Introduction to Macromolecular Chemistry

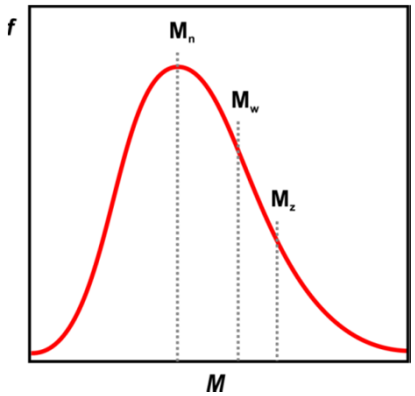
aka polymer chemistry

Mondays, 8.15-9.45 am, NC 02/99

Dr. Christian Merten, Ruhr-Uni Bochum, 2019

Last lecture

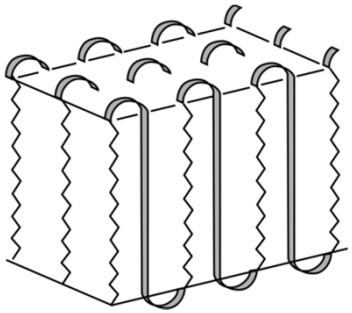
Mass distributions



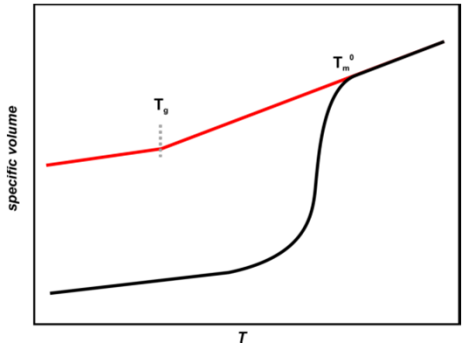
$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

