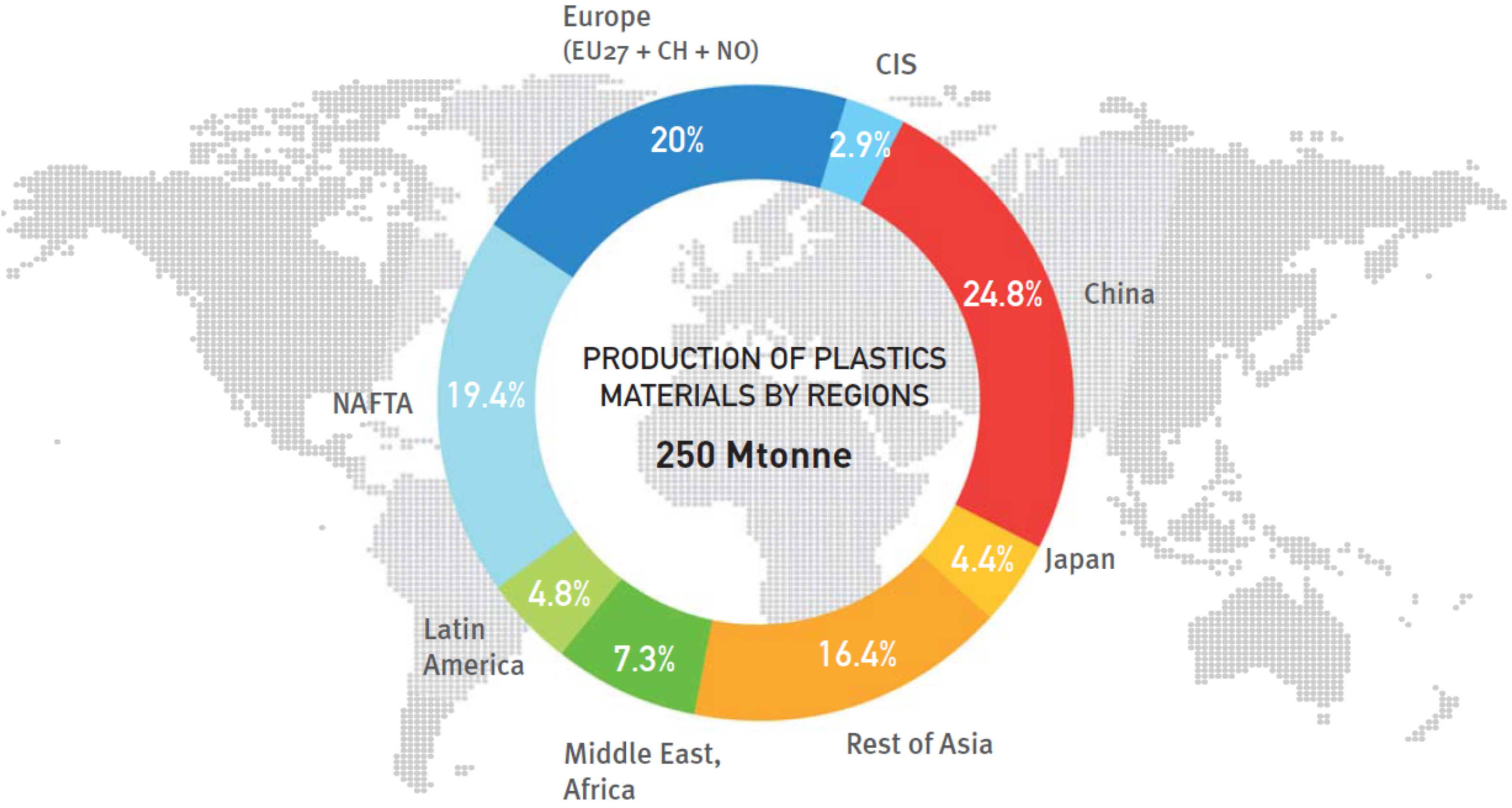
Applications

- Plastics (*e.g.,* packaging materials)
- Coatings & adhesives (*e.g.* paints)
- Fibers (*e.g.,* clothes)
- Rubbers & elastomers (*e.g.* tires)
- Agriculture (*e.g.,* promoting plant growth)
- Medicine (*e.g.,* replacement of heart valves)
- Specialty polymers (high thermal stability)
- Plastic electronics (*e.g.,* PLED, solar cells)

Source: British Plastics and rubber, www.mpes.co.uk

Motivation 1

World plastics production



2013 World production of plastics materials (thermoplastics and polyurethanes)

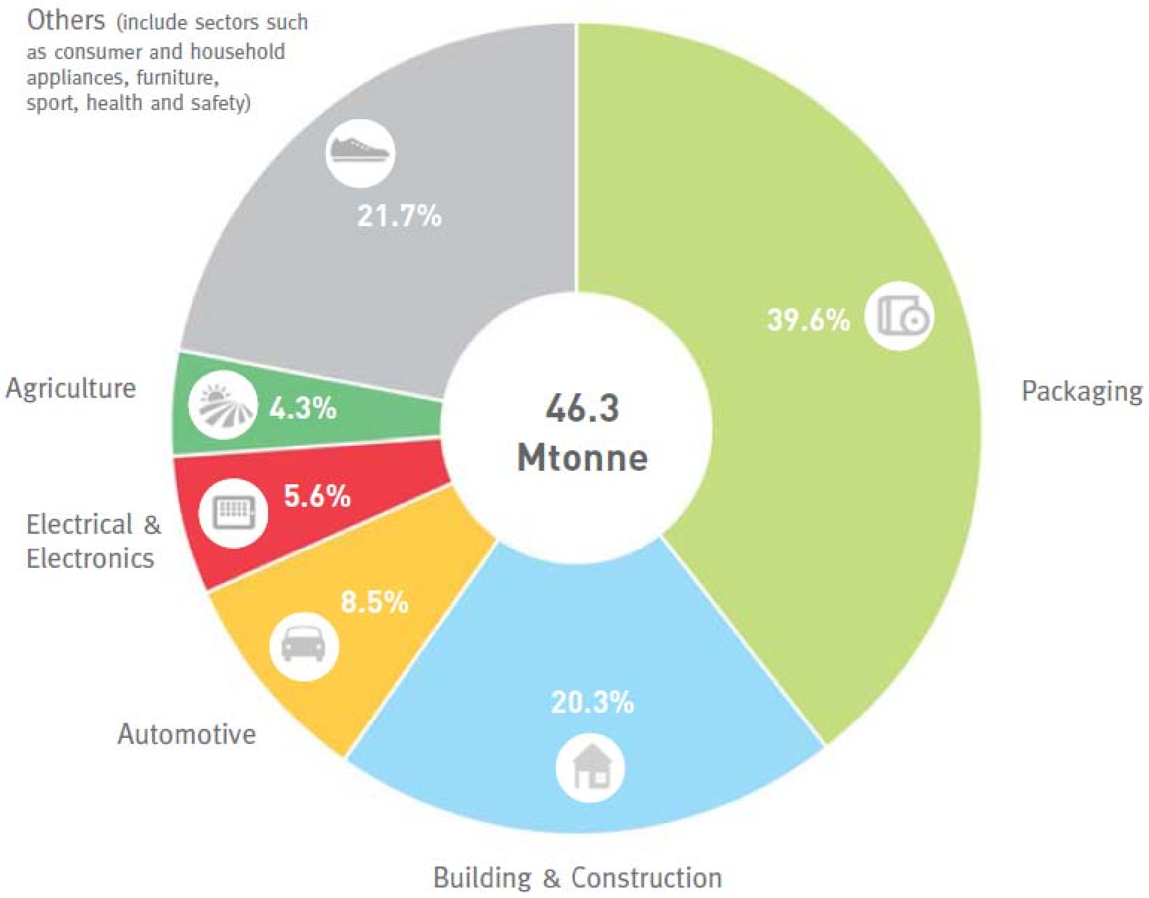
Does not include other plastics (thermosets, adhesives, coatings and sealants) nor PP-fibers.

Source: PlasticsEurope (PEMRG) / Consultic

Plastics – the Facts 2014/2015 - PlasticsEurope

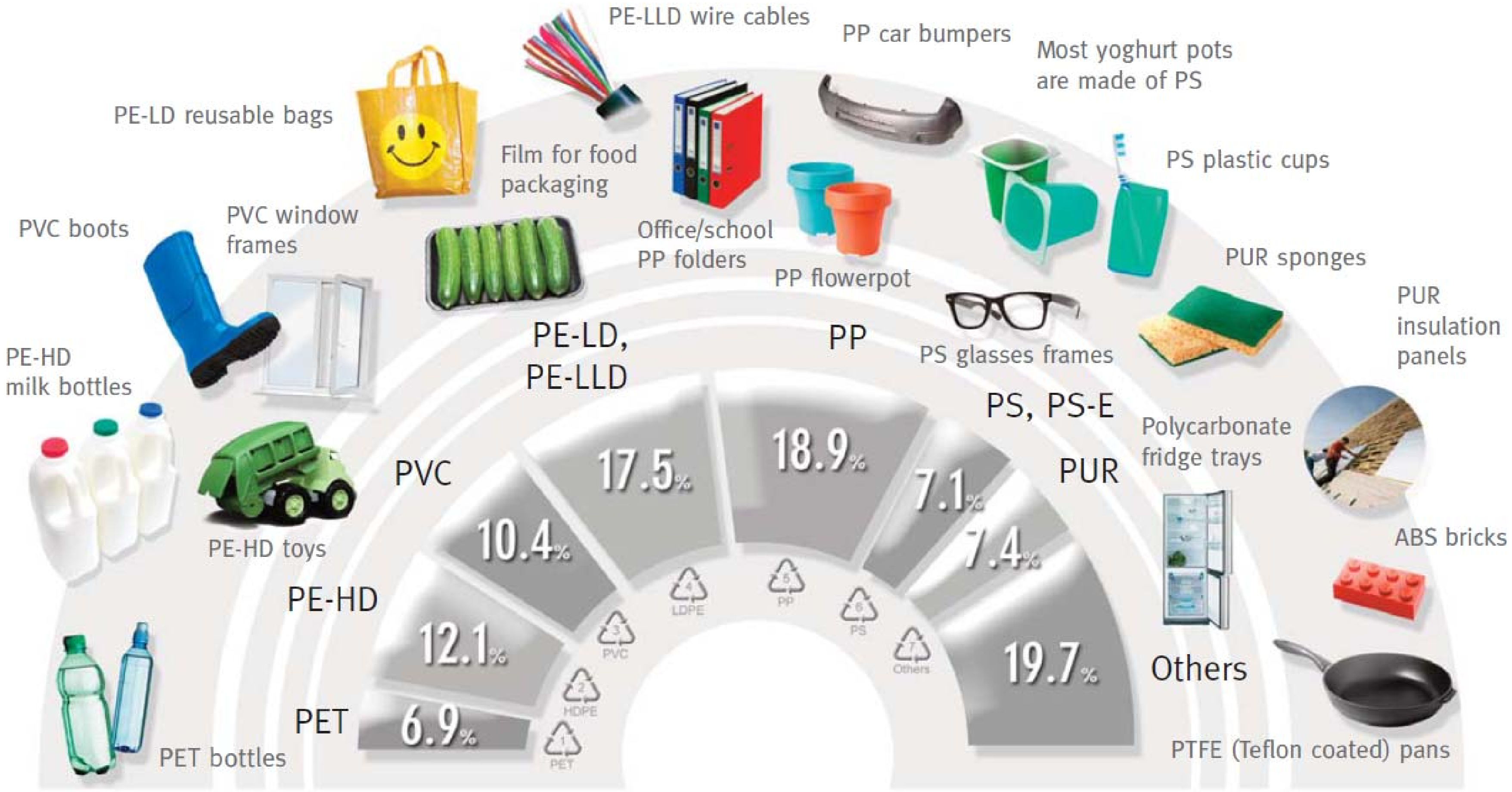
Motivation 2

European plastic demand



Plastics – the Facts 2014/2015 - PlasticsEurope

Motivation 3



European plastics demand* by polymer type 2013

Plastics – the Facts 2014/2015 - PlasticsEurope

Motivation 4

European plastics industry

Jobs

The plastics industry gives direct employment to over **1.45** million people in Europe

Companies

An industry in which more than **60.000** companies operate, most of them SME's

Turnover

The European plastics industry had a turnover of **320** billion euro in 2013

Multiplier effect

The European plastics industry has a **multiplier effect of 2.4 in GDP** and **almost 3 in jobs***

Innovation

The plastics sector is part of the **top 5** most innovative sector in the EU representing 1 in 25 patents submitted by the industry between 2003 and 2012

Recycling

More than **6.6** million tonnes of plastics waste recycled in 2012

Plastics – the Facts 2014/2015 - PlasticsEurope

What are polymers? History

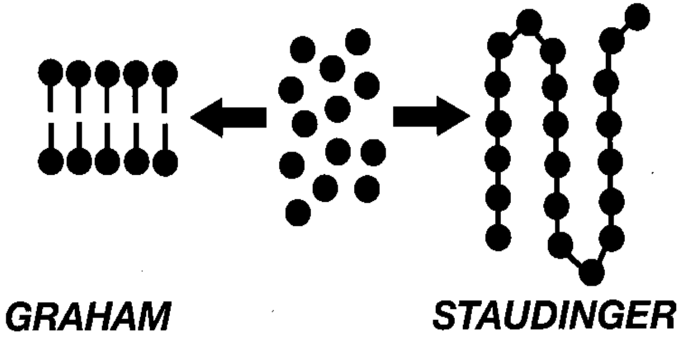
On the other hand....rubber was once thought (~1910) to be two isoprene units ($-CH_2-C(CH_3)=CH-CH_2-$) joined in a circle. The high viscosity was attributed to secondary forces grouping the circles into great aggregates. If so, then brominating the isoprene should dramatically alter the viscosity. It did not.

Still people were not convinced...because where were the end groups if the chains were really linear?

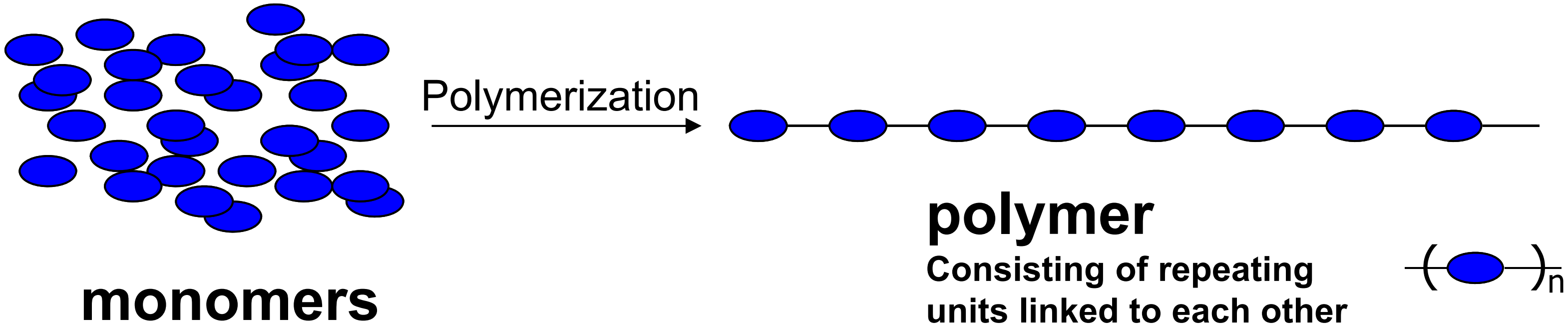
No one could find them, and no one could admit such a failure of chemical analysis...so linear polymerization was a mystery. Maybe polymers were large rings???

(Leaping ahead for awhile: In fact, it was a failure of chemical analysis that the end groups were not found. On a polystyrene of M=104,000 there are only 2 ends: Only 1 in 500 styrene units is different.)

→ Polymers were assigned as organic colloids (loose physical aggregates) or as impure stuff.



What are polymers? – Definitions 1



Polymer: a substance composed of macromolecules

Oligomer: A molecule of **intermediate relative molar mass**, the structure of which essentially comprises a **small plurality of units** derived, actually or conceptually, from molecules of lower relative molecular mass. A molecule is regarded as having an intermediate relative molecular mass if it has **properties which do vary significantly with the removal of one or a few of the units**. If a part or the whole of the molecule has an intermediate relative molar mass and essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass, it may be described as **oligomeric**, or by **oligomer** used adjectivally.

IUPAC Gold Book

Polymer (IUPAC-definition):

A substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that does not vary markedly with the addition or removal of one or a few of the constitutional units.

www.iupac.org

Timeline

- Use of natural polymers: cellulose, skins, wools, resin, natural rubber since prehistoric times
- 1839 first trials of vulcanization of natural rubber by Charles Goodyear
- 1865 Parker: 1. Patent for celluloid
- 1901 Röhm: Polyacrylicacidesters
- 1906 Hofmann: Polyisoprene
- 1907 Bakeland: Bakelite (phenol-formaldehyd-resin); typical black
- 1915 Bayer: polydimethylbutadiene (synthetic rubber)
- Not until 1920 development of macromolecular chemistry by Hermann Staudinger (nobelprize 1953)
- 1926 PVC: Waldon Semeon of B.F. Goodrich (method to plastize)
- 1930 BASF: Polystyrene, Polyacrylonitrile
- 1933 Röhm: Plexiglass (PMMA)
- 1937 IG Farben: BUNA (first synthetic rubber)
  DuPont: Nylon-6,6 (Carothers)
  Bayer: Polyurethanes by using isocyanates (Otto Bayer)

History of macromolecular chemistry 2

1938/39	BASF: Nylon-6 = Perlon (ε-Caprolactam) (Dr. P. Schlack)
1939	ICI: HD-PE
1945	ICI: Terylen (Poly(ethylene terephthalate)) Hoechst: Trevira (Poly(ethylene terephthalate))
1946	DuPont: Teflon (Polytetrafluoroethylene)
1952/53	Ziegler: ZIEGLER-catalysts -> Polymerization of ethylene at normal pressure Natta: ZIEGLER-catalysts for the synthesis of substituted polyethylenes -> regular (= isotactic) polypropylene result: Ziegler-Natta-Polymerization for the synthesis of tactic polymers
1956	DuPont: Polyoxymethylene -(-CH_2-O-)- (POM)
1957	General Electric and Bayer: Polycarbonates
1962	DuPont: Polyimides and Polyphenylenes
1964/65	Polyphenylenoxides, -sulfides, - sulfones
1970	PET/PBT (Polybutyleneterephthalate), SBS (Stryrene-Butadiene-Styrene)
1975	Kevlar (aromatic polyamide, high performance polymer)
1970‘s	Intensive investigations of block-, grafted- and star polymers
1977	Electrically conducting polymers (doped polyacetylene)

History of macromolecular chemistry 3

- Since 80s: Dentritic polymers, highly branched polymers
- Since 90s: Controlled radical polymerization
- 1986: First solar cell consisting of conducting polymer and C_{60}, Sariciftci
- 1989: Patent (Bayer) PEDOT for antistatic applications
  → later OLEDs, solar cells
- 90s: Polylactide: Discovery 1990, biodegradable polymers

Four generations of polymeric materials

1. Polymers introduced to the market before 1950, simple plastics (PS, PVC, PMMA, LD-PE, Nylon)

2. Polymers with improved properties as construction materials, 1950-65 (HD-PE, PC, isotact. PP, PU)

3. Speciality polymers, since 1965, more complex chemical structure, high mechanical strength, high softening temperature (Poly(phenylenesulfide, Polyimide, Kevlar, Teflon)

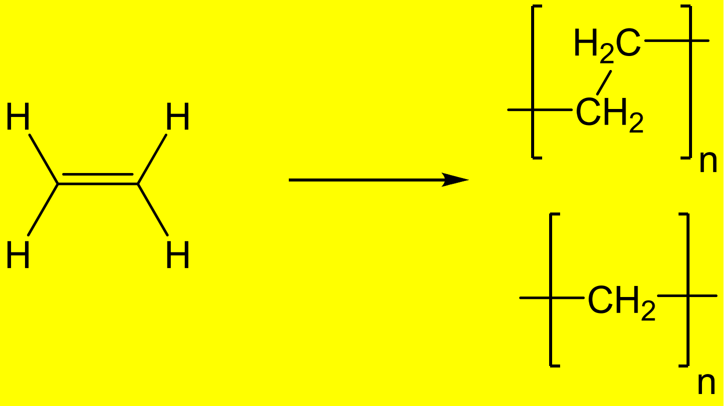
4. Electrically conducting polymers, since 1977

B. Rånby: Background – polymer science before 1977

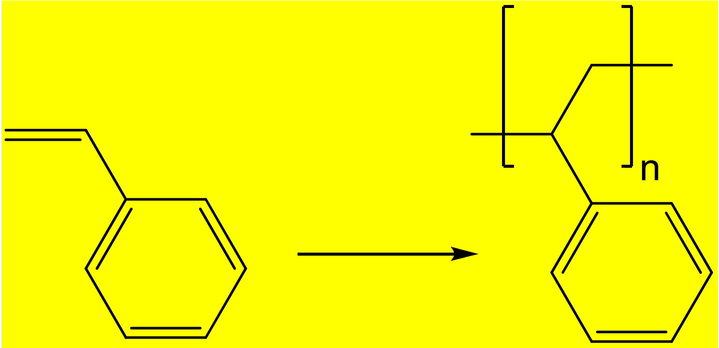
Nomenclature 1

Normally the monomer determines the name of the polymer:

Poly(ethylene)/Polymethylene

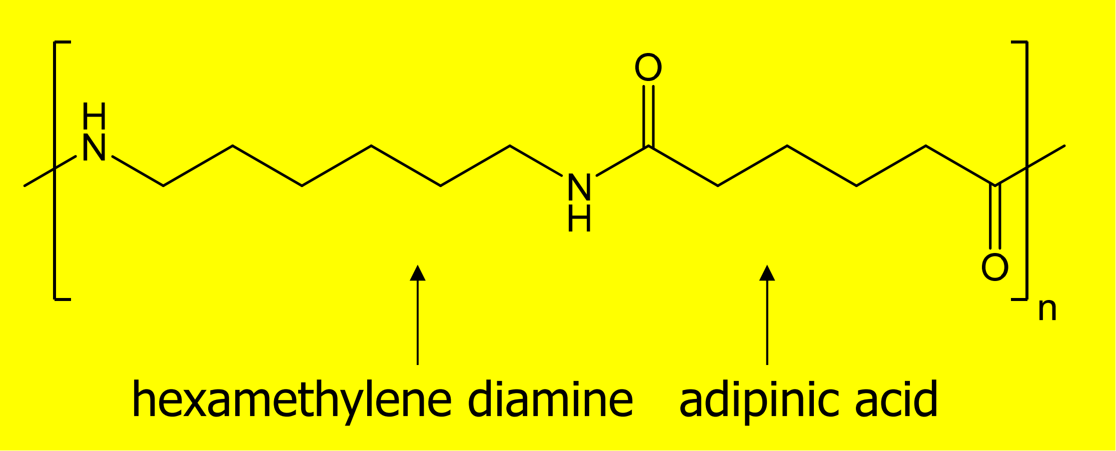


Polystyrene

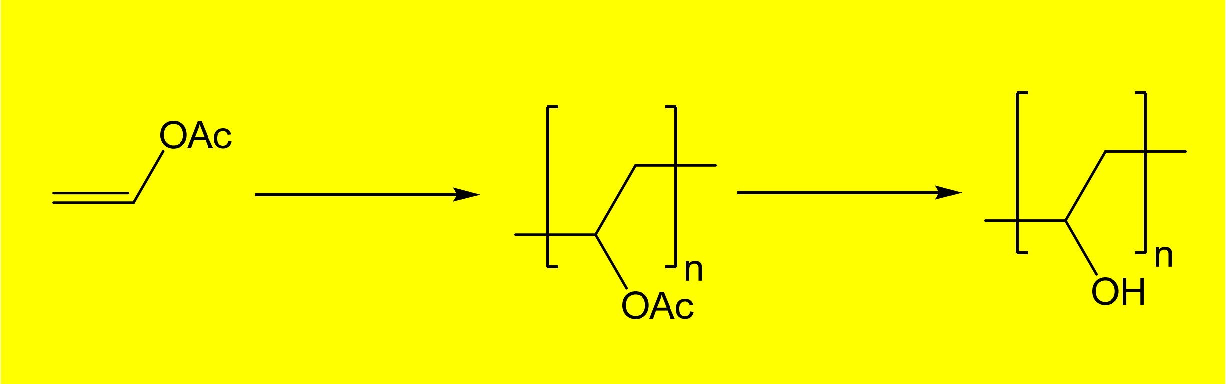


Nomenclature 2

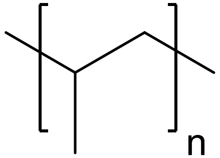
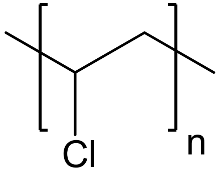
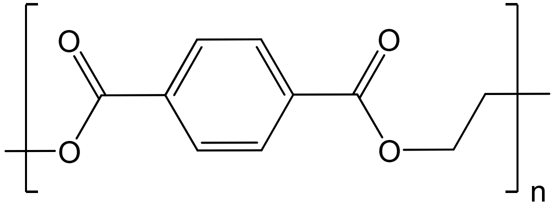
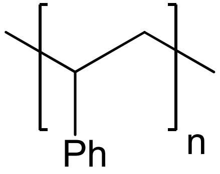
Poly(hexamethylene-adipinic acidamide)
Nylon 66



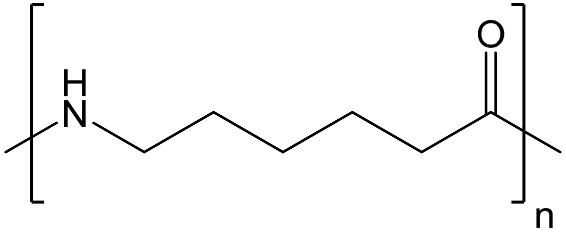
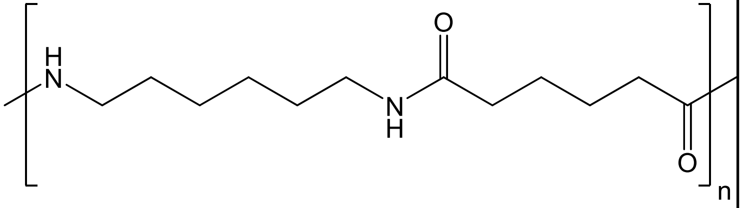
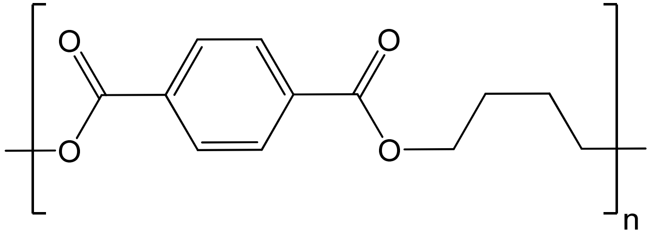
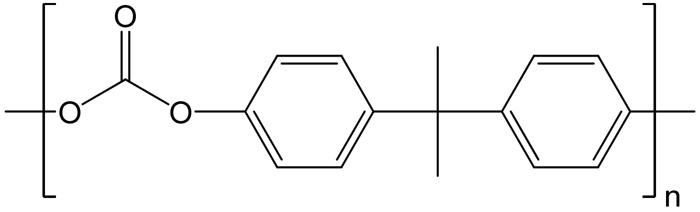
But:
Polyvinylalcohol



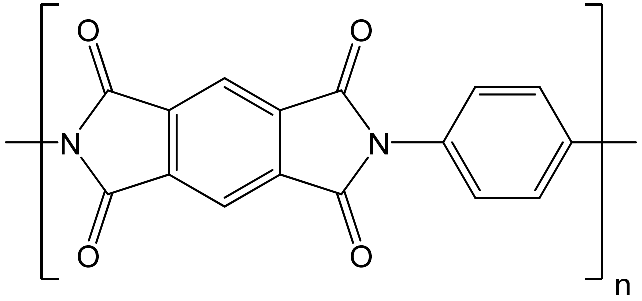
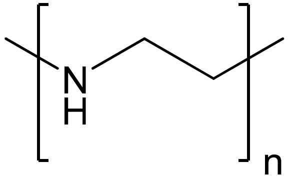
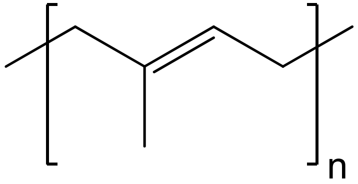
Important industrial polymers 1

PE	Polyethylene	$-\!\!\left[-CH_2CH_2-\right]_n\!\!-$	packaging gas pipes
PP	Polypropylene		packaging plastic mouldings
PVC	Polyvinylchloride		pipelines building material
PET	Poly(ethylene terephthalate)		food and liquid containers
PS	Polystyrene		insulation packaging

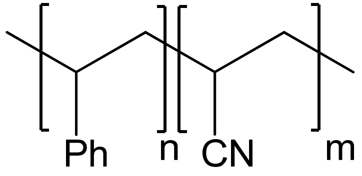
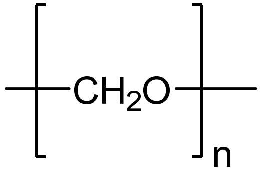
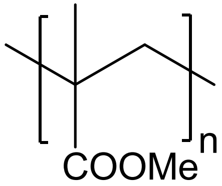
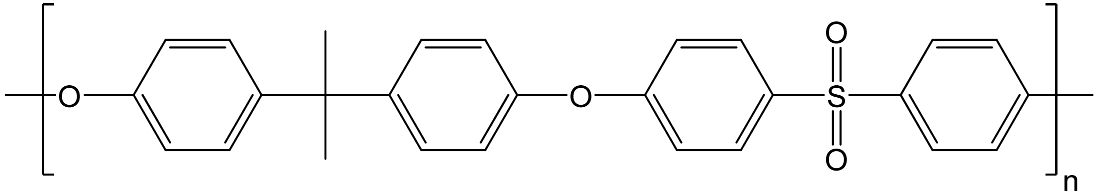
Important industrial polymers 2

PA6	Polyamide 6		synthetic fibers
PA6	Polyamide 66		synthetic fibers
PBT	Poly(butylene-terephthalate)		enclosure of electric devices
PC	Polycarbonate		greenhouses CD, DVD

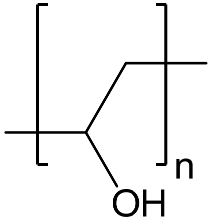
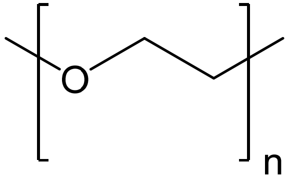
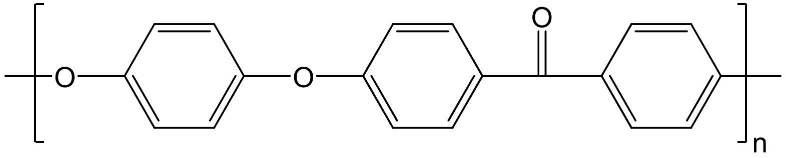
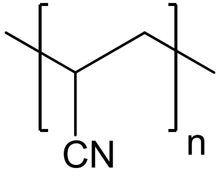
Important industrial polymers 3

	Polyimide		electronic industry
PEI	Poly(ethyleneimine)		cell extraction
PI	Poly(isoprene)		rubber
PTFE	Poly(tetrafluoro-ethylene)	$\left[CF_2CF_2 \right]_n$	Teflon

Important industrial polymers 4

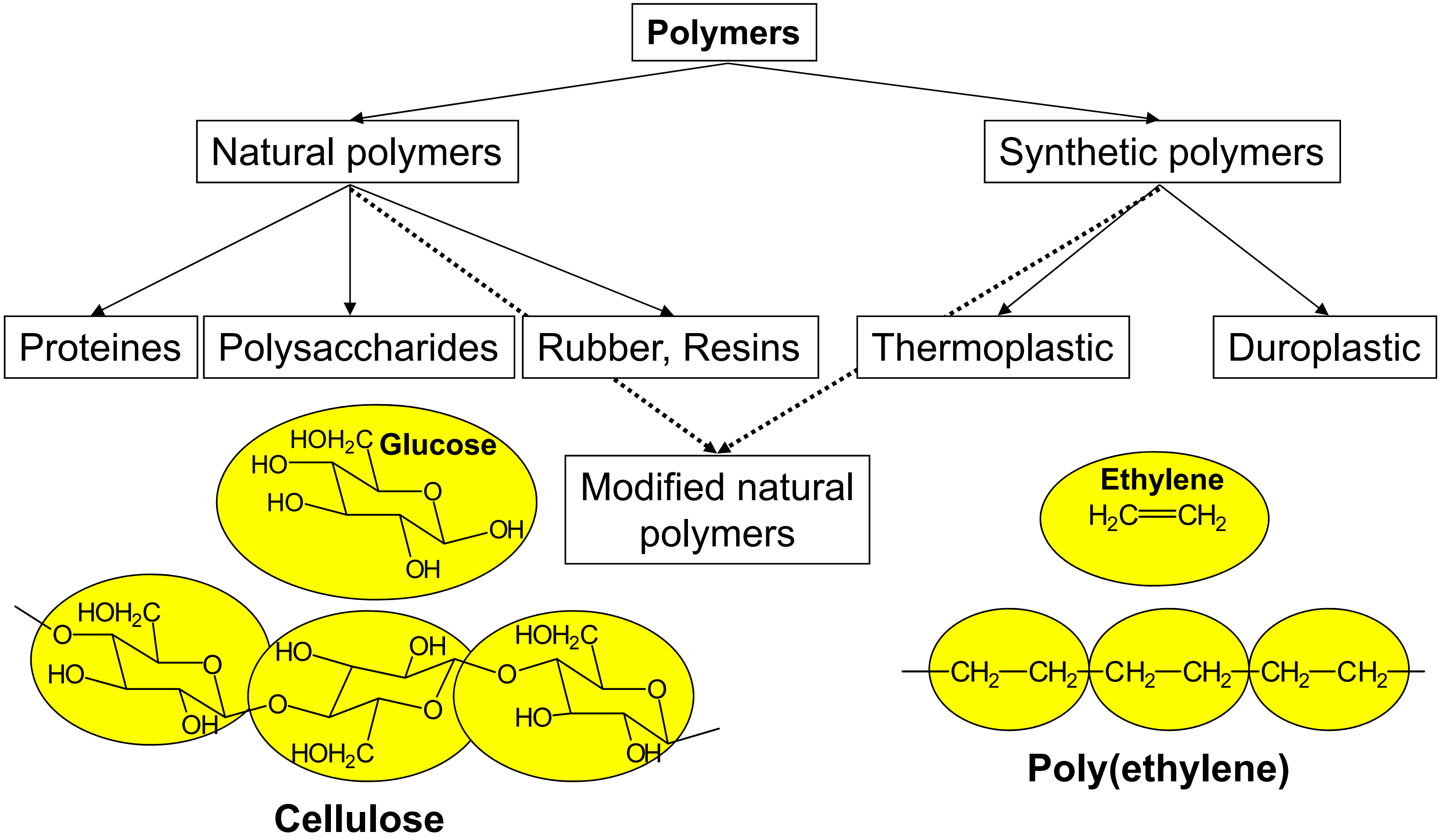
SAN	Poly(styrene-acrylonitrile)		optics reflectors
POM	Poly(oxymethylene)		automobile parts fixative
PMMA	Poly(methylmeth-acrylate)		optics glass-like appl.
PSU	Poly(sulfone)	Membranes, composite material 	

Important industrial polymers 5

PVA	Polyvinyl alcohol		carbon dioxide barrier
PEG	Polyethylene glycol		clinical use cosmetics
PEEK	Poly(etherether-ketone)		medical implants parts of pumps
PAN	Poly(acrylnitrile)		fibers

Classifications of polymers 1

Distinction of origin and manufacturing



Polymers

Natural polymers

Synthetic polymers

Proteines

Polysaccharides

Rubber, Resins

Thermoplastic

Duroplastic

Modified natural polymers

Glucose

Ethylene

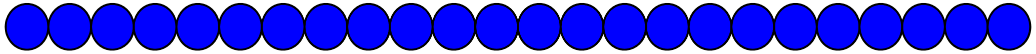
$H_2C{=}CH_2$

Cellulose

Poly(ethylene)

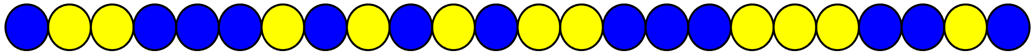
Classifications of polymers 2

Homopolymer
only one monomer species

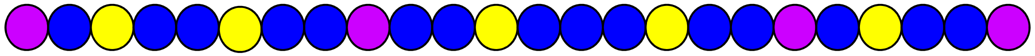

poly(A)

Copolymers
more than one monomer species

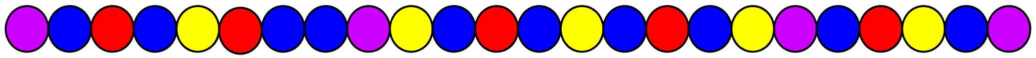
Bipolymers/Copolymers
two different monomers


poly(A-*co*-B)

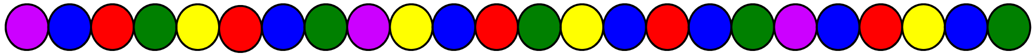
Terpolymers
three monomer species


poly(A-*co*-B-*co*-C)

Quarterpolymers
four differnt monomers


poly(A-*co*-B-*co*-C-*co*-D)

Pentapolymer, ...

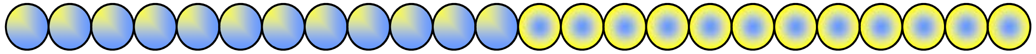

poly(A-*co*-B-*co*-C-*co*-D-*co*-E)

No constitution, only composition

Classifications of polymers 3

Block polymers

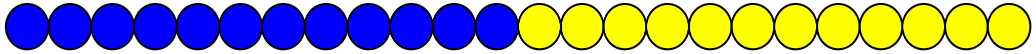
composed of blocks in sequence



Block copolymer

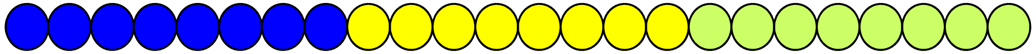
more than one monomer, sequence of blocks, each block consists only out of one monomer

Diblock copolymer



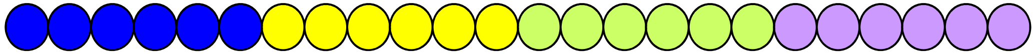
poly(A)-*block*-poly(B)

Triblock terpolymer



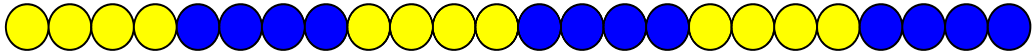
poly(A)-*block*-poly(B)-*block*-poly(C)

Tetrablock quaterpolymer



poly(A)-*block*-poly(B)-*block*-poly(C)-*block*-poly(D)

Multiblock copolymer

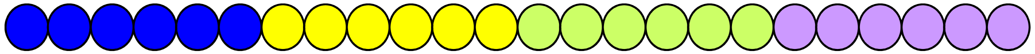


poly(A-B)$_n$

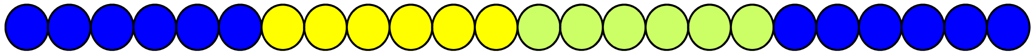
Classifications of polymers 4

Examples

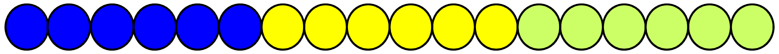
Tetrablock quarterpolymer



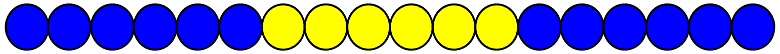
Tetrablock terpolymer



Triblock terpolymer



Triblock bipolymer

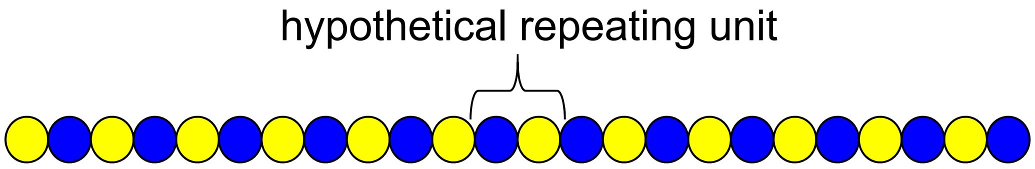


number of blocks, number of different monomers
(latin) (greek)

Classifications of polymers 5

Alternating copolymer

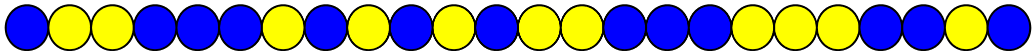
may be considered as homopolymer



Poly(A-*alt*-B)

Statistical copolymer

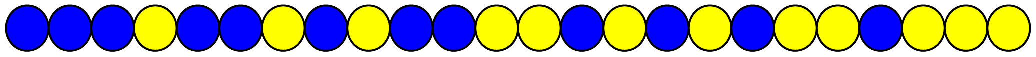
distribution obeys statistical laws,
otherwise random



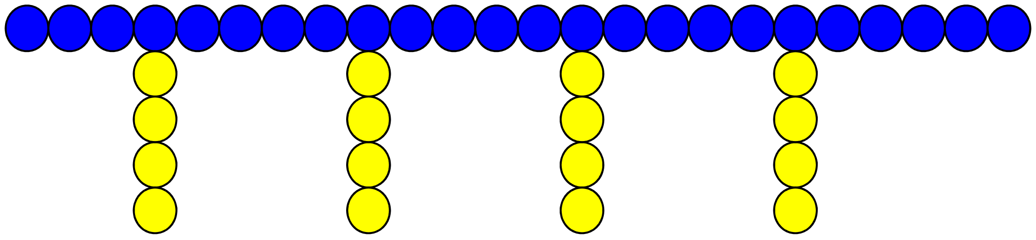
Poly(A-*stat*-B) **Poly(A-*ran*-B)**

Gradient copolymer

two monomers (one end many of monomer A, monomer B *vice versa*)



Graft copolymer

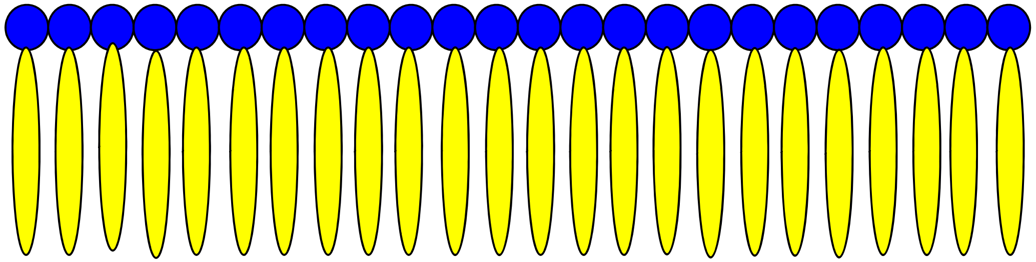


Poly(A)-*graft*-poly(B)

Classifications of polymers 6

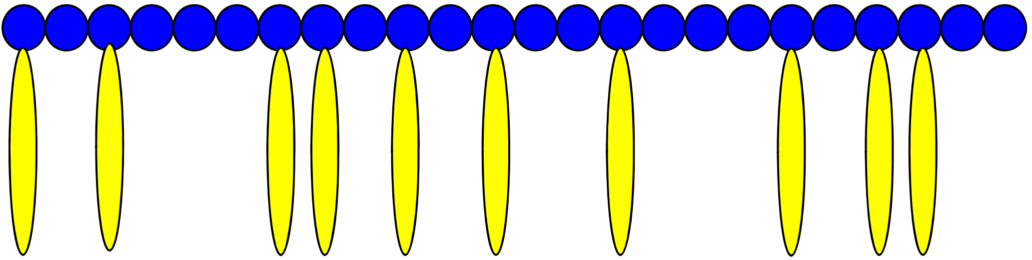
Comb copolymers

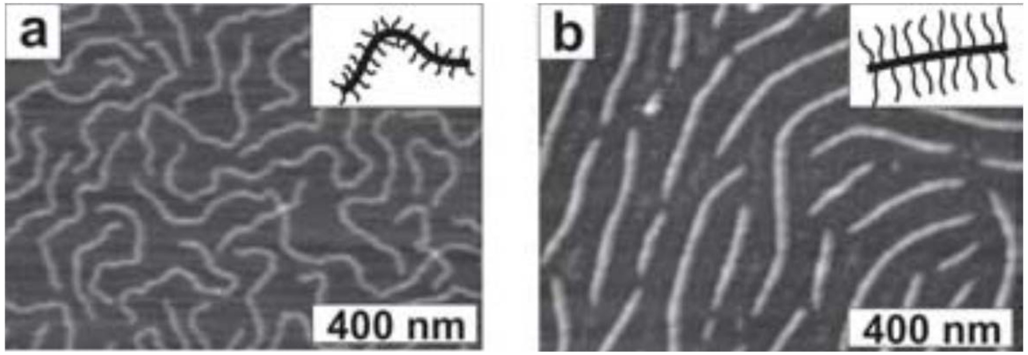
each monomer has a side chain



Graft copolymers

some monomers have a side chain





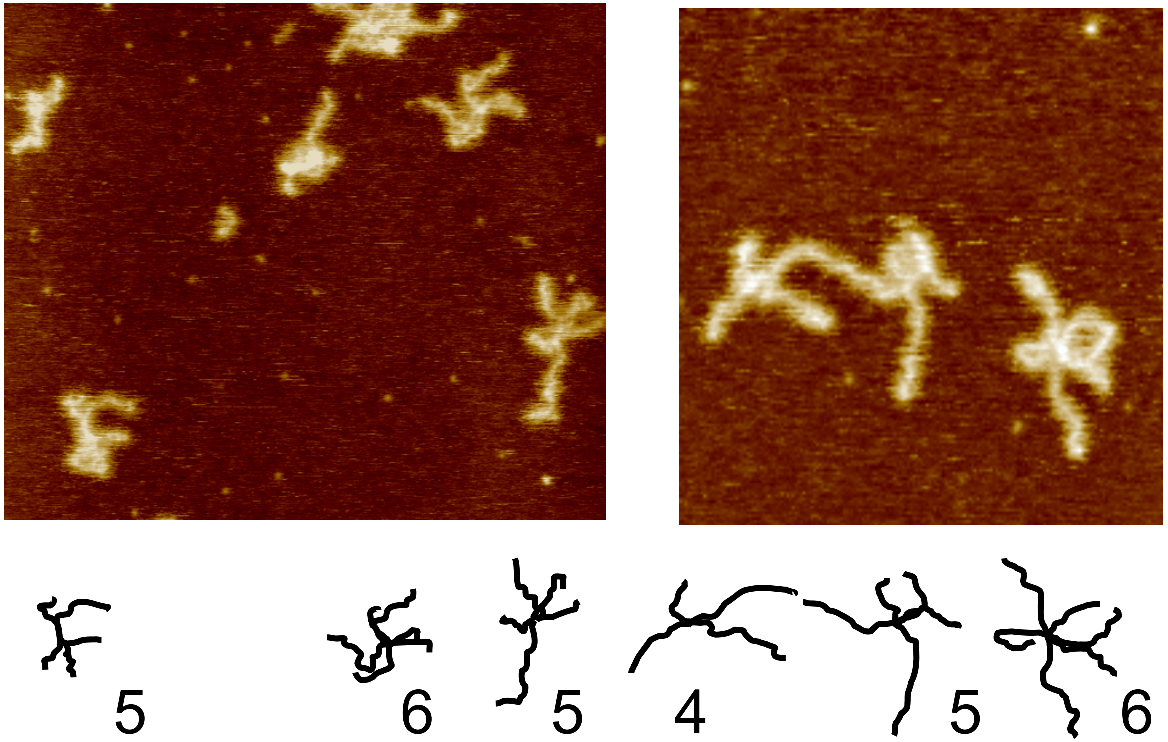
a) Short side chains
b) Long side chains

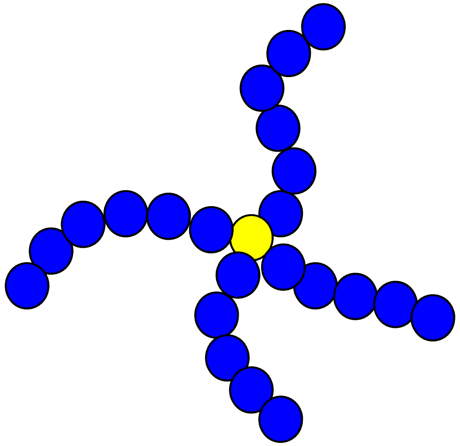
M. Matyjaszewski, *et al., Nature* **2006**, *440*, 191

Classifications of polymers 7

Star-shaped polymers

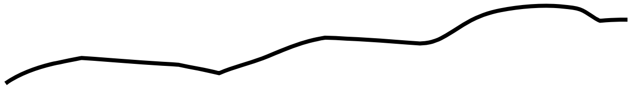
several side chains (arms) are connected with one core



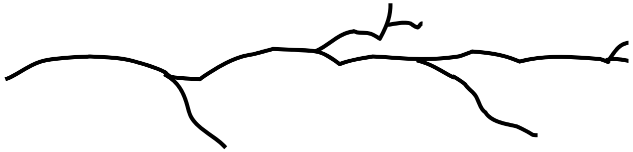


Classifications of polymers 8

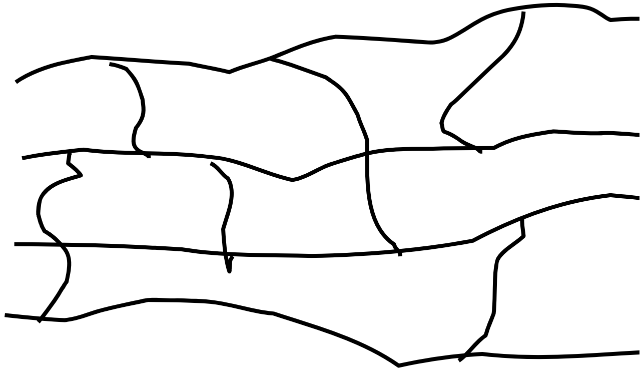
linear polymers



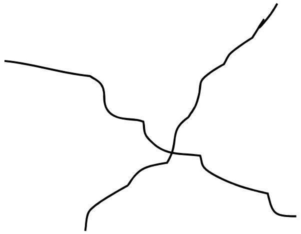
branched polymers



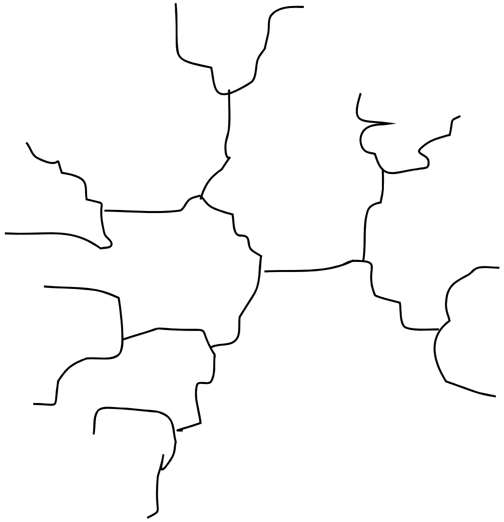
crosslinked polymers



star-polymers



dendrimers (3rd generation)



branched polymers: short-chain branches = oligomeric subunits
long-chain branches = polymeric subunits

Different reaction types

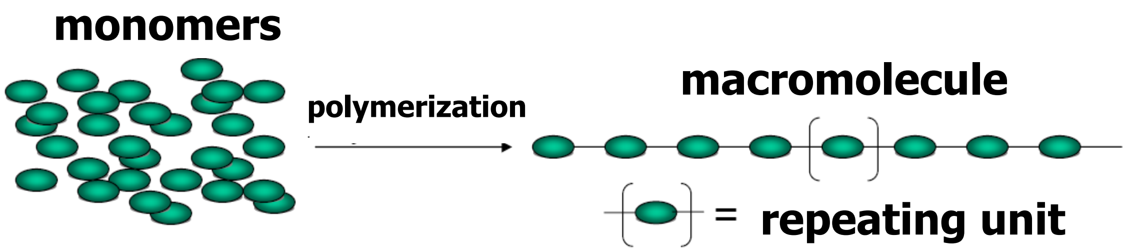
Polymerization

Step-growth reactions

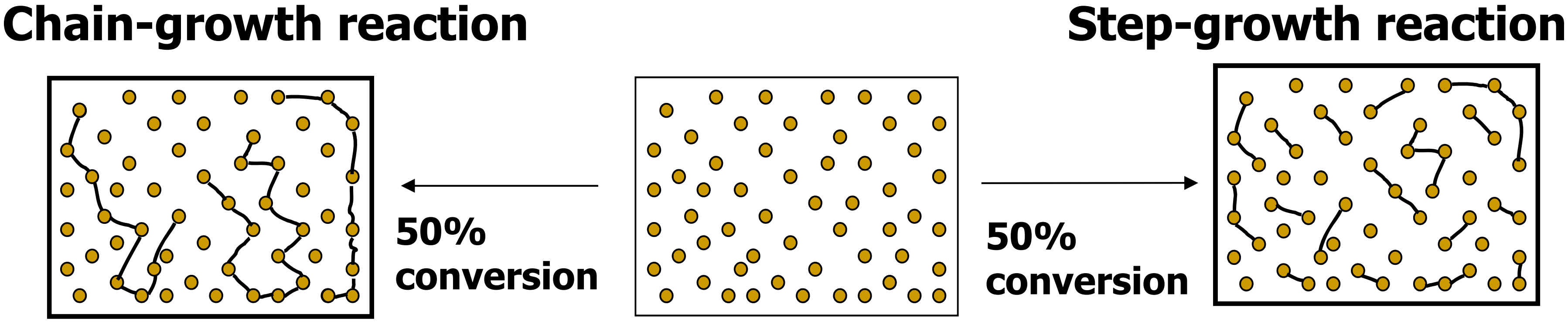
- **Polycondenzation**
- **Polyaddition**

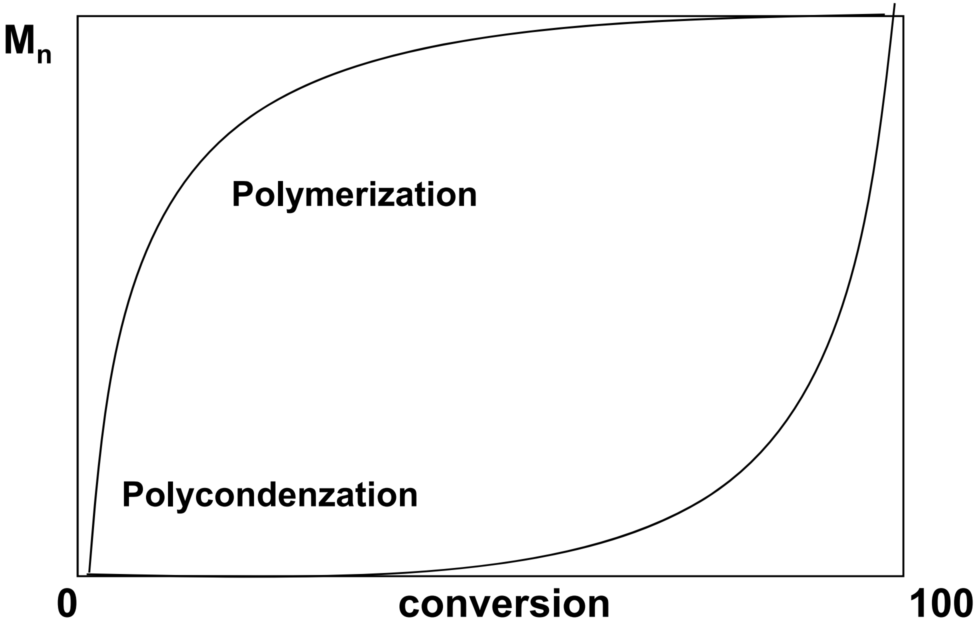
Chain-growth reactions

- **radical polymerization**
- **cationic polymerization**
- **anionic polymerization**
- **coordinative polymerization**



Chain-growth vs. step-growth reactions 1





Chain-growth vs. step-growth reactions 2

Chain growth:

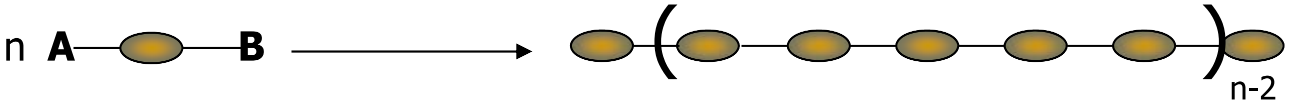
- Chain reaction
- Intermediate products and stages not always isolatable
- Highly reactive intermediates (radicals, ions)
- High energy of activation
- High molar masses are achievable very fast

Step growth:

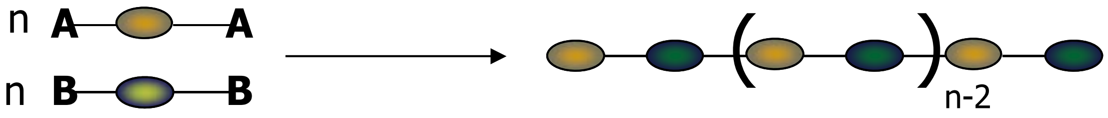
- Stepwise build-up of the polymer
- Same energy of activation for each reaction step
- Usually: intermediate products and stages isolatable
- High molar masses only at high conversions

Linear step-growth reactions

AB-Monomer



AA-Monomer
and
BB-Monomer



Polycondenzation: Coupling of two M/O/P involving the elimination of small molecule (e.g., water)

Polyaddition: Coupling of two M/O/P without loss of molecules

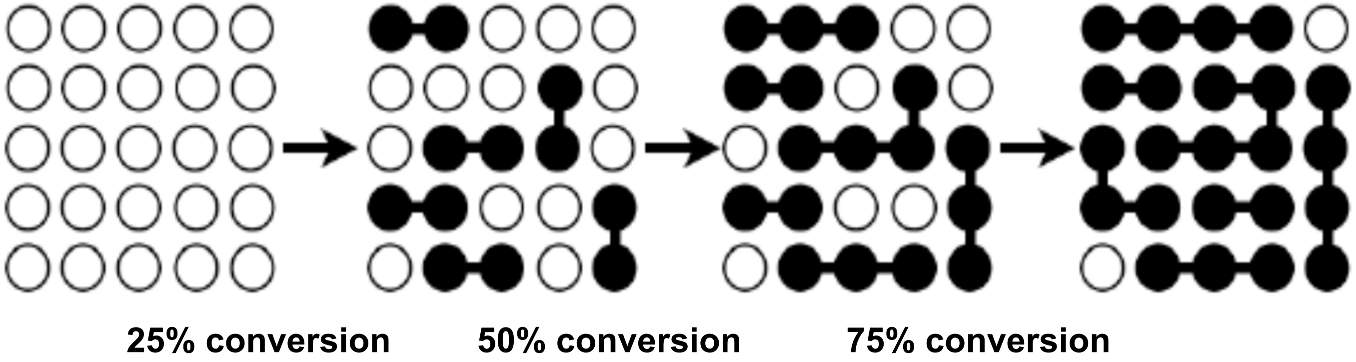
- No initiator necessary
- Use of catalysts is possible
- Theoretically: All molecules (M/O/P) have the same reactivity
- All molecules (M/O/P) react

M/O/P = monomer/oligomer/polymer

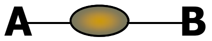
Tieke.

Carothers equation 1

A high conversion is necessary for high molar masses



AB-system:

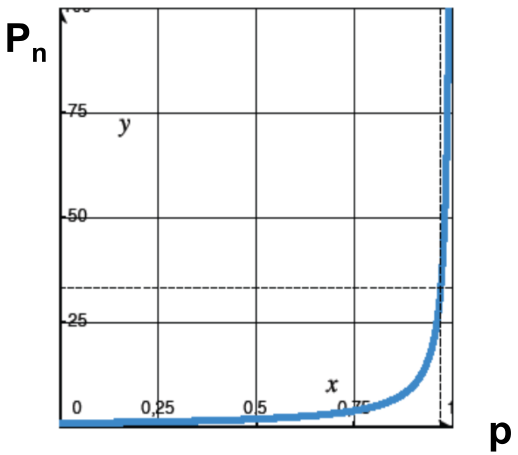


$$p = \frac{N_0 - N_t}{N_0} \quad \text{and} \quad P_n = \frac{N_0}{N_t} = \frac{1}{1-p}$$

Carothers equation

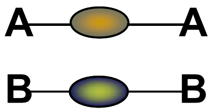
p	P_n
0.5	2
0.95	20
0.990	100
0.9990	1000
0.9999	10000

Tieke.



p – conversion
P_n – degree of polymerisation
N_0 – number of functional units at t = 0
N_t – number of Functional units at t

Carothers equation for AA/BB-systems:



$$P_n = \frac{q + 1}{q + 1 - 2pq}$$

$q = n_A / n_B$ $n_A \leq 1$; p = conversion,
n_A, n_B – mols of monomer A and B resp.

$$\boxed{q = 1 \Rightarrow P_n = 1/(1-p); \quad p = 1 \Rightarrow P_n = (1 + q)/(1 - q)}$$

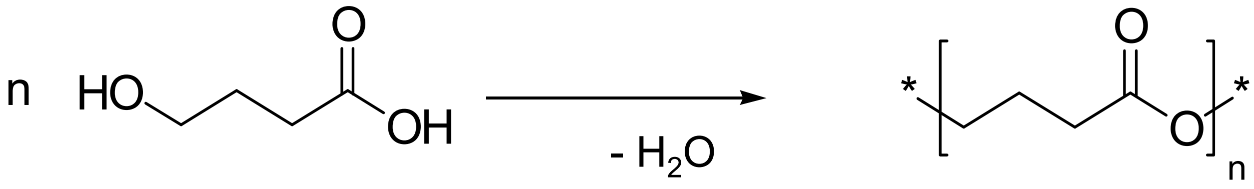
aberrations: Formation of cycles, aberrations from equilibrium, reactivity of the endgroups is not independend of the molecule length, side reactions

r	p	P_n
0.9524	0.999	39.4
1	0.999	1000
0.9524	1	41.0

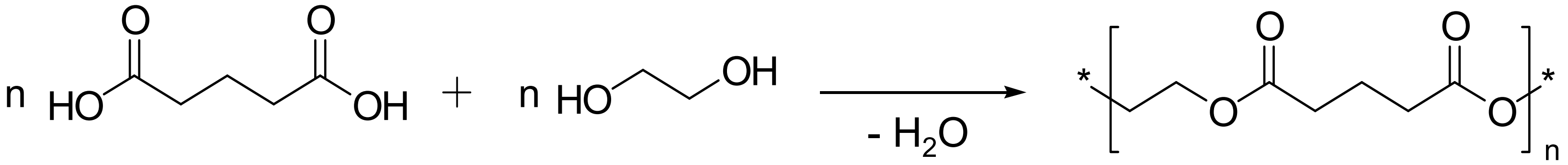
r = 1/1.05
= A/B

Important:
High molar masses are only achievable when the exact same monomer amounts are used !

Synthesis of polyesters



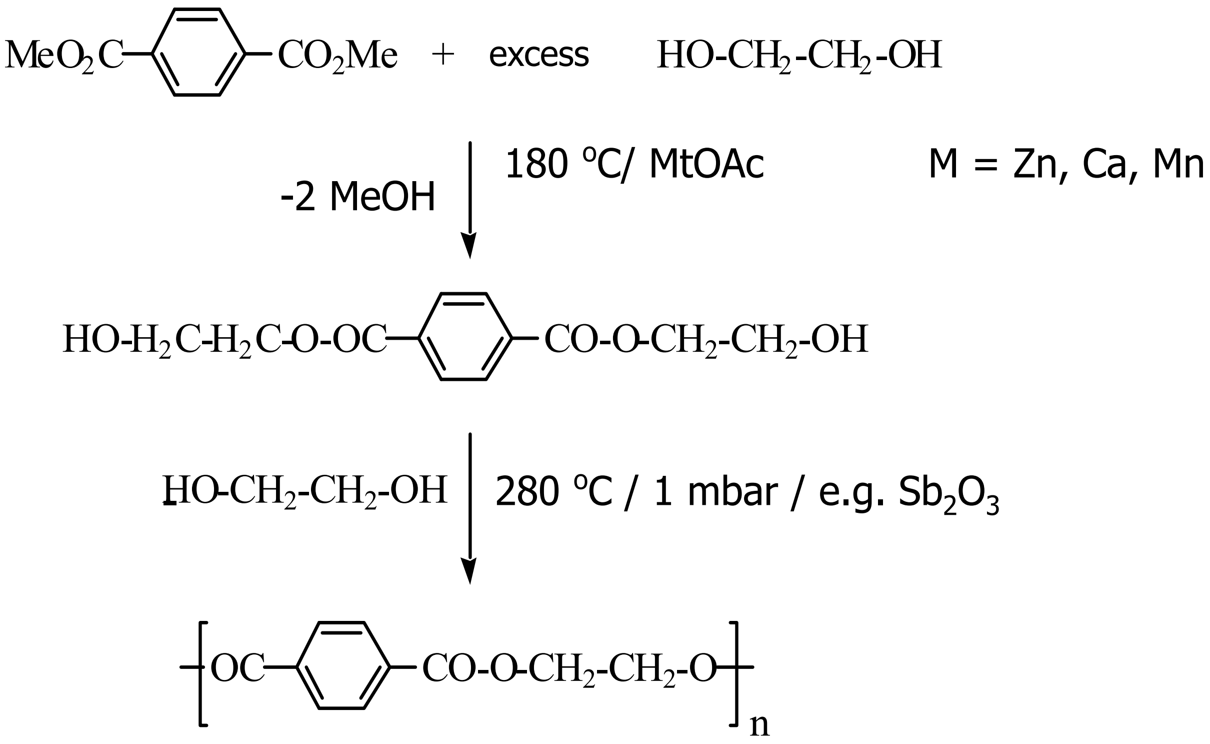
Polycondenzation
of hydroxy carbonacids
(AB-monomer)



Polycondenzation of dicarboxlic acids
and dialcohols
(AA- und BB-monomer)

Polyesters 2

Polyethyleneterephthalate (PET)



-2 MeOH

180 °C/ MtOAc

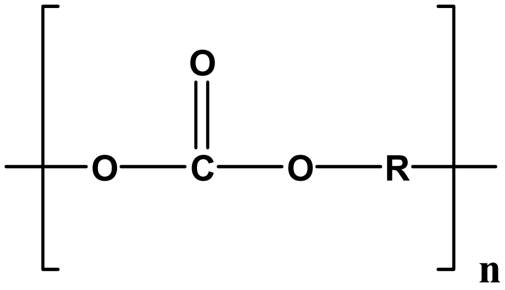
M = Zn, Ca, Mn

$HO\text{-}CH_2\text{-}CH_2\text{-}OH$

280 °C / 1 mbar / e.g. Sb_2O_3

Also: other diols (1,4-butandiol → polybutyleneterephthalate)
Semi-crystalline (T_m = 265 °C, T_g = 80 °C)
Melt-spinning of fibers (textile industry)
Bottles

Polycarbonates 1



$$\left[-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-R-\right]_n$$

Thermoplasts

Semi-crystalline with low crystallinity ➔ transparent

Hard, impact-proof

Heat resistant (glass transition ~150 °C, processing 300 °C)

Solubility: Insoluble in water and alcohols

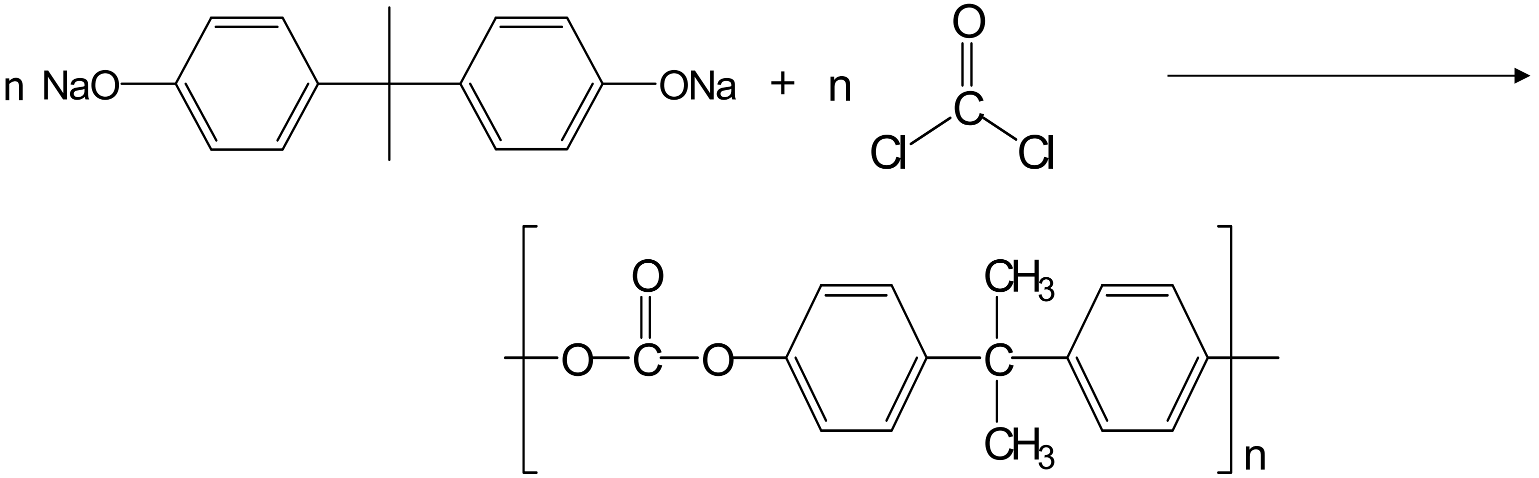
Soluble in many organic solvents (e.g. CH_2Cl_2, $CHCl_3$, pyridine)

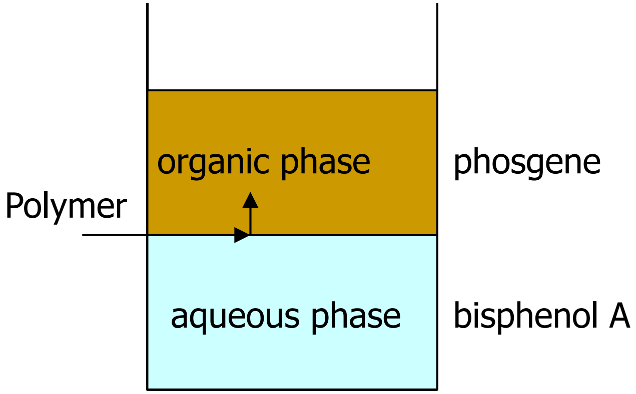
Application: Injection molding, isolation foils, Makrolon (Bayer), CD and DVD

Bayer - Makrolon

Synthesis I

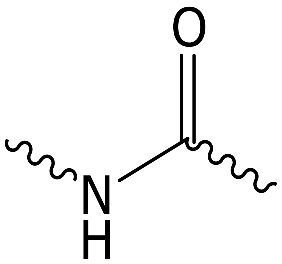
Interface polycondenzation (Schotten-Baumann)



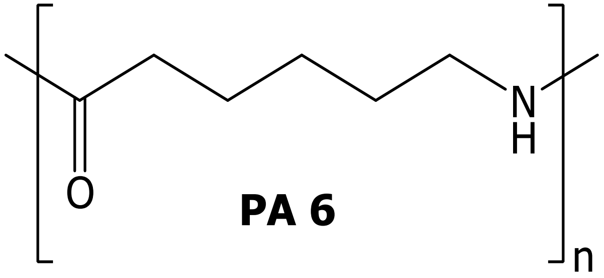


high molar masses are achievable
but
removing of NaCl is difficult

Polyamides 1

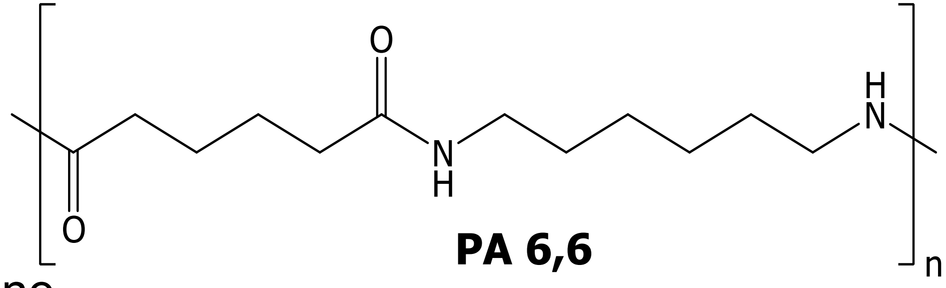


Perlons: constitutional unit and monomer identical
ω-amino carboxylic acids or lactams


PA 6

Nylons: constitutional unit consists of two different monomers
diamino and dicarboxylic acid monomer

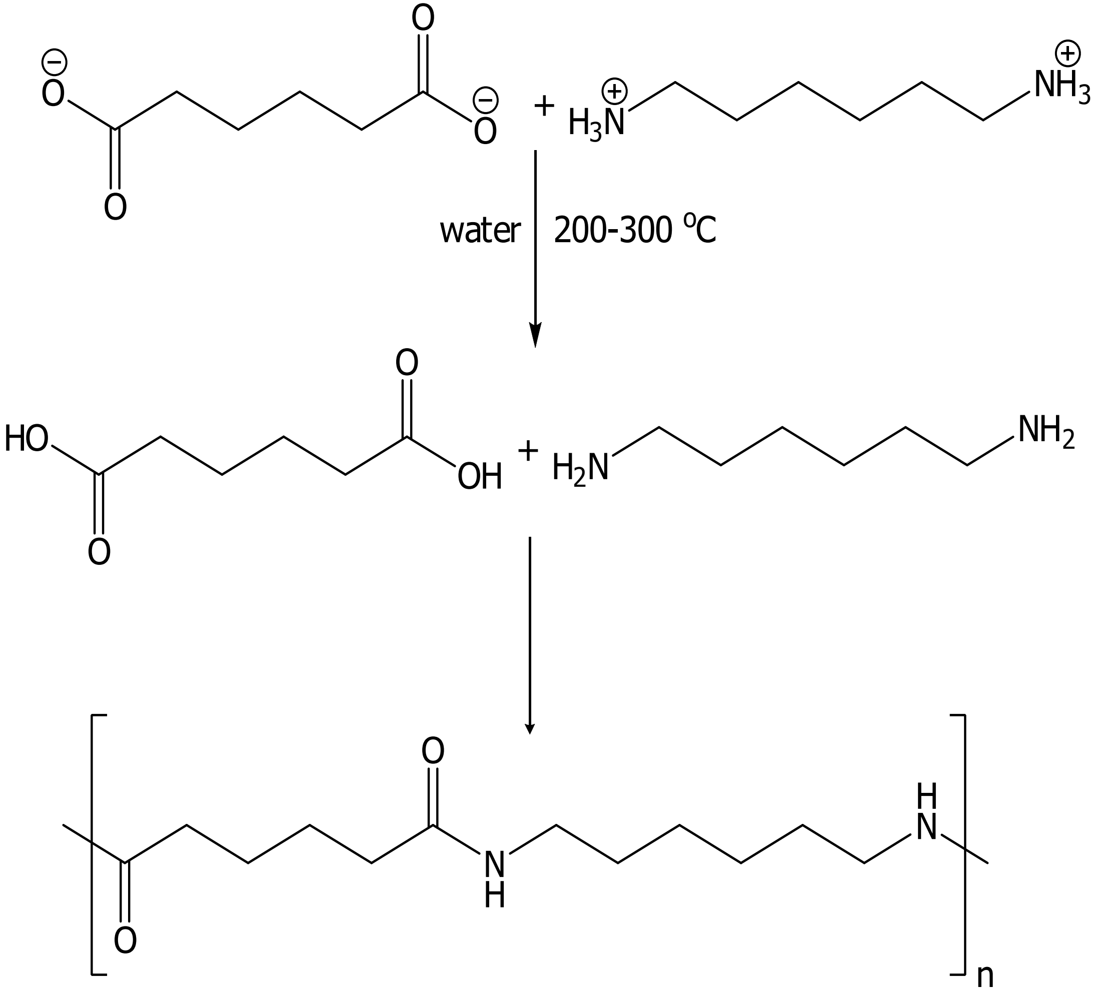
- Polyamides contain –NHOC-group
- Proteines, polyaramides (aromatic amines and carboxylic acids)
- Nylon xy
  x = number of the C-atoms of the amine
  y = number of the C-atoms of the carboxylic acids
- Hydrogen bonding → high mechanical strength


PA 6,6

Applications: Fibers, engineering plastics
Melting point 260 °C, 30-50% crystallinity,
M_n = 15000-50000 g/mol, PDI ~ 2

Synthesis

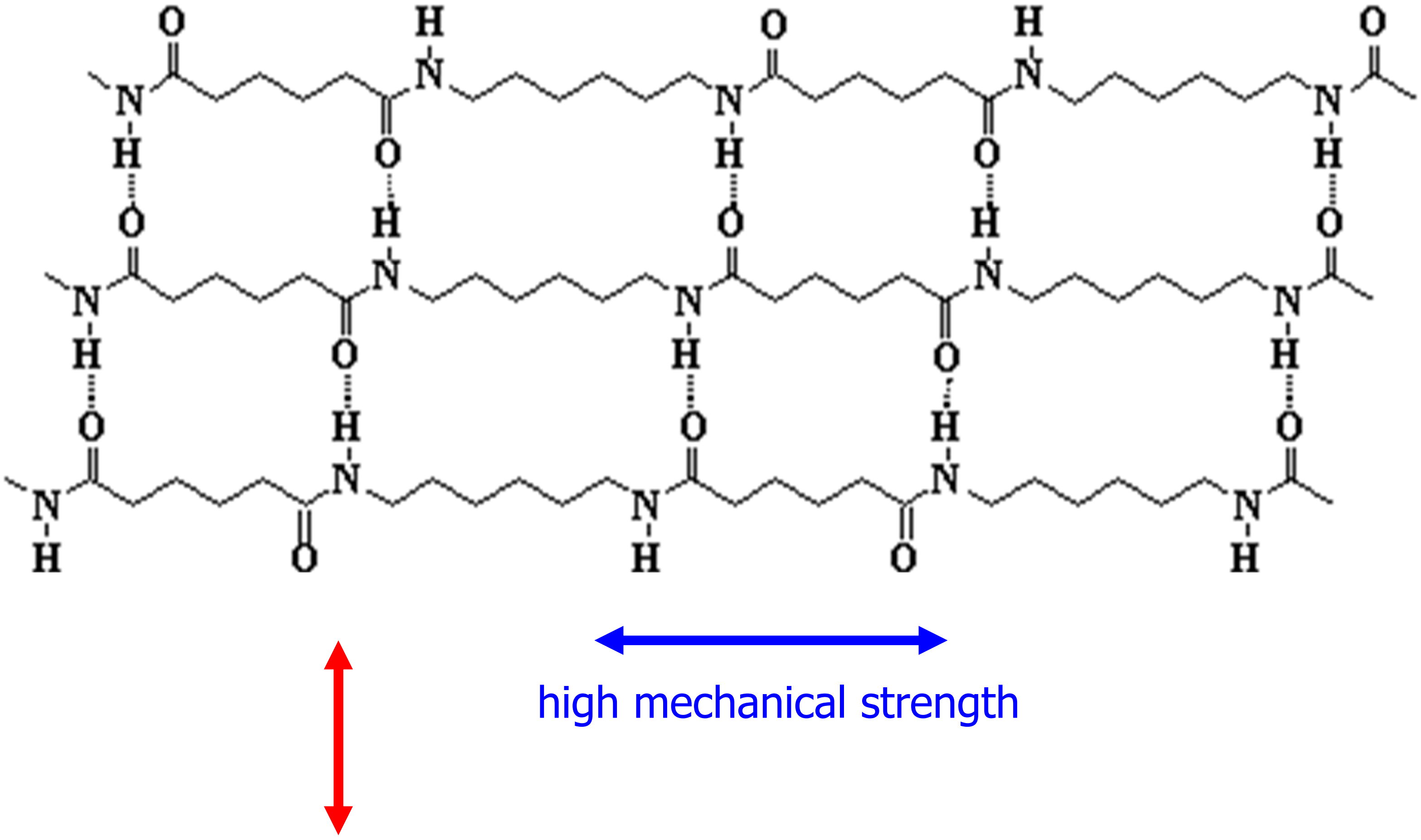
Nylons:



AH-salt (made of dicarboxylic acid [adipinic acid] and diamine [hexamethylene diamine)
Purification by recrystallization
→ exact stoichiometry
Molar mass is adjusted by addition of mono carboxylic acid

But also interface polycondenzation is possible:

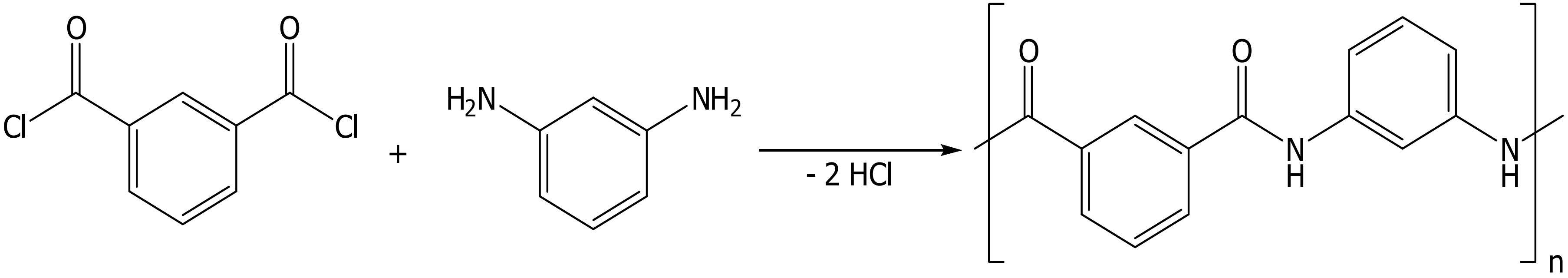
Hydrogen bonding in Nylon 6,6



high mechanical strength

lower mechanical strength

poly(*m*-phenylene-isophthalamide) (DuPont: Nomex)



High melting point (380-390 °C), soluble in DMF/LiCl

High permanent heat resistance

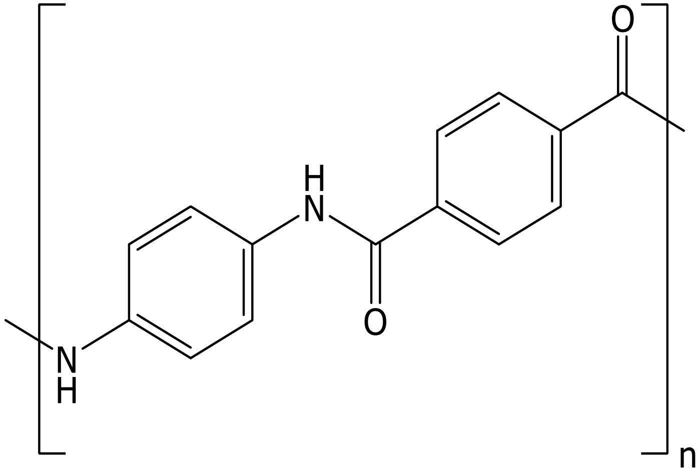
poly(*p*-phenylene-terephthalamide) (DuPont: Kevlar)

Unmeltable (decomposition 425 °C)

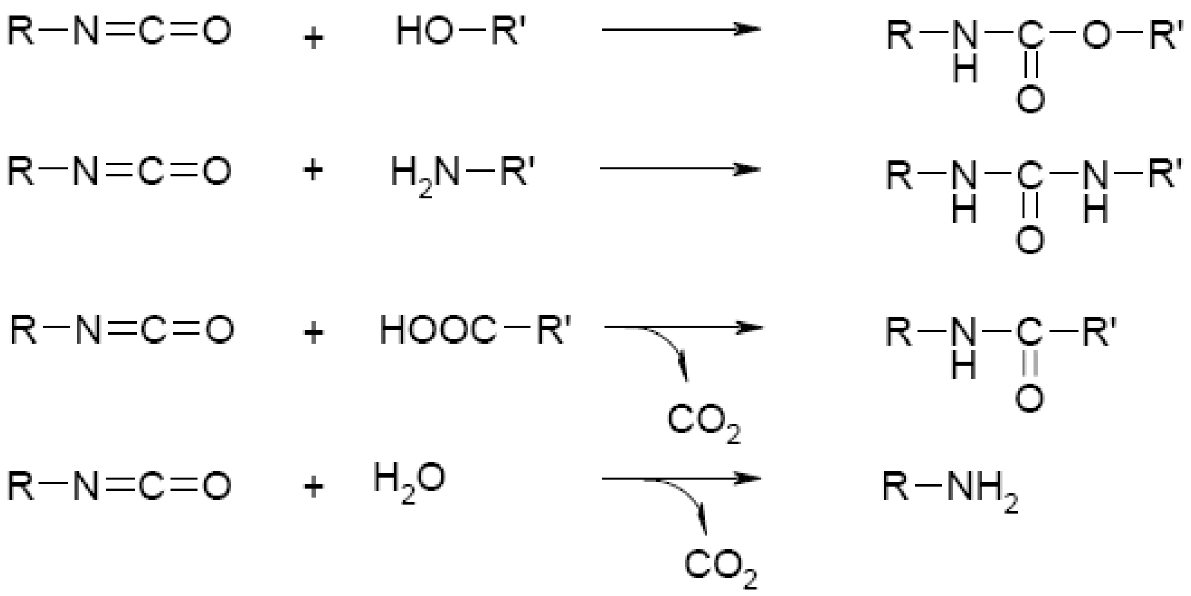
Soluble in DMAc/LiCl, sulfric acid

High permanent heat resistance, mechanical strength

Polycondenzation has to be carried out in solution



Isocyanate chemistry – basic reactions



$$R{-}N{=}C{=}O + HO{-}R' \longrightarrow R{-}\underset{H}{N}{-}\underset{O}{\underset{\|}{C}}{-}O{-}R'$$

urethane

$$R{-}N{=}C{=}O + H_2N{-}R' \longrightarrow R{-}\underset{H}{N}{-}\underset{O}{\underset{\|}{C}}{-}\underset{H}{N}{-}R'$$

urea

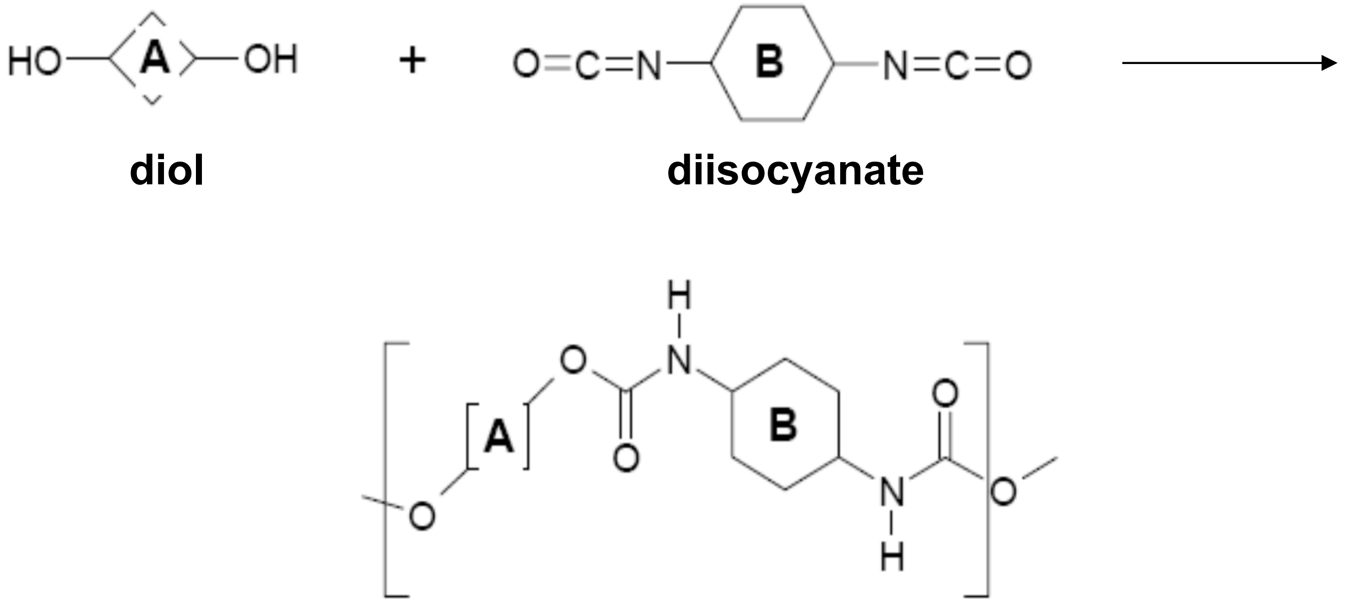
$$R{-}N{=}C{=}O + HOOC{-}R' \xrightarrow[CO_2]{} R{-}\underset{H}{N}{-}\underset{O}{\underset{\|}{C}}{-}R'$$

amide

$$R{-}N{=}C{=}O + H_2O \xrightarrow[CO_2]{} R{-}NH_2$$

hydrolysis yielding amine

Isocyanate chemistry – polyurethanes



diol

diisocyanate

polyurethane

Variation of diol and diisocyanate → adjustment of chain flexibility
→ adjustment of physical properties

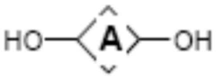
Alkyl polyurethanes → reaction in melt; aromatic polyurethanes → reaction in solution

Catalysts: Tertiary amines (DABCO), tin compounds [$n\mathrm{Bu}_2\mathrm{Sn(OAc)}_2$]

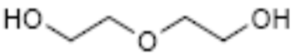
Lecture Prof. Menzel, TU Braunschweig.

Polyurethanes 3

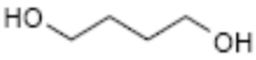
Isocyanate chemistry – different building blocks



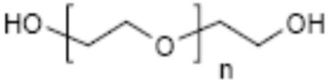
Ethylene glycol



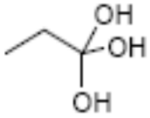
diethylene glycol



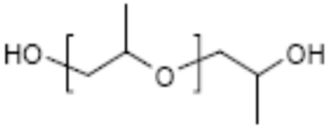
Butandiol



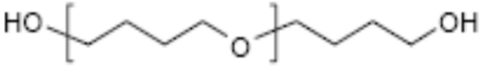
Poly(ethylene glycol)



Trimethylolpropane

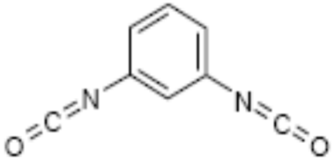


Poly(propylene glycol)

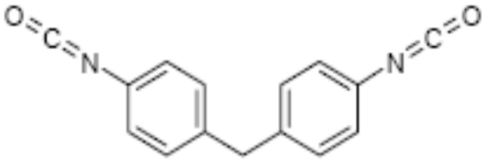


Poly(oxytetramethylene)

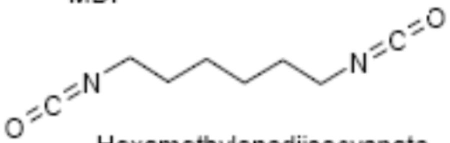
and many more



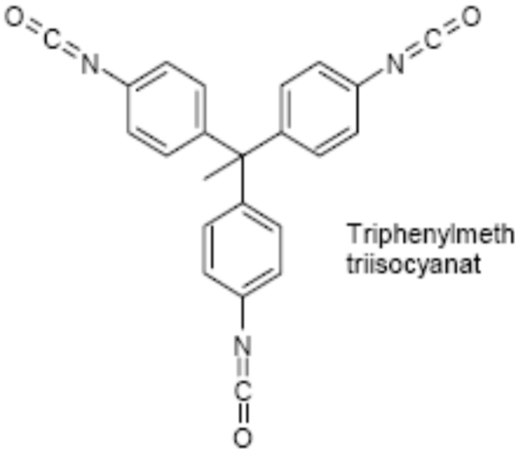
Toluenedisocyanate
TDI



Diphenylmethanediisocyanate
MDI



Hexamethylenediisocyanate
HDI



Triphenylmethane-
triisocyanat

and many more

Lecture Prof. Menzel, TU Braunschweig.

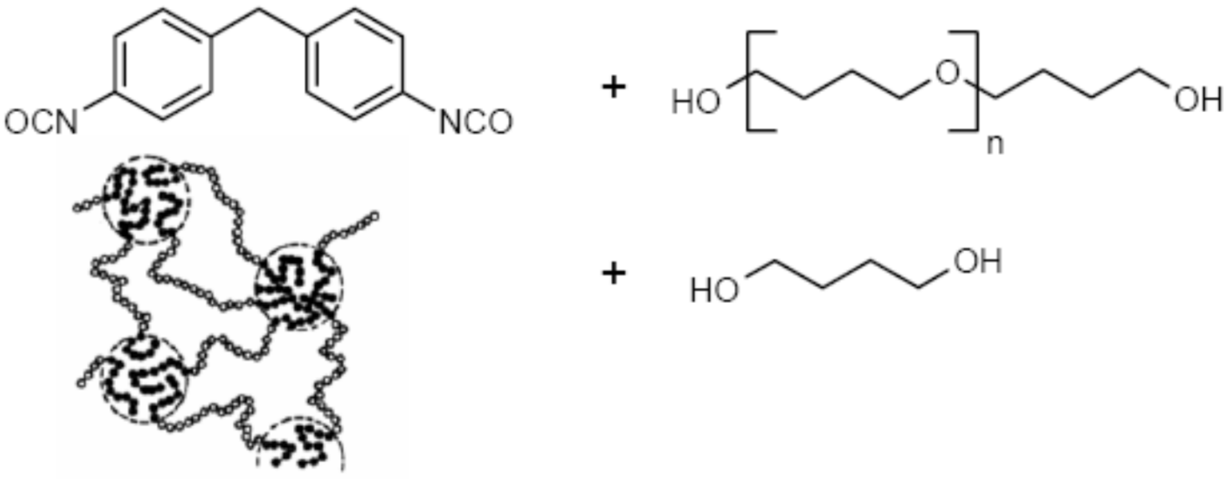
Polyurethanes 4

Thermoplastic elastomers (TPU):

Diisocyanates and oligomers (diols) → prepolymer (isocyanate endgroups)
soft segment

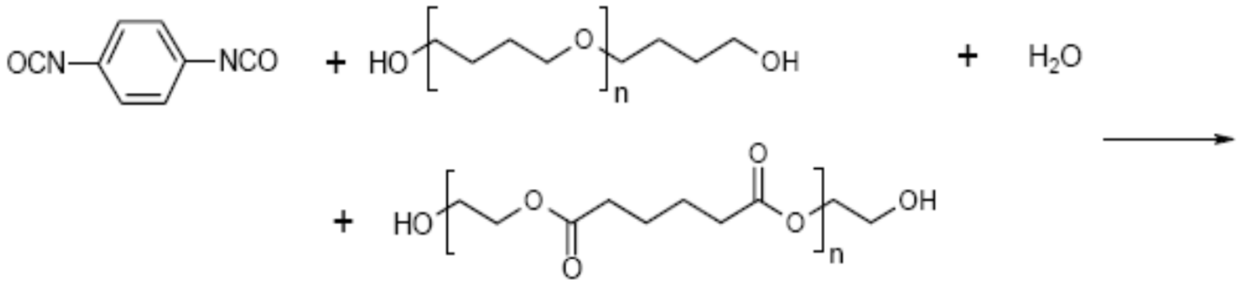
Diisocyanate and butanediol → prepolymer (OH-endgroups)
hard segment

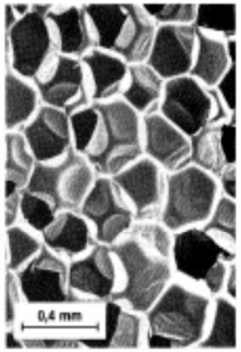
Combination of the two prepolymers



Lecture Prof. Menzel, TU Braunschweig.