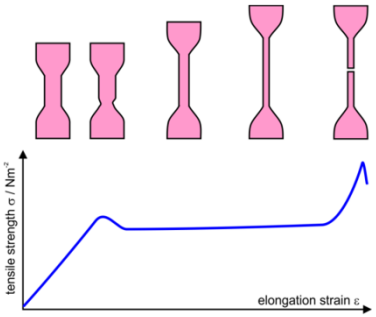
Solid state structures



Thermal properties



Mechanical properties



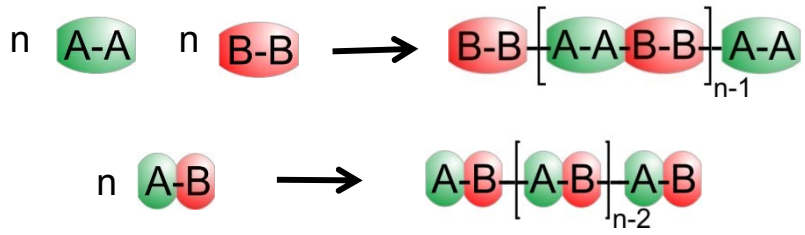
Polymerization reactions

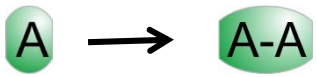
KINETICS

STEP GROWTH REACTION

CHAIN GROWTH REACTION

SCHEME





MECHANISM

Polyaddition

Polycondensation

Radical chain reaction

Cationic polymerization

Anionic polymerization

Coordination polymerization

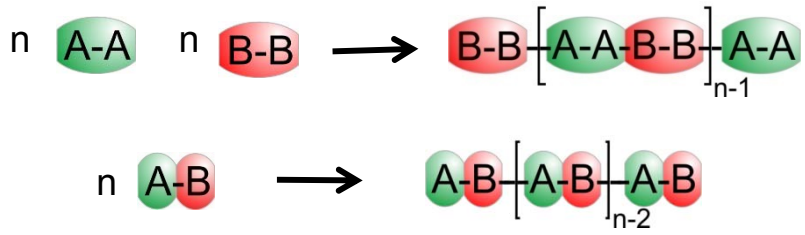
Polymerization reactions

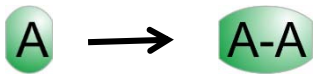
KINETICS

STEP GROWTH REACTION

CHAIN GROWTH REACTION

SCHEME





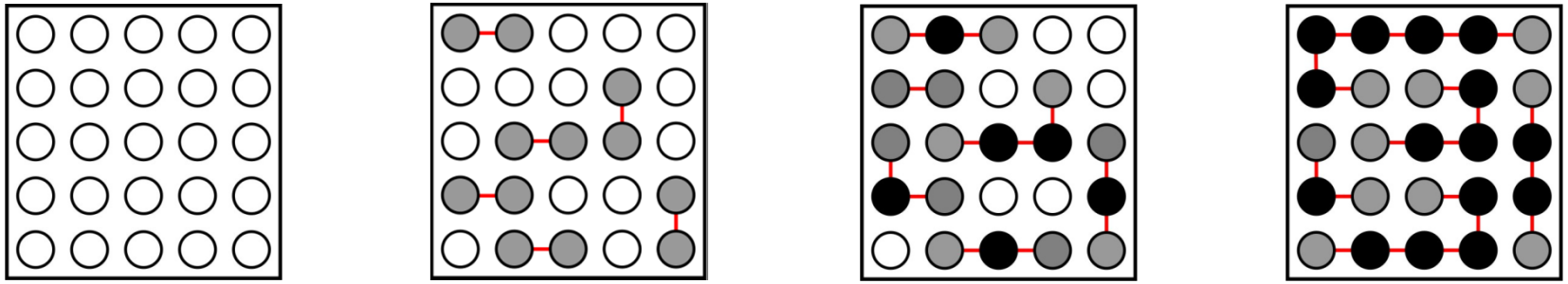
CHARACTERISTICS

- No initiation step with highly reactive starter necessary
- All molecules have similar reactivities and participate in the polymerization process
- High molecular weights only when high turnover is reached

- Initiation through a highly reactive species (e.g. radical starter)
- Only small part of the molecules are actually involved in the polymerization process
- Chain grows fast, high molecular weights are often achieved within seconds

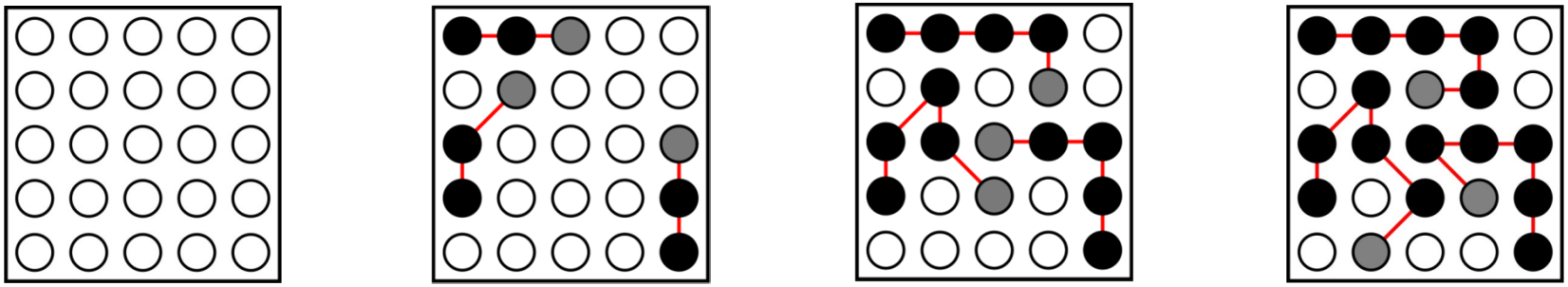
Polymerization reactions: Chain length vs. turnover

Step growth reaction



Turnover: **0%** **24%** **48%** **80%**

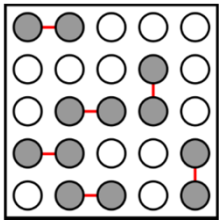
Chain growth reaction

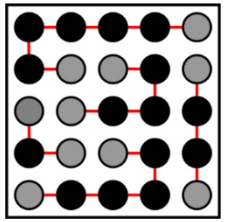


Turnover: **0%** **24%** **48%** **60 %**

Polymerization reactions: Summary

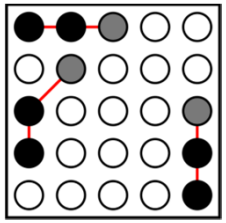
STEP GROWTH REACTION

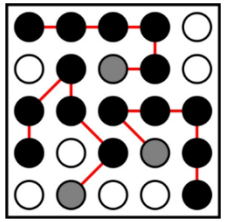




- Monomer with ≥2 polymerizable groups
- Multiple reactive chain ends
- Molecular weight increases slowly
- High molecular weight only at high conversion

CHAIN GROWTH REACTION





- Monomer has one polymerizable group
- Active chain end, i.e. growth in one direction

Step growth and chain growth have different kinetics!