Polyurethane foams





two phase system:
gas and polymer

→ gas for foaming

Hardness and pore structure depends on ratios of monomers, water content, …

Lecture Prof. Menzel, TU Braunschweig.

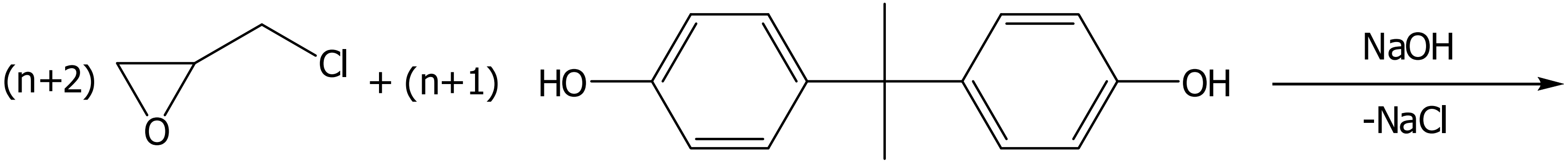
Applications:

insulation

www.basf.pfe.com, www.technicalfoams.nl.

History

1936 Pierre Castan (Switzerland) produced an amber colored, low melting solid from the reaction of bisphenol A with epichlorhydrin, at the same time S. O. Greenlee (USA) discovered this reaction



Ciba (licensed Castan's work) became one of the major epoxy resin manufactorers

1946 introduction of Araldite adhesive resin by Ciba

Still present today → Huntsman

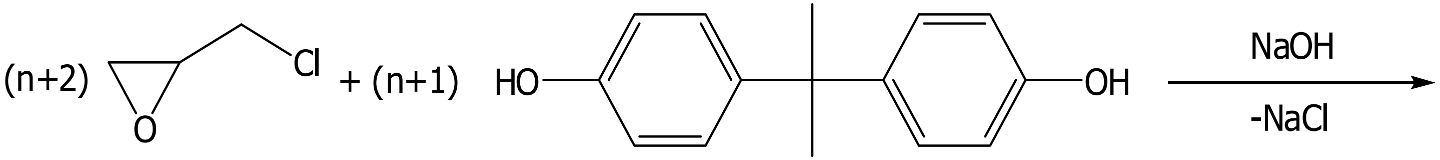
1952 start of the industrial production of epoxyresins

two component adhesive

www.glue-shop.com, www.it-logistics.de.

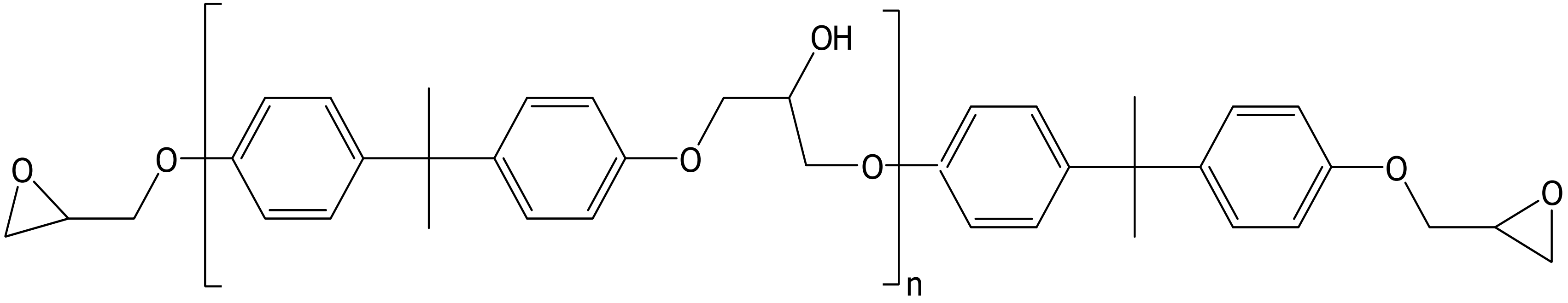
Epoxy resins

No pure polyaddition, also polycondenzation steps are involved.



epichlorhydrin

Bisphenol A

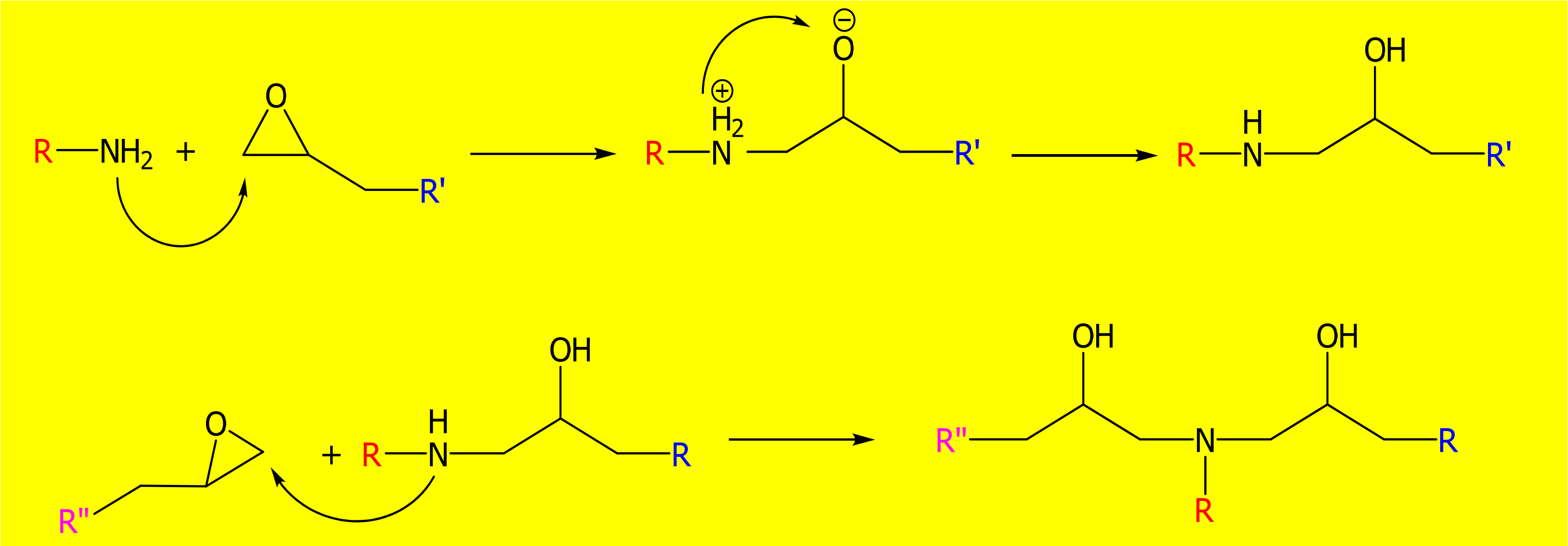


Bisphenol-A-diglycidyl ether (n = 0-30)

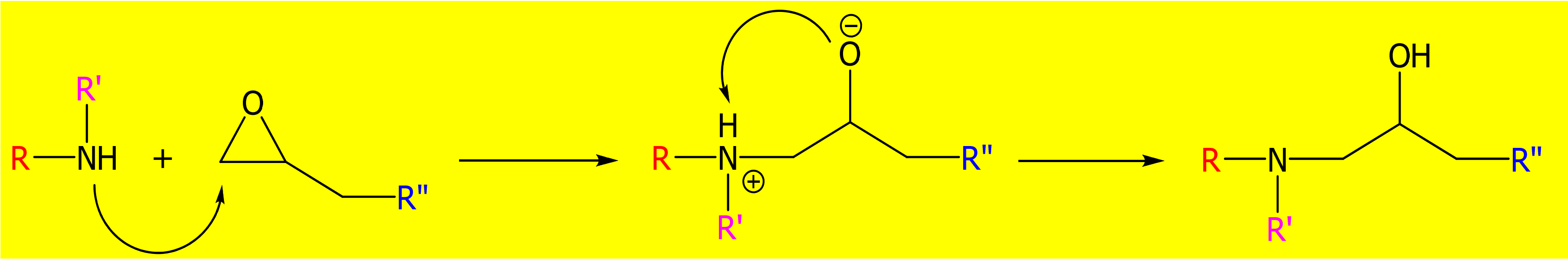
Epoxy resins 3

Crosslinking:

Primary amines

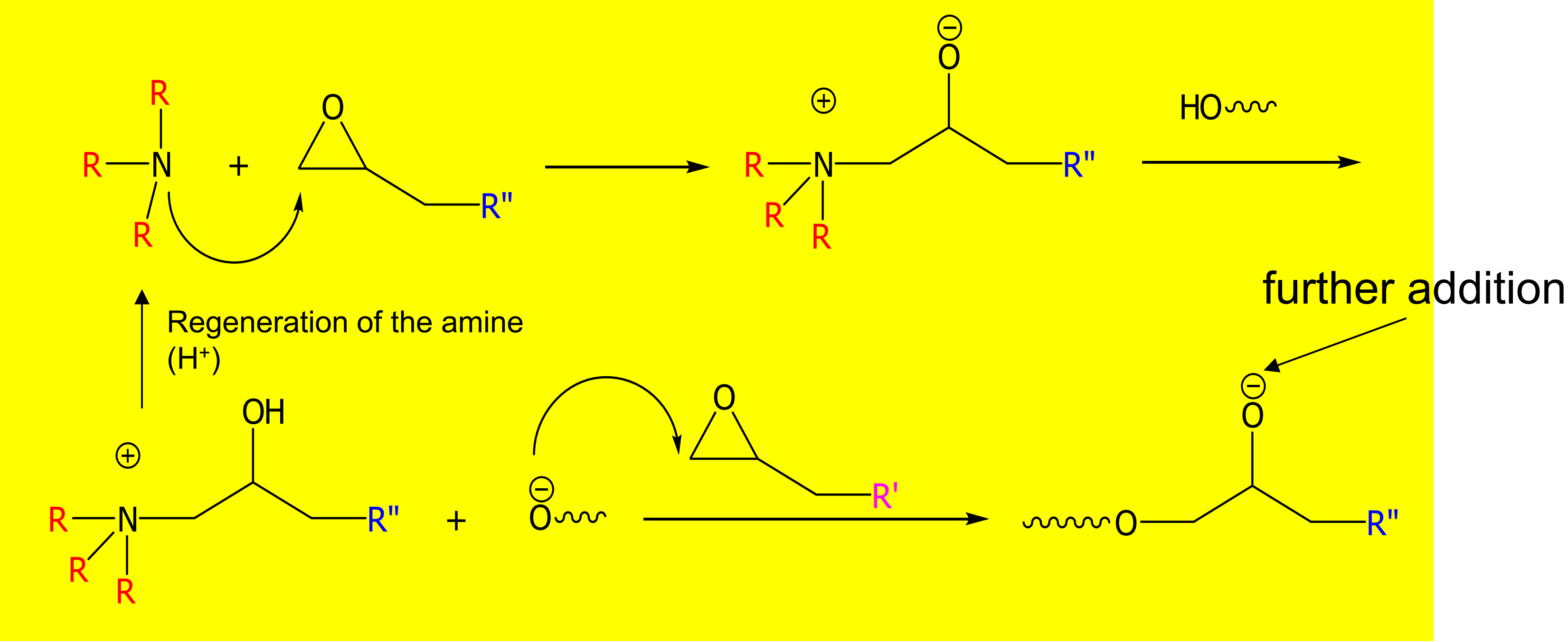


Secondary amines



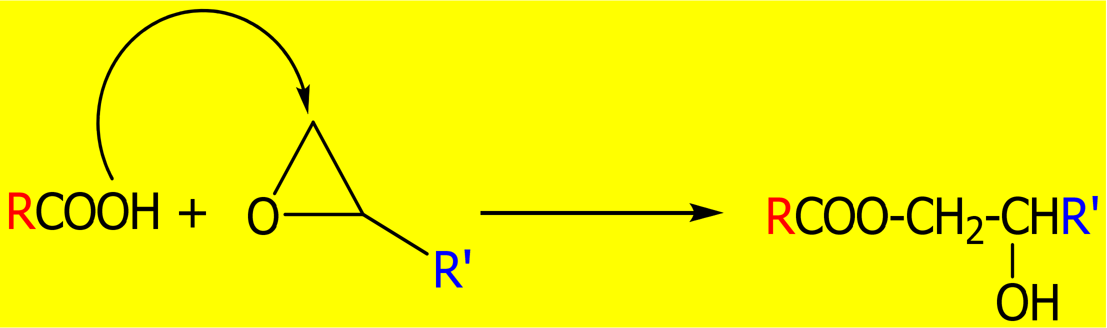
Crosslinking:

Tertiary amines

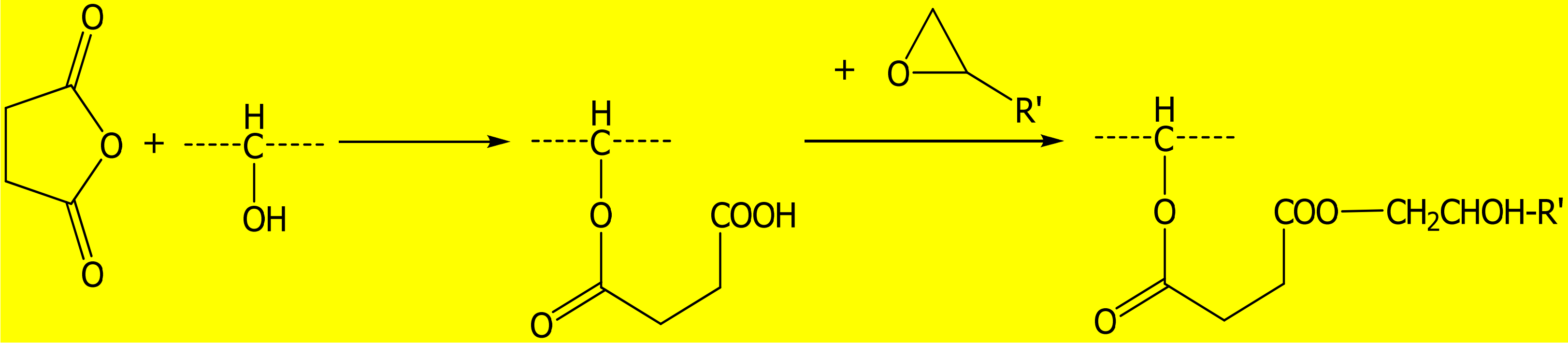


Crosslinking:

Carboxylic acids



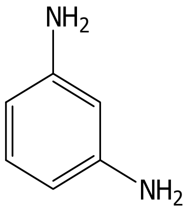
Anhydrides



Epoxy resins

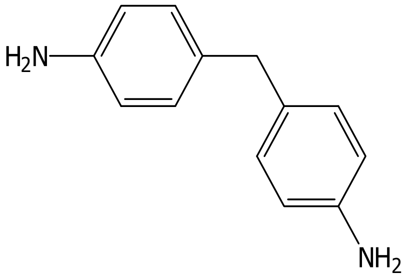
Typical curing agent:

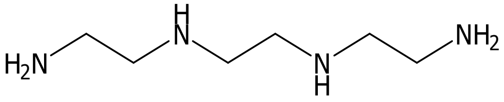
Amines



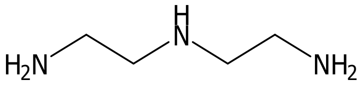
m-phenylene diamine

4,4’-diamino-diphenylmethane

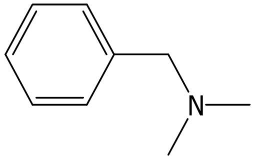




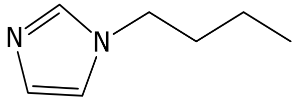
triethylene diamine



diethylene diamine

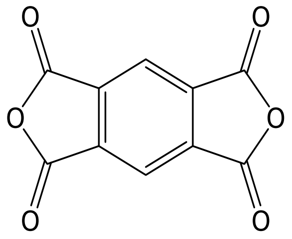


benzyldimethylamine

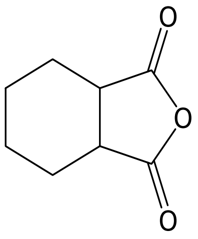


N-n-butylimidazole

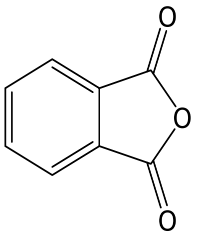
Anhydrides



pyromellithic acid anhydride



hexahydrophthalic anhydride

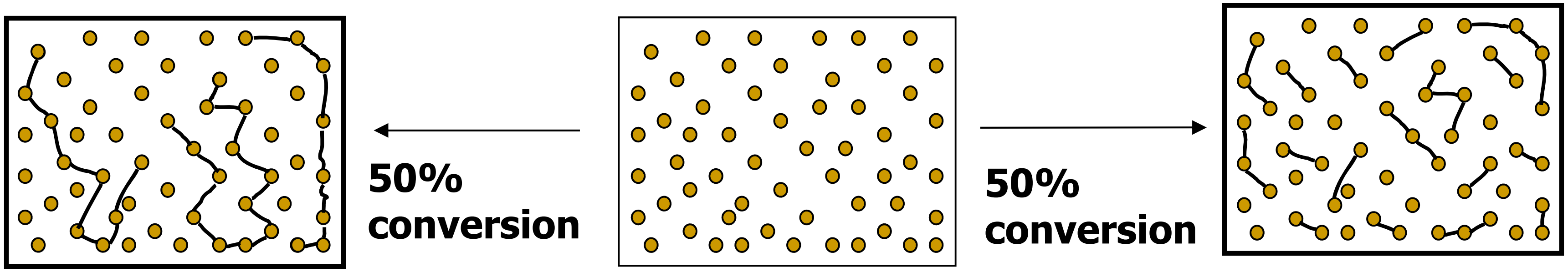


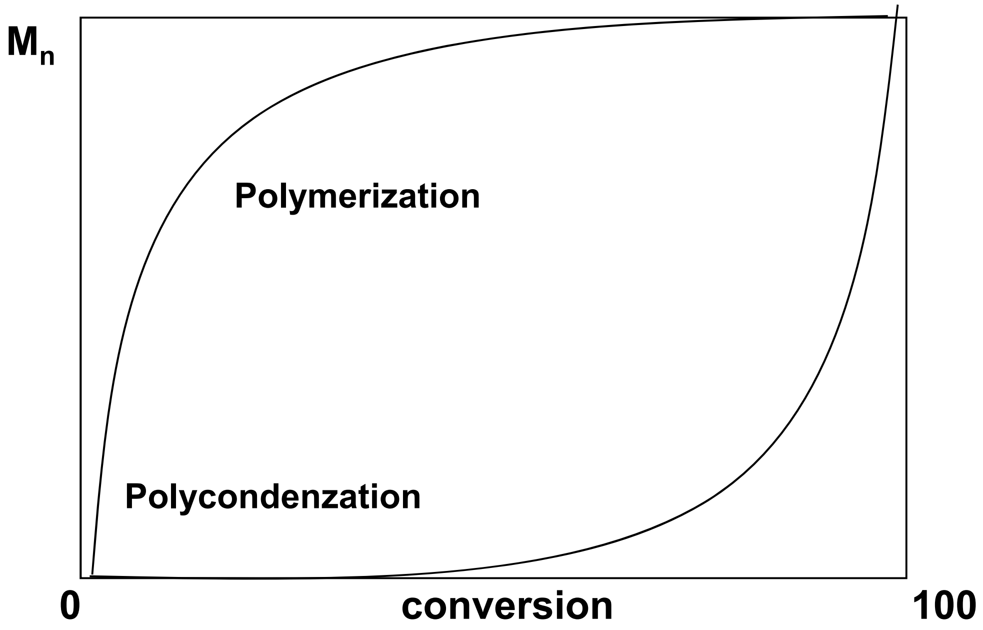
phthalic anhydride

Chain-growth vs. step-growth reactions

Chain-growth reaction

Step-growth reaction



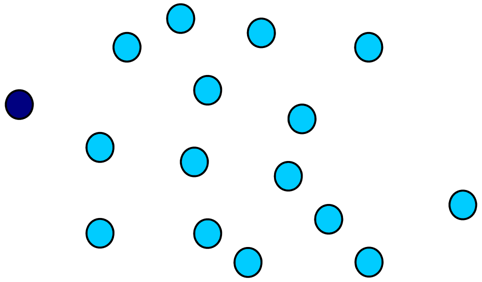


Chain growth reactions 1

reactive monomer $\xrightarrow[\textbf{initiator}]{\hspace{4em}}$ **polymer**

radical polymerization	**anionic polymerization**	**cationic polymerization**	**coordinative polymerization**
$R\bullet$	$R^{\ominus}$	$R^{\oplus}$	$\square ML_n$
radical former (*e.g.*, peroxo-compounds)	**anions** (*e.g.*, BuLi)	**cations** (*e.g.*, TosOMe)	**metall complexes** (*e.g.*, Ti-complex)

Chain growth reactions 2



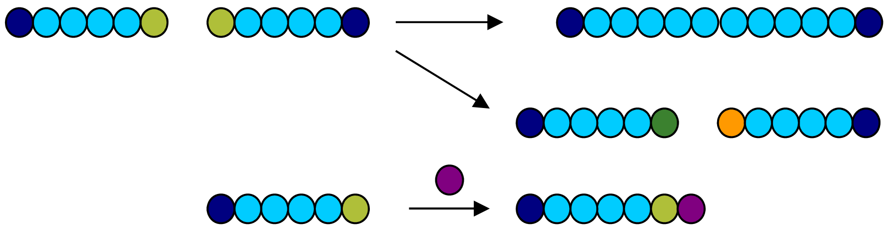
monomers

0. addition of initiator ●

initiating of a monomer → "reactive monomer"

growing chain

termination



recombination

disproportionation

reaction with a molecule, which catches the active species

reactive polymer chains

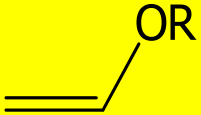
"dead" polymer chains

Monomers 1

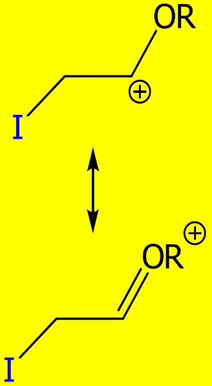
Not all monomers can be polymerized by all four methods

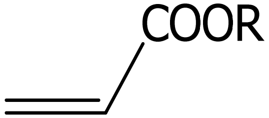
Kind of the monomer and substitution of the double bond determines the reactivity of the monomer

→ possibilities to polymerize it

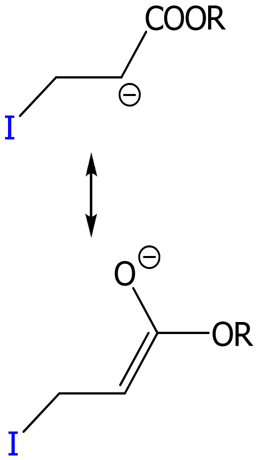


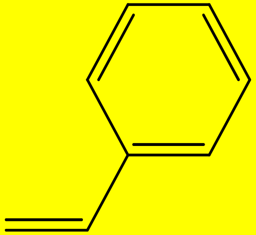
cationic polymerization (cationic species is stabilized)



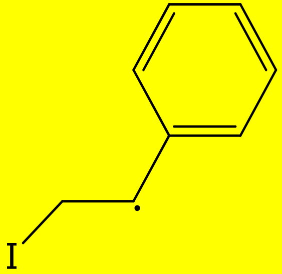


anionic polymerization (anionic species is stabilized)





radical polymerization (radical species is stabilized)



mesomerism

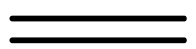
Monomers 2

Polymerizations of selected monomers:

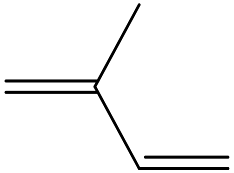
☑ industrial scale ✓ possible

Monomer	radical	anionic	cationic	polyinsertion
ethylene	☑			☑
propylene			✓	☑
isobutylene			☑	✓
isoprene	✓	✓	✓	☑
cyclopentene				☑
butadiene	☑	☑	✓	☑
tetrahydrofurane			☑	
ethylene oxide		☑	✓	
caprolactam		☑	✓	
vinylether			☑	✓
acrylonitrile	☑			
styrene	☑	✓	✓	✓

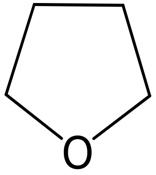
Monomers 3



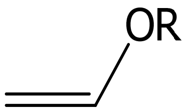
ethylene



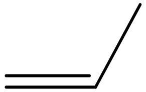
isoprene



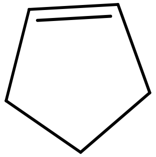
tetrahydrofurane



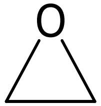
vinylether



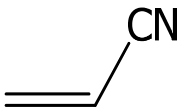
propylene



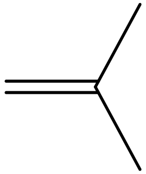
cyclopentene



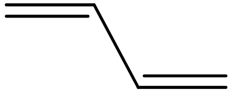
ethylene oxide



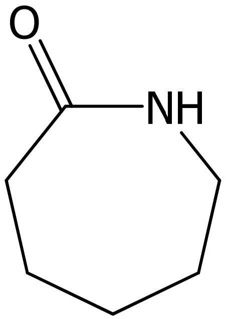
acrylonitrile



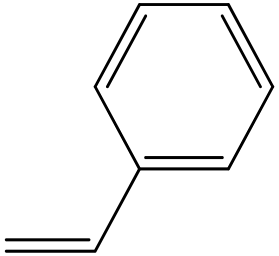
isobutylene



butadiene



ε-caprolactam



styrene

Free radical polymerization 1

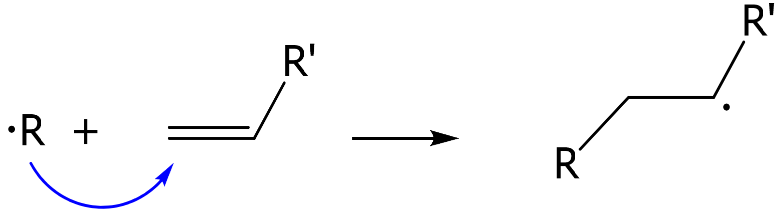
1) Initiation

$R{-}X \longrightarrow {\cdot}R + X{\cdot}$

$R{-}R \longrightarrow {\cdot}R + R{\cdot}$

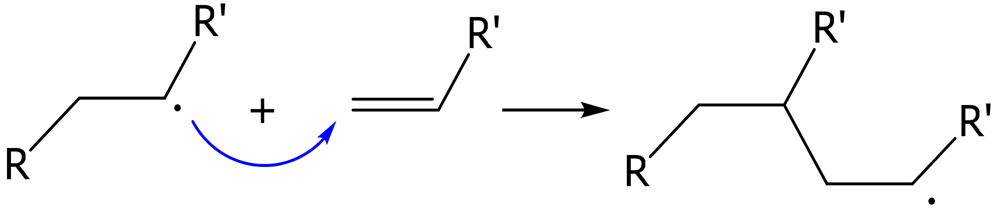
one or more reactive radical(s) are formed

2) Start reaction

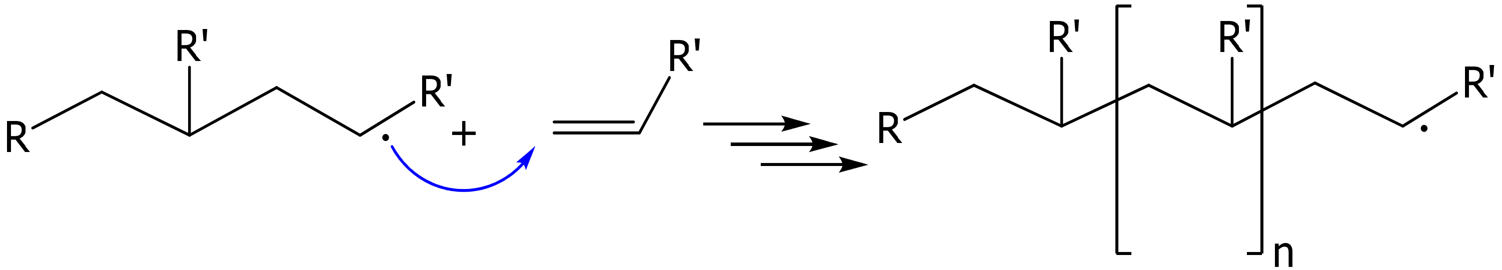


addition of initiator to monomer
→ reactive monomer

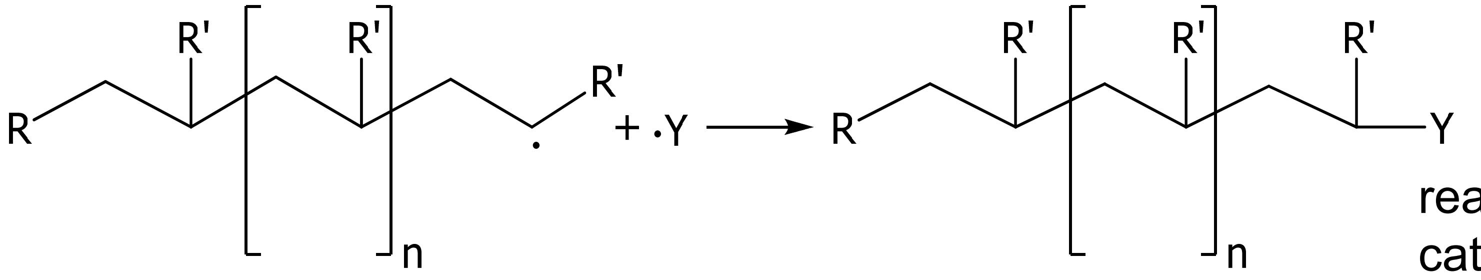
3) Chain reaction (propargation)



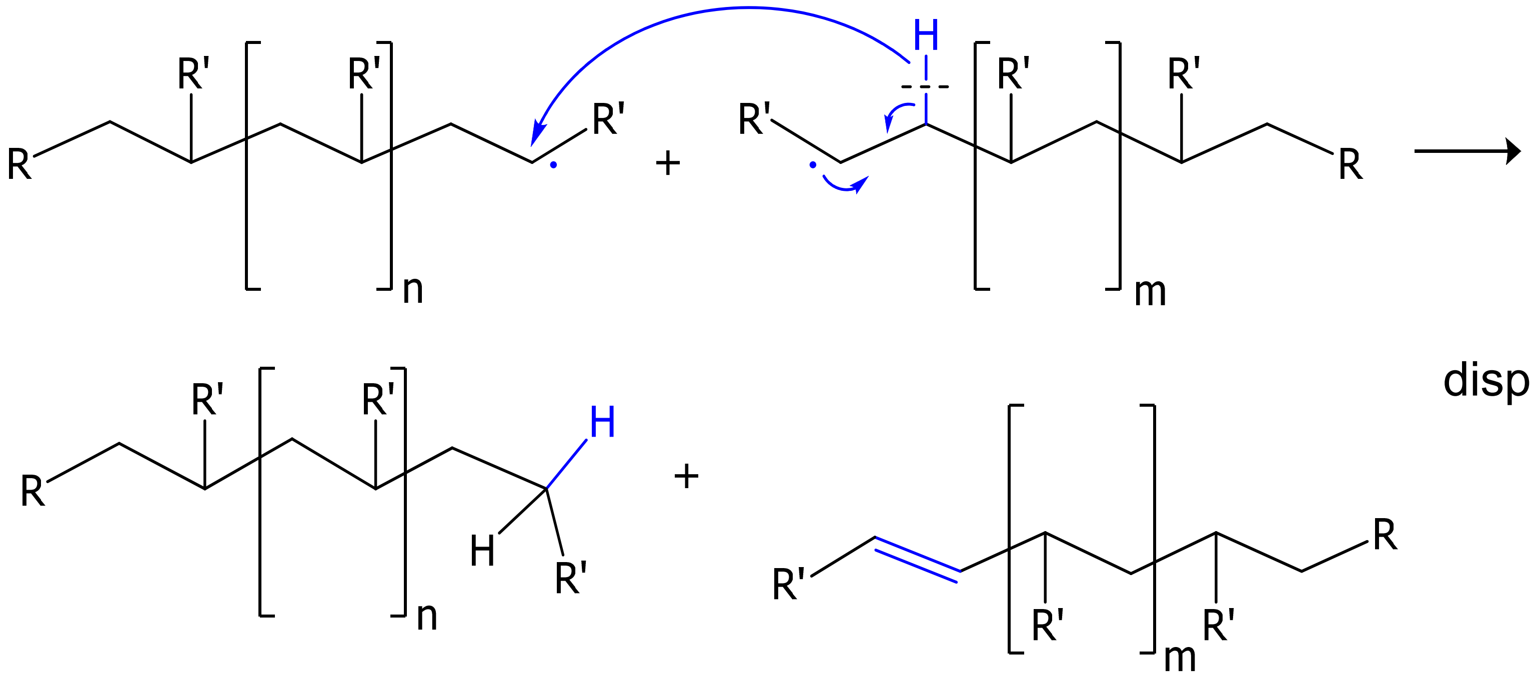
addition of monomers
→ growing polymer chain



4) Termination I

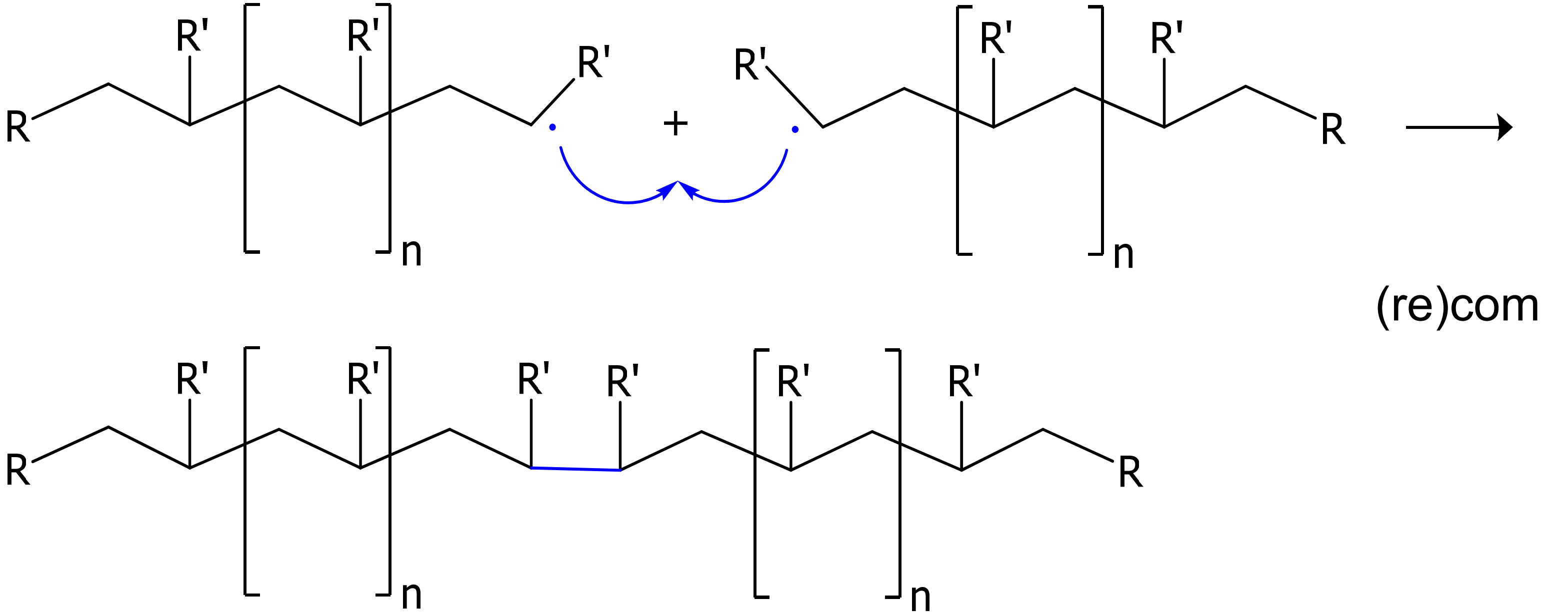


reaction with radical catching species



disproportionation

4) Termination II



(re)combination

termination depends on monomer and temperature:

styrene (up to 160 °C)	mainly recombination
MMA (> 60 °C)	mainly disproportionation
acrylonitrile	recombination
vinylacetate	disproportionation

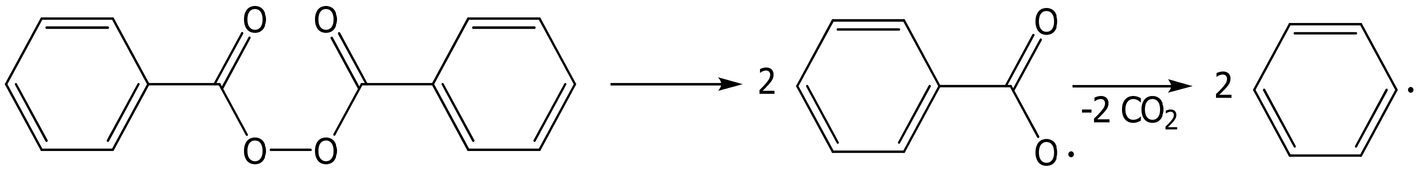
Initiation 1

Radicals are produced by homolytic thermal decomposition of:
- carbon-carbon-bonds (no great importance)
- organic and inorganic peroxides
- azoinitiators

By high energetic radiation

By redox reactions

Peroxides



dibenzoyl peroxide

Organic peroxides are potentially explosive!

Organic peroxides are used in technical scale

Mass polymerization of styrene, ethylene, vinylchloride

Both radicals can initiate the polymerization (influenced by environment, monomer)

Inorganic peroxides and redoxreactions

Predominantly for polymerizations in aqueous phase
H_2O_2: unsafe (formation of oxygen), used in redoxsystems

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + OH^{\bullet}$$

also others:

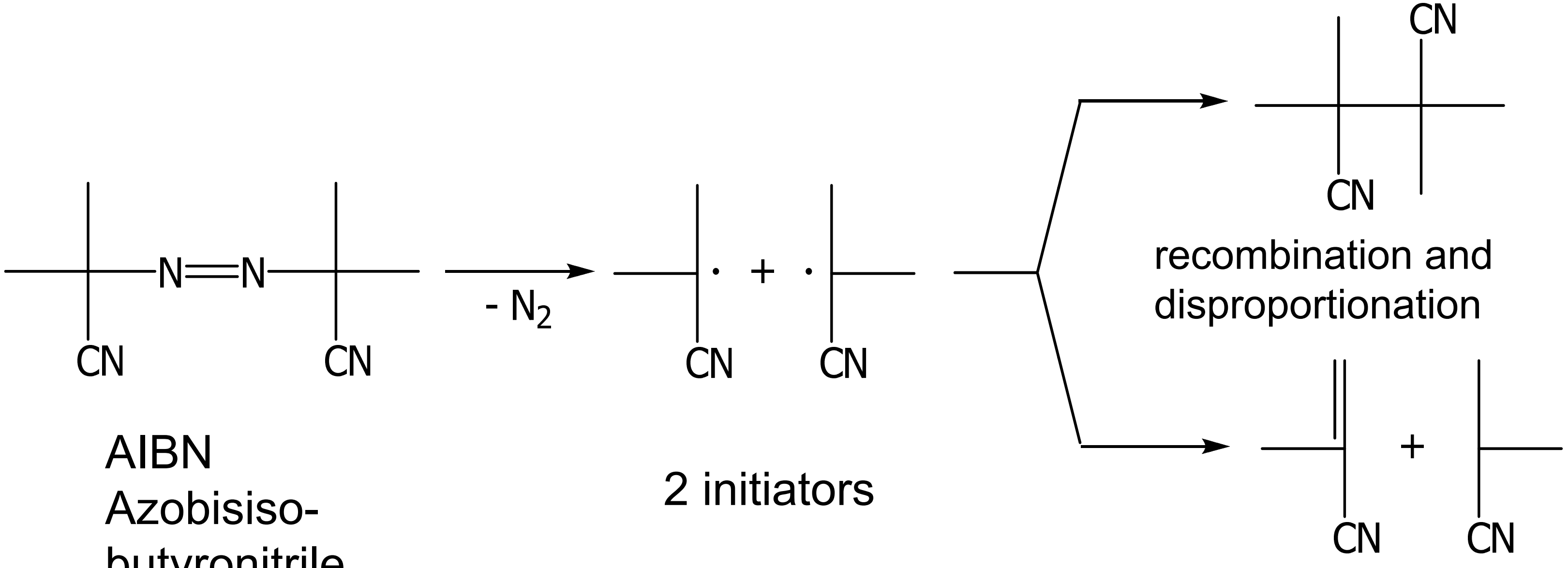
$$R{-}CH_2{-}OH + Ce^{4+} \longrightarrow R{-}\underset{\bullet}{CH}{-}OH + Ce^{3+}$$

Peroxodisulfate $S_2O_8^{2-}$ (potassium, ammonium salt),
reaction mechanism still unclear:

Homolytic cleavage: $S_2O_8^{2-} \rightarrow 2\ SO_4^{-\cdot}$ or
radical formation: $S_2O_8^{2-} + H_2O \rightarrow SO_4^{-} + HSO_4^{-} + OH^{\cdot}$
Both reactions have first order kinetics

Initiation 3

Azoinitiators



AIBN
Azobisisobutyronitrile

2 initiators

recombination and disproportionation

cage-effect → high amount

Thermal decomposition or photolysis (360 nm)
Two radicals are formed
Also unsymmetrical initiators

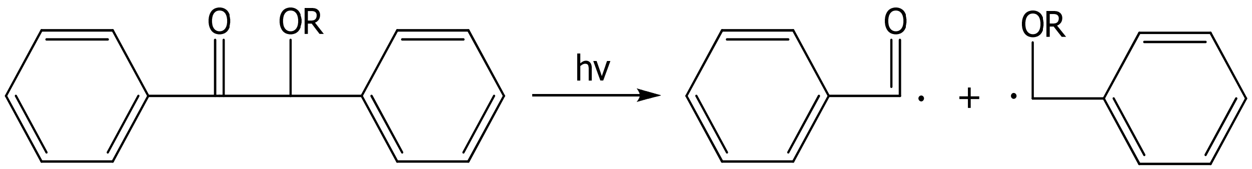
Photoinitiators

Two different types: type I → bond cleavage; type II → H-abstraction

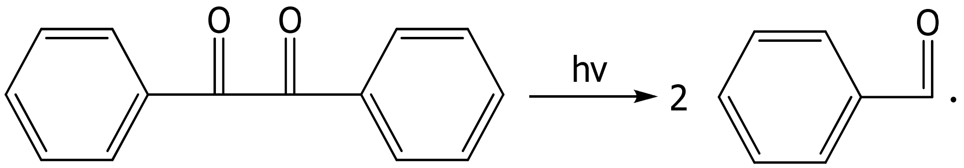
Disulfides (I)

RSSR → 2 RS·

Benzoin and –ethers (I) (approx. 250 nm)



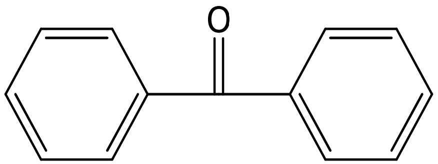
Benzil (approx. 260 nm) (I)



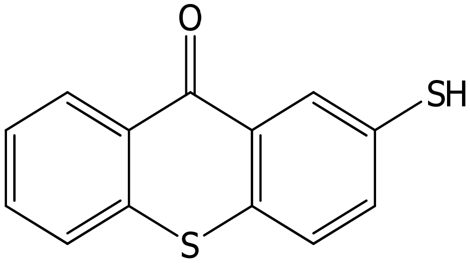
Initiation 5

Photoinitiators

Ketones (II)

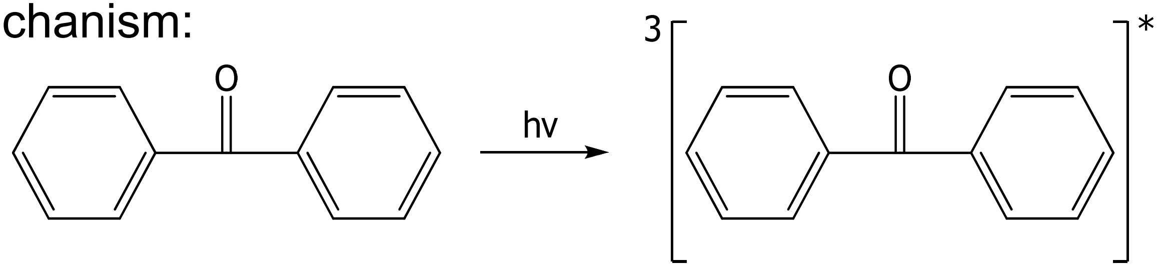


benzophenone
(250 nm)

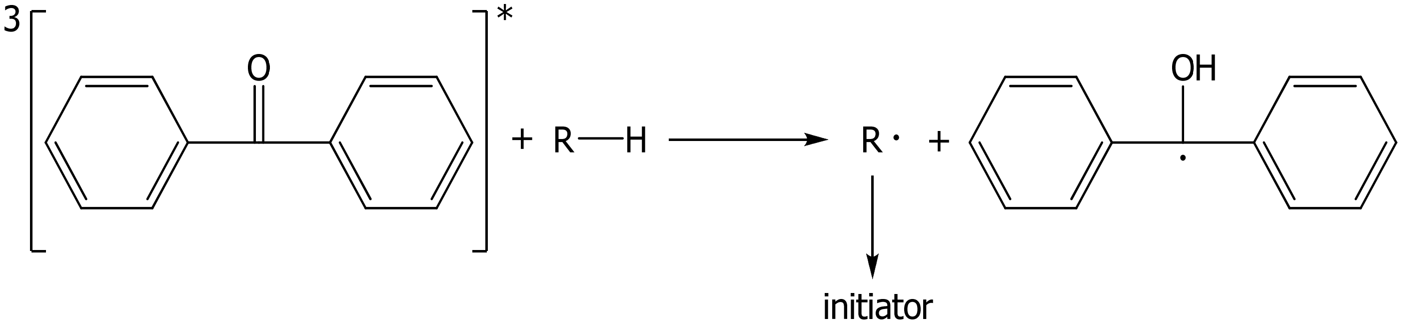


thioxanthone-thiol
(260 nm)

mechanism:

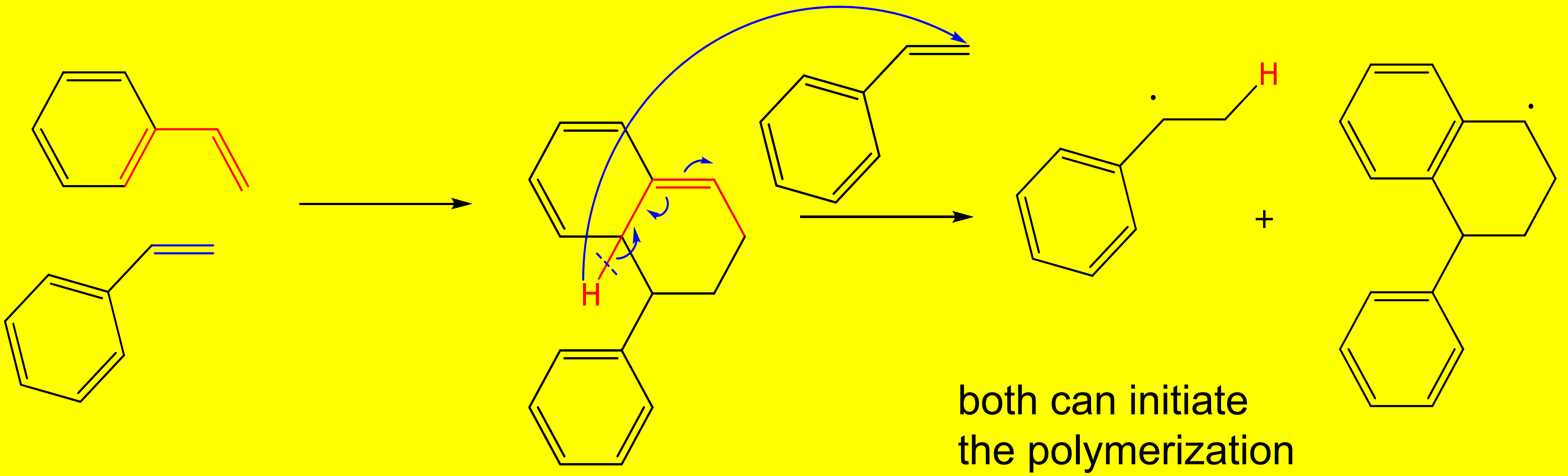


RH = alcohols, ethers,
amines, thiols
(right ketone RH = SH)



Self-initiation

Rare cases, monomers themselves can start reaction
No "spontaneous" polymerization (light, impurities, ...)
e. g. styrene and derivatives, MMA, 2-vinyl-pyridine
Not all self-initiated reactions are radical reactions, but difficult to investigate: MMA conversion of 50% after 5.3 years
Styrene (self-initiated in the dark): 50% conversion of styrene 400 days at 29 °C, 4 hours at 127 °C



both can initiate the polymerization

Combined kinetics 1

Initiation

$$I \equiv R-R \rightarrow 2R\cdot$$

$$v_{init} = k_i\,[\,I\,]$$

Startreaction

$$R\cdot + M \rightarrow R-M\cdot$$

$$v_{start} = k_{st}\cdot[\,R\cdot\,] = k_{st}\cdot k_i\cdot 2\cdot f\cdot[\,I\,]$$

Growth

$$R-M\cdot + n\,M \rightarrow R-M-(M-)_{n-1}-M\cdot \equiv P\cdot$$

$$v_{growth} = k_{gr}\cdot[\,P\cdot\,][\,M\,]$$

Combined kinetics 2

4. Termination

$$v_{term} = k_t \cdot [P\cdot]^2$$

4.1 Coupling

$$R-(M-)_n M\cdot + R-(M-)_m M\cdot \rightarrow$$
$$R-(M-)_{m+n+2} - R$$

4.2 Disproportionation

$$R-(M-)_n M\cdot + R-(M-)_m M\cdot \rightarrow$$
$$R-(M-)_n M + R-(M-)_m M$$

Combined kinetics 3

Steady state: formation of new radicals = consumption of radicals otherwise reaction will stop or explode

$$\frac{d[R\cdot]}{dt} = 0 = \underbrace{2\cdot f\cdot k_i\cdot[I]}_{\textbf{formation}} - \underbrace{k_{st}\cdot[R\cdot]\cdot[M]}_{\textbf{consumption}}$$

rearrange:

$$\boxed{[R\cdot] = \frac{2\cdot f\cdot k_i\cdot[I]}{k_{st}\cdot[M]}}$$

growing chains also constant

$$\frac{d[P_1\cdot]}{dt} = 0 = k_{st}\cdot[R\cdot]\cdot[M] - k_{gr,1}\cdot[P_1\cdot]\cdot[M]$$

$$\frac{d[P_2\cdot]}{dt} = 0 = k_{gr,1}\cdot[P_1\cdot]\cdot[M] - k_{gr,2}\cdot[P_2\cdot]\cdot[M]$$

Combined kinetics 4

$$\frac{d[P_1\cdot]}{dt} = 0 = k_{st} \cdot [R\cdot] \cdot [M] - k_{gr,1} \cdot [P_1\cdot] \cdot [M]$$

$$\frac{d[P_2\cdot]}{dt} = 0 = k_{gr,1} \cdot [P_1\cdot] \cdot [M] - k_{gr,2} \cdot [P_2\cdot] \cdot [M]$$

all growing chains possess same reactivity → all [P_n·] are equal → replacement by [P ·]

$$\frac{d[P\cdot]}{dt} = 0 = k_{st} \cdot [R\cdot] \cdot [M] - k_t \cdot [P\cdot]^2$$

startreaction **termination**

rearrange:

$$\boxed{[P\cdot] = \sqrt{\frac{k_{st} \cdot [R\cdot] \cdot [M]}{k_t}}}$$

Overall rate of polymerization 1

monomer concentration decreases with time:

$$v_{overall} = -\frac{d[M]}{dt}$$

monomer is used in the start reaction and in the growth reaction

$$R\cdot + M \rightarrow R-M\cdot$$

$$v_{start} = k_{st} \cdot k_i \cdot 2 \cdot f \cdot [I]$$

$$R-M\cdot + n\,M \rightarrow$$

$$R-M-(M-)_{n-1}-M\cdot$$

$$v_{growth} = k_{gr} \cdot [P\cdot][M]$$

much more monomers react in the growth reaction
→ start reaction can be neglected

$$v_{overall} = -\frac{d[M]}{dt} = k_{gr} \cdot [P\cdot] \cdot [M]$$

Overall rate of polymerization 2

$$v_{overall} = -\frac{d[M]}{dt} = k_{gr} \cdot [P\cdot] \cdot [M]$$

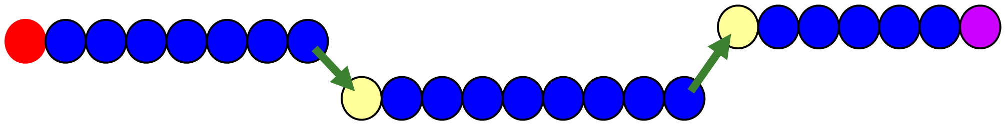
$$[R\cdot] = \frac{2 \cdot f \cdot k_i \cdot [I]}{k_{st} \cdot [M]}$$

$$[P\cdot] = \sqrt{\frac{k_{st} \cdot [R\cdot] \cdot [M]}{k_{ab}}}$$

$$v_{overall} = k_{gr} \cdot \left[\frac{k_{st} \cdot [M]}{k_{ab}} \cdot \frac{2 \cdot f \cdot k_i \cdot [I]}{k_{st} \cdot [M]} \right]^{0.5} \cdot [M]$$

$$v_{overall} = K \cdot \sqrt{[I]} \cdot [M]$$

Chain transfer: Termination of the molecule growth without termination of the kinetic chain



$$P\cdot + QX \rightarrow PX + Q\cdot$$

$$Q\cdot + M \rightarrow QM\cdot$$

QX can be any molecule:

Monomer

Initiator

Polymer (→ branching)

Solvent

Chain transfer agents

thiol:

$$P\cdot + HS-R \rightarrow P-H + R-S\cdot$$

CBr_4:

$$P\cdot + CBr_4 \rightarrow P-Br + CBr_3\cdot$$

$$v_{transfer} = -\frac{d[QX]}{dt} = k_{transfer}\cdot[P\cdot]\cdot[QX]$$

Kinetic chain length:

$$v' = \frac{v_{growth}}{v_{termination} + \sum v_{transfer}}$$

Chain transfer 2

Mayo-equation

$$\frac{1}{\overline{P}_n} = \frac{1}{\overline{P}_{n,0}} + C_{transfer}\frac{[QX]}{[M]}$$

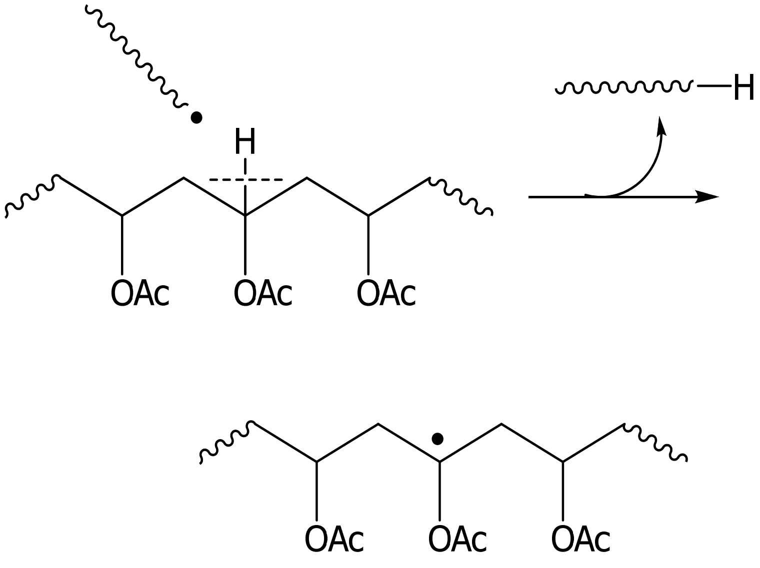
$$C_{transfer} = \frac{k_{transfer}}{k_{growth}}$$

degree of polymerization without chain transfer

amount and efficiency of chain transfer agent

	to momomer $C_{transfer,M}$ x 10^5	to polymer $C_{transfer,P}$ x 10^5
acrylonitrile	2.6	35
MMA	1.0	21
styrene	6.0	19
vinylacetate	20.0	30

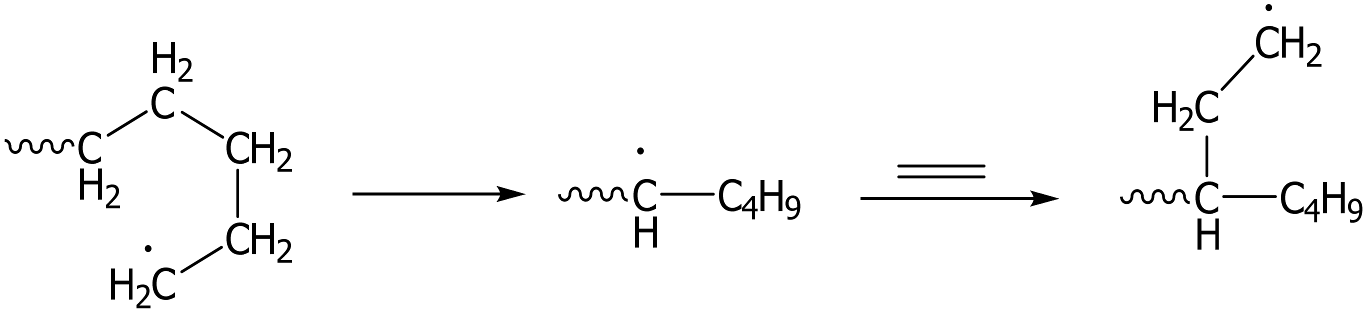
Elias.

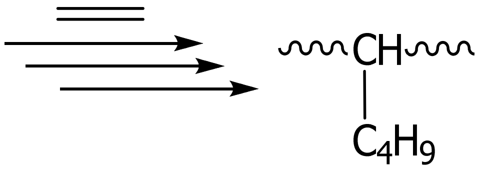


intermolecular transfer

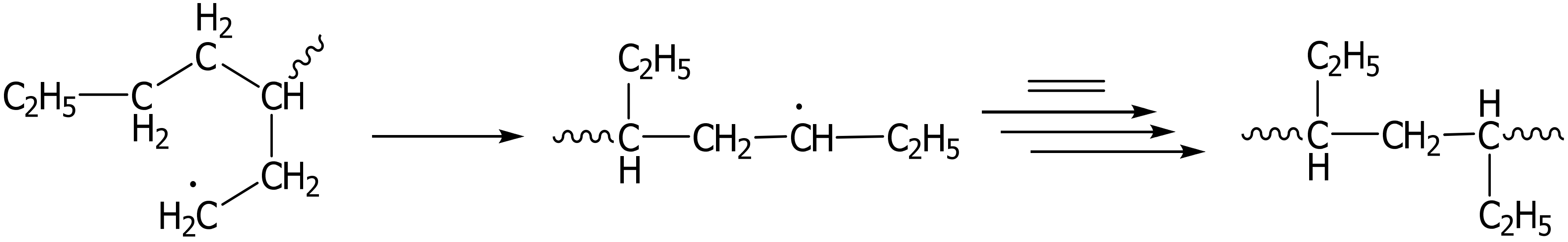
Chain transfer 3

intramolecular transfer - backbiting





Anzahl / 1000 C-Atome	
Methyl	- 0
Ethyl	- 1
Propyl	- 0
Butyl	- 9.6
Pentyl	- 3.6
Hexyl	- 5.6



→ short chain branching

Chain transfer 4

transfer to solvent

	$C_{transfer,M}$ x10^5
benzene	0.23
toluene	1.6
ethylbenzene	8.3
isopropylbenzene	10.4
tert-butylbenzene	0.6
triphenylmethane	65
butylalcohol	0.6
propargylalcohol	70
allylalcohol	15.0

transfer to modifier

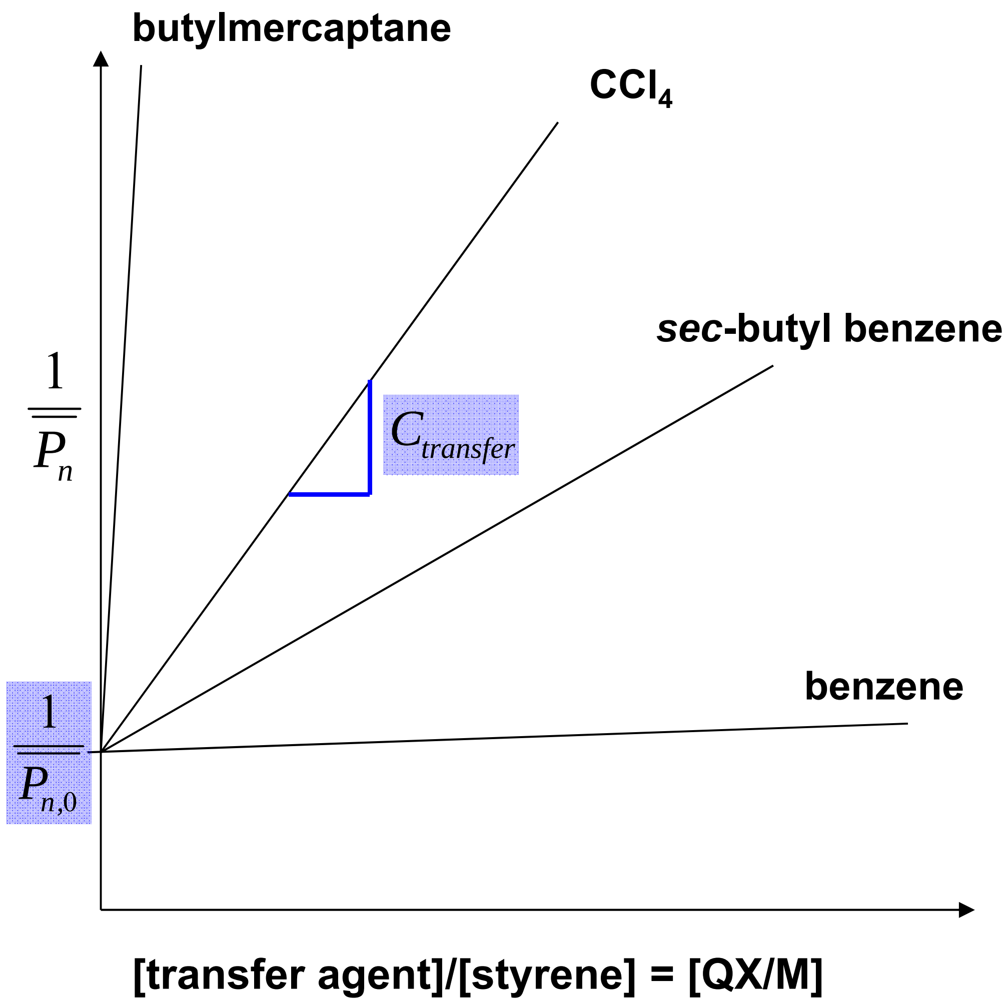
	$C_{transfer,M}$ x10^5
CCl_4	900
CBr_4	220,000
dodecylmercaptane	1,480,000
butylmercaptane	2,100,000

Chain transfer 5

Chain transfer leads to a decrease of the polymer chain length.
Large $C_{transfer}$ → telomerization
(only oligomers are formed)

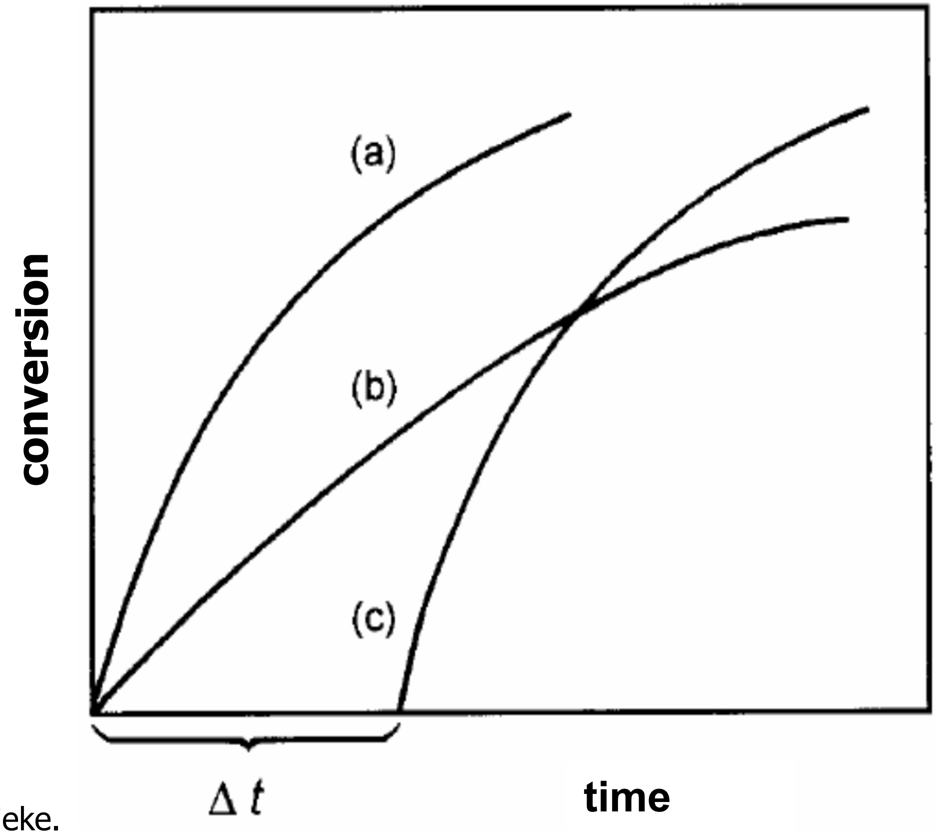
$$\frac{1}{\overline{P}_n} = \frac{1}{\overline{P}_{n,0}} + C_{transfer}\frac{[QX]}{[M]}$$

↑ intercept ↑ slope



Inhibition 1

Inhibition = intended chain termination (e. g. storage of monomers)
Inhibitor = substance that suppresses a radical polymerization completely
(formation of stable inactive radicals)
Retarder = substance that decelerates a radical polymerization
(chain transfer, only few reactive radicals, slow transfer)



Tieke.

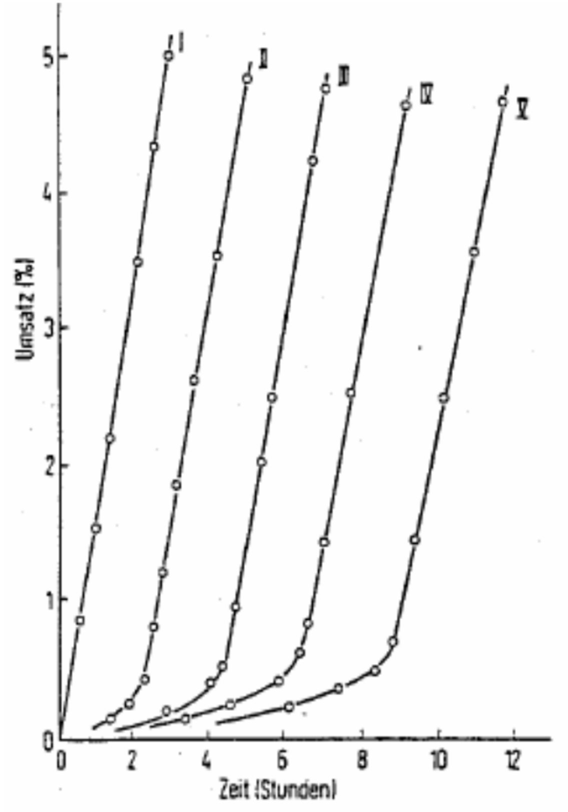
Radical polymerization

Radical polymerization
in the presence of a **retarder**
→ rate of polymerization is lowered, lower degree of polymerization

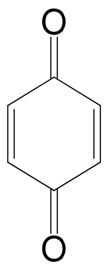
Radical polymerization in the presence of an **inhibitor**, polymerization is stopped until all inhibitor is consumed

Inhibition 2

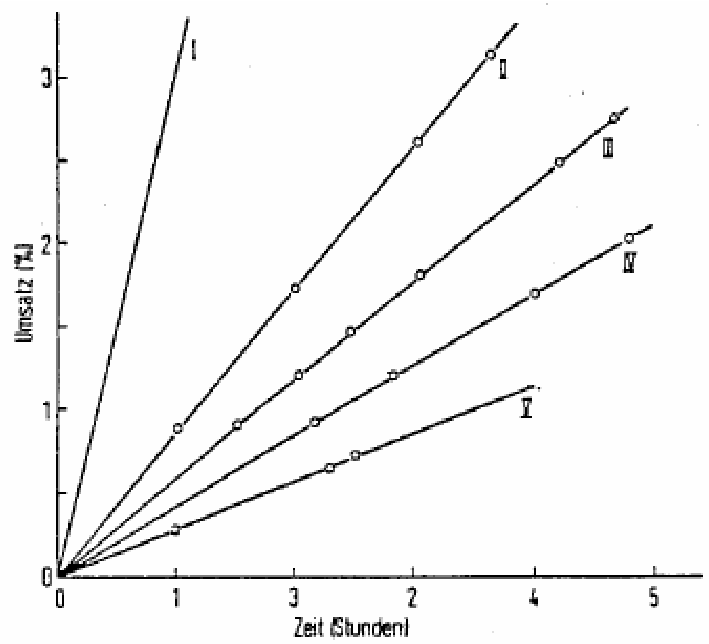
Single substance can be inhibitor or retarder depending on the reaction conditions and the used monomer.



styrene



I-V increasing concentration



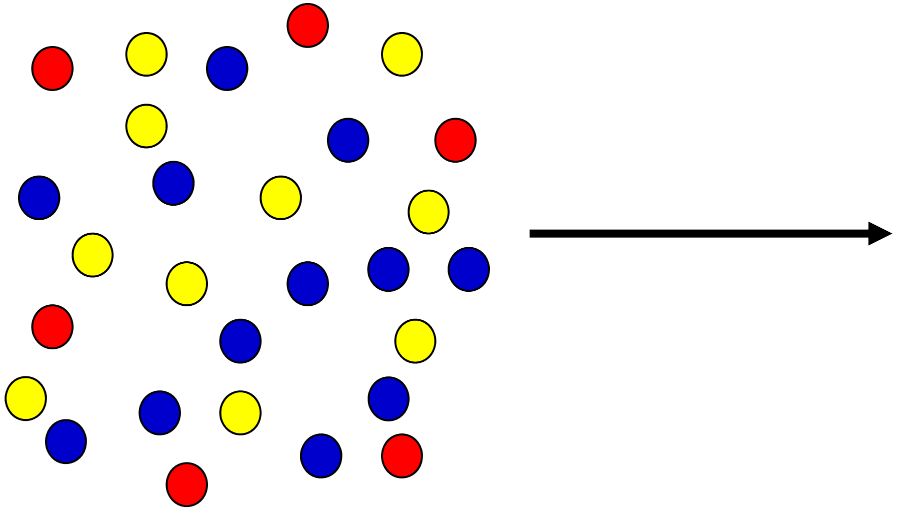
MMA

→ **inhibitor**

→ **retarder**

Copolymerization 1

Copolymerization:
Polymerization of at least two different monomers → copolymers

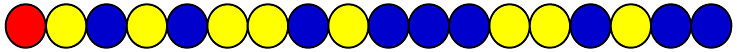


● **Initiator**

● **Monomer A**

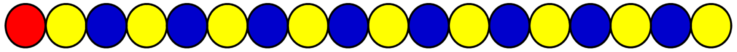
● **Monomer B**

Statistical copolymer



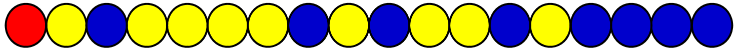
approx. same reactivities of A and B

Alternating copolymer



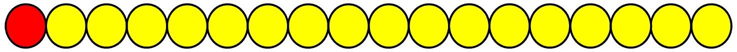
A and B do not homopolymerize or A or B does not homopolymerize, but one monomer is very reactive

Gradient copolymer



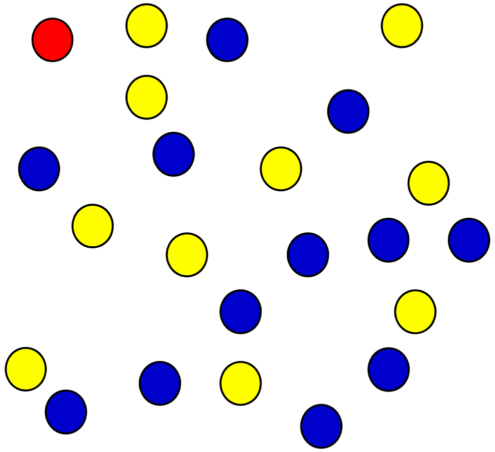
B is more reactive than A

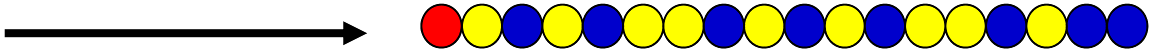
Homopolymer(s)



B is much more reactive than A (unreactive)

Copolymerization - Kinetics1





● **Initiator**

● **Monomer A**

● **Monomer B**

Molar fractions in monomer feed

$$F_A = \left(\frac{[A]}{[A]+[B]} \right)_{mon}$$

$$F_B = 1 - F_A$$

$$F_A = \frac{12}{10+12} = 0.54$$

$$F_B = 0.46$$

Molar fractions in copolymer

$$f_A = \left(\frac{[A]}{[A]+[B]} \right)_{poly}$$

$$f_B = 1 - f_A$$

$$f_A = \frac{8}{8+9} = 0.47$$

$$f_B = 0.53$$

$$f_A = \frac{d[A]_{pol}}{d[A]_{pol} + d[B]_{pol}}$$

Assumptions:

Reactivity independent from chain length

Growth via an active chain end

Start reaction, termination and chain transfer can be neglected

4 different propagation steps (terminal model – only last monomer unit of the chain influences reactivity)

reaction rates of all steps

$$\sim M_1\cdot + M_1 \xrightarrow{k_{11}} \sim M_1 - M_1\cdot \qquad v_{11} = k_{11}\cdot[\sim M_1\cdot]\cdot[M_1]$$

$$\sim M_1\cdot + M_2 \xrightarrow{k_{12}} \sim M_1 - M_2\cdot \qquad v_{12} = k_{12}\cdot[\sim M_1\cdot]\cdot[M_2]$$

$$\sim M_2\cdot + M_1 \xrightarrow{k_{21}} \sim M_2 - M_1\cdot \qquad v_{21} = k_{21}\cdot[\sim M_2\cdot]\cdot[M_1]$$

$$\sim M_2\cdot + M_2 \xrightarrow{k_{22}} \sim M_2 - M_2\cdot \qquad v_{22} = k_{22}\cdot[\sim M_2\cdot]\cdot[M_2]$$

Addition of monomer M_1

$$v_{11} = k_{11} \cdot [\sim M_1 \cdot] \cdot [M_1]$$

$$v_{21} = k_{21} \cdot [\sim M_2 \cdot] \cdot [M_1]$$

Addition of monomer M_2

$$v_{12} = k_{12} \cdot [\sim M_1 \cdot] \cdot [M_2]$$

$$v_{22} = k_{22} \cdot [\sim M_2 \cdot] \cdot [M_2]$$

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

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

Reactivity ratio of monomers M_1 and M_2

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

Mayo-Lewis equation 1

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

Assumptions:

$[\sim M^{\cdot}]$ is constant

equilibrium: $v_{21}=v_{12}$

Steady state conditions

Monomer ratio in polymer

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}\cdot\frac{r_1\cdot[M_1]+[M_2]}{[M_1]+r_2\cdot[M_2]}$$

$$r_i = \frac{\text{rate of add. of same M}}{\text{rate of add. of other M}} \Rightarrow r_1 = \frac{k_{11}}{k_{12}};\ r_2 = \frac{k_{22}}{k_{21}}$$

Mayo-Lewis equation 2

$$r_i = \frac{\text{add. of same M}}{\text{add. of other M}} \Rightarrow r_1 = \frac{k_{11}}{k_{12}};\, r_2 = \frac{k_{22}}{k_{21}}$$

Five different cases for r_i:

$r_i = 0$	Rate constant for homopolymerizations are zero → active chain end adds only the other type of monomer
$r_i < 1$	The other type of monomer is added preferentially
$r_i = 1$	Both monomers are added with equal probability if $[M_1] = [M_2]$
$r_i > 1$	The same monomer is added preferentially
$r_i = \infty$	Only homopolymerization, no copolymerization

M_1	r_1	M_2	r_2
tetrafluoroethylene	1	chlortrifluoroethylene	1
ethylene	0.88	vinylacetate	1.03
styrene	56	vinylacetate	0.01
styrene	17.24	vinylchloride	0.058
styrene	0.84	butadiene	1.44
vinylchloride	0.04	butadiene	8.8
acrylonitrile	0.04	butadiene	0.36
methylmethacrylate	0.027	butadiene	0.5
methylmethacrylate	0.41	styrene	0.48
acrylonitrile	1.68	butylacrylate	1.06
stilbene	0.03	maleic acid anhydride	0.03

$$r_1 \approx r_2;\ r_1 \cdot r_2 = 1 \Rightarrow \text{random copolymerization, ideal copolymerization}$$

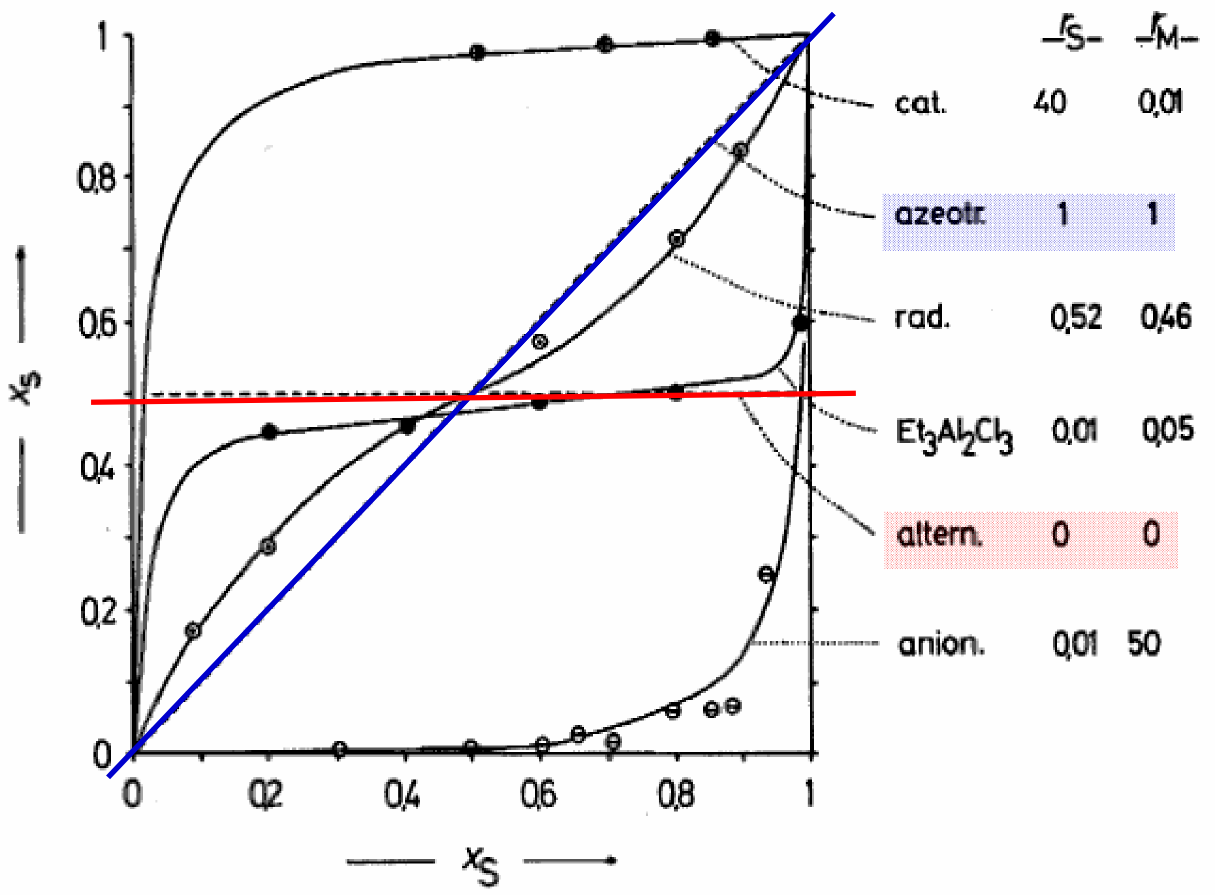
$$r_1 > 1, r_2 < 1;\ r_1 \cdot r_2 = 1 \Rightarrow \text{composition drift, ideal copolymerization}$$

$$r_1 > 1, r_2 < 1;\ r_1 \cdot r_2 > 1 \Rightarrow \text{composition drift, deviation from ideal copolymerization}$$

$$r_1 = r_2 = 0;\ r_1 \cdot r_2 = 0 \Rightarrow \text{strictly alternating copolymer}$$

$$r_1 < 1, r_2 < 1;\ 0 < r_1 \cdot r_2 < 1 \Rightarrow \text{more or less alternating copolymer}$$

Influence of reaction mechanism



Copolymerization of styrene (S) and methylmethacrylat (M)
with different initiators (cationic, radical, anionic, coordinative polymerization)
(x_s = ratio of styrene in polymer *vs.* x_s = ratio of styrene in monomer mixture)

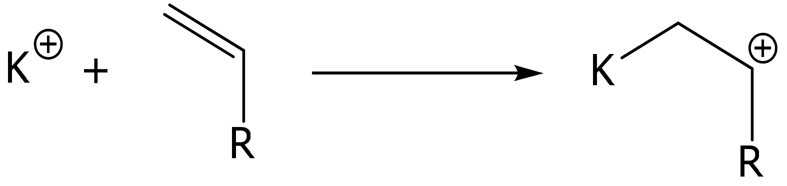
Cowie.

Cationic polymerization 1

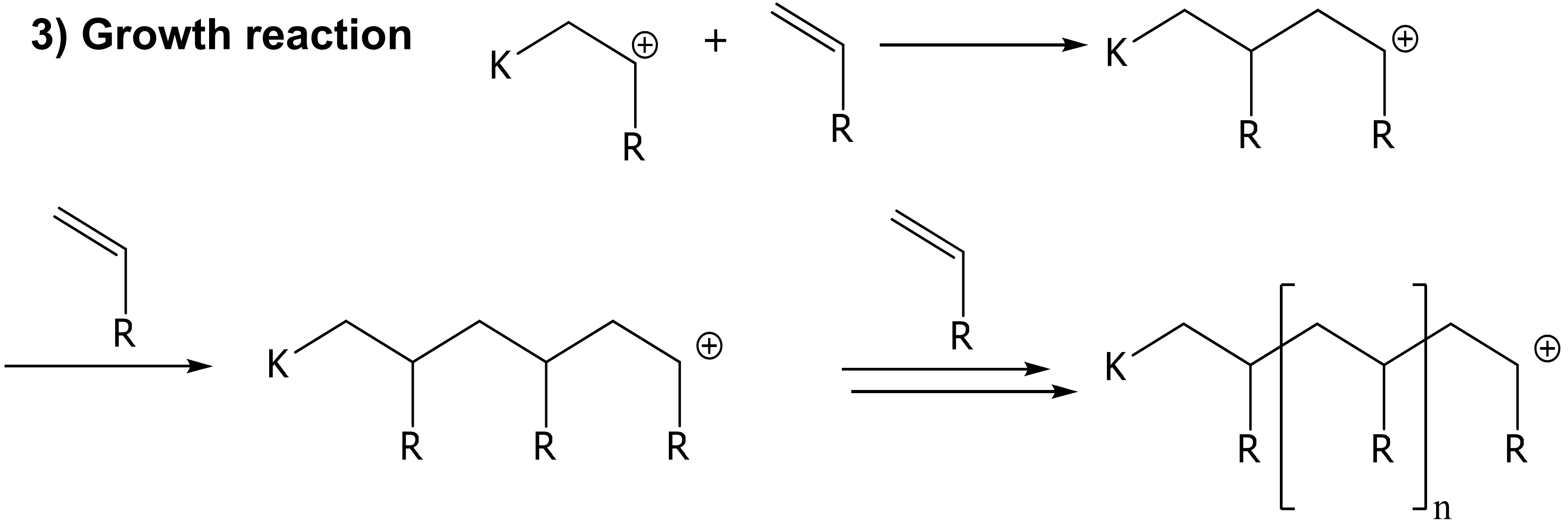
1) Initiation

$$KA \longrightarrow K^{\oplus} + A^{\ominus}$$

2) Start reaction

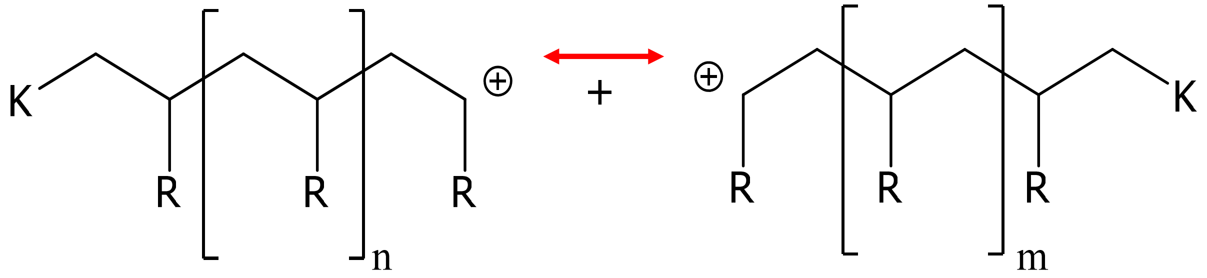


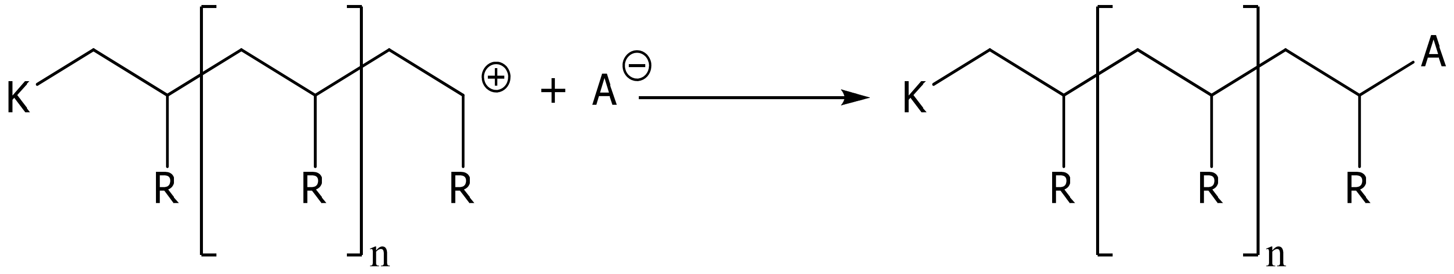
3) Growth reaction



Cationic polymerization 2

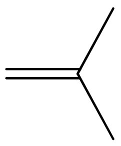
4) Termination



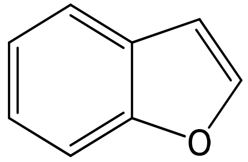


+ many other reactions

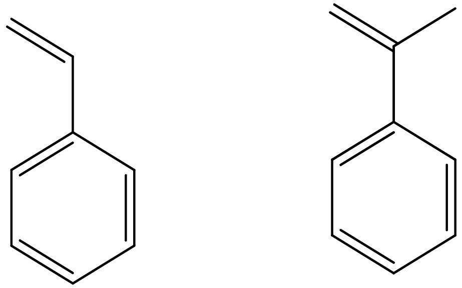
Monomers



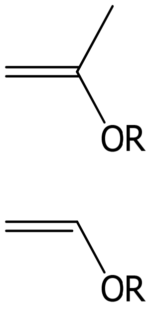
isobutene



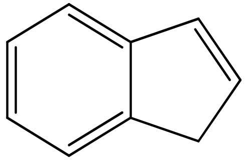
benzofurane



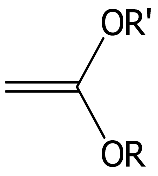
styrene derivates and
α-methyl-styrene derivates



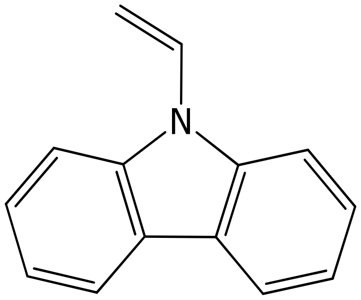
vinylethers



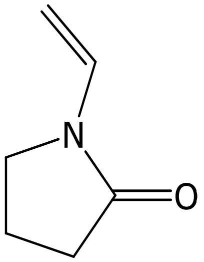
indene



vinylacetales



vinylcarbazole



N-vinyl-pyrrolidone

Monomers are electronrich and stable against deprotonation.

Initiators 1

- **Protic acids**

H_2SO_4, $HClO_4$, FSO_3H, F_3CSO_3H, F_3CCOOH → sterically demanding anion

- **Lewis acids**

BF_3, $AlCl_3$, $AlBr_3$, $SnCl_4$, SbF_5, $SbCl_5$, $TiCl_4$
Coinitiator is necessary:
$BF_3 + H_2O \rightarrow H^+ + BF_3OH^-$
$AlCl_3 + RCl \rightarrow R^+ + AlCl_4^-$

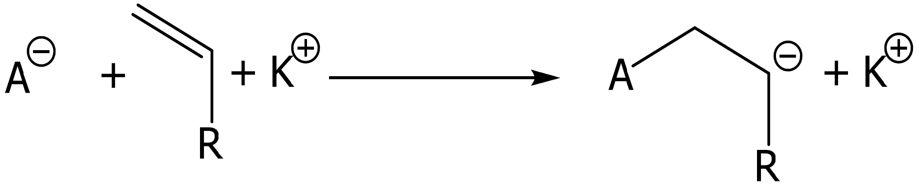
higher molar masses
acidity of cocatalyst determines reaction rate:
acetic acid > nitroethane > phenol > water

Anionic polymerization 1

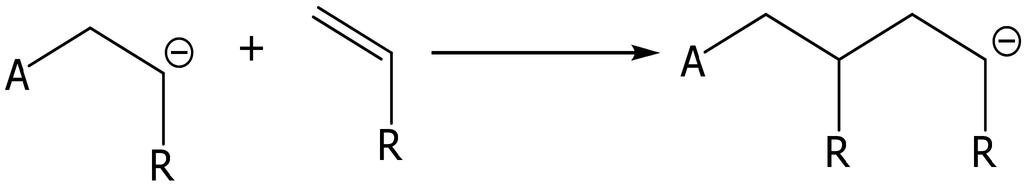
1) Initiation

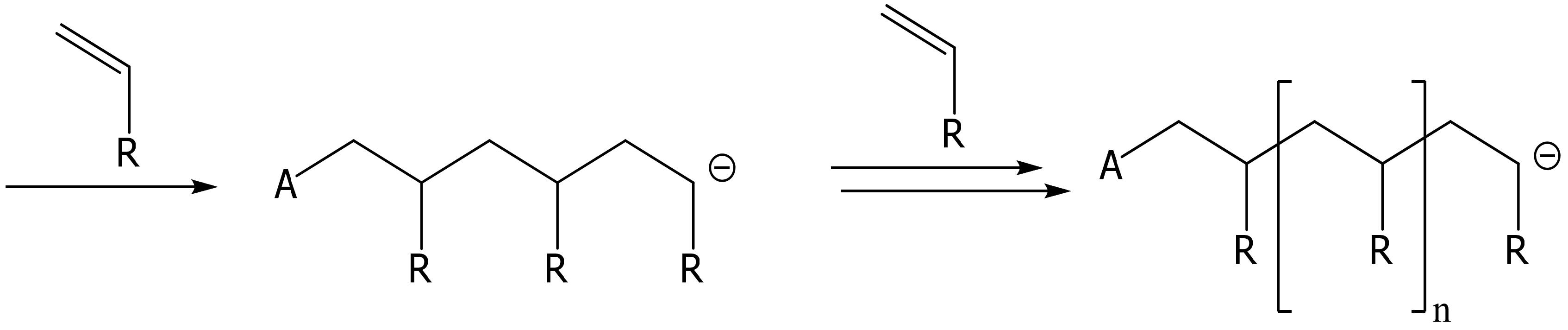
$$KA \longrightarrow K^{\oplus} + A^{\ominus}$$

2) Start reaction

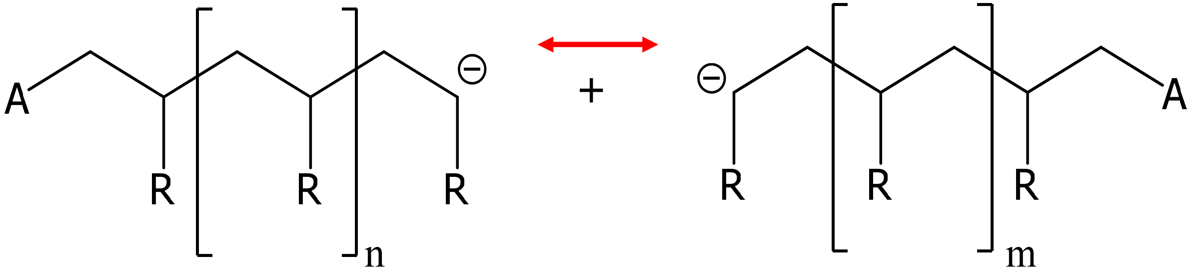


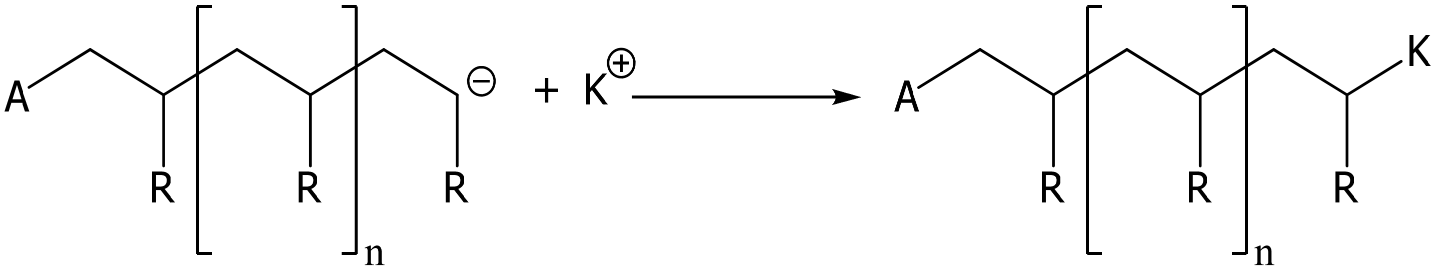
3) Growth reaction





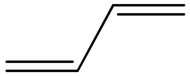
4) Termination



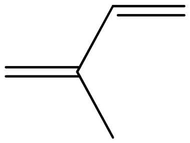


+ many other reactions

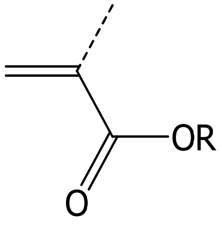
Monomers for anionic polymerization



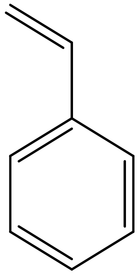
butadiene



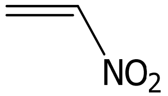
isoprene



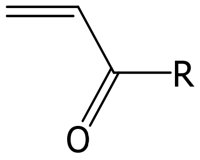
acrylates and
methacrylates



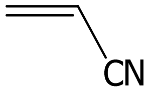
styrene



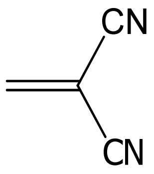
nitroethene



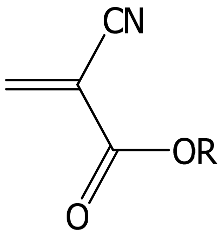
vinylketons



acrylonitrile



vinylidene cyanide



cyanoacrylate

Monomers are electronpoor and have electronwithdrawing substituents.

Initiators

$NH_2^{\ominus}$

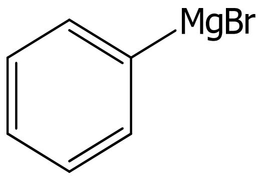
$NR_2^{\ominus}$

metal amides

$OH^{\ominus}$

$CN^{\ominus}$

“normal” anions



Grignard compounds

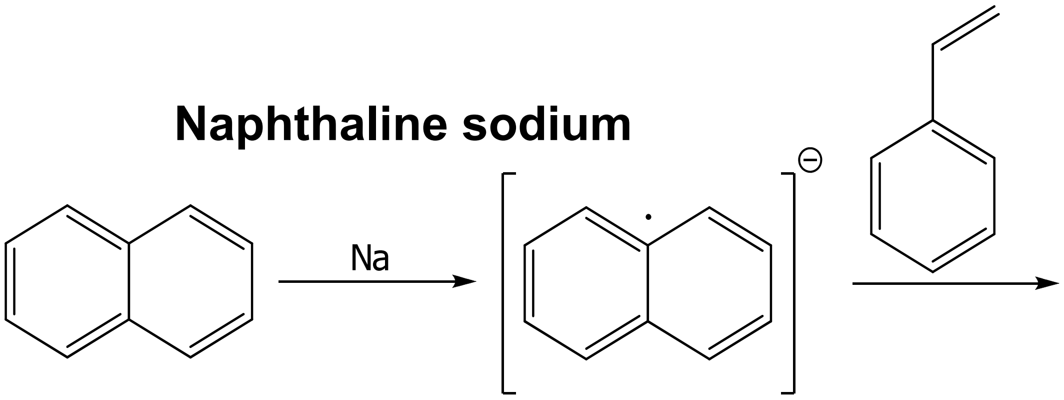
n-BuLi
sec-BuLi

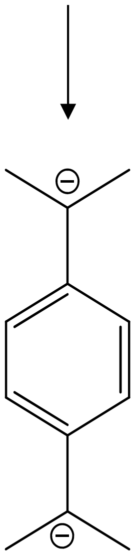
Lithium compounds

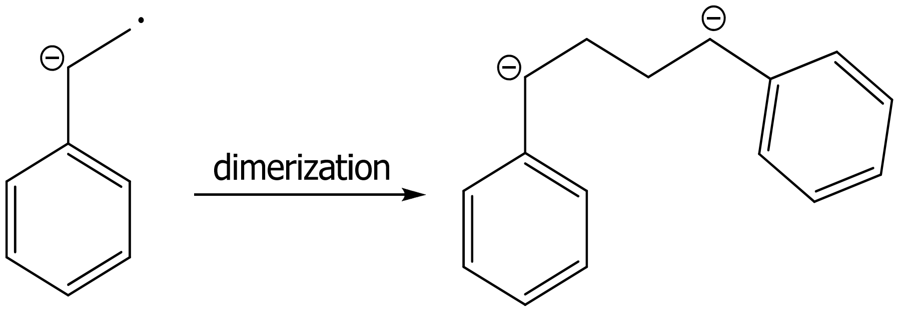
$OR^{\ominus}$

alkoxides

Naphthaline sodium

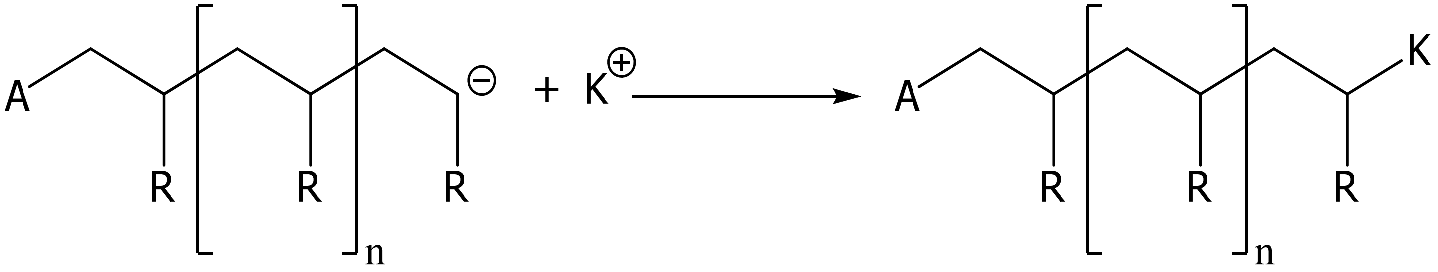




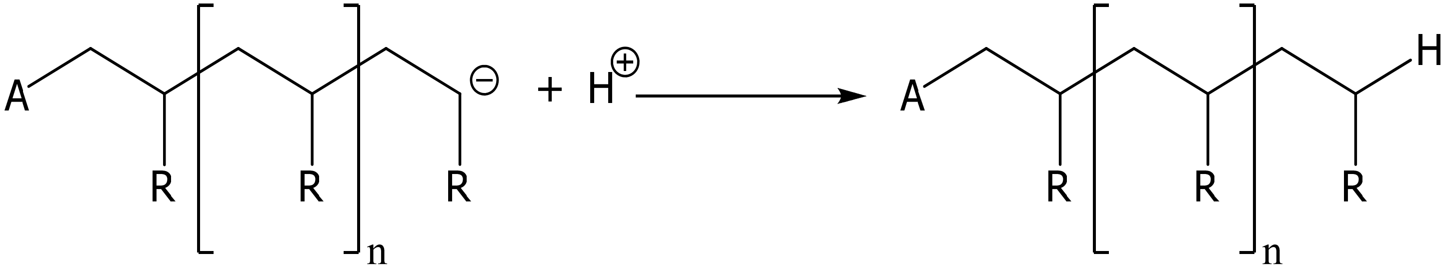


Ideal anionic polymerization (“living polymerization”) → no termination

Reaction of anion with counter ion

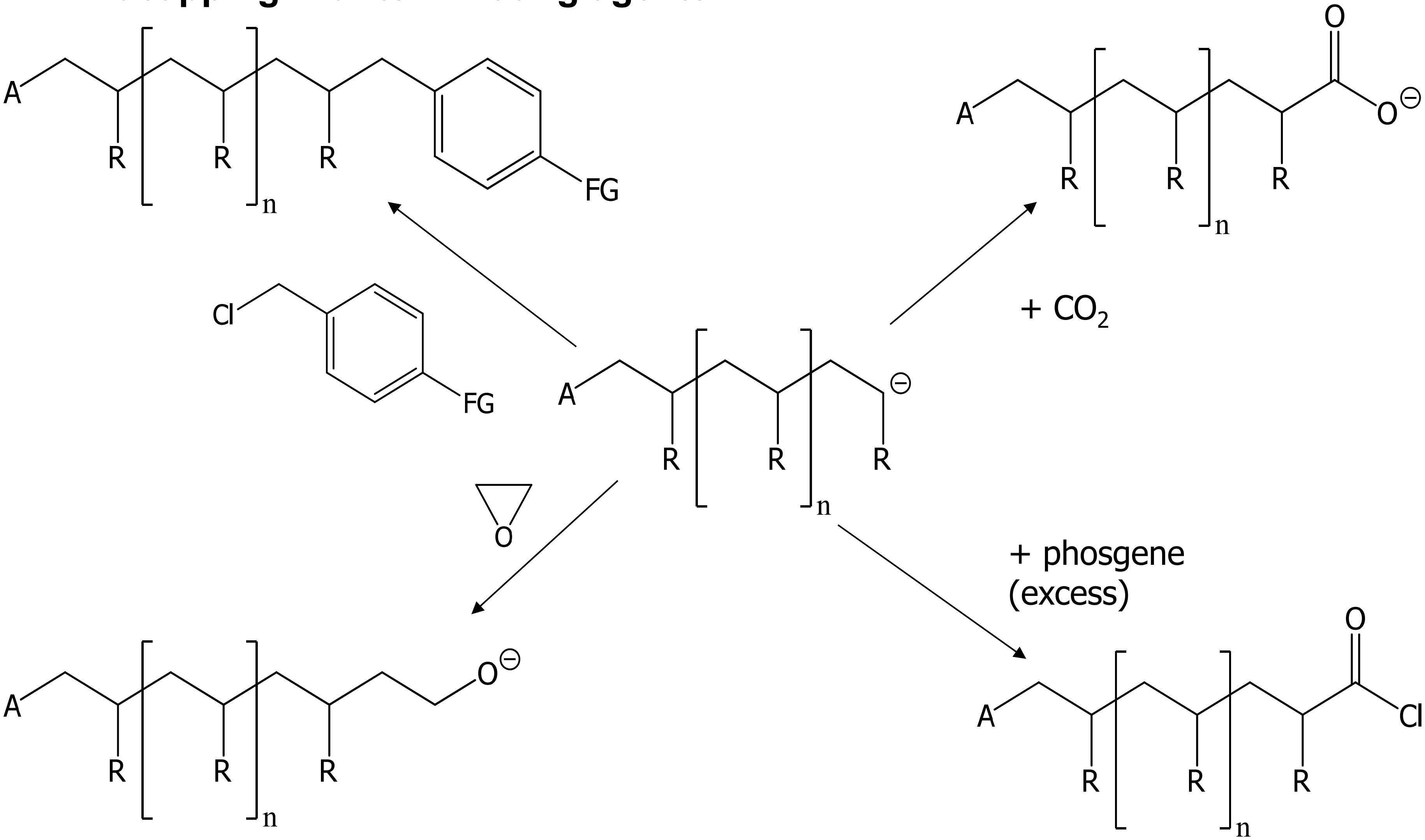


Anion (base) reacts with proton



Termination 2

Endcapping with terminating agents



Special considerations for experimental work

high nucleophilicity of the initiators (and propargating chain ends)
absolutely necessary to **avoid oxygen, water and protic impurities**

aprotic solvents (dry)
- polar: THF, diethyl ether, …
- non-polar: toluene, cyclohexane, hexane, …

purification of all reagents
handling of reagents **in vacuum or under inert gas**

no termination → high concentration of active species → very high reaction rate

(*e.g.* the half of the amount of MMA reacts in less than 1 s in THF at room temperature)

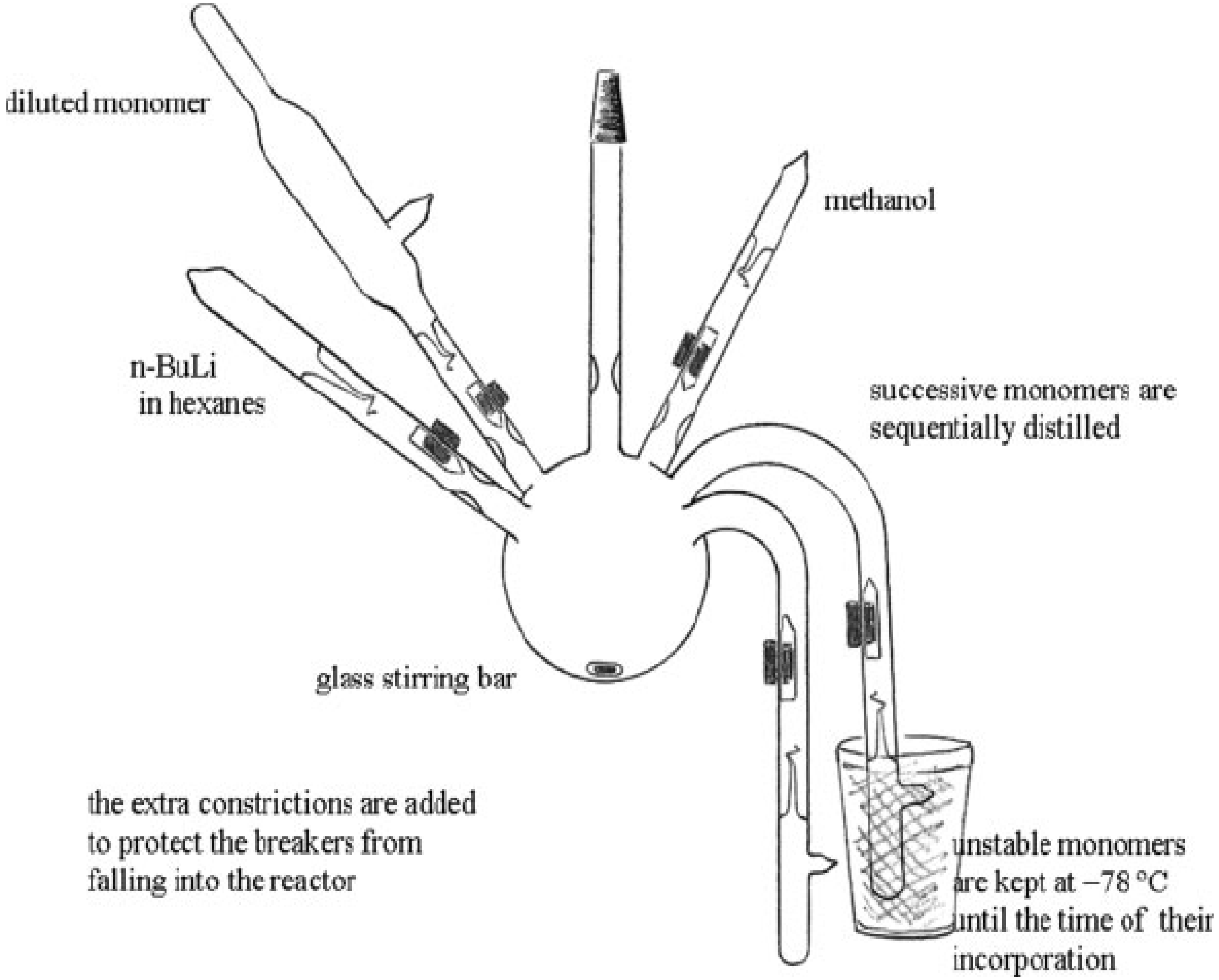
→ polymerization at very **low temperatures**

Anionic polymerization equipment 2

„The high-vacuum technique employed in classical anionic polymerization methodology requires highly developed and specialized skills. The polymer scientist must possess both an adept glassblowing ability and a thorough understanding of the behavior of compounds, volatile and nonvolatile, in a vacuum environment.“

J. Polym. Sci., Part A., Polym. Chem. **2005**, *43*, 6179–6222.

Anionic polymerization equipment 3



N. Hadjichristidis, University of Athens

Anionic polymerization equipment 4

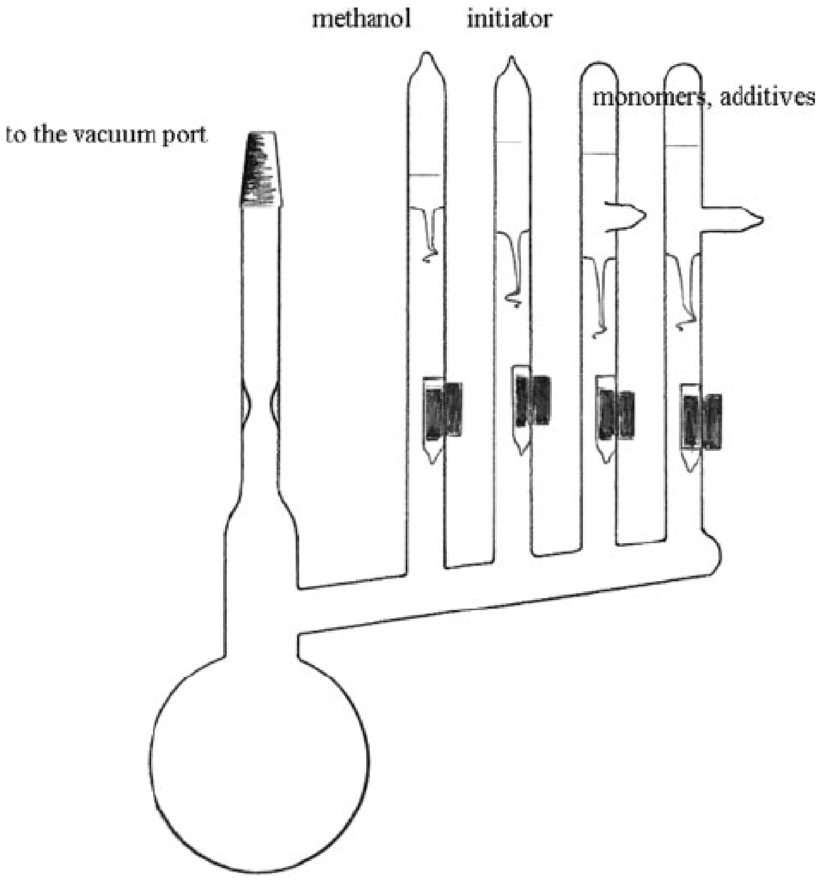
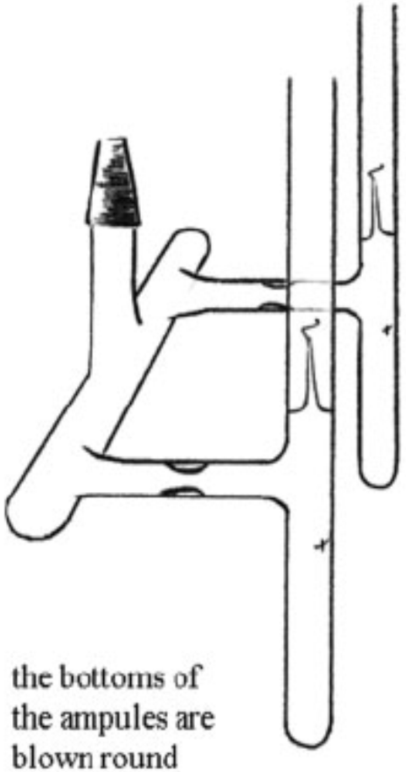


Figure 46. Simple polymerization apparatus.

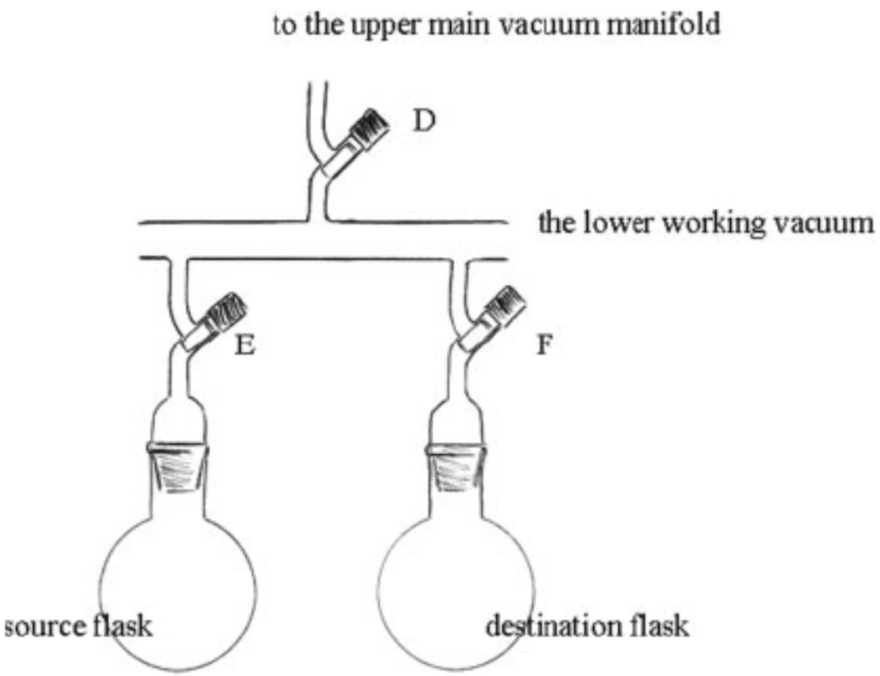
N. Hadjichristidis, university of Athens

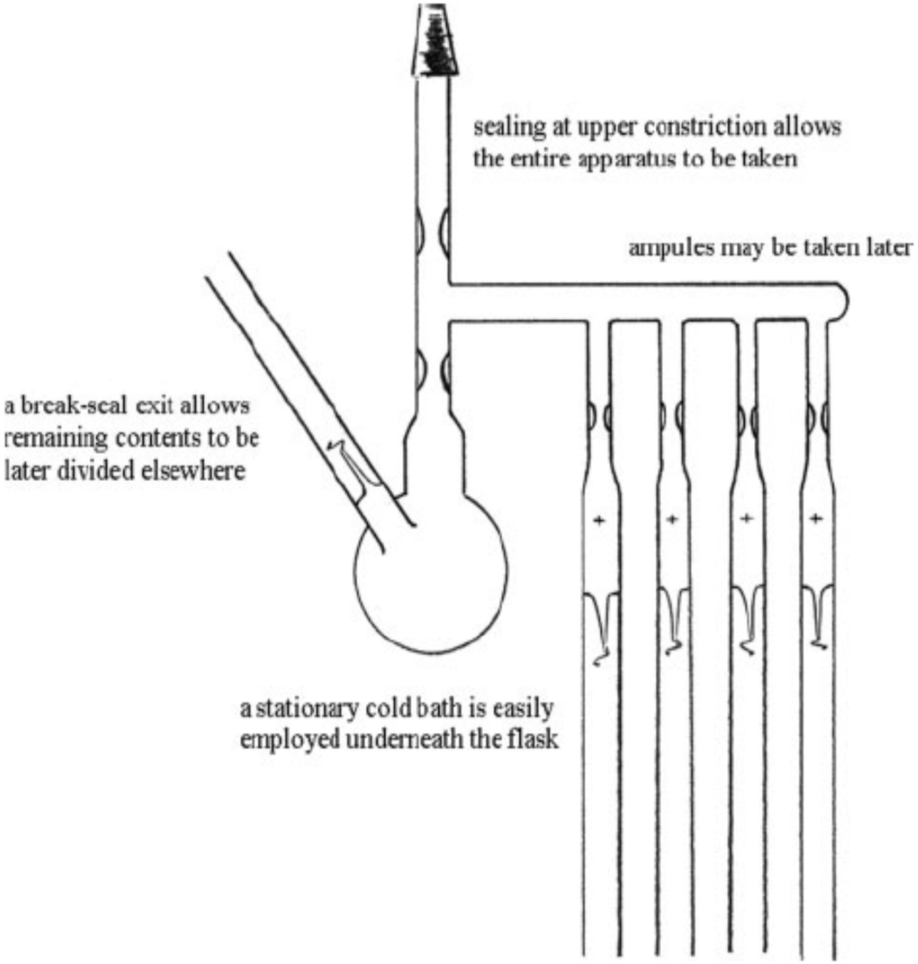


the ampules are calibrated with a scratch on the glass

the bottoms of the ampules are blown round and uniform in thickness

Anionic polymerization equipment 5



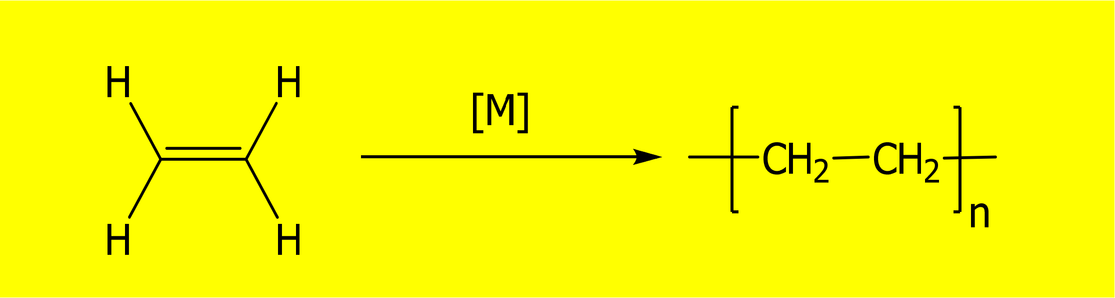

sealing at upper constriction allows the entire apparatus to be taken

ampules may be taken later

a break-seal exit allows remaining contents to be later divided elsewhere

a stationary cold bath is easily employed underneath the flask

N. Hadjichristidis, University of Athens



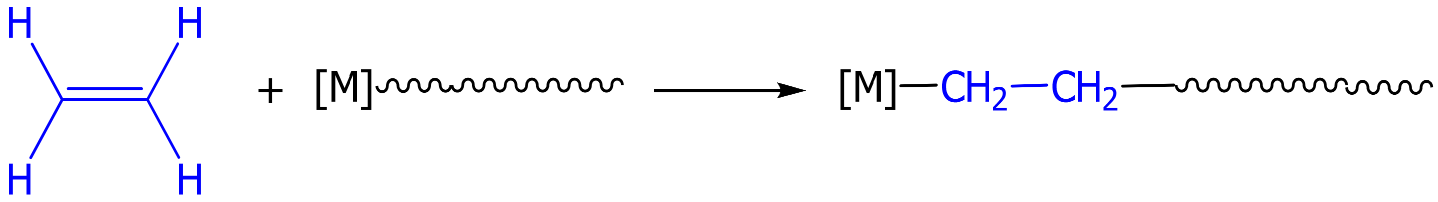
History:

1953 Karl Ziegler and his coworkers discovered the polymerization of ethene with triethylaluminium and nickel complexes

1954 Giulio Natta discovered the stereoregular polymerization of propylene

1963: Nobel prize for K. Ziegler and G. Natta

also: polyinsertion



Stereoisomerism

- configuration of monomers (stereoisomers)
- configurational isomers → high energy barrier
- conformational isomers → low energy barrier

two different configurations

$(CH_2CHX)_m-C(H)(X)-(CH_2CHX)_p$

$(CH_2CHX)_m-C(X)(H)-(CH_2CHX)_p$

asymmetric, but usually no optical activity

heteroatoms (main chain) → absolute configuration → optical activity

$-OH_2C-C(H)(X)-OCH_2-$

$-OH_2C-C(X)(H)-OCH_2-$

Tieke

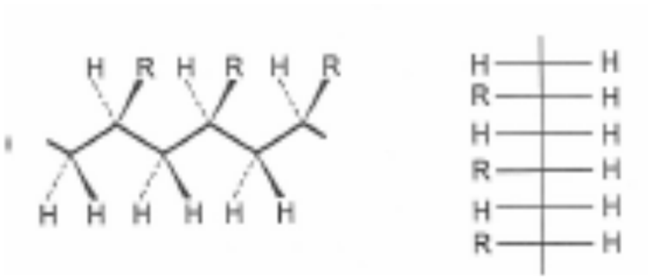
Structure of polymers – tacticity 2

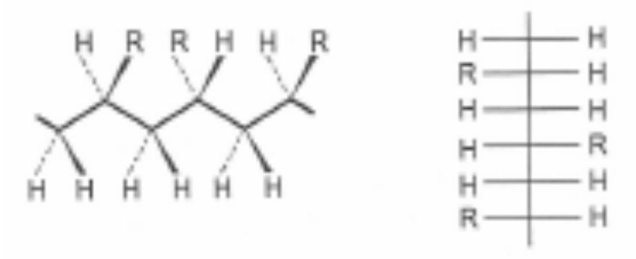
Tacticity: steric order of R-substitution along the main chain
→ Fischer projection

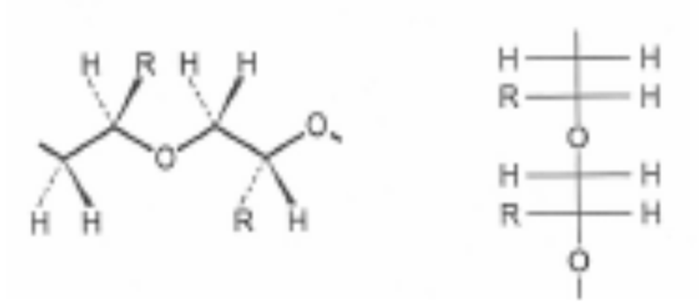
When all substituents are

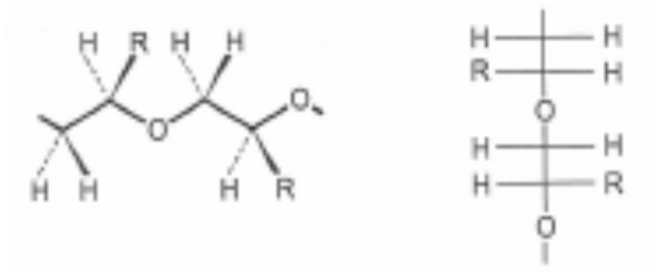
on one side → isotactic

alternating → syndiotactic





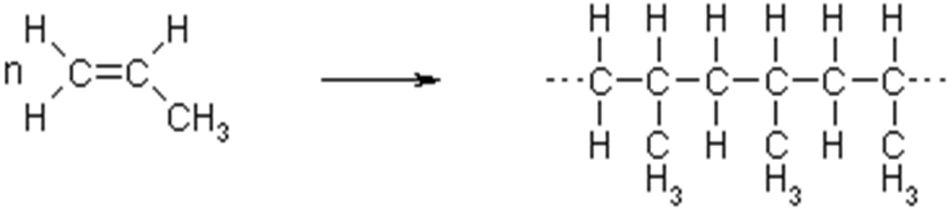




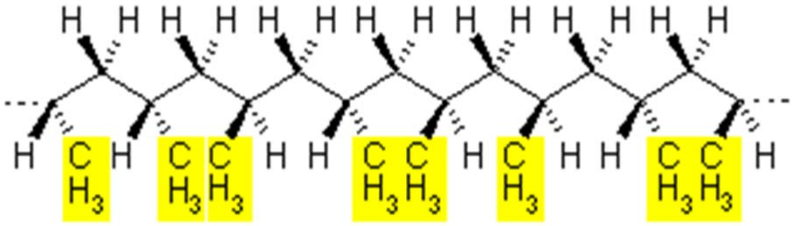
irregular polymers → atactic

Tieke

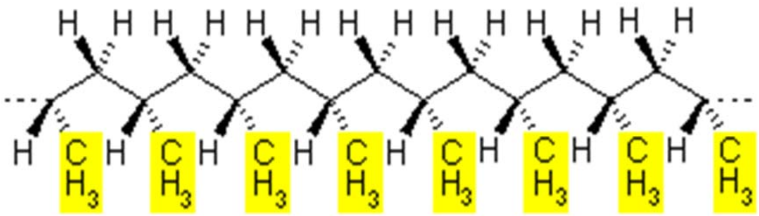
Example for tacticity: poly(propylene)



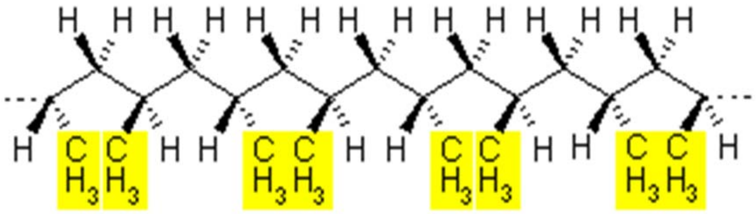
propene **poly(propylene)**



atactic poly(propylene)



isotactic poly(propylene)



syndiotactic poly(propylene)

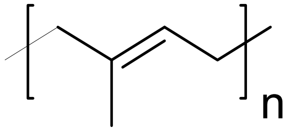
- atactic: no long-range order, amorphous
- isotactic: helical, crystalline; best mechanical properties
- syndiotactic: crystalline, zig-zag conformation

- melting point: at < st < it
  $120<130<165\ ^{o}C$
- crystallinity: st < it

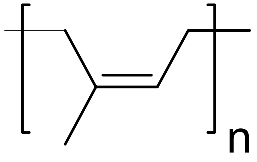
- industry: mainly isotactic PP

Structure of polymers – isomers 1

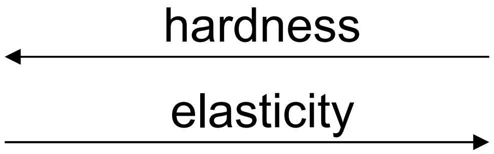
***cis* – *trans* isomers:**
poly(isoprene)



trans: guttapercha



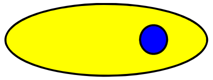
cis: natural rubber



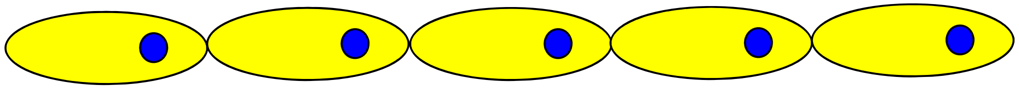
hardness

elasticity

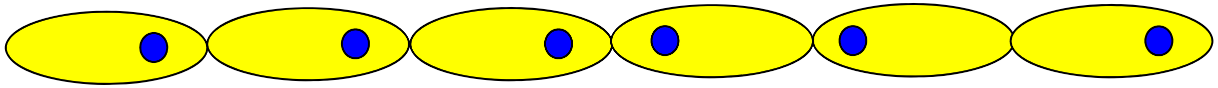
head-tail/head-head and tail-tail-polymers:
Vinyl polymers



tail head

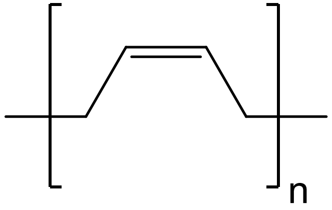


head-tail

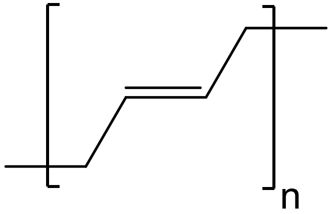


head-head **tail-tail**

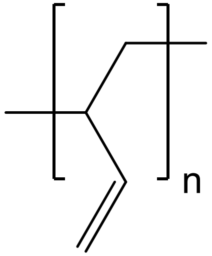
Geometric isomerism - poly(butadiene)



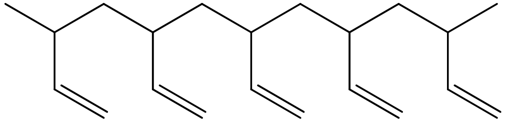
cis-1,4-poly(butadiene) (a)



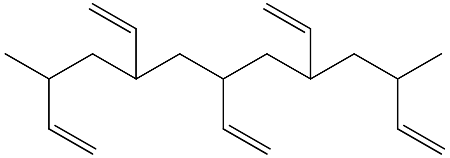
trans-1,4-poly(butadiene) (b)



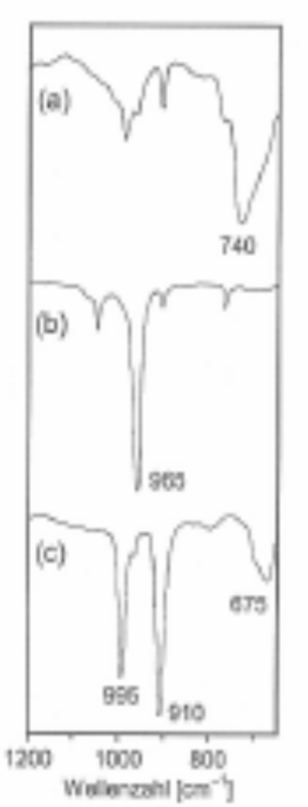
1,2-poly(butadiene) (c)



isotactic



syndiotactic 1,2-poly(butadiene)

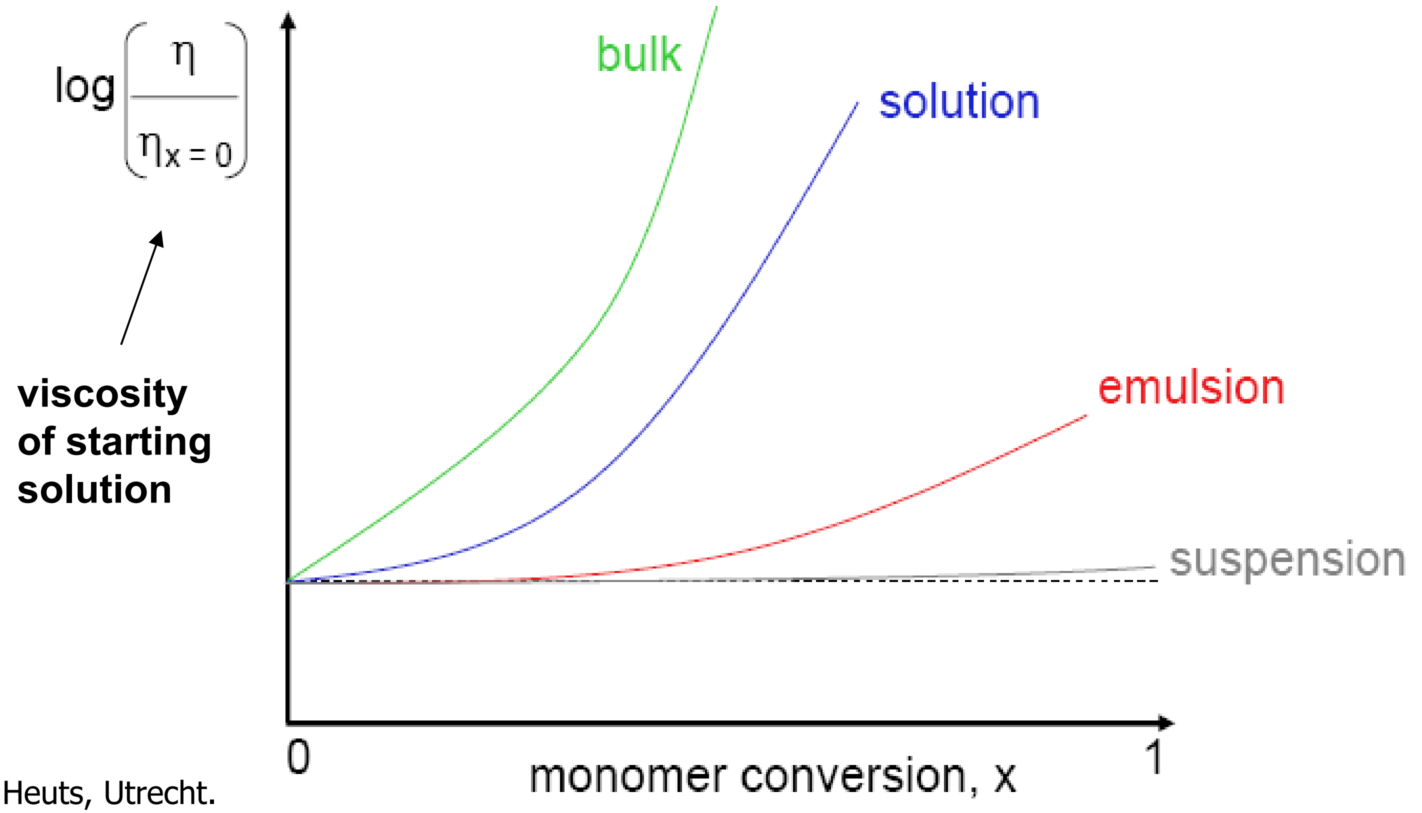


out-of-plane CH vibrations

www.chemgapedia.de; Tieke

Homogeneous: Bulk: With monomer only
Solution: In a solvent

Heterogeneous: Emulsion: With monomer dispersed in an aqueous phase
Suspension: In a solvent
[Gas phase: In gaseous monomer, solid catalyst]



Lecture Prof. Heuts, Utrecht.

Polymerization of the monomer without any solvent
Polymer is dissolved in the monomer
Low conversions → residual monomer is stripped off

Advantages:	Disadvantages:
➢ Pure products, freedom from contaminations → high optical clarity ➢ No solvent ➢ Polymerization → endform (*e.g.* sheets)	➢ Highly increasing viscosity → difficult to stir → difficult heat removal ➢ Very broad molar mass distribution ➢ Removal of residual monomer is necessary ➢ Viscous polymer/monomer solution is difficult to handle

Used for polystyrene, poly(vinyl chloride), PMMA
PMMA sheets: Unstirred reaction: Prepolymer (lower molar mass)
main polymerization to higher molar mass
→ better heat control

Solution polymerization

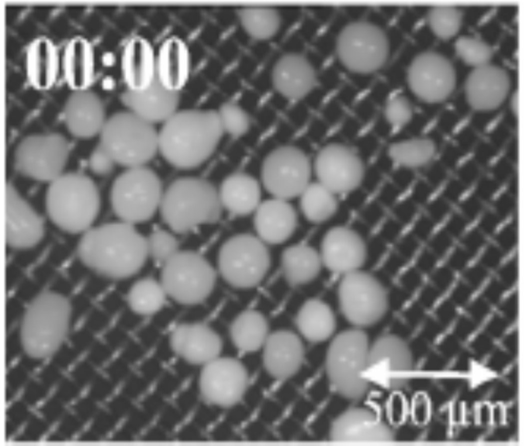
Polymerization of the monomer in the presence of a solvent
Polymer and monomer are dissolved in the solvent

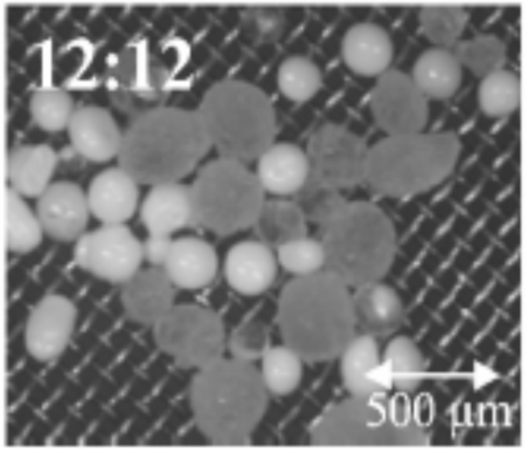
Advantages:	Disadvantages:
➢ Lower viscosities → better control of the gel effect ➢ Better temperature control ➢ Polymer solution can be used for some applications (coatings)	➢ Removal and recycling of solvents ➢ Toxicity/flammability of solvents ➢ Chain transfer to solvent

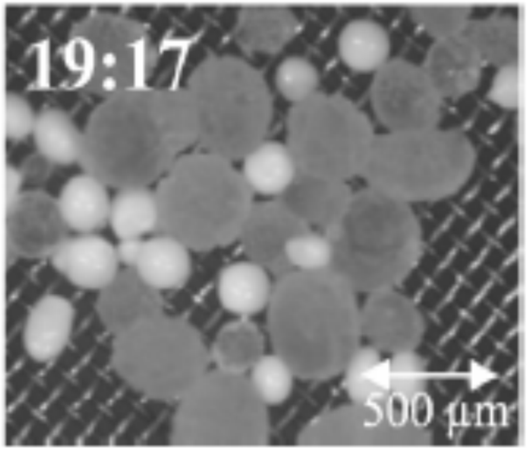
Used for poly(vinyl acetate) [methanol, *tert*-butanol], ethylene [*e.g.,* cyclohexane]

Gasphase polymerization

Polymerization of the monomer in the gas-phase
Catalyst is immobilized on particle (mainly metal catalysts)
Only for gaseous monomers (*e.g.* ethylene, butadiene)

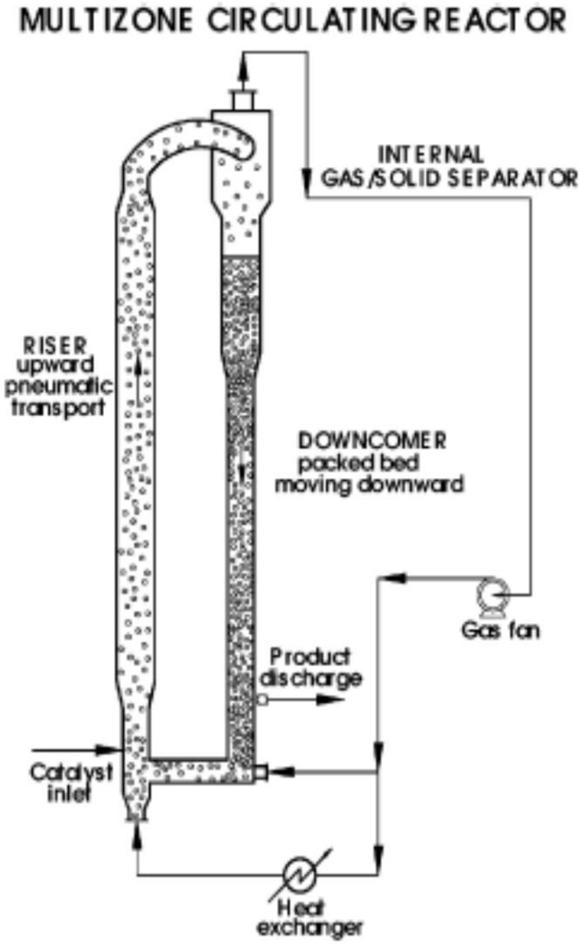






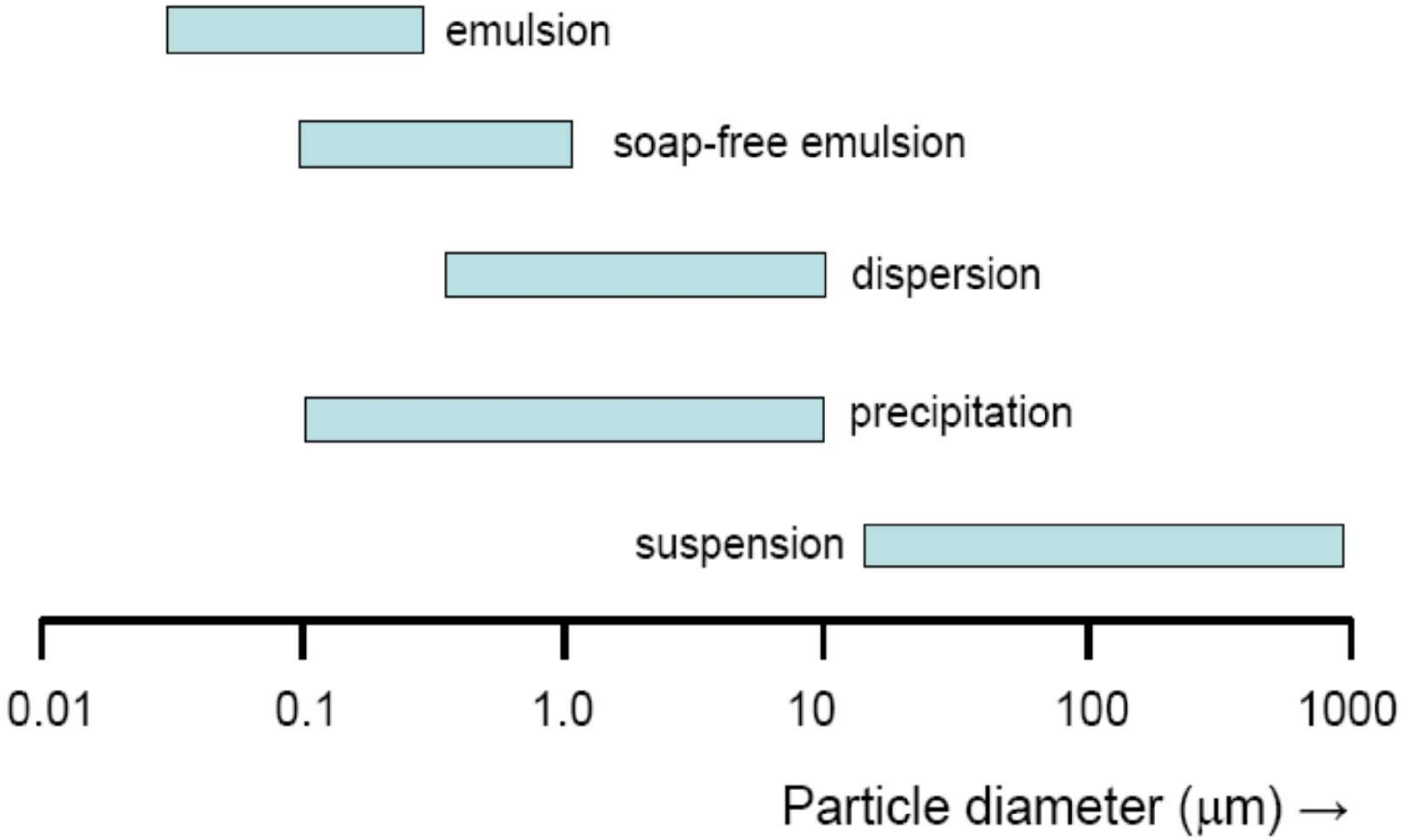
growing particles
(polybutadiene)
time in minutes

K. Zoellner, K.-H. Reichert, *Chem. Eng. Sci.* **2001**, *56*, 4099-4106.



Heterogeneous polymerization: two phase system, polymer particles are formed immiscible with liquid phase

Size of polymer particles



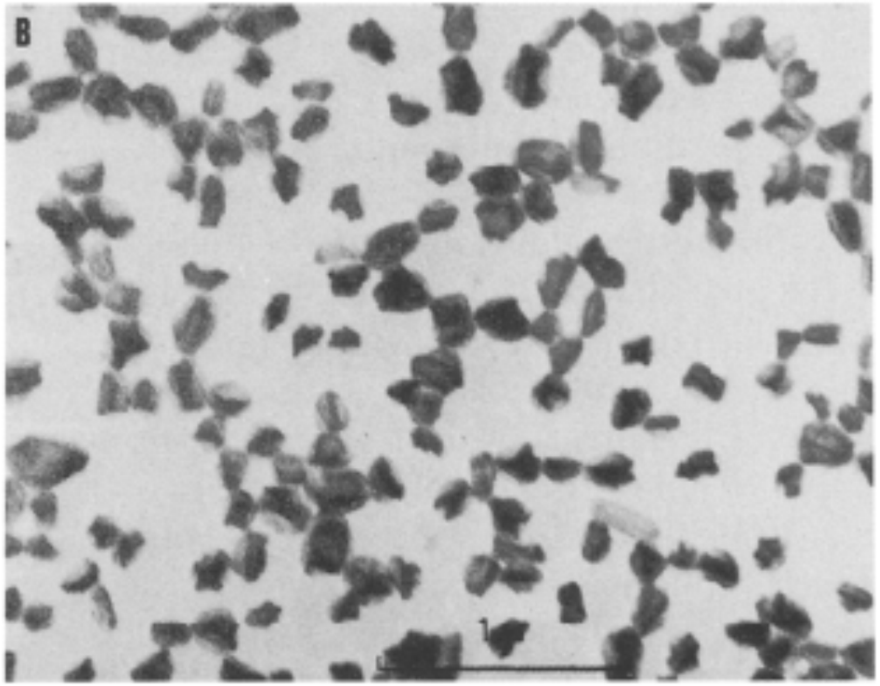
Lecture Prof. Heuts, Utrecht.