Step growth: Degree of polymerization (DP)

Degree of polymerization P_n:

$$P_n = \frac{N_0}{N_t}$$

How many monomers have (on average) been incorporated into the polymer?

Turnover of a reaction p:

$$p = \frac{N_0 - N_t}{N_0}$$

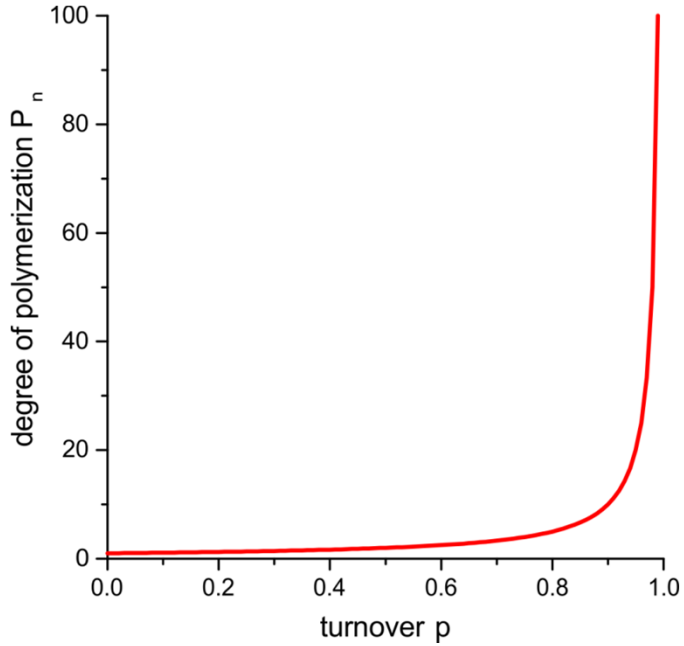
How many monomers have reacted?

N_0: number of molecules at start
N_t: number of molecules at time

Step growth: Degree of polymerization (DP)

For AB monomers

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



p: turnover (how many monomers have been used up?)
N_0: number of molecules at start
N_t: number of molecules at time

Step growth: Degree of polymerization (DP)

For AB monomers

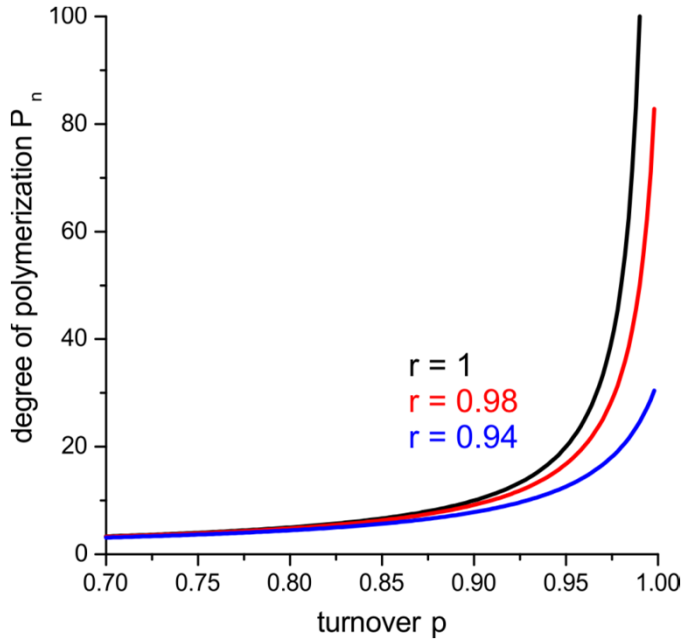
$$P_n = \frac{N_0}{N_t} = \frac{1}{1-p} \quad \text{with} \quad p = \frac{N_0 - N_t}{N_0}$$