Precipitation polymerization

Polymerization of the monomer in the presence of a solvent or in bulk
Polymer is not soluble in the monomer or the solvent
Monomer and initiator are soluble
Monomer does not swell the polymer

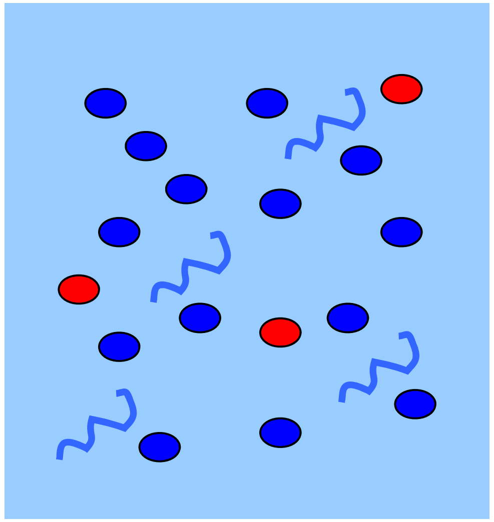
→ **polymer precipitates** (irregularly shaped particles)

used for polymerization
of acrylonitrile in water



Lecture Prof. Heuts, Utrecht.

Monomer, initiator and stabilizer are soluble in the solvent
Polymer is not soluble in the monomer or the solvent
Precipitated polymer forms stabilized particles, swollen by monomer
Polymerization in particles (monodisperse particles)

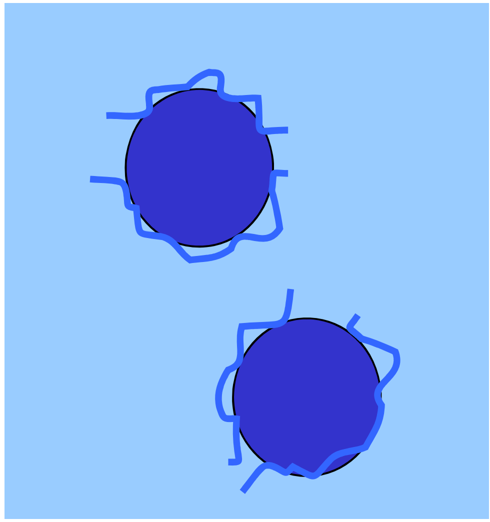


Polymerization →

● **monomer**

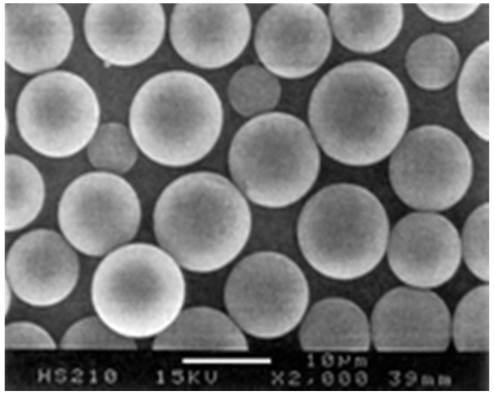
● **initiator**

∿ **stabilizer**



0.1-10 µm

e.g. polystyrene or PMMA in hydrocarbons or alcohols

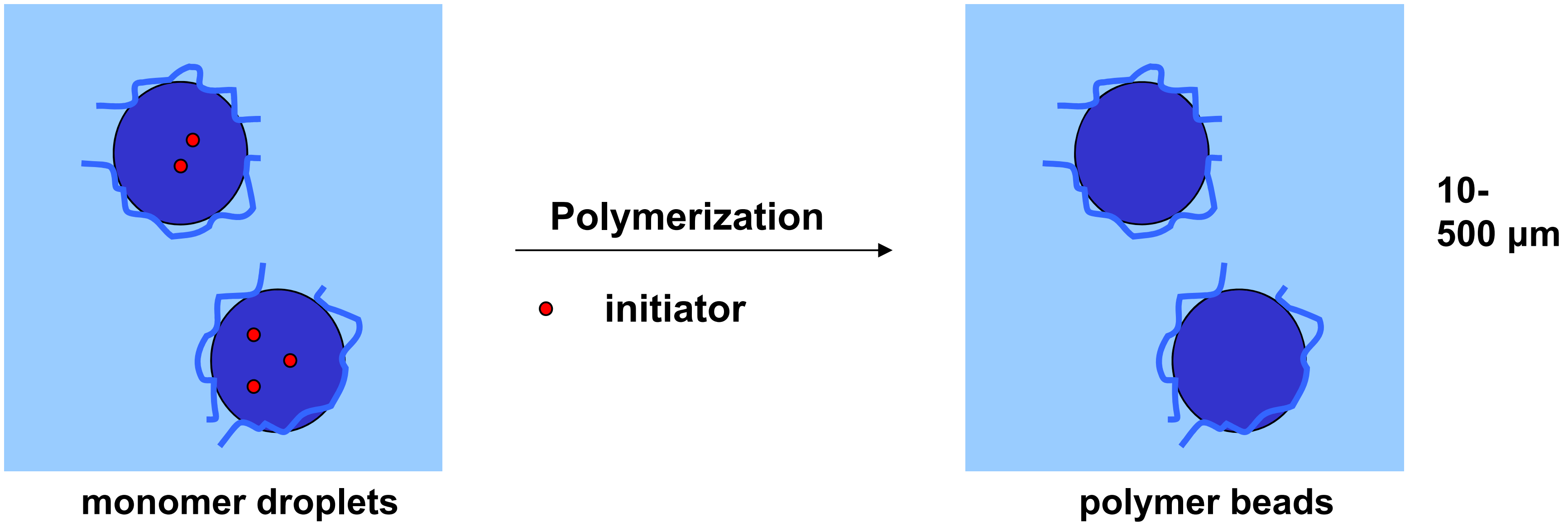


SEM of polystyrene in $scCO_2$,
AIBN as initiator
and fluorinated polyacrylate as stabilizer

A. I. Cooper, *J. Mater. Chem.* **2000**, *10*, 207-234.

Suspension polymerization 1

Monomer and initiator are not soluble in the solvent
Polymer is not soluble in the monomer or the solvent
Colloidal stabilizer (*e. g.* polyvinylalcohol)
Monomer forms stabilized droplets, initiator is dissolved in the monomer droplets
Polymerization in particles (monodisperse particles)
“Mini-bulk polymerization” → same kinetics
Improved heat transfer



Suspension polymerization 2

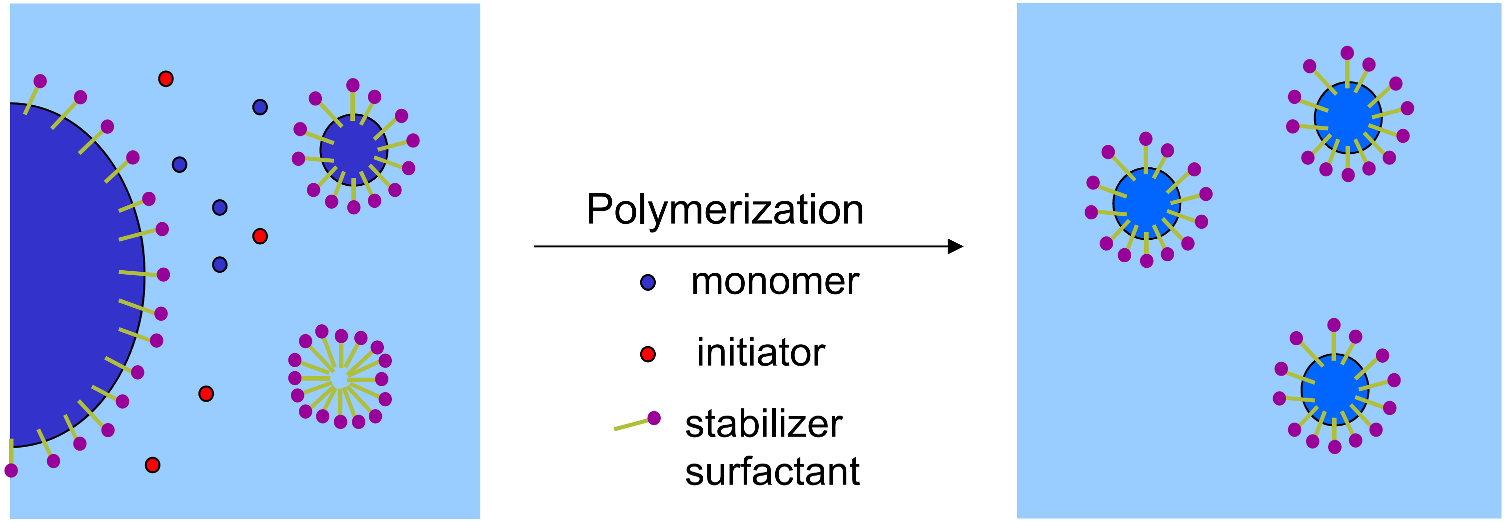
Advantages:	Disadvantages:
➢ Low viscosity ➢ Good heat transfer ➢ Easy separation of polymer and liquid phase (filtration) ➢ Product: Polymer beads (easy to handle)	➢ Mostly only batch reactor ➢ Reactor wall fouling

Used for polystyrene, poly(vinyl chloride), PMMA
Ion exchange resins

www.indiamart.com.

Emulsion polymerization 1

Monomer and polymer are not soluble in the solvent (water)
Initiator is soluble in the solvent
Monomer droplets are dispersed in the non-solvent, micelle forming surfactant
Polymerization takes place in nucleated polymer particles
Large monomer droplets, micelles and micelles filled with monomer



Polymerization

● monomer

● initiator

stabilizer surfactant

0.05 - 5 µm

monomer droplet

micelle filled with monomer

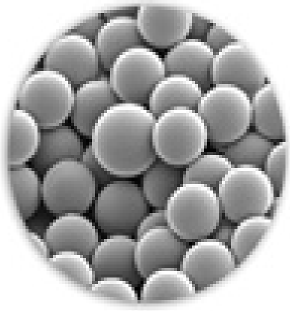
micelle

latex particles

Emulsion polymerization 2

Advantages:	Disadvantages:
➢ Low viscosity ➢ Good heat transfer ➢ Easy separation of polymer and liquid phase (filtration) ➢ High molar masses ➢ Direct application of latices	➢ Mostly only batch reactor ➢ Reactor wall fouling ➢ Separation costs ➢ Surfactant is necessary

Used for poly(vinyl chloride), polyvinylacetate, coatings, etc.
Application for latices: Paintings and coatings, glues and adhesives
textiles (fleece binder, textile coating)



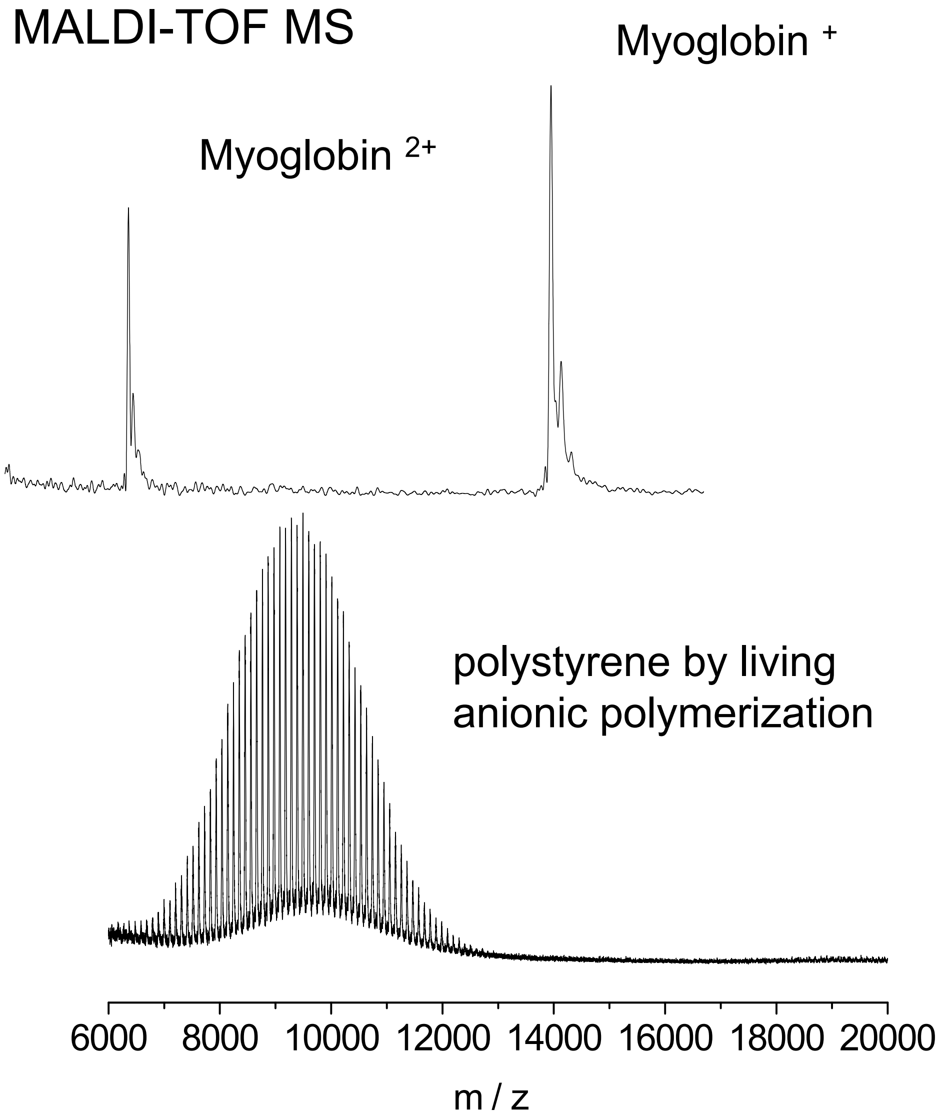
polystyrene latex particles

www.microgenecs.com.

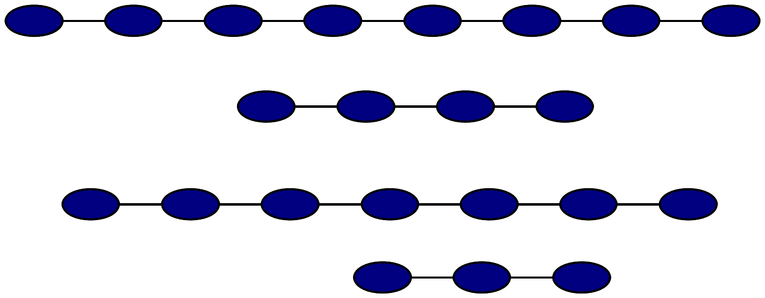
Emulsion vs. suspension polymerization

	Suspension polymerization	**Emulsion polymerization**
Monomer-water ratio	1 : 1 – 4 : 1	Typically < 2: 1
Initiator	Oil soluble	Water soluble
Stabilizing colloid/surfactant	< 0.1 weight%	1 – 5 weigth% > critical micellation concentration
Locus of polymerization	Stabilized colloid monomer droplets	Polymer particles (micelles)
Final particle size	10 – 500 µm	0.05 – 5 µm
Molecular weight	≈ bulk	≥ bulk

Monodispersity vs. polydispersity



Synthetic polymers do not have a specific molar mass.
They have a molar mass distribution.



Number average molar mass (M_n)

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i w_i}{\sum_i \frac{w_i}{M_i}}$$

N_i – number of polymer-chains with weight M_i

w_i – weigthfraction of polymerchains with weight M_i

This value is defined as the summation of the molar mass of a chain times the number of moles having that weight, divided by the total moles of polymer.

The number average molar mass of a polymer can be determined by
Osmometry,
End-group titration,
Colligative properties (cryoscopy, ebulliometry),
SEC,
MALDI-TOF-MS.

Weight average molar mass (M_w)

$$M_w = \frac{\sum_i N_i M_i^{2}}{\sum_i N_i M_i} = \frac{\sum_i w_i M_i}{\sum_i w_i}$$

N_i – number of polymer-chains with weight M_i

w_i – weigthfraction of polymerchains with weight M_i

Weigh a number of polymer molecules, add the squares of these weights, and then divide by the total weight of the molecules.

The weight average molar mass of a polymer can be determined by
Light scattering (LS),
Small angle neutron scattering (SANS),
Sedimentation velocity,
SEC,
MALDI-TOF-MS.

Sedimentation average molar mass (M_z)

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i}$$

N_i – number of polymer-chains with weight M_i

w_i – weigthfraction of polymerchains with weight M_i

The sedimentation average molar mass of a polymer can be determined by Sedimentation equilibrium.

Viscosity average molar mass (M_v)

$$M_\eta = \left(\frac{\sum N_i M_i^{1+\alpha}}{\sum N_i M_i} \right)^{\frac{1}{\alpha}}$$

usually:

$0.5 \le \alpha \le 1$ → $M_n \le M_\eta \le M_w$

$\alpha = -1 \rightarrow M_\eta = M_n$

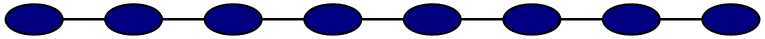
$\alpha = 1 \rightarrow M_\eta = M_w$

→ detailed information will follow:
Viscosimetry

Degree of polymerization

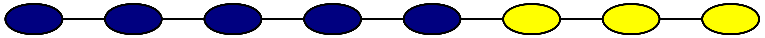
$$DP = \frac{M_{macromolecule}}{M_{reapeating\ unit}}$$

Number of building blocks per macromolecule



DP =9

different building blocks → determination of each fraction to obtain DP

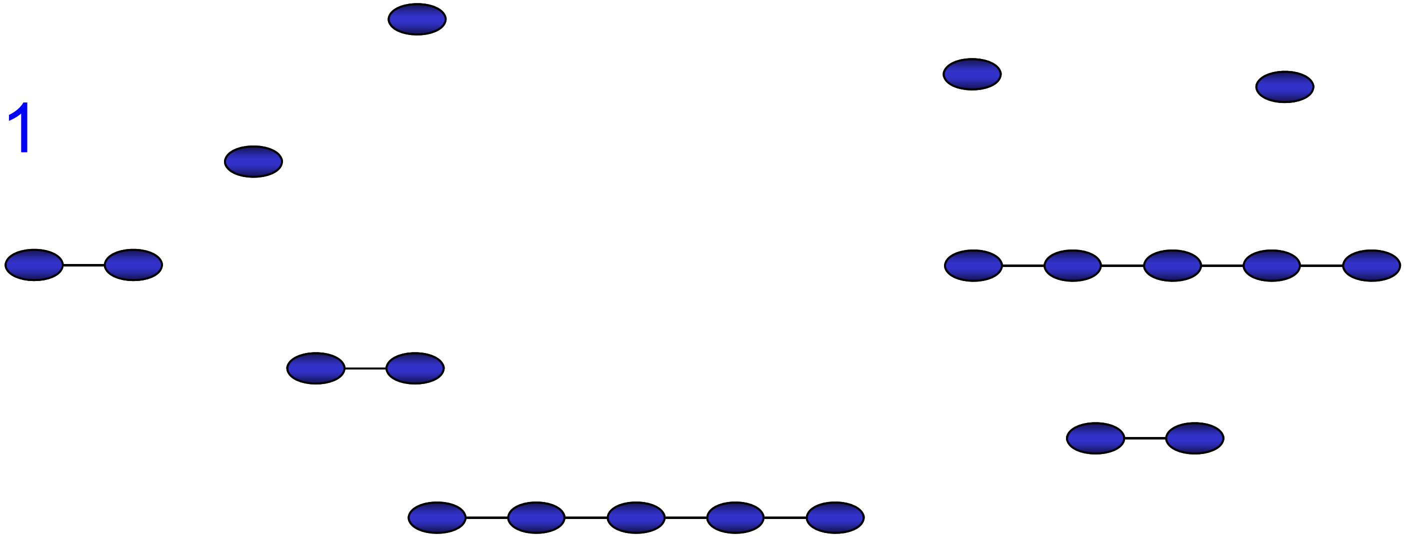


DP = 8 (5 A + 3 B)

Example 1

Sample with the following polymers
(number is equal to a certain molar mass or repeating unit):

1,1,1,1
2,2,2
5,5



Calculate M_n, M_w and M_z

Example 1

Number average molar mass

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

$$M_n = \frac{(4\times1)+(3\times2)+(2\times5)}{4+3+2} = \frac{4+6+10}{9} = \frac{20}{9} = 2.22$$

Weight average molar mass

$$M_w = \frac{\sum_i N_i M_i^{\;2}}{\sum_i N_i M_i}$$

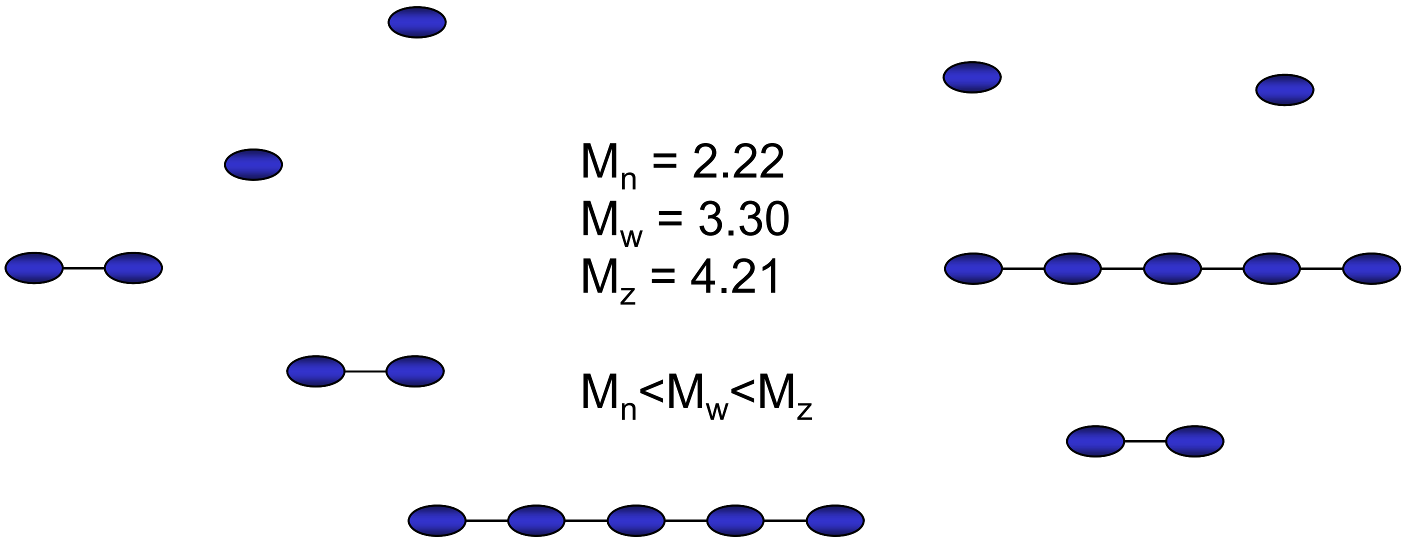
$$M_w = \frac{(4\times1^2)+(3\times2^2)+(2\times5^2)}{(4\times1)+(3\times2)+(2\times5)} = \frac{4+12+50}{4+6+10} = \frac{66}{20} = 3.30$$

Example 1

Sedimentation average molar mass

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2}$$

$$M_z = \frac{(4\times 1^3)+(3\times 2^3)+(2\times 5^3)}{(4\times 1^2)+(3\times 2^2)+(2\times 5^2)} = \frac{4+24+250}{4+12+50} = \frac{278}{66} = 4.21$$



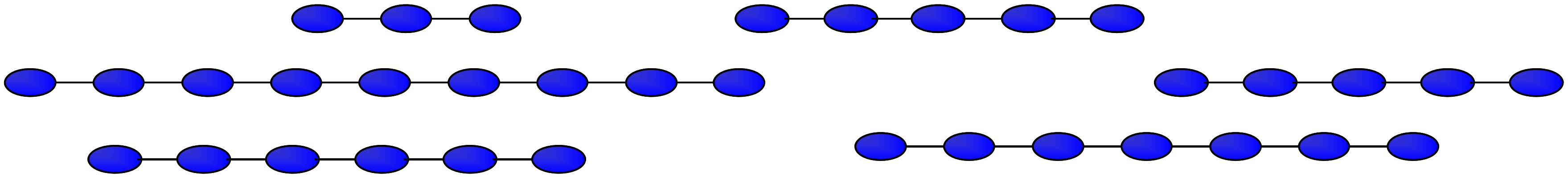
$M_n = 2.22$
$M_w = 3.30$
$M_z = 4.21$

$M_n < M_w < M_z$

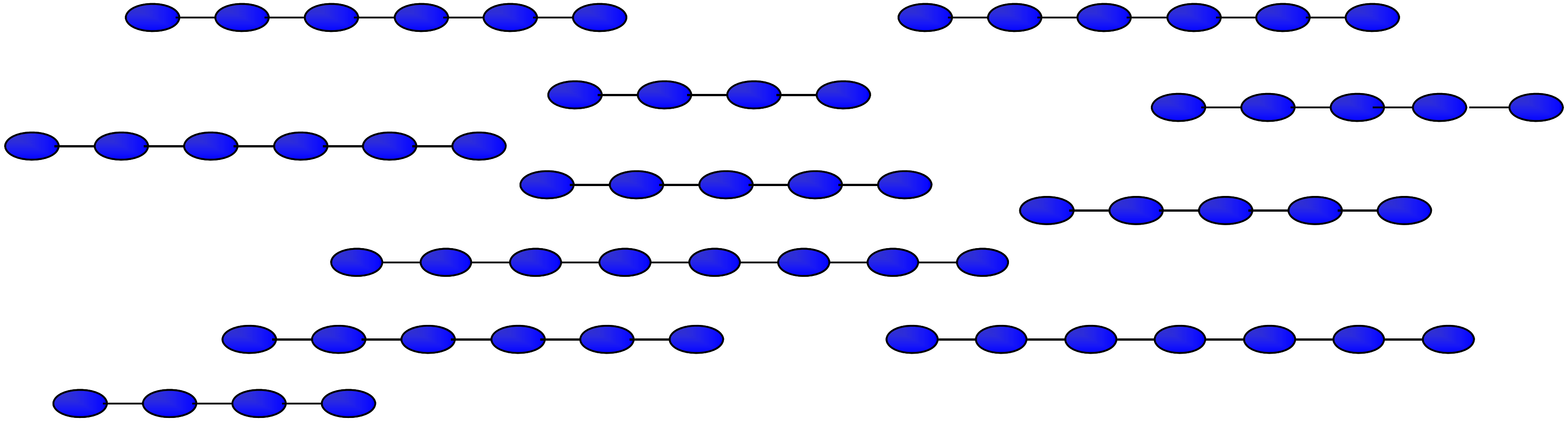
Example 2

More realistic:

M	0	1	2	3	4	5	6	7	8	9	10
N	0	0	0	1	2	5	4	2	1	1	0



Calculate M_n, M_w and M_z



Example 2

More realistic:

M	0	1	2	3	4	5	6	7	8	9	10
N	0	0	0	1	2	5	4	2	1	1	0

$$M_n = \frac{(1\times3)+(2\times4)+(5\times5)+(4\times6)+(2\times7)+(1\times8)+(1\times9)}{1+2+5+4+2+1+1} =$$

$$M_n = \frac{3+8+25+24+14+8+9}{16} = \frac{91}{16} = 5.69$$

$$M_w = \frac{(1\times3^2)+(2\times4^2)+(5\times5^2)+(4\times6^2)+(2\times7^2)+(1\times8^2)+(1\times9^2)}{(1\times3)+(2\times4)+(5\times5)+(4\times6)+(2\times7)+(1\times8)+(1\times9)} =$$

$$M_w = \frac{9+32+125+144+98+64+81}{91} = \frac{553}{91} = 6.07$$

Example 2

More realistic:

M	0	1	2	3	4	5	6	7	8	9	10
N	0	0	0	1	2	5	4	2	1	1	0

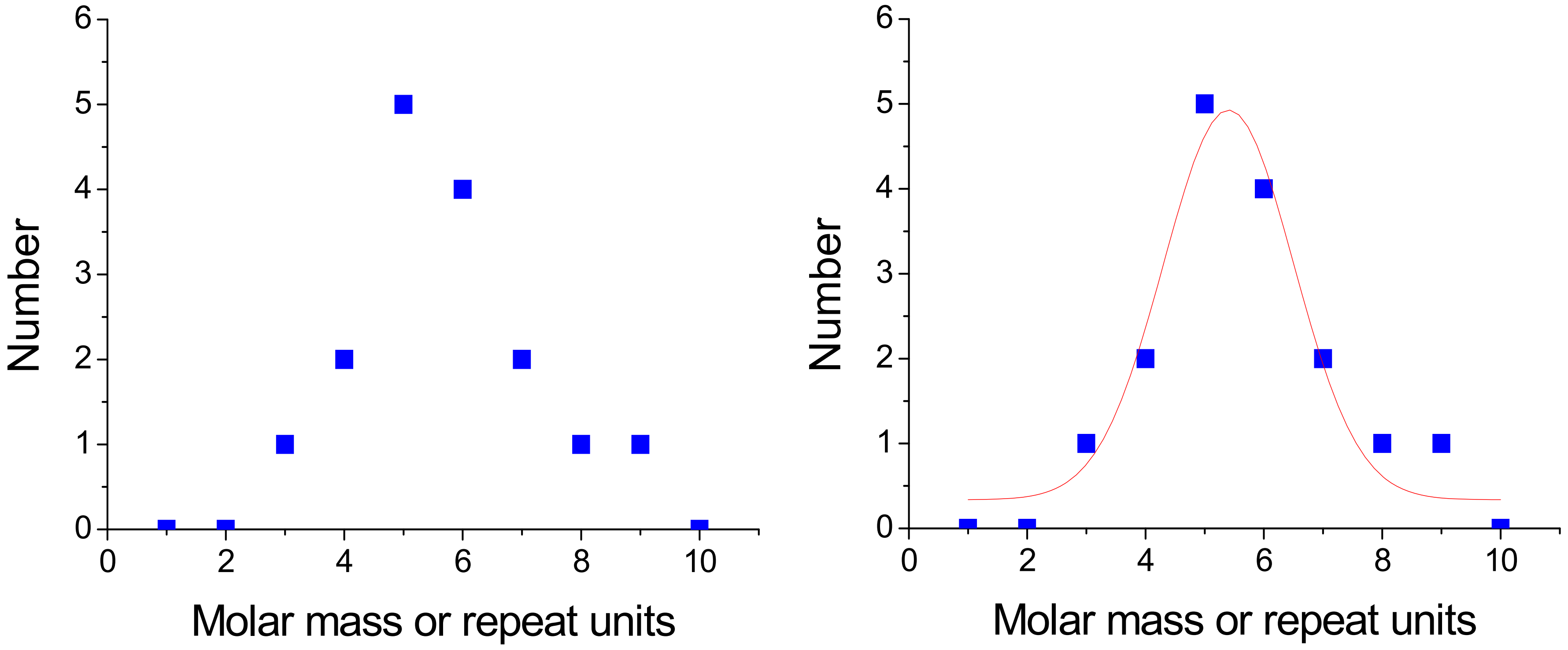
$$M_z = \frac{(1\times 3^3)+(2\times 4^3)+(5\times 5^3)+(4\times 6^3)+(2\times 7^3)+(1\times 8^3)+(1\times 9^3)}{(1\times 3^2)+(2\times 4^2)+(5\times 5^2)+(4\times 6^2)+(2\times 7^2)+(1\times 8^2)+(1\times 9^2)} =$$

$$M_z = \frac{27+128+625+864+686+512+729}{553} = \frac{3571}{553} = 6.46$$

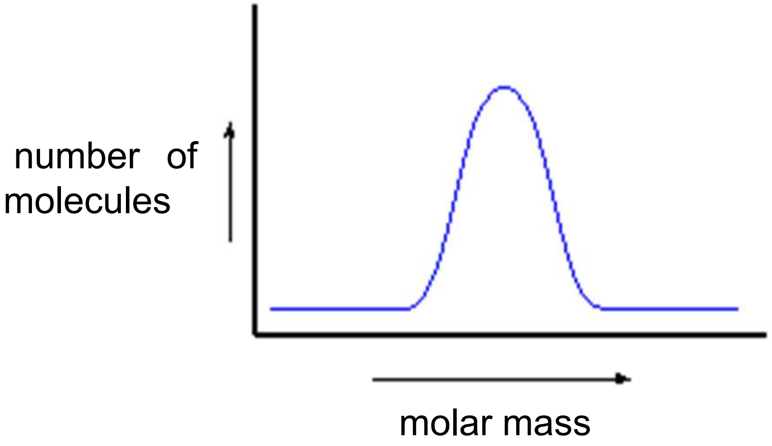
$M_n = 5.69$
$M_w = 6.07$
$M_z = 6.46$
$M_n < M_w < M_z$

Example 2 – graphical illustration

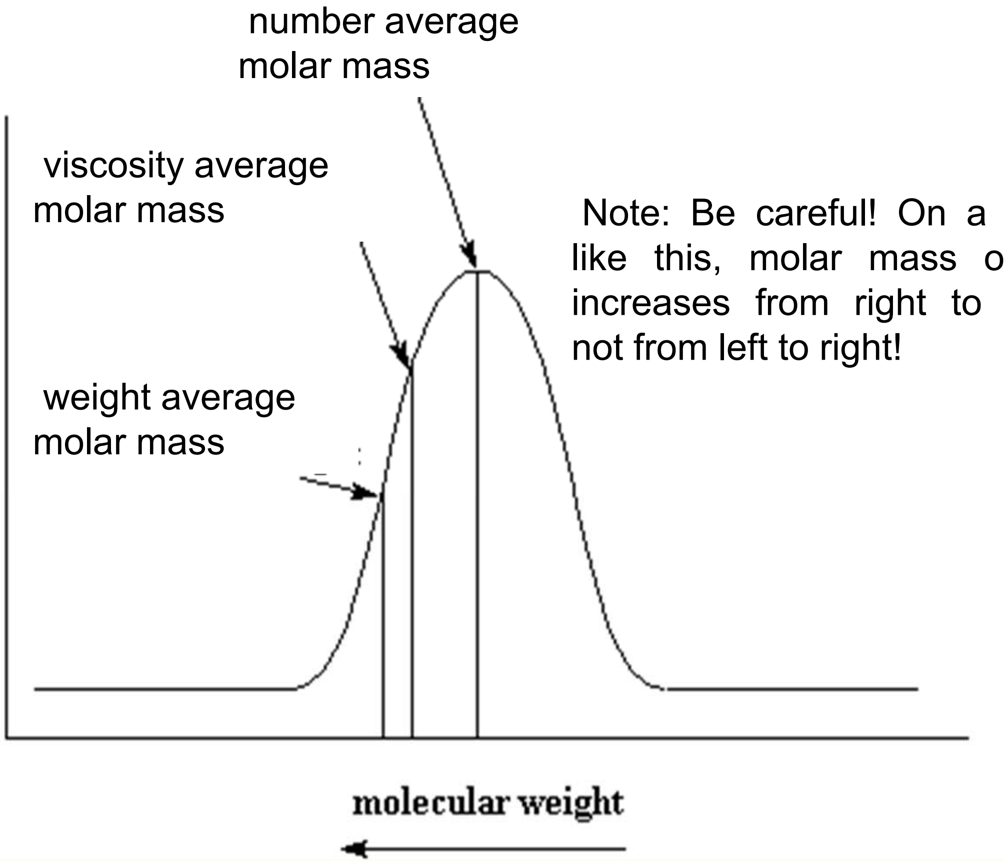
$M_n = 5.69$
$M_w = 6.07$
$M_z = 6.46$



General discussion



$$Mn \le M\eta \le Mw \le Mz$$



Note: Be careful! On a plot like this, molar mass often increases from right to left, not from left to right!

Polydispersity index (PDI) - Dispersity

The dispersity (Đ) / polydispersity index (PDI) is the ratio of the weight average molar mass to the number average molar mass.

The Đ / PDI indicates the distribution of individual molar masses in a batch of polymers.

$$PDI = \frac{M_w}{M_n}$$

Example 1:

$$PDI = \frac{M_w}{M_n} = \frac{3.30}{2.22} = 1.49$$

Example 2:

$$PDI = \frac{M_w}{M_n} = \frac{6.07}{5.69} = 1.07$$

Example 3

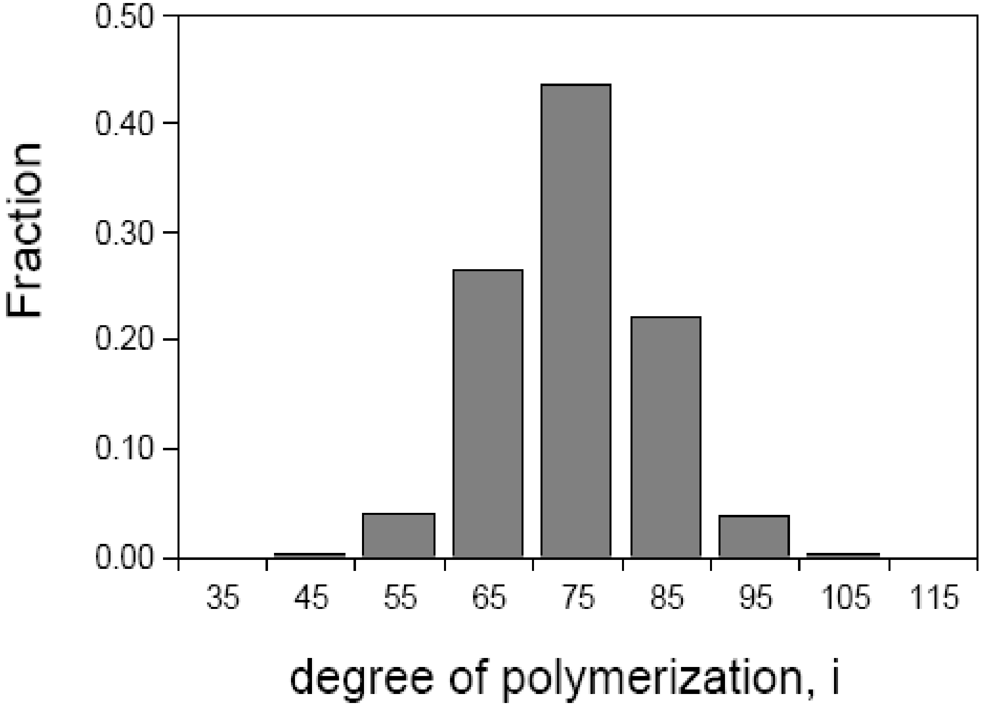
Comparison of two polymers with same M_n

P1	M	46	47	48	49	50	51	52	53	54
	N	2	1	4	5	3	8	0	4	1
P2	M	11	21	34	40	50	65	72	83	93
	N	3	6	5	6	3	8	4	4	2

	M_n	M_w	DPI
P1	50	50.09	1.002
P2	50	61.28	1.226

Example 4

Polymer with DP_n = 75 and PDI 1.01 → nearly monodisperse?



only 5% of the chains DP = 75
only 47% have DP = 75±5

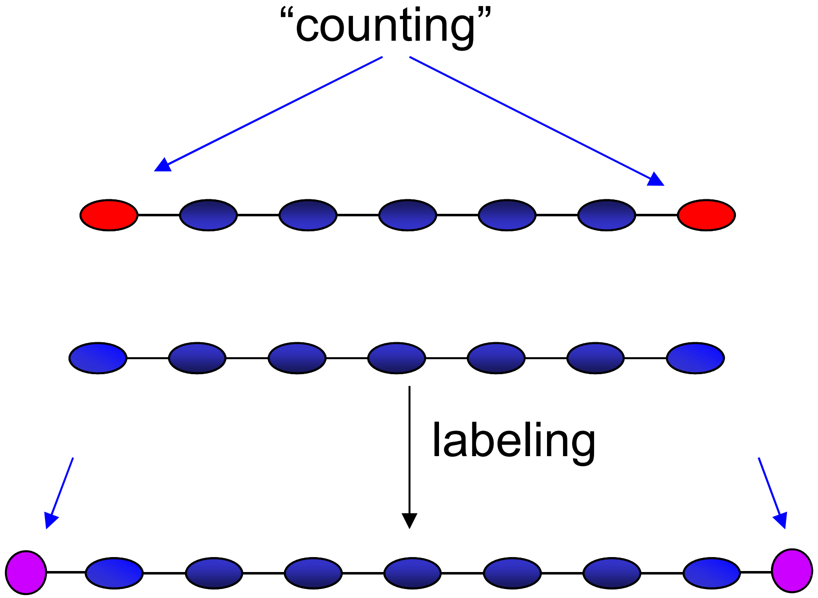
Lecture Heuts

Methods

method	**type**	**range**	**average**
membrane osmometry	absolut	$10^4 – 10^6$	M_n
endgroup analysis	absolut	$< 5\ 10^4$	M_n
vaporpressure osmometry	absolut	$< 2 \times 10^4$	M_n
ebulliometry / cryoscopy	absolut	$< 5\ 10^4$	M_n
light scattering	absolut	$> 5\ 10^3$	M_w
MALDI-TOF-MS ESI-TOF-MS	absolut	up to 10^6	$M_{n,}\ M_w$
analytical ultracentrifuge	absolut	100 to $5\ 10^8$	M_w, M_z
viscosimetry in diluted solutions / viscosimetry of melting	relative	$>10^2$	M_η
gelpermeation chromatography **size exclusion chromatography**	relative	$< 5\ 10^6$	$M_{n,}\ M_w$

Endgroup analysis

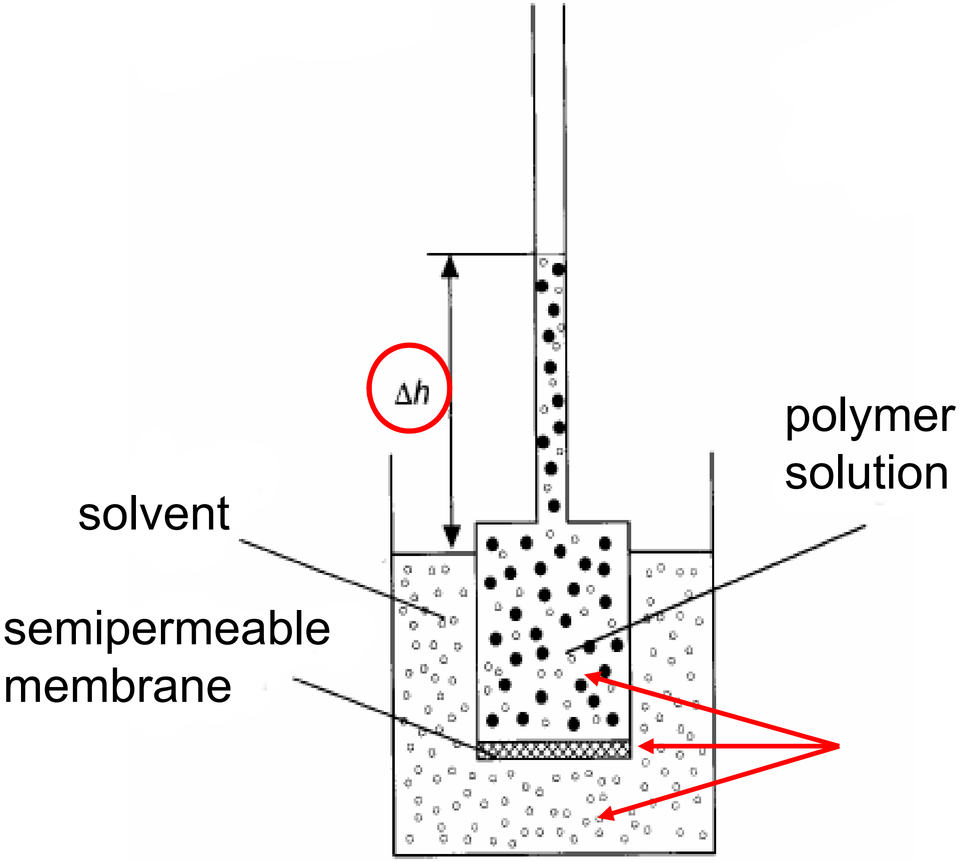
Analysis of endgroups by:
- Titration
- NMR-spectroscopy
- UV/vis-spectroscopy
- IR-spectroscopy
- Radiochemical
- Labeling of endgroups



- Most common method (→ M_n): titration (chemical reactions on endgroup)
- Number of reacted end groups can be quantified by spectroscopy or pH measurement
- Number of endgroups in known amount of polymer → M_n
- Difficulties: solubility, viscosity, steric hindrance, mechanisms of initiation and termination (→ which endgroup? one or two?)
- Best suited in the range from 5,000 to 10,000 molar mass

Photo source: http://www.dartmouth.edu/~chemlab/techniques/titration.html.