For non-stoichiometric polymerizations, e.g. if $n_{AA} \neq n_{BB}$

$$P_n = \frac{N_0}{N_t} = \frac{1+r}{2r(1-p)+1-r}$$

(Carother equation)

$$r = n_A / n_B$$



Step growth: Degree of polymerization (DP)

General definition of DP: $\boldsymbol{P_n = \frac{n_0}{n_t}}$ with

n_0: number of molecules at start

n_t: number of molecules at time t

turnover / extend of reaction: $\boldsymbol{p = \frac{n_0 - n_t}{n_0} = 1 - \frac{n_t}{n_0}}$

---

1) n AB → $(AB)_n$
n A + n B → $(AB)_n$ → $\boldsymbol{n_t = (1-p)n_0}$

$$\Rightarrow \boldsymbol{P_n = \frac{n_0}{n_t} = \frac{n_0}{(1-p)n_0} = \frac{1}{1-p}}$$

---

2) n_A A + n_B B → $(AB)_n$ + (n_A-n) A + (n_B-n) B

If $n_A \neq n_B$ ⇒ stoichiometric ratio: $\boldsymbol{\frac{n_A}{n_B} = r \leq 1}$ ⇒ $\boldsymbol{P_n = \frac{n_A + n_B}{n_{A,t} + n_{B,t}} = \frac{n_a\left(1+\frac{1}{r}\right)}{n_{A,t} + n_{B,t}}}$

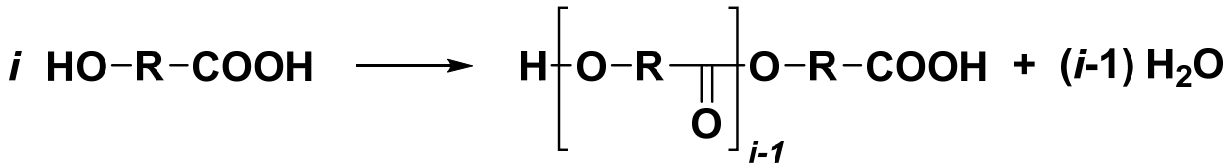
As A is limiting, there will be more B left at turnover p:

$$\left.\begin{aligned} \boldsymbol{n_{A,t}} &= \boldsymbol{(1-p)n_A} \\ \boldsymbol{n_{B,t}} &= \boldsymbol{(1-rp)n_B} \end{aligned}\right\} \boldsymbol{n_{A,t} + n_{B,t} = (1-p)n_A + (1-rp)n_B = \frac{n_A}{r}(r - 2rp + 1)}$$

$$\boldsymbol{P_n = \frac{N_0}{N_t} = \frac{1+r}{2r(1-p)+1-r}}$$

(Carother equation)

Step growth: Reaching maximum turnover



Equilibrium constant of esterification: $K = \frac{[COOR][H_2O]}{[COOH][ROH]}$

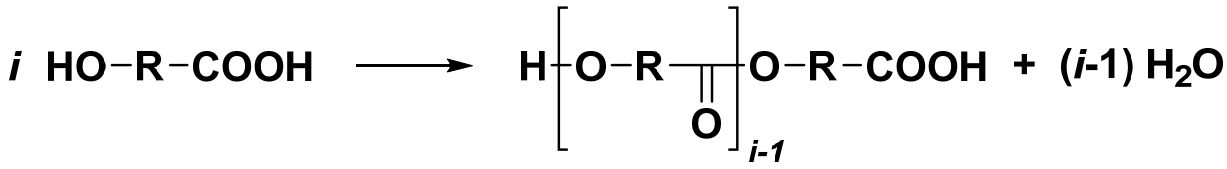
Turnover can be given as $p = \frac{[COOR]}{[COOH]_0} = \frac{[H_2O]}{[ROH]_0}$ and $(1-p) = \frac{[COOH]}{[COOH]_0} = \frac{[ROH]}{[ROH]_0}$

$$\Rightarrow \boldsymbol{K = \frac{p^2}{(1-p)^2}} \Rightarrow \boldsymbol{p = \frac{\sqrt{K}}{1+\sqrt{K}}} \Rightarrow \boxed{\boldsymbol{P_n = \frac{1}{1 - \frac{\sqrt{K}}{1+\sqrt{K}}}}}$$

High DP can only be reached by removing products from equilibrium, e.g. by

- removing water
- precipitating polymer

Step growth reactions: Molecular weight distribution



What is the probability χ_i that a polymer with i-1 monomer units is formed?

➢ χ_i is product of the the probabilities for ester group formation

- Formation of polymer requires (i-1) reaction steps
- Probability for an end group to react = turnover p

$p^{(i-1)}$: probability that (i-1) bonds are formed

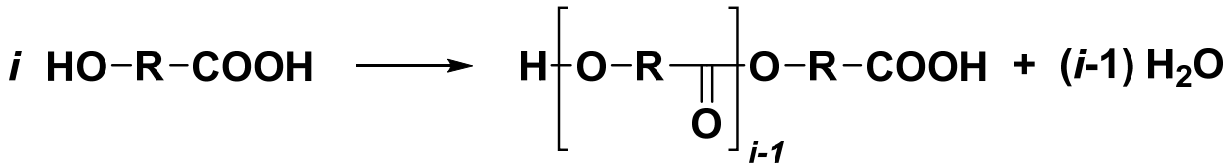
But there are unreacted groups at the ends left:

- Probability for an end group not to react = (1-p)

It follows for χ_i:

$$\chi_i = p^{(i-1)}(1-p)$$

Step growth reactions: Molecular weight distribution



What is the number of molecules $\boldsymbol{n_i}$ with *i* monomer units after time *t* ?

- $\boldsymbol{n_i = \chi_i \cdot n_t = n_t \cdot p^{(i-1)}(1-p)}$

with $\boldsymbol{n_t = n_0(1-p)}$ (cf. definition of turnover), we can write

- $\boldsymbol{n_i = n_0 \cdot p^{(i-1)}(1-p)^2}$

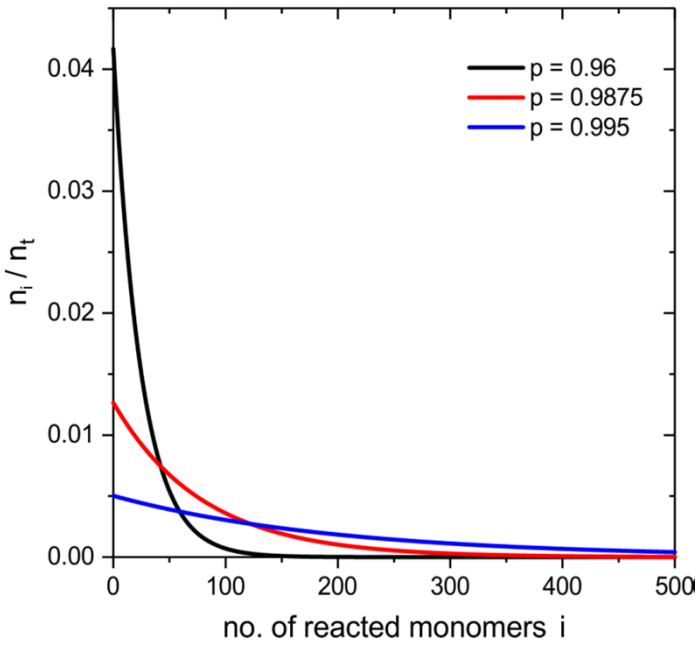
What is the mass fraction of molecules $\boldsymbol{w_i}$ with *i* monomer units of mass M_0?