Membrane osmometry



Determination of M_n

Two chambers, separated by semipermeable membrane

Polymer solution ←→ pure solvent

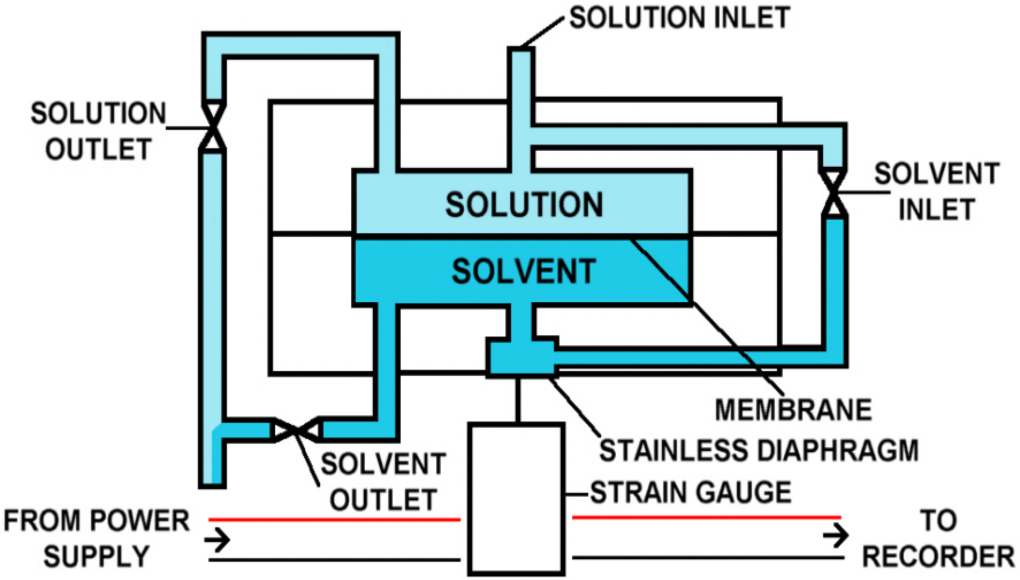
Solvent diffusion of solvent into the polymer solution

Δh proportional to osmotic pressure

Tieke, www.gonotec.com/img/GER/bild_osmomat90.gif

Osmometry 2

membrane osmometer



http://www.uicinc.com/SysSheet_HTMs/Model230.htm.

Osmometry 3

$$\Pi = \rho \cdot g \cdot \Delta h$$

correlation osmotic pressure and Δh

can be measured

osmotic pressure → molecular weight (analogue van't Hoff: equation for gases)

$$\Pi \cdot V = n \cdot R \cdot T$$

$$\Pi \cdot V = R \cdot T \cdot \frac{m}{M}$$

only for infinite
diluted solutions

$$\Pi = \left(\frac{m}{V}\right) \cdot \frac{R \cdot T}{M} = \frac{c \cdot R \cdot T}{M} = \frac{c \cdot R \cdot T}{\overline{M}_n}$$

monodisperse
polydisperse
sample

Π – osmotic pressure
ρ – density of solution
g – acceleration of gravity
(Erdbeschleunigung)
V – volume of solution

T – temperature [K]
n = number of mols (polymer)
R – gas constant (83143 mbar mL/mol K)
M – molar mass

Osmometry 4

$$\frac{\Pi}{c} = \left(\frac{R \cdot T}{\overline{M}_n}\right) + A_2 \cdot c + A_3 \cdot c^2 + \dots$$

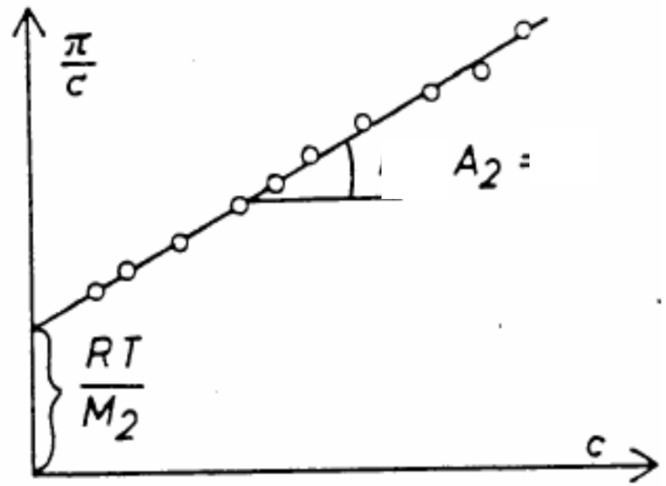
A_2 – virial coefficient
polymer – solvent interaction

approximation

real solutions

measurement of osmotic pressure
for different concentrations

$$\overline{M}_n = \frac{RT}{(\pi / c)_{c \to 0}}$$



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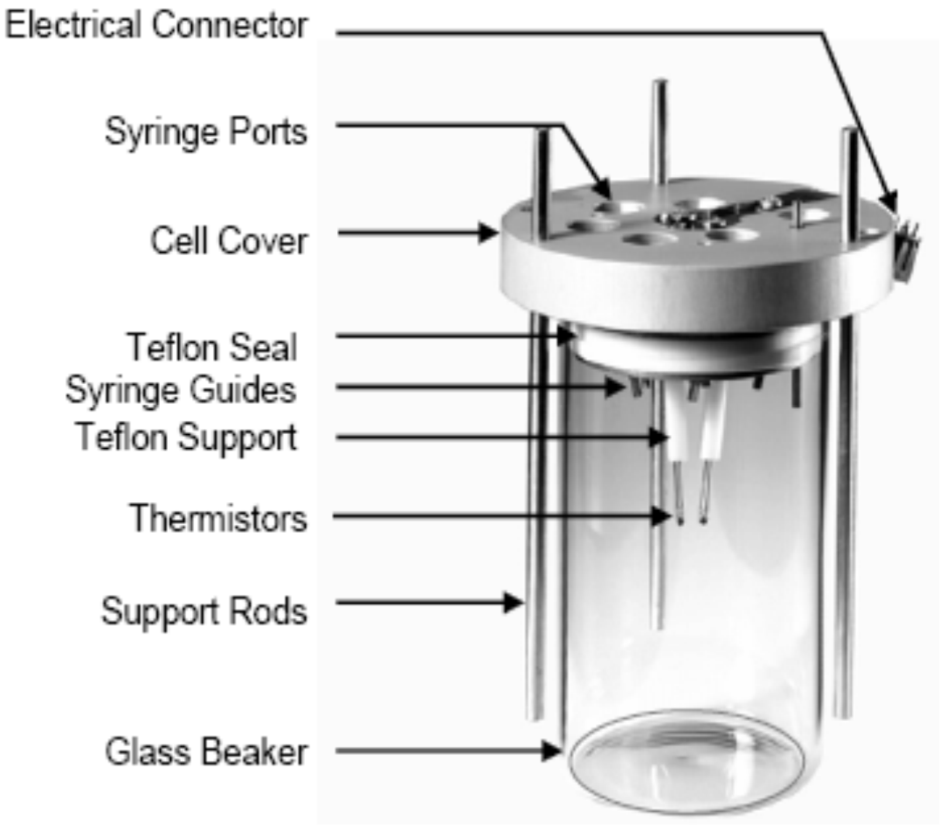
Osmometry 6

Vapor pressure osmometry



www.knauer.net.

Vapor pressure osmometry – theory I

$$\frac{p_1}{p_1^0} = x_1 = 1 - x_2$$ Raoult's law

$$1 - \frac{p_1}{p_0^1} = \frac{\Delta p}{p_1^0} = x_2 = \frac{n_2}{n_1 + n_2}$$

$$\frac{\Delta p}{p_0^1} \approx \frac{n_2}{n_1}$$ very diluted solutions

p_1 – vapor pressure of solution
$p^0{}_1$- vapor pressure of solvent
x_1 – mole fraction of solvent
Δp – relative vapor pressure lowering (pure solvent → solution)
n – number of mols

Tieke; Lechner, Gehrke, Nordmeier.

Vapor pressure osmometry – theory II

Measurement in saturated (solvent) atmosphere

Droplet of polymer solution is placed on thermistor

Beginning: the droplet has the same temperature as the surrounding

Droplet: lower vapor pressure → condenzation of solvent → heat of condenzation

Temperature difference between droplet and surrounding

$$\frac{\Delta T_{th}}{c} = \frac{R \cdot T^2}{L_1 \cdot \rho_s} \cdot \frac{1}{\overline{\overline{M_n}}}$$

ΔT_{th} – temperature difference theory
c – concentration of polymer solution
R – gas constant
T – temperature [K]
L_1 – vaporization heat of solvent (per g)
ρ_s – density of solution

→ Clausius-Clapeyron

Tieke; Lechner, Gehrke, Nordmeier.

Vapor pressure osmometry – theory III

Thermal contact between droplet and surrounding:

$$\Delta T_{\exp} = const. \cdot \Delta T_{th}$$

$$\frac{\Delta T_{\exp}}{c} = const. \cdot \frac{R \cdot T^2}{L_1 \cdot \rho_s} \cdot \frac{1}{\overline{M}_n}$$

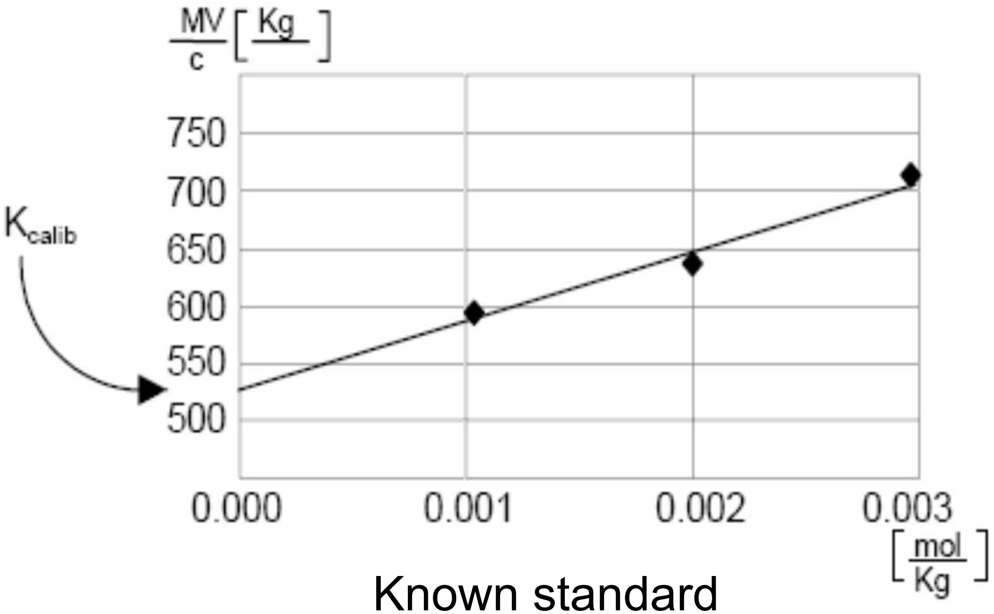
$$\frac{\Delta T_{\exp}}{c} = K_E \cdot \frac{1}{\overline{M}_n}$$

↑ calibration with known model substance

ΔT_{th} – temperature difference (theory)
ΔT_{exp}- experimental difference
c – concentration of polymer solution
R – gas constant
T – temperature [K]
L_1 – vaporization heat of solvent (per g)
ρ_s – density of solution
K_E – constant (calibration)

Tieke; Lechner, Gehrke, Nordmeier.

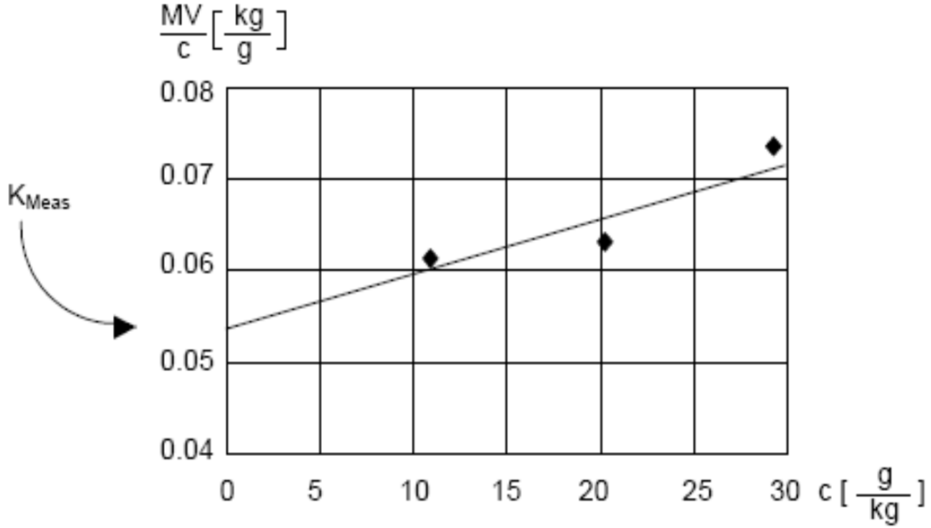
Osmometry 10



MV – measured value

Known standard

Polymer sample



$$M\left[\frac{g}{mol}\right] = \frac{K_{calib}}{K_{Meas}}$$

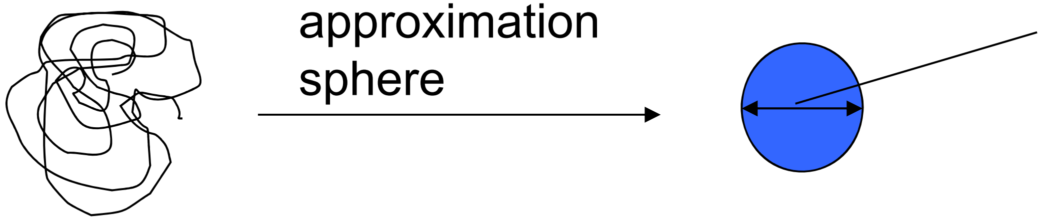
www.knauer.net.

Solution viscosity 1

Polymer solutions are viscous. Viscosity is influenced by:

Solvent
Kind of polymer
Molar mass of polymer
Concentration of polymer
Temperature

Theory – Kuhn's Law



approximation sphere

d – proportional to radius of gyration $\sqrt{\langle s^2 \rangle}$

ideal coil

$$\langle s^2 \rangle = K_{geometry} \cdot N = K_{geometry} \cdot \frac{M_{coil}}{M_{monomer}} = K^2 \cdot M \longrightarrow \sqrt{\langle s^2 \rangle} = K \cdot \sqrt{M}$$

M_{coil} – molar mass of the coil
$M_{monomer}$ – molar mass of the monomer

$$\rho_{sphere} = \frac{m}{\frac{1}{6}\pi \cdot d^3} \Rightarrow \frac{M}{\sqrt{M}^3} \cdot K_\rho = \frac{K_\rho}{\sqrt{M}} = \rho_{equ.}$$

Tieke; Lechner, Gehrke, Nordmeier.

Solution viscosity 2

$$\eta_{rel} = \frac{\eta}{\eta_0} = \left(\frac{\text{viscosity of solution}}{\text{viscosity of solvent}} \right) = 2.5 \cdot \varphi + 1$$

according to Einstein the relative viscosity η_{rel} of a solution with spherical particles depends only on volume ratio ρ of the particles and the solution

$$\varphi = \frac{V}{V_L} = \frac{\text{volume of dispersed phase}}{\text{volume of solution}}, V = \frac{m}{\rho} \Rightarrow V_{equ.} = \frac{m}{\rho_{equ.}}$$

problem: Is m the mass of the polymer plus solvent shell or the mass of the coil without solvent shell?

⟶ solution: We use equivalent spheres, which behave like the coil.

Tieke; Lechner, Gehrke, Nordmeier, Lecture Prof. Menzel, TU Braunschweig.

Solution viscosity 3

$$\varphi = \frac{V}{V_L} = \frac{\text{volume of dispersed phase}}{\text{volume of solution}}, V_{equ.} = \frac{m}{\rho_{equ.}}$$

c – concentration
$V_{equ.}$ – equ. volume
$\rho_{equ.}$ – equ. density
m – mass

$$\varphi = \frac{\frac{m}{\rho_{equ.}}}{V_L} = \frac{m}{V_L} \cdot \frac{1}{\rho_{equ.}} = \frac{c}{\rho_{equ.}}$$

Einsteins viscosity law:

$$\eta_{rel} = 2.5 \cdot \varphi + 1 = \frac{2.5}{\rho_{equ.}} \cdot c + 1$$

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\eta - \eta_0}{\eta_0} = \frac{2.5}{\rho_{equ.}} \cdot c$$

specific viscosity η_{sp}

$$\eta_{red} = \frac{\eta_{sp}}{c} = \frac{2.5}{\rho_{equ.}}$$

reduced viscosity η_{red}

Tieke; Lechner, Gehrke, Nordmeier, Lecture Prof. Menzel, TU Braunschweig.

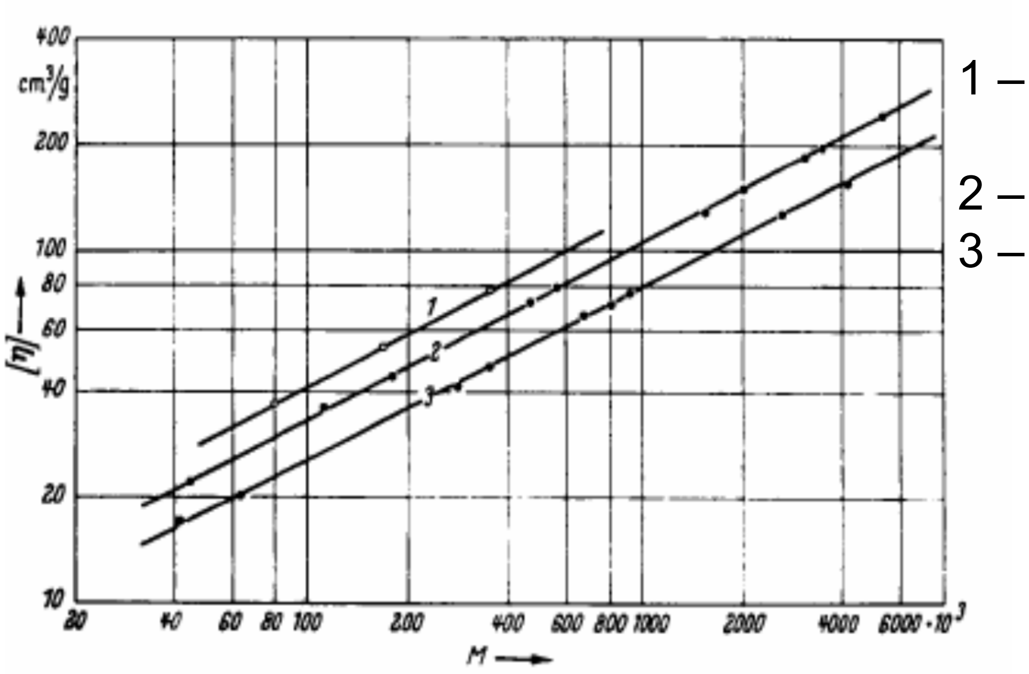
Solution viscosity 4

Staudinger:

$$\lim_{c\to 0}\frac{\eta_{sp}}{c}=[\eta]=\frac{2.5}{\rho_{equ.}}=\frac{2.5}{K_{\rho}}\cdot M^{0.5}=K_{\eta}\cdot M^{0.5}$$

$$\frac{K_{\rho}}{\sqrt{M}}=\rho_{equ.}$$

Kuhn's Law



1 – cellulosetricaprylate in γ-phenylpropylalcohol (321 K)
2 – polyisobutylene in benzene (297 K)
3 – polystyrene in cyclohexane (307 K)

These values are only obtained under these special conditions (right solvent and temperature) polymer → "ideal coil"

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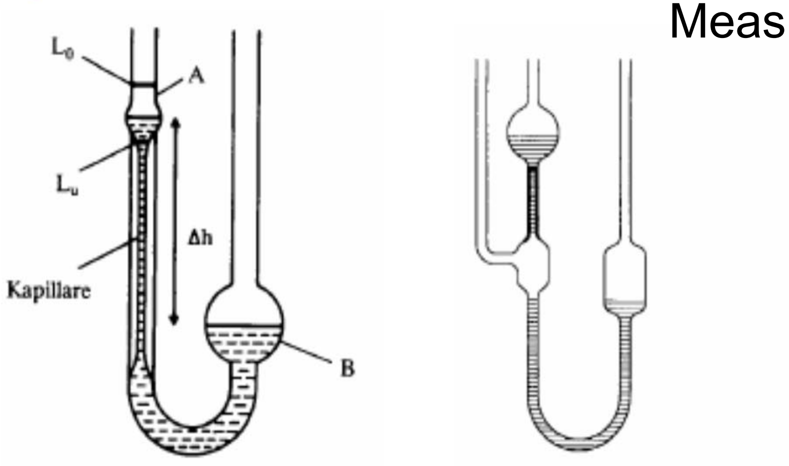
Solution viscosity 6



Measurement of viscosity

Determination of the time in which the solution flows through a capillary

Ostwald-, and Ubbelohde-Viscosimeter

polymer solution

Law of Hagen-Poiseuille:

$$t = \frac{8 \cdot \eta \cdot l \cdot V}{\pi \cdot \rho \cdot r^4 \cdot g \cdot h}$$

$$\eta = \frac{\pi \cdot r^4 \cdot \Delta p \cdot t}{8 \cdot l \cdot V}$$

$$\Delta p = \rho \cdot g \cdot h$$

r – diameter of capillary
Δp – pressure difference
V/t – volume which flows in a certain time through capillary
l – length of capillary
h – high difference

$$t_0 = \frac{8 \cdot \eta_0 \cdot l \cdot V}{\pi \cdot \rho_0 \cdot r^4 \cdot g \cdot h}$$

pure solvent

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Solution viscosity 7

$$t = \frac{8 \cdot \eta \cdot l \cdot V}{\pi \cdot \rho \cdot r^4 \cdot g \cdot h}$$

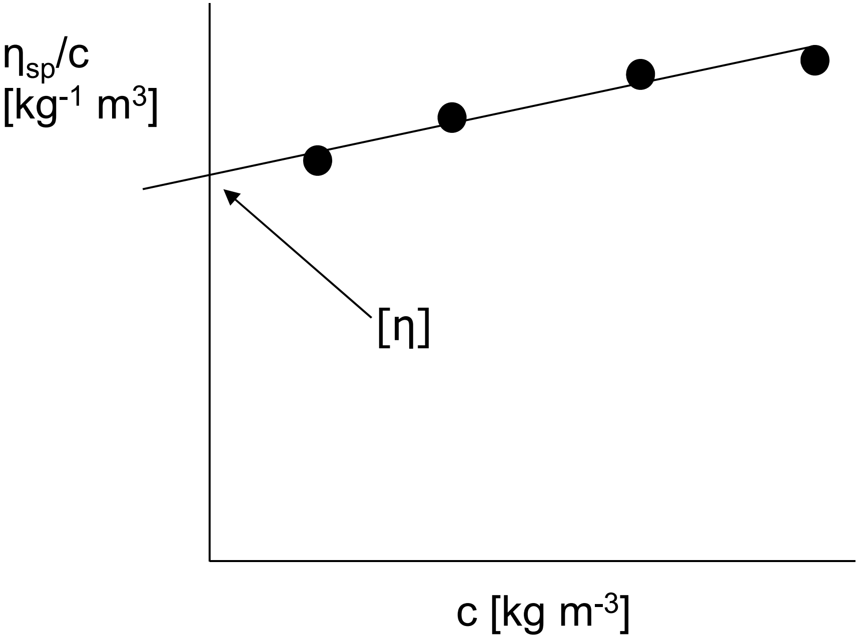
$$t_0 = \frac{8 \cdot \eta_0 \cdot l \cdot V}{\pi \cdot \rho_0 \cdot r^4 \cdot g \cdot h}$$

$\longrightarrow$

diluted solution: $\rho = \rho_0$

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{\rho \cdot t}{\rho_0 \cdot t_0} \approx \frac{t}{t_0};$$

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} = \eta_{rel} - 1$$



graphical analysis:

$$\frac{\eta_{sp}}{c} = [\eta] + K[\eta]^2 c$$

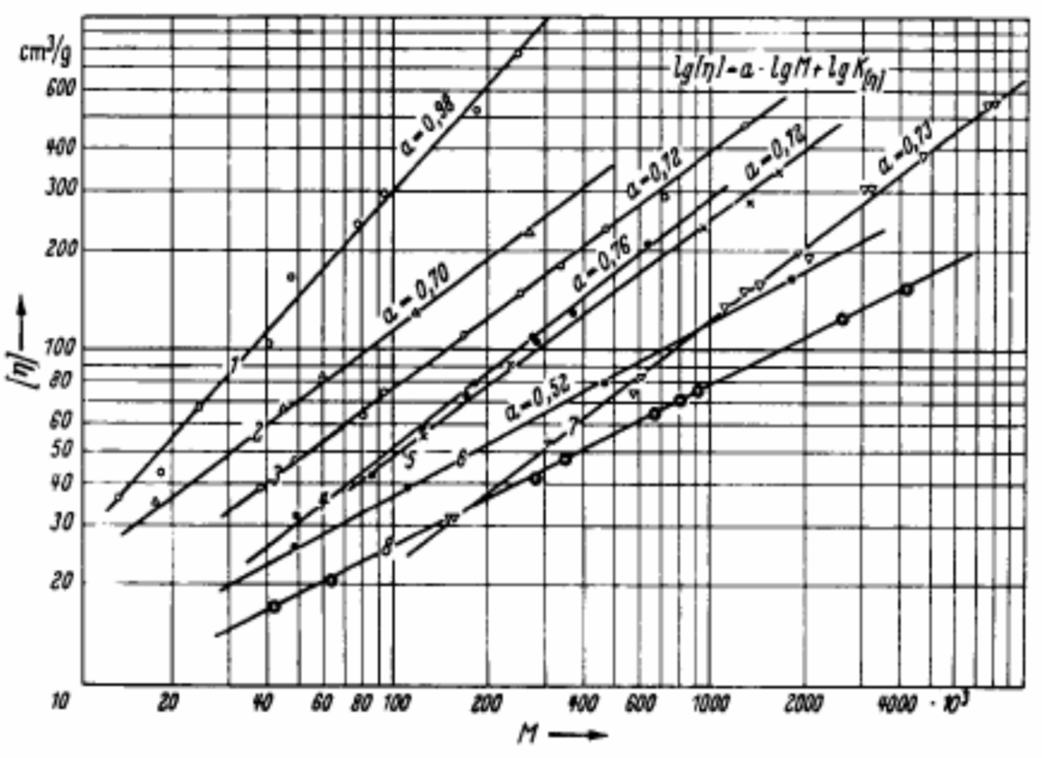
(Huggins)

empirical equation to fit
the measured values

Tieke.

Solution viscosity 8

Mark-Houwink



[η]-M-plots in double logarithmic scale

1 (○) Cellulosenitrate in acetone at 293 K;

2 (Δ) Polycarbonate in THF at 293 K;

3 (⊙) Polyisobutylene in Cyclohexane at 303K;

4 (●) Polypropylene isotactic in α-Chlornaphthaline at 418K;

5 (×) Polystyrol in Toluol bei 295 K;

6 (⊕) Polyisobutylen in Benzol bei 298 K;

7 (∇) PMMA in Aceton bei 293 K;

8 (Θ) Polystyrol in Cyclohexan in 307 K

(according to G.V. Schulz, Meyerhoff, Flory, Zimm)

$$\boxed{[\eta] = K_\eta \cdot M^{0.5}}$$

not all polymers obey this equation!

$$\boxed{[\eta] = K_\eta \cdot M^{a}}$$

Mark-Houwink

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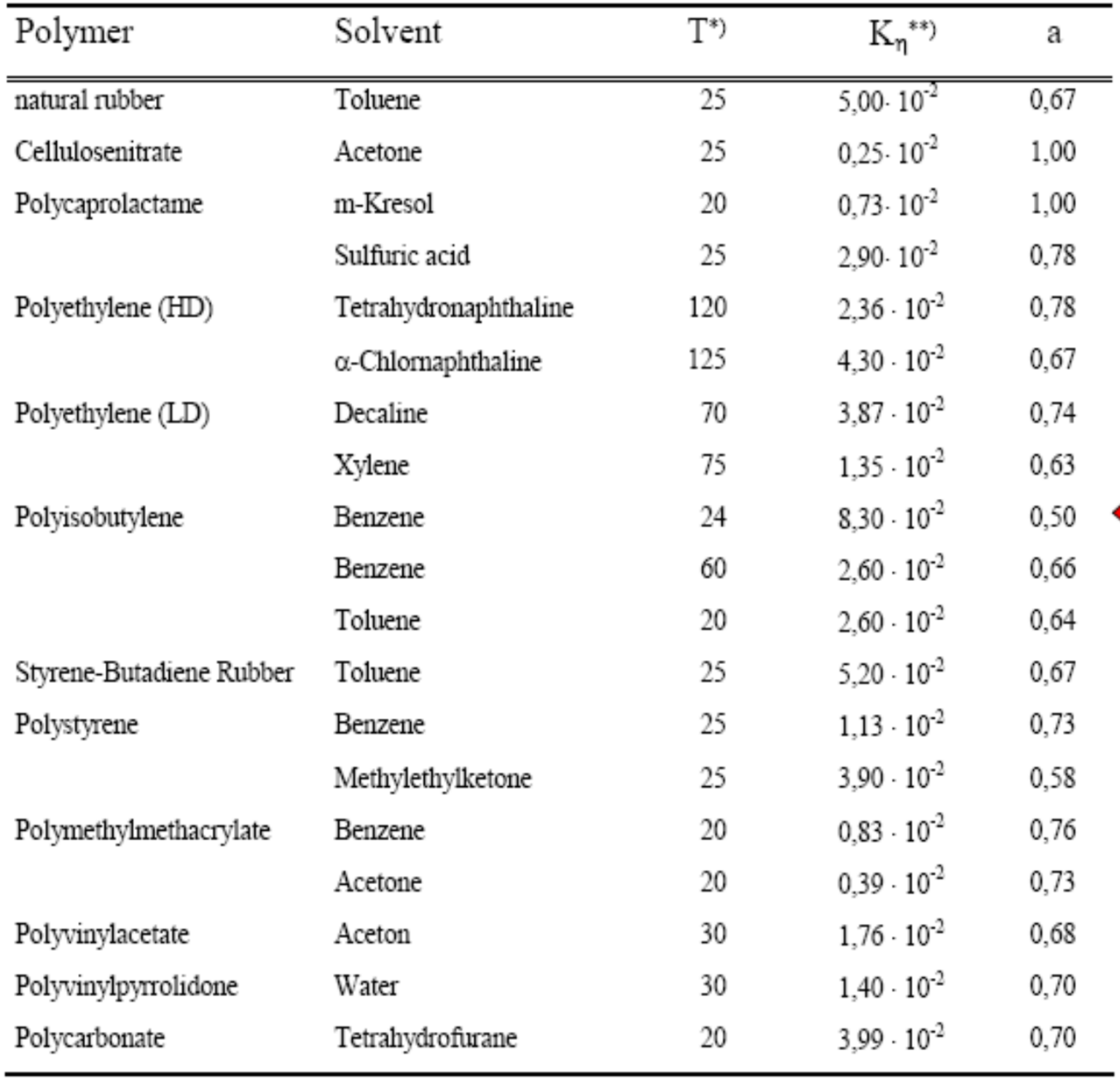
Solution viscosity 9



Polymer	Solvent	T*)	K_η**)	a
natural rubber	Toluene	25	$5{,}00 \cdot 10^{-2}$	0,67
Cellulosenitrate	Acetone	25	$0{,}25 \cdot 10^{-2}$	1,00
Polycaprolactame	m-Kresol	20	$0{,}73 \cdot 10^{-2}$	1,00
	Sulfuric acid	25	$2{,}90 \cdot 10^{-2}$	0,78
Polyethylene (HD)	Tetrahydronaphthaline	120	$2{,}36 \cdot 10^{-2}$	0,78
	α-Chlornaphthaline	125	$4{,}30 \cdot 10^{-2}$	0,67
Polyethylene (LD)	Decaline	70	$3{,}87 \cdot 10^{-2}$	0,74
	Xylene	75	$1{,}35 \cdot 10^{-2}$	0,63
Polyisobutylene	Benzene	24	$8{,}30 \cdot 10^{-2}$	0,50
	Benzene	60	$2{,}60 \cdot 10^{-2}$	0,66
	Toluene	20	$2{,}60 \cdot 10^{-2}$	0,64
Styrene-Butadiene Rubber	Toluene	25	$5{,}20 \cdot 10^{-2}$	0,67
Polystyrene	Benzene	25	$1{,}13 \cdot 10^{-2}$	0,73
	Methylethylketone	25	$3{,}90 \cdot 10^{-2}$	0,58
Polymethylmethacrylate	Benzene	20	$0{,}83 \cdot 10^{-2}$	0,76
	Acetone	20	$0{,}39 \cdot 10^{-2}$	0,73
Polyvinylacetate	Aceton	30	$1{,}76 \cdot 10^{-2}$	0,68
Polyvinylpyrrolidone	Water	30	$1{,}40 \cdot 10^{-2}$	0,70
Polycarbonate	Tetrahydrofurane	20	$3{,}99 \cdot 10^{-2}$	0,70

Mark-Houwink constants

$$\boxed{[\eta] = K_\eta \cdot M^a}$$

*) temperature in °C
**) ([η] in mL/g)

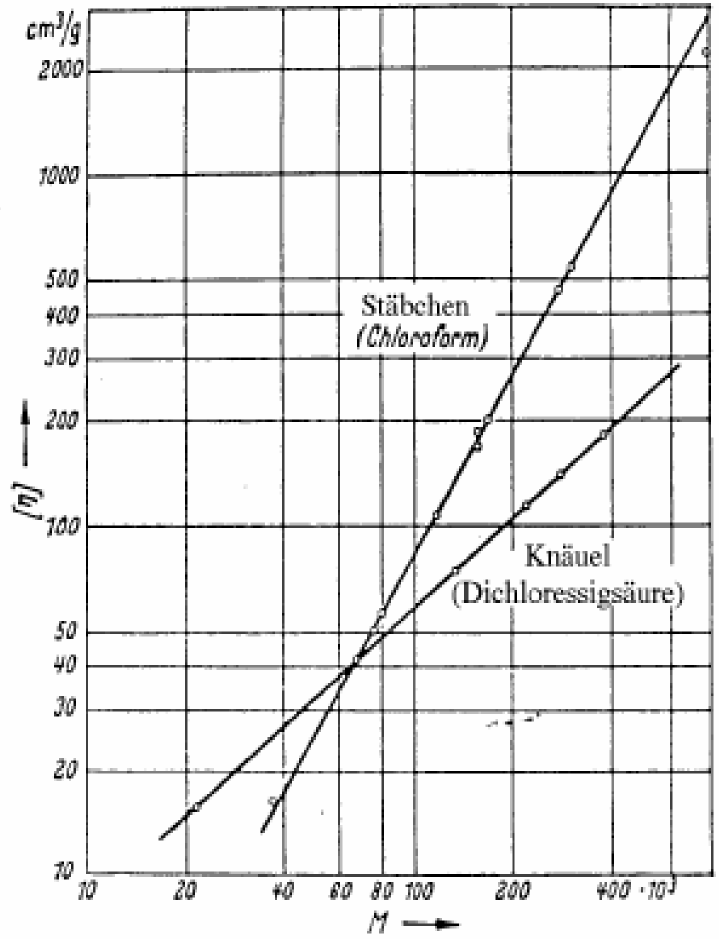
Lecture Prof. Menzel, TU Braunschweig

Mark-Houwink constants

a	shape
0	Hard sphere
0.5	Ideal coil
0.6-0.8	Real coil
≈1	Some cellulose derivatives
1.3-1.4	Rigid rod like polymers
2	Ideal rod

$$\boxed{[\eta] = K_\eta \cdot M^a}$$

a – measure for the shape of the macromolecule



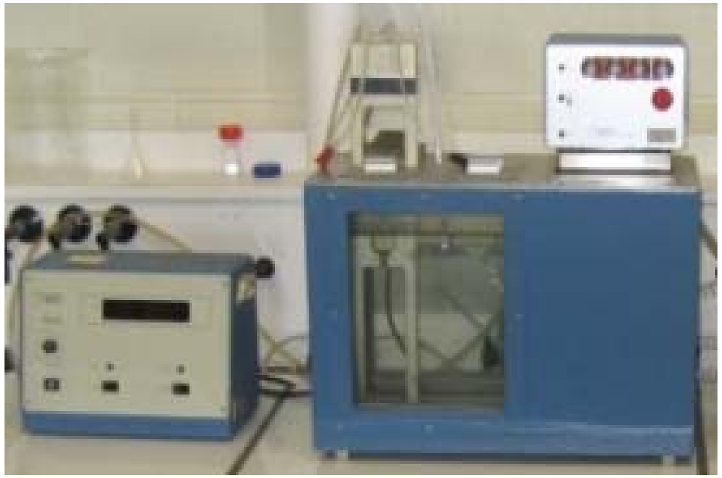
poly(benzylglutamate) in chloroform
→ helical structure → rigid rod
in dichloro acetic acid → coil

Lecture Prof. Menzel, TU Braunschweig.

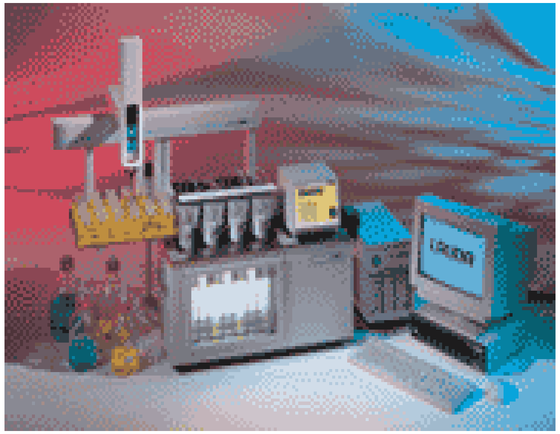
Solution viscosity 11

Ostwald-viscosimeter

Ubbelohde-viscosimeter



Ubbelohde-viscosimeter with thermostat

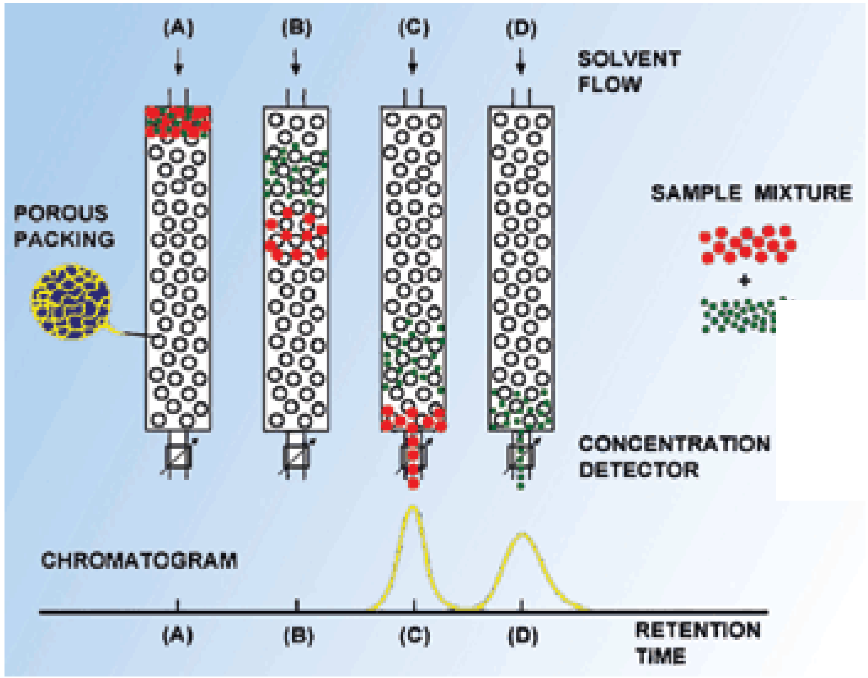


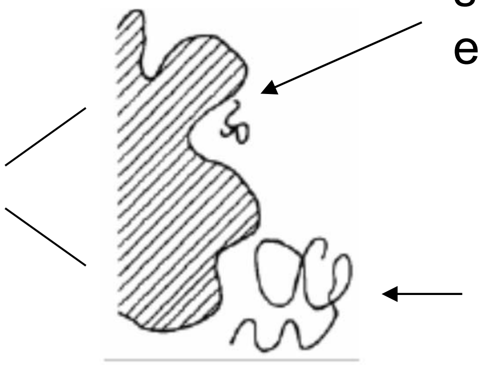
www.natuurkunde.nl, www.uibk.ac.at, www.wefcol.vub.ac.be/wefcol/instr.htm

SEC 1

Gel permation chromatography - GPC
Size exclusion chromatography - SEC

Principle:





short chains
enter pores

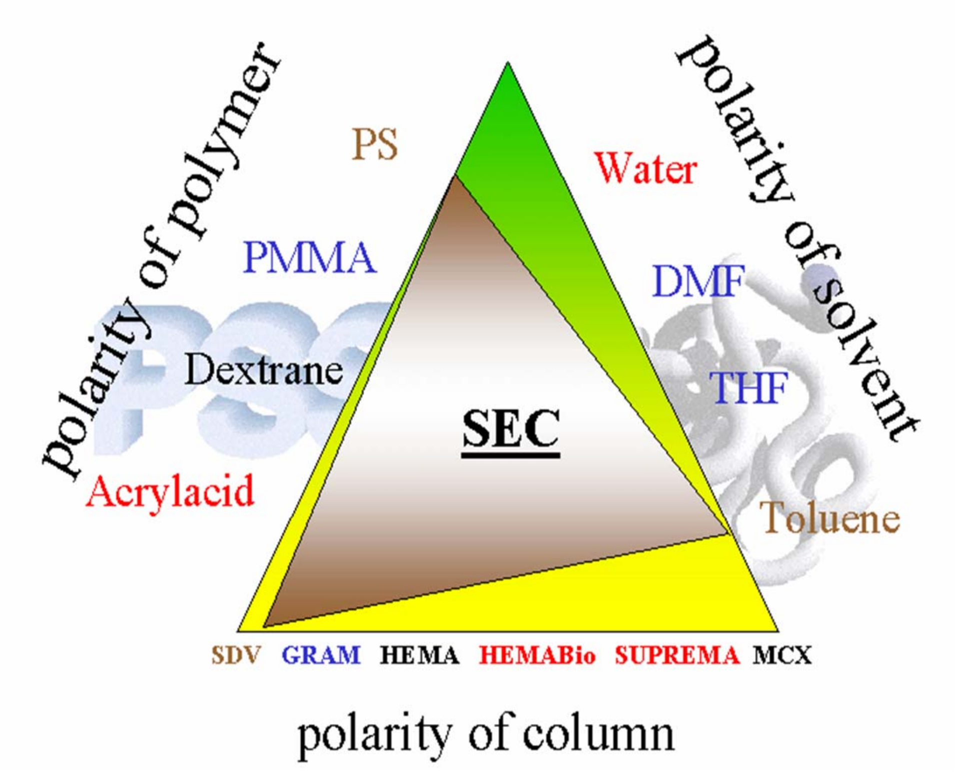
long chains
pass pores

short chains → long retention time
long chains → shorter retention time

chromatogram: signal of a detector
as a function of volume

No absolute method!
Calibration is necessary.

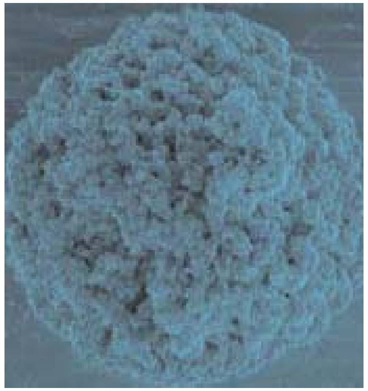
Tieke, www.viscotek.com.



Choice of column and solvent depends on polymer, which will be analyzed.

http://www.polymer.de/bilder/secani.gif.

SEC-columns



Material:
- Polystyrene (crosslinked with divinylbenzene)
- Silica
- Glucose attached to DVB polymer
- Modified DVB polymer (-OH, $-SO_3H$, -F, $-NH_2$)
- Monolithic columns

thin columns → analytical SEC
wider columns → preparative SEC

www.polymerlabs.com.