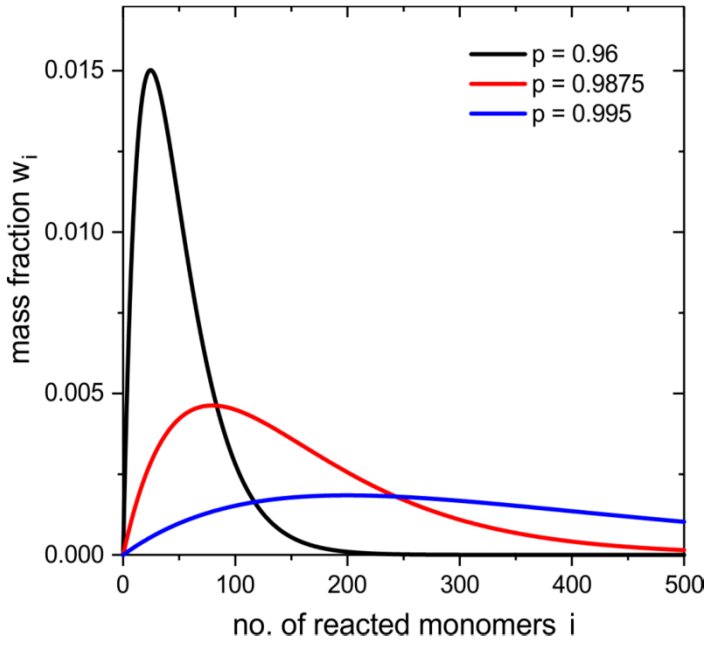
- $\boldsymbol{w_i = \frac{m_i}{m_{tot}}} \quad \Rightarrow \quad \boldsymbol{w_i = \frac{n_i(i \cdot M_0)}{n_0 M_0} = \frac{i \cdot n_i}{n_0}} \quad \Rightarrow \quad \boxed{\boldsymbol{w_i = i \cdot p^{(i-1)}(1-p)^2}}$

Step growth reactions: Molecular weight distribution

In terms of numbers, always more low molecular weight fragments:

But, in terms of mass fraction, contribution goes down with $p \rightarrow 1$





Step growth reactions: Average molecular weights

If $\boldsymbol{N_i}$ and $\boldsymbol{w_i}$ are known, the average molecular weights $\boldsymbol{\bar{M}_n}$ and $\boldsymbol{\bar{M}_w}$ can easily be calculated:

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} \qquad \bar{M}_w = \sum w_i M_i$$

with $\sum n_i = n_t$ $\quad n_i = n_0 p^{(i-1)}(1-p)^2$
$M_i = i \cdot M_0$ $\quad n_t = n_o(1-p)$

$$\bar{M}_n = \frac{\sum n_0 p^{(i-1)}(1-p)^2 \cdot i M_0}{n_0(1-p)}$$

$$= M_0(1-p) \cdot \sum i \cdot p^{(i-1)}$$

$\sum i \cdot p^{(i-1)} = \frac{1}{(1-p)^2}$ for p<1

$$\boxed{\bar{M}_n = \frac{M_0}{1-p}}$$

with $M_i = i \cdot M_0$ $\quad w_i = i \cdot p^{(i-1)}(1-p)^2$

$$\bar{M}_w = \sum i \cdot p^{(i-1)}(1-p)^2 \cdot i \cdot M_0$$

$$= \mathrm{M}_0(1-\mathrm{p})^2 \cdot \sum i^2 p^{(i-1)}$$

$\sum i^2 \cdot p^{(i-1)} = \frac{1+p}{(1-p)^3}$

$$\boxed{\bar{M}_w = M_0 \cdot \frac{(1+p)}{(1-p)}}$$

Step growth reactions: Average molecular weights

$$\bar{M}_n = \frac{M_0}{1-p}$$

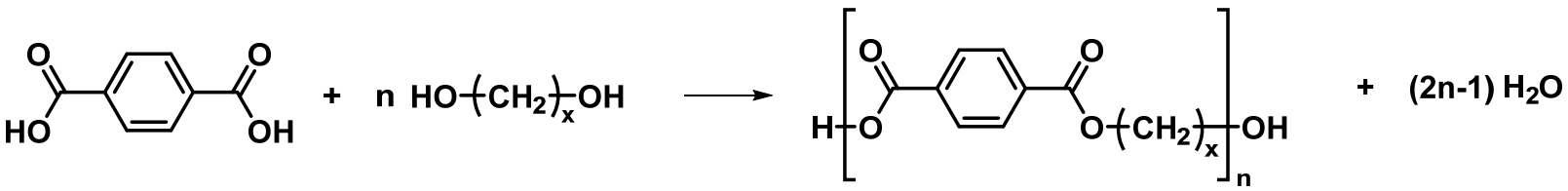
$$\bar{M}_w = M_0 \cdot \frac{(1+p)}{(1-p)}$$