Detectors:

UV/vis spectrometer: Polymer or some functional groups absorb light
very sensitive and selective detector
one specific wavelength (254 nm → aromatic groups in the polymer)

Diode array: Detection by several diodes (light is dispersed in front of diodes → UV-vis spectrum of eluated polymer)

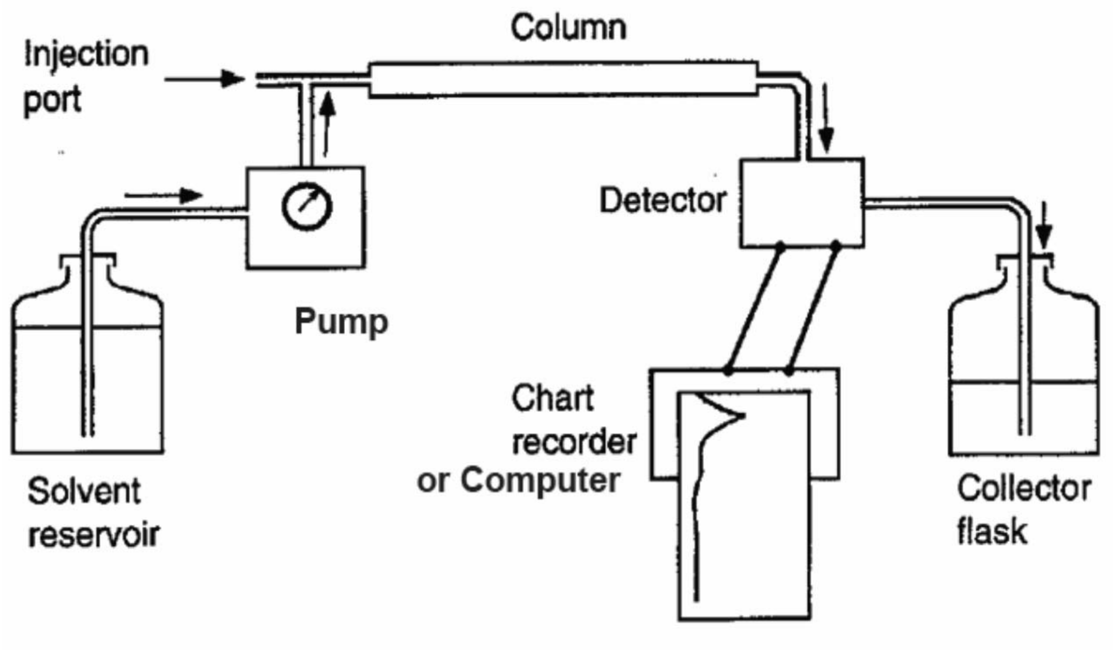
Differential-refractometer RI: Refractive index of solution and the one of the pure solvent are compared; applicable to most polymers; strong dependence on the pressure and temperature → exact temperation of column and detector

Viscosity detector: Universal calibration

Light scattering LS: Very sensitive for high molar mass compounds
RI proportional to c, LS proportional to c*M

Evaporative light scattering detector ELSD: Solvent emerging from column is evaporized in a steam of air, solute does not evaporate and is nebulized → formation of small droplets → scattering of light → amount of scattered light is proportional to concentration of material

SEC-setups

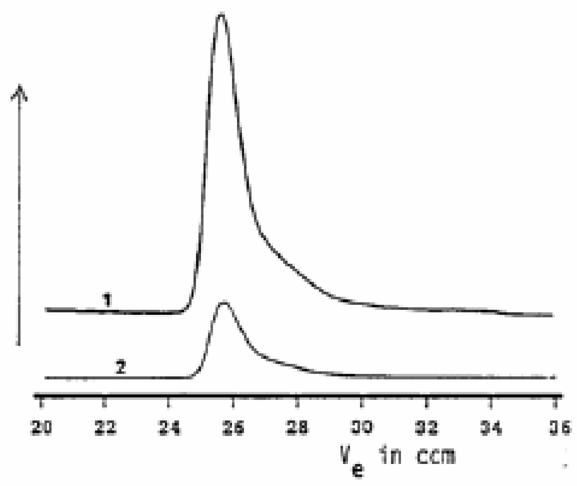


schematic set-up

real set-up:
3 columns
autosampler

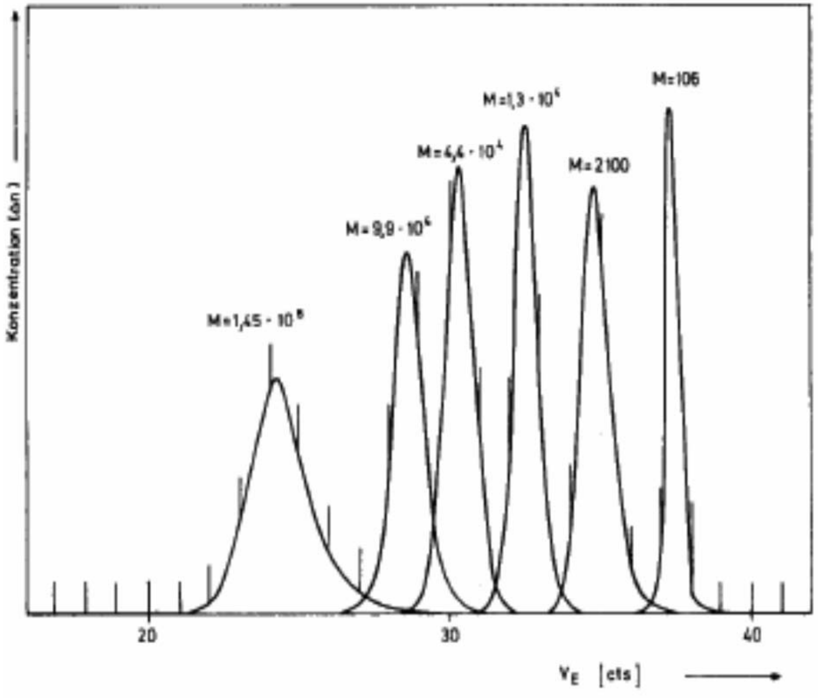
www.polymer.de.

Calibration



detector signal is proportional to polymer concentration
c(1) > c(2)
→ calibration

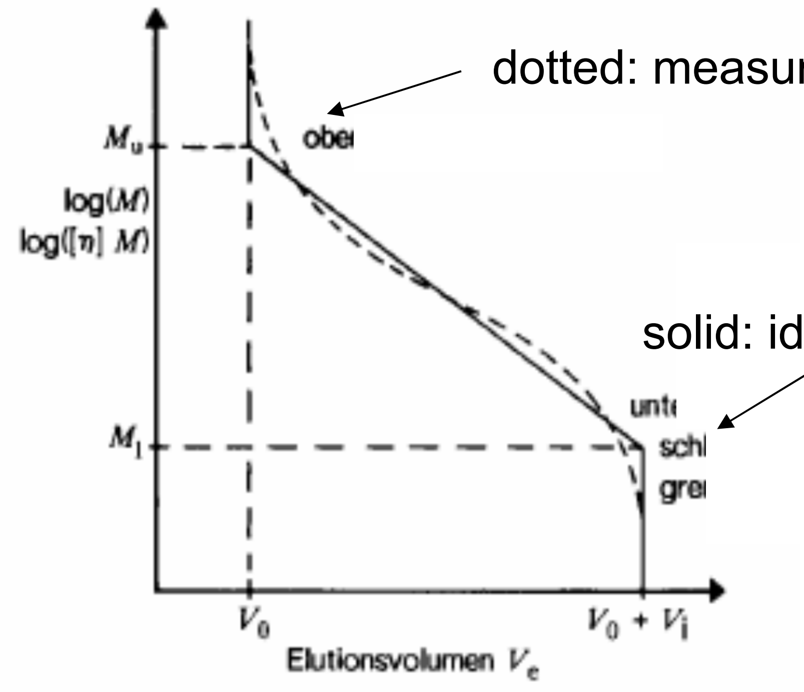
well known polymers (narrow distribution) are used as standards
molar mass is compared with eluted volume V_E



SEC curves of different polystyrenes and ethylbenzene in THF

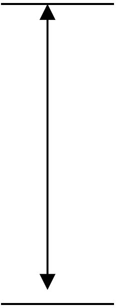
Lecture Prof. Menzel, TU Braunschweig.

Calibration



dotted: measured curve

solid: ideal curve



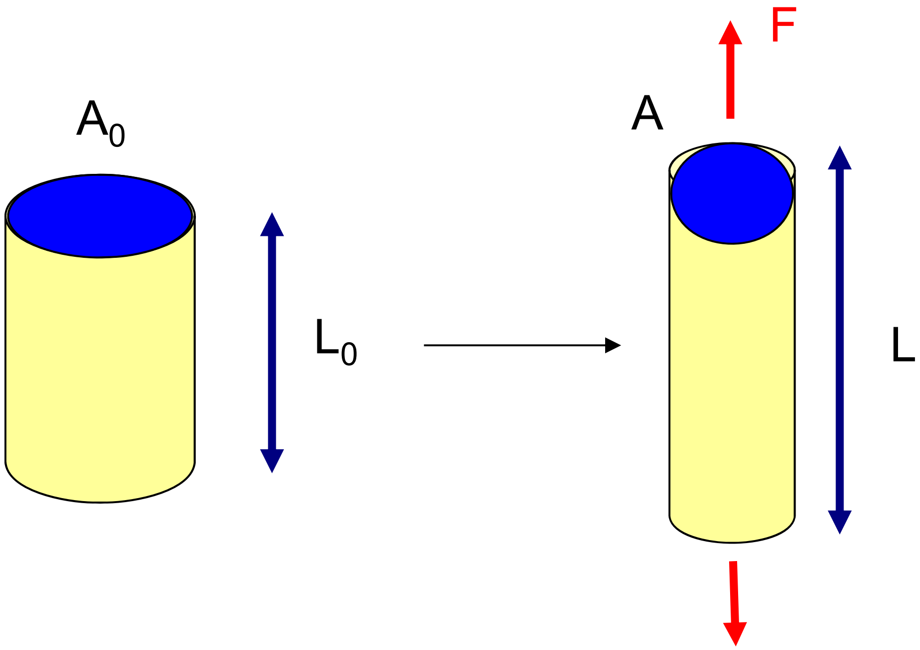
range in which can be measured

upper exclusion limit: no more pores accessible
lower exclusion limit: all pores accessible

Calibration is only valid for the polymer used for calibration!

Lecture Prof. Menzel, TU Braunschweig.

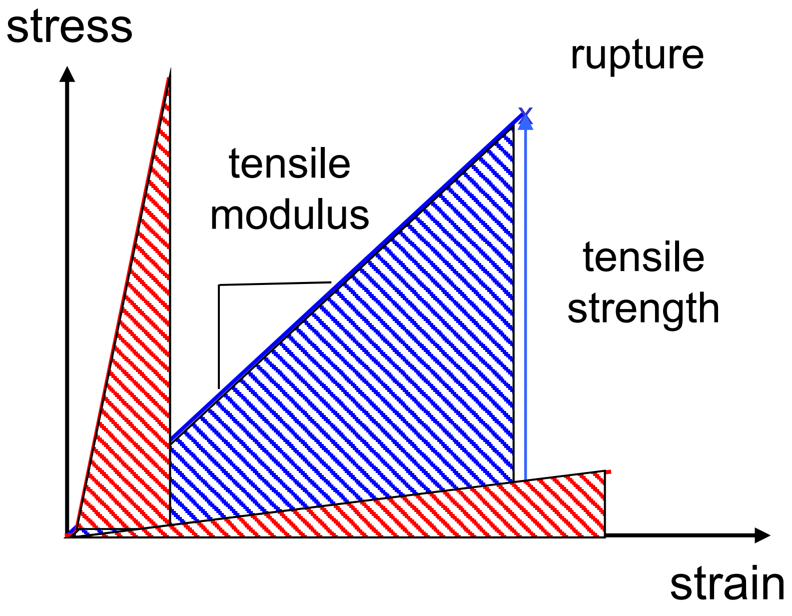
Mechanical properties



Stress = F/A
Strain = change of length/initial length

tensile load → stretching in direction of load
→ narrowing in perpendicular plane

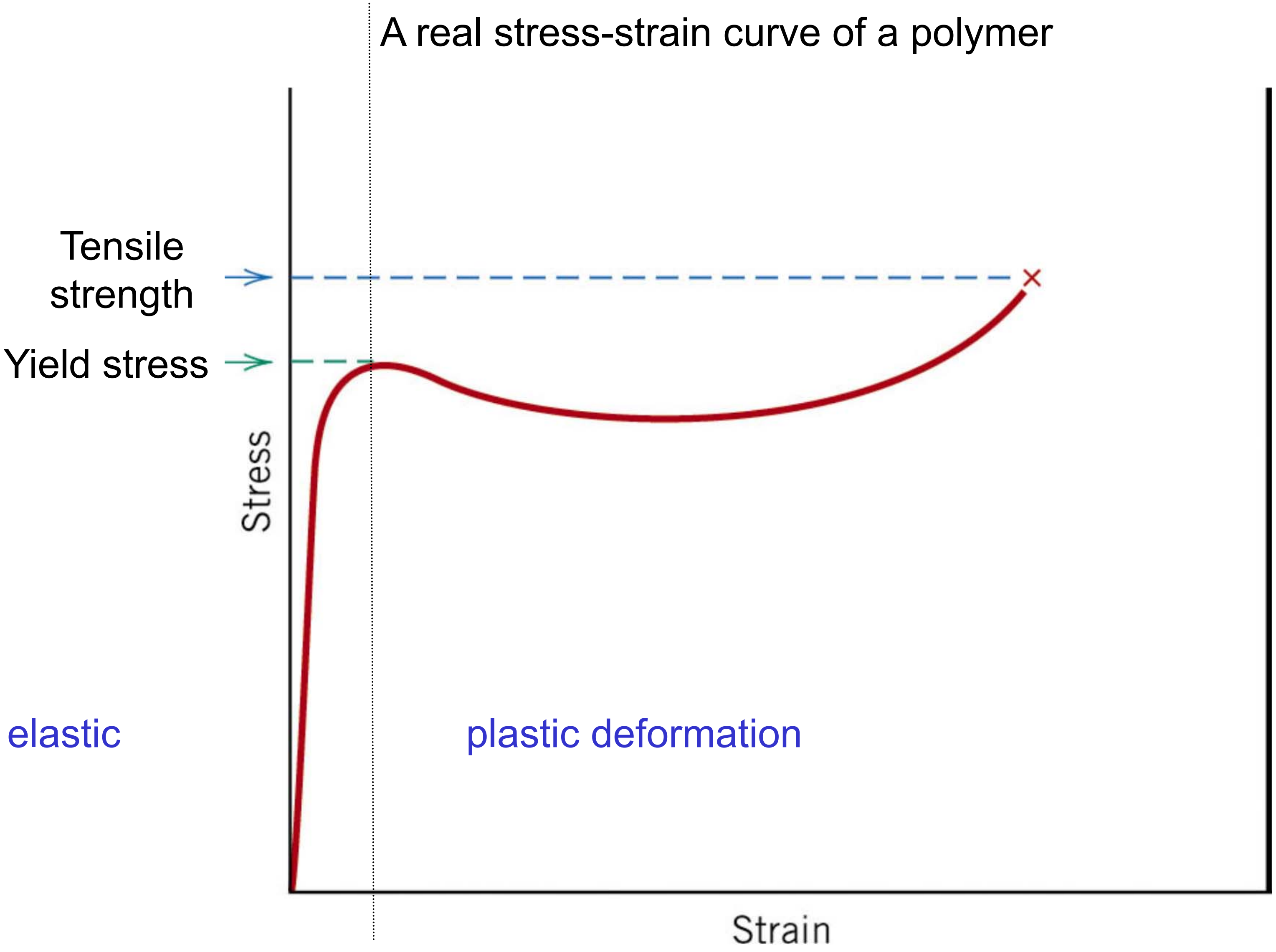
Stress-strain-curve



tensile modulus = Young’s modulus

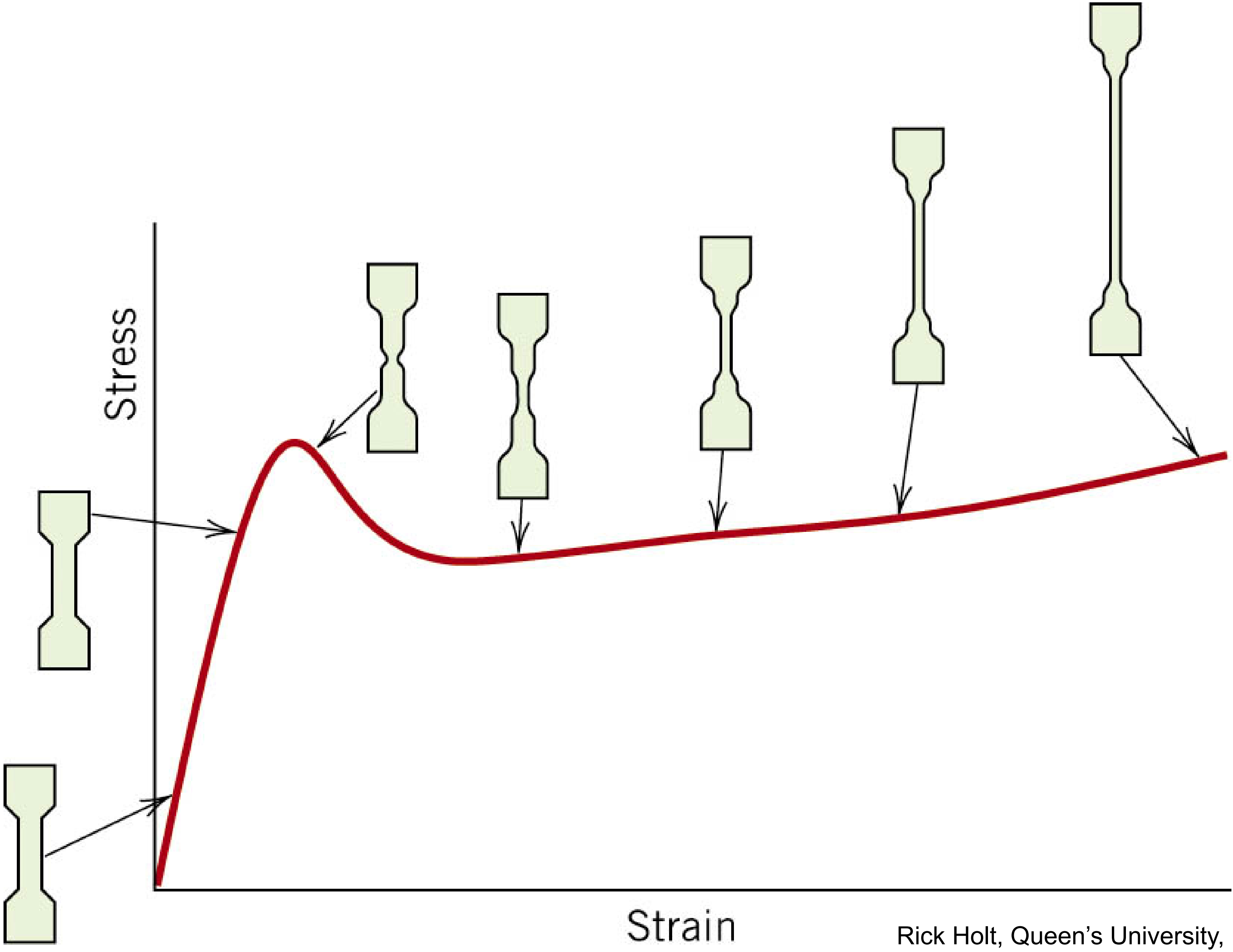
Mechanical properties 4

A real stress-strain curve of a polymer



Rick Holt, Queen's University, Kingston.

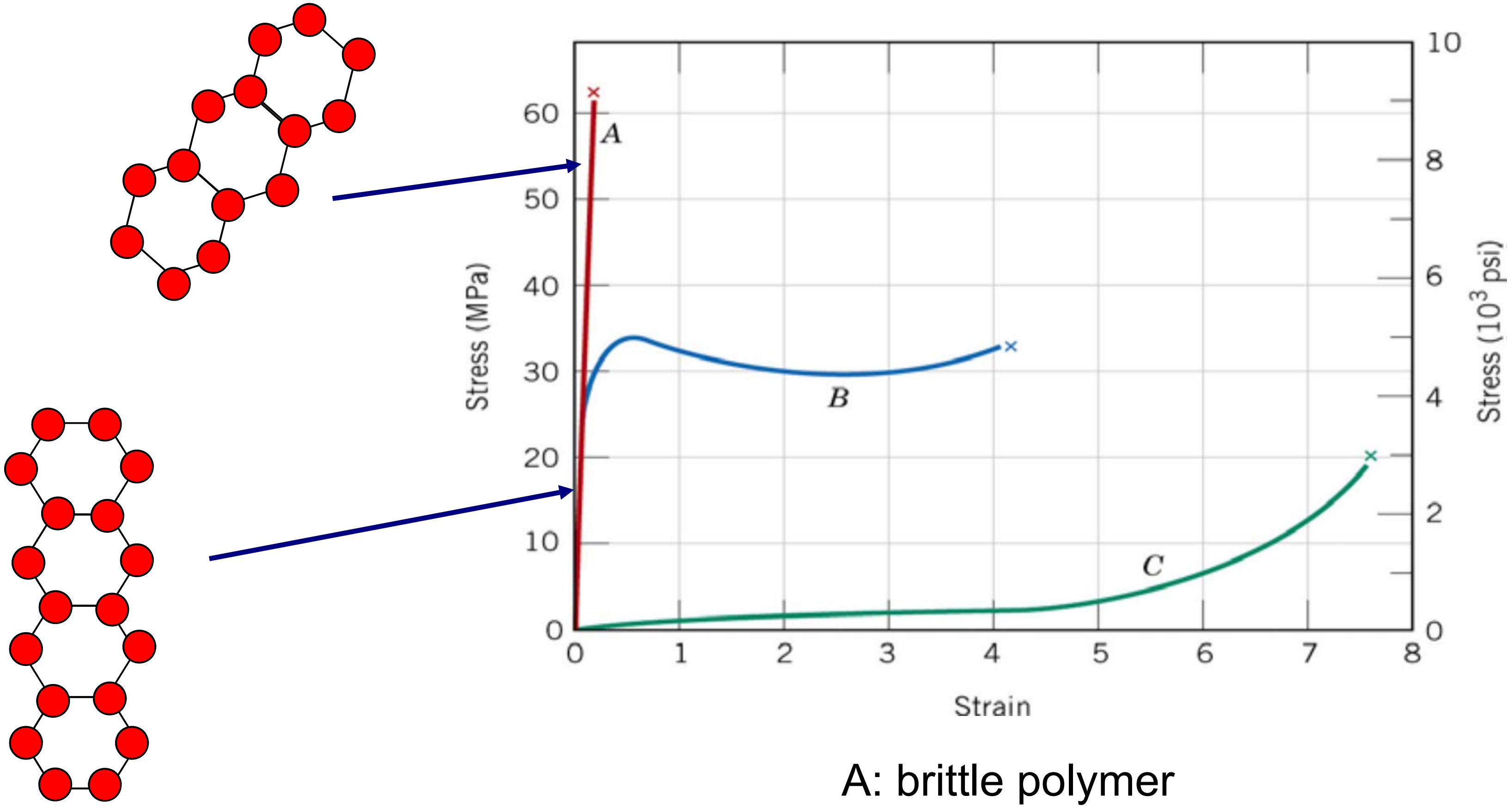
Mechanical properties 5



Rick Holt, Queen's University, Kingston.

Mechanical properties 6

What is happening on the molecular level?



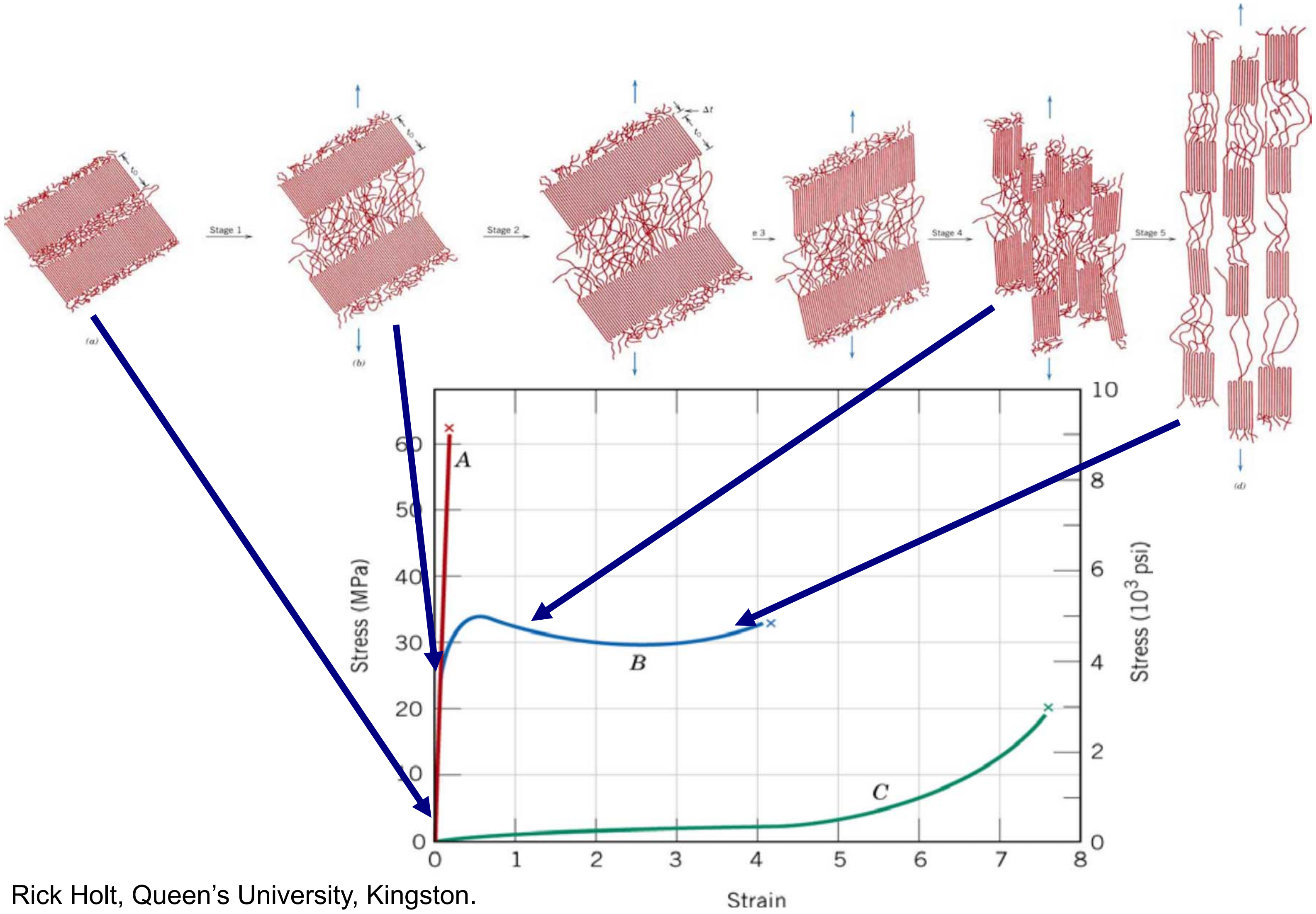
A: brittle polymer

e.g. polymer network

Rick Holt, Queen's University, Kingston.

Mechanical properties 7

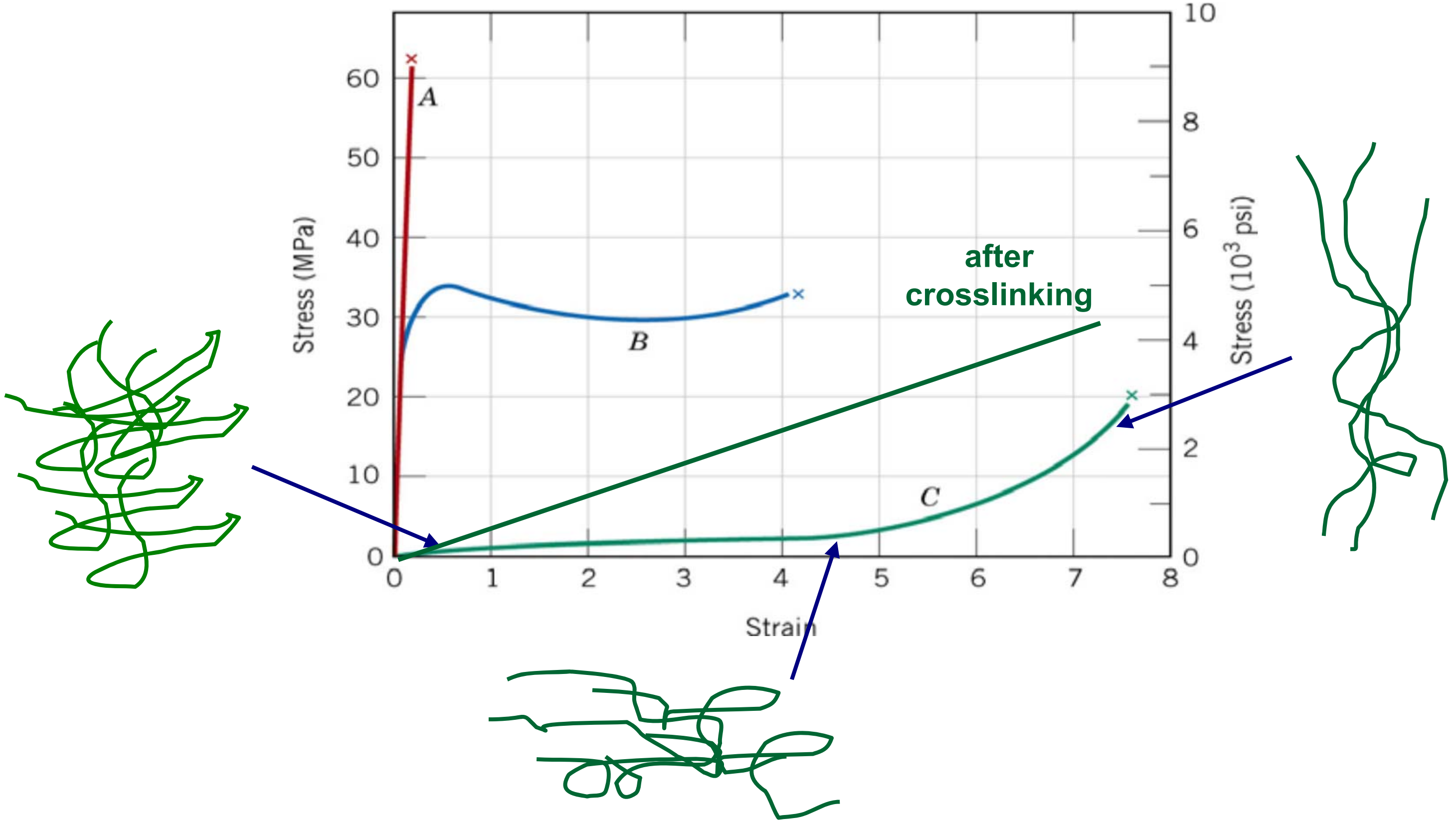
What is happening on the molecular level?



Rick Holt, Queen's University, Kingston.

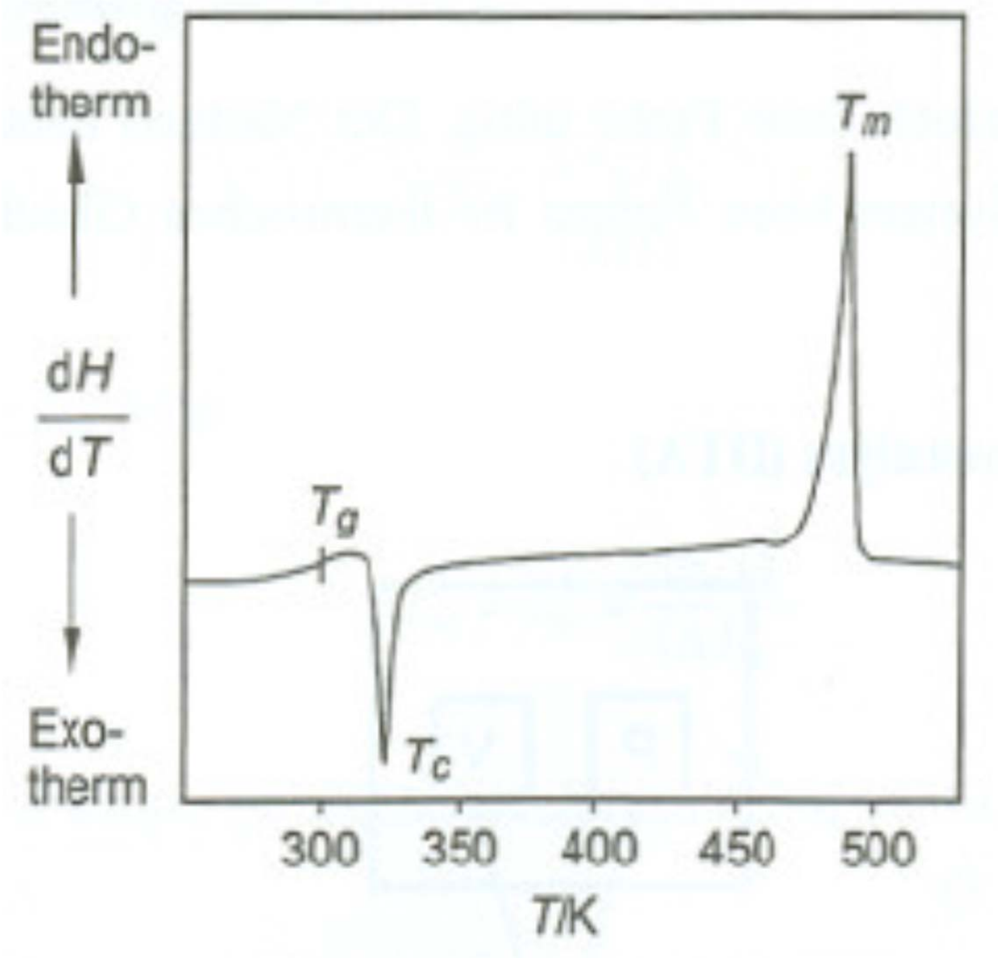
Mechanical properties 8

What is happening on the molecular level?



after crosslinking

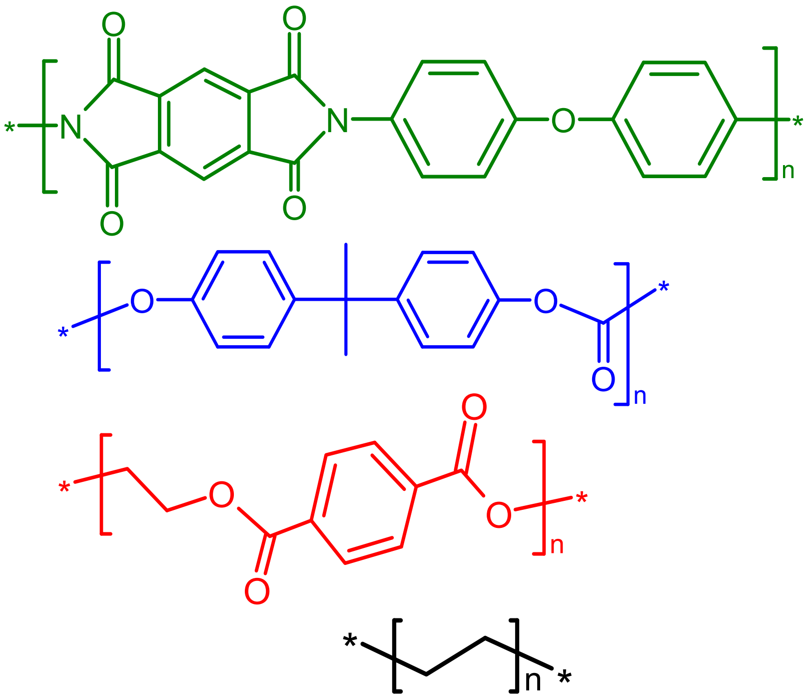
DSC Diagram

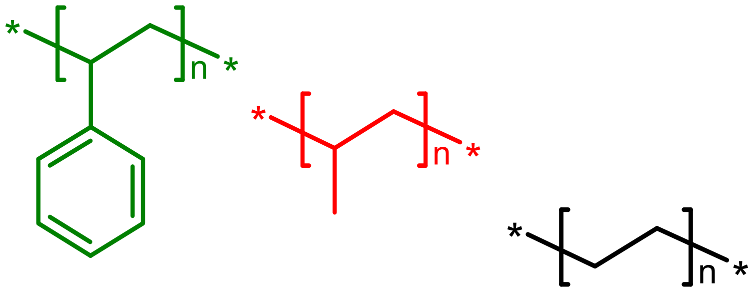


T_g – glass transition
T_c – crystallization temperature
T_m – melting temperature

Tieke

Thermal properties – glass transition 2





More flexible chain → lower T_g

<u>Lower main chain stiffness</u>

Polyimide	> 400 °C
Polycarbonate	150 °C
Polyethyleneterephthalate	70 °C
Polyethylene	-120 °C

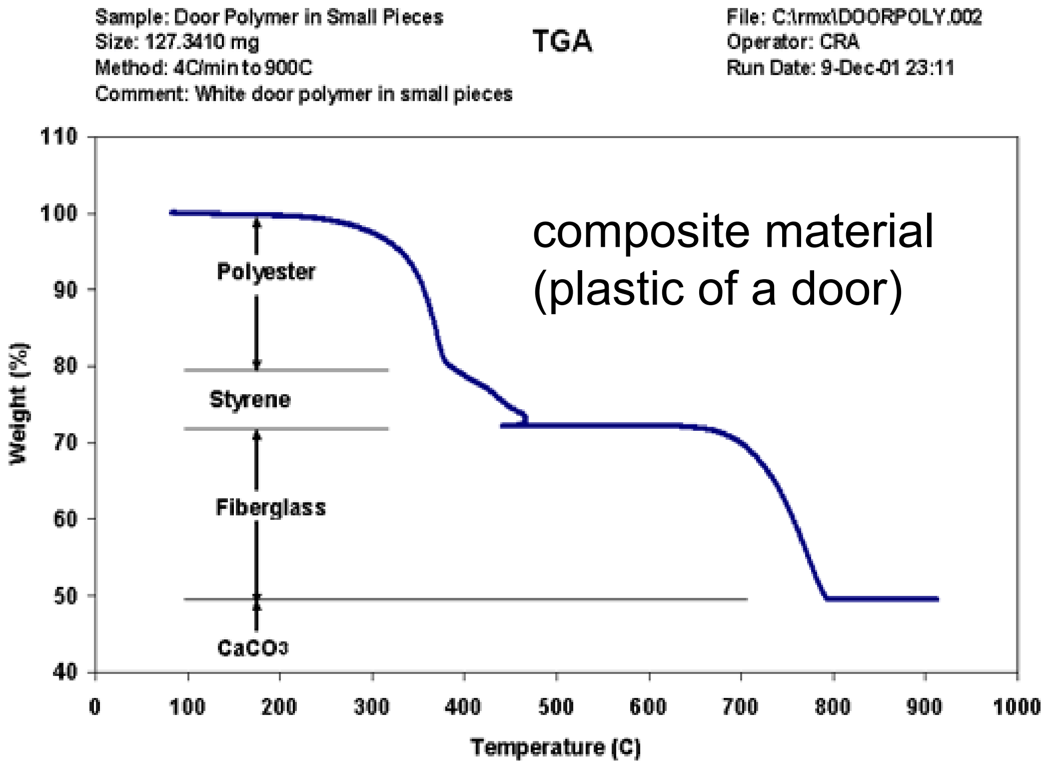
<u>Chemical cross-linking</u> increases T_g

<u>Smaller side group</u>

Polystyrene	100 °C
Polypropylene	15 °C
Polyethylene	-120 °C

Thermogravimetric analysis (TGA)

- thermal stability of polymers
- measurement weight loss against temperature
- residual solvent
- thermal decomposition

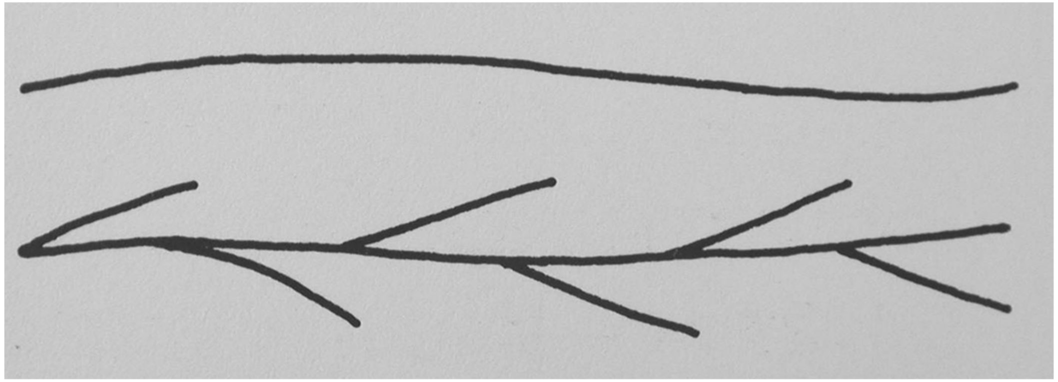


composite material
(plastic of a door)

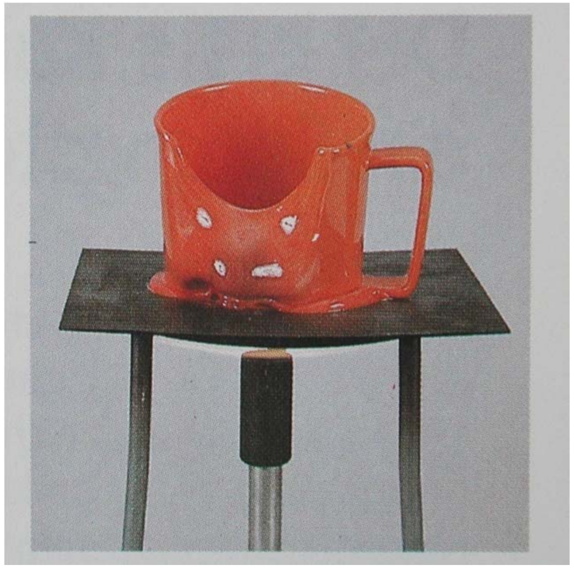
www.andersonmaterials.com/images/tga.gif

http://www.netzsch-thermal-analysis.com

Thermoplastics

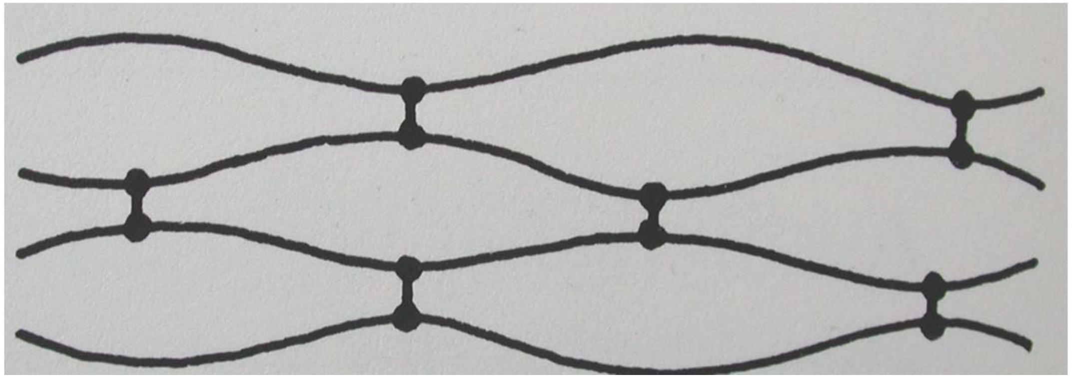


linear, branched polymers

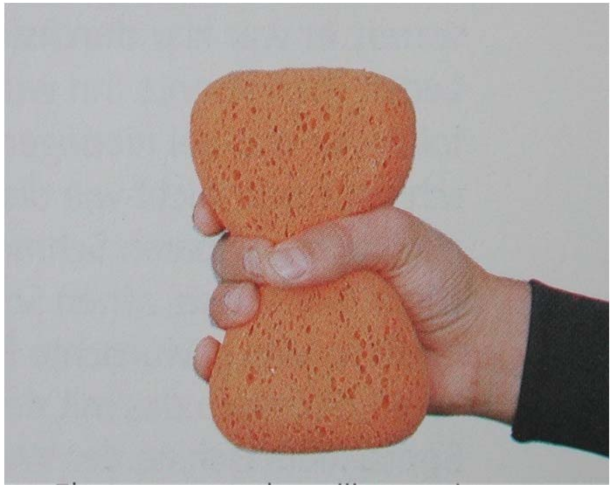


Thermoplastics above T_g and T_m are capable of flowing
Manufacture by extrusion and injection moulding

Elastomers



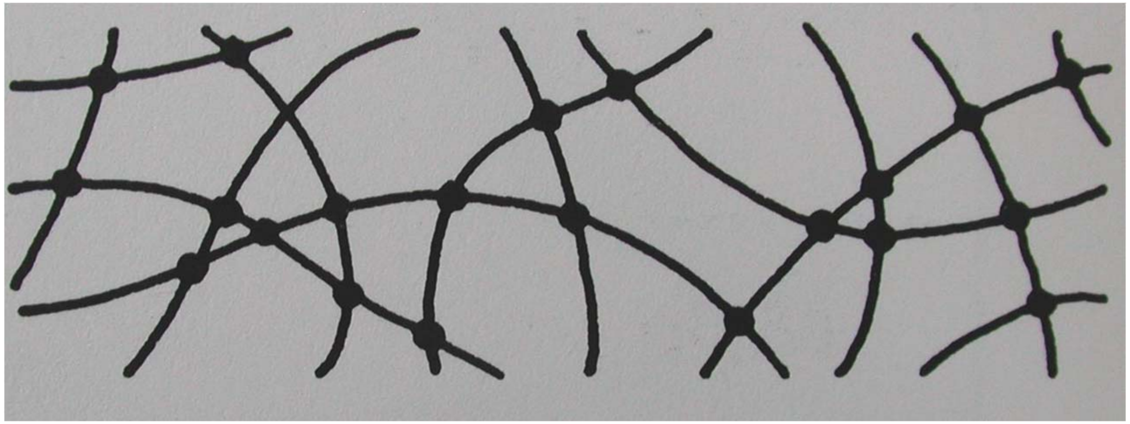
crosslinked polymers (wide meshed)



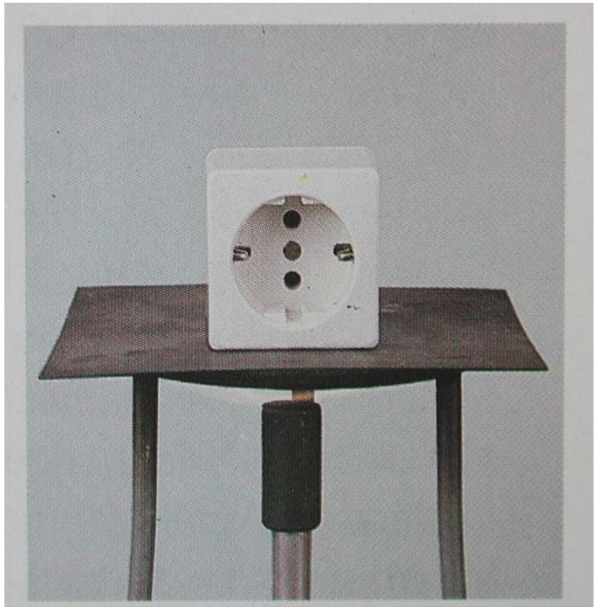
elastomers are swellable and elastic like rubber

rigid, but elastically deformable T_g< room temperature

Duroplastics



crosslinked polymers



Manufacture only by casting of monomers/oligomers
→ Thermal crosslinking (polymer unsoluble)