polydispersity index

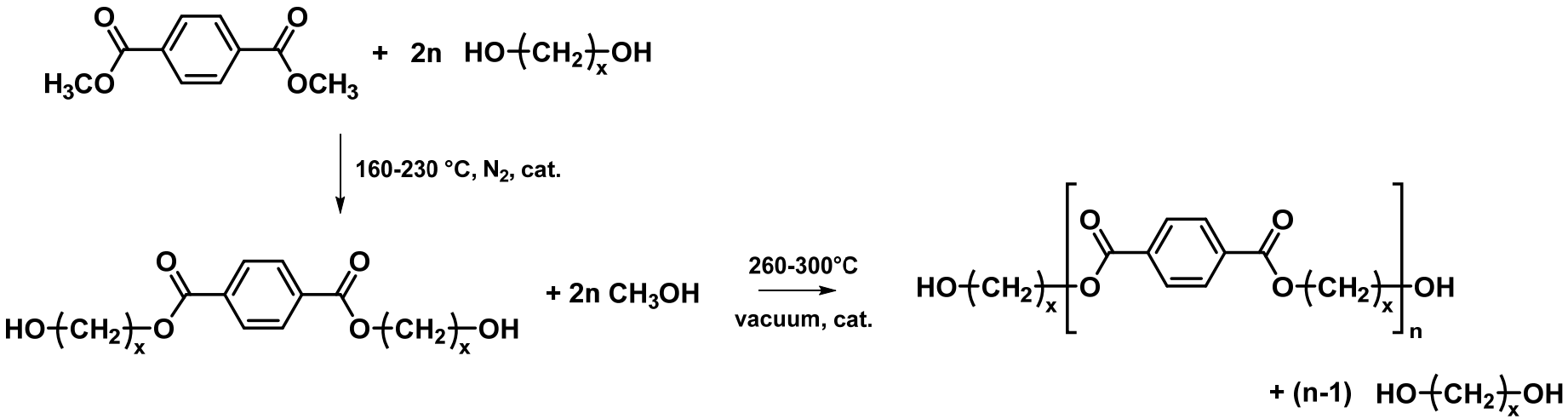
$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + p = PDI$$

Step growth reactions: Industrially relevant 1

Polyesters

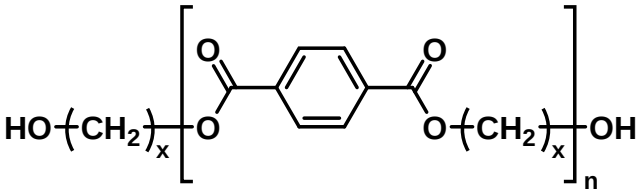


or more commonly on industrial scale:



Step growth reactions: Industrially relevant 1

Polyesters



Polyethylene terephthalate (PET, x=2)

trade names: Rynite (DuPont), Arnite-A (DSM)

Semi-crystalline PET-C:

medium strength, high stiffness and hardness, low impact resistance
→ *Electrical engineering*: phones, computers; *mechanical engineering*

Amorphous PET-A:

Optically transparent up to 5 mm thickness, low permeability for O_2 and CO_2
→ Preferred in *packaging industry*

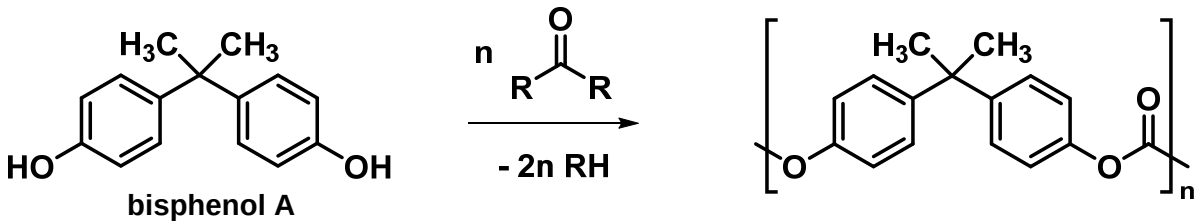
Polybutylene terephthalate (PBT, x=4)

typical applications: engineering polymer

trade names: Ultradur (BASF), Vestodur (Evonik Degussa)

Step growth reactions: Industrially relevant 1

Polycarbonates (PC): linear polyesters of carbonic acid



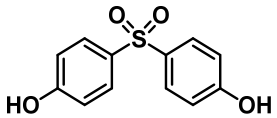
Makrolon (Bayer Materials)
Lexan (GEP)
Xantar (DSM)

with diphenylcarbonat (R= OPh): melt polymerization

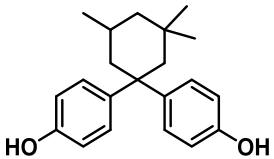
with phosgene: interfacial polymerization (DCM/water) with Na-salt of bisphenol A

Variation of properties like glass transition or refractive index

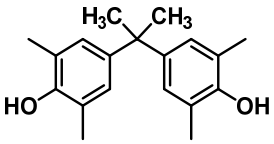
by choice of bisphenol:



bisphenol S

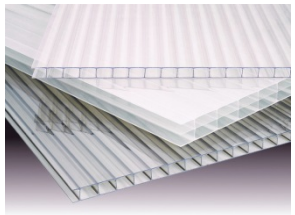


BPTMC



Tetramethyl-bisphenol A

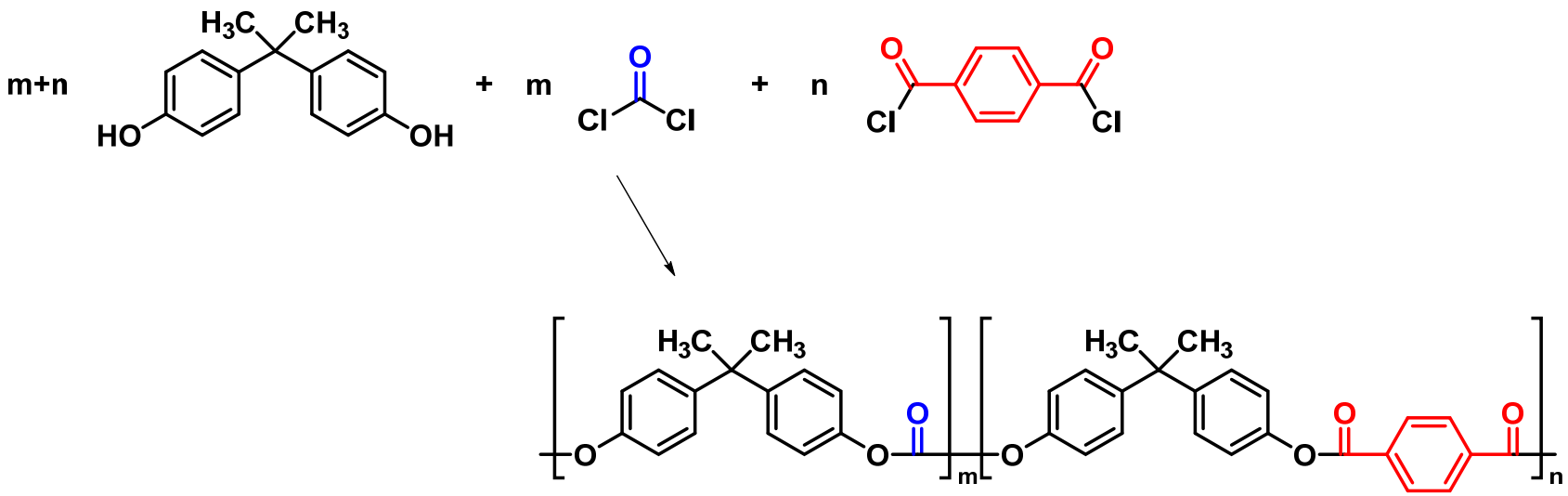
Typical applications:



Step growth reactions: Industrially relevant 1

Polyestercarbonates (PEC):

co-condensation of bisphenol A with terephthalic chloride and phosgene



Advantage over PC:

Replacement of CO- by CO-Ar-CO leads to higher form stability at high temperatures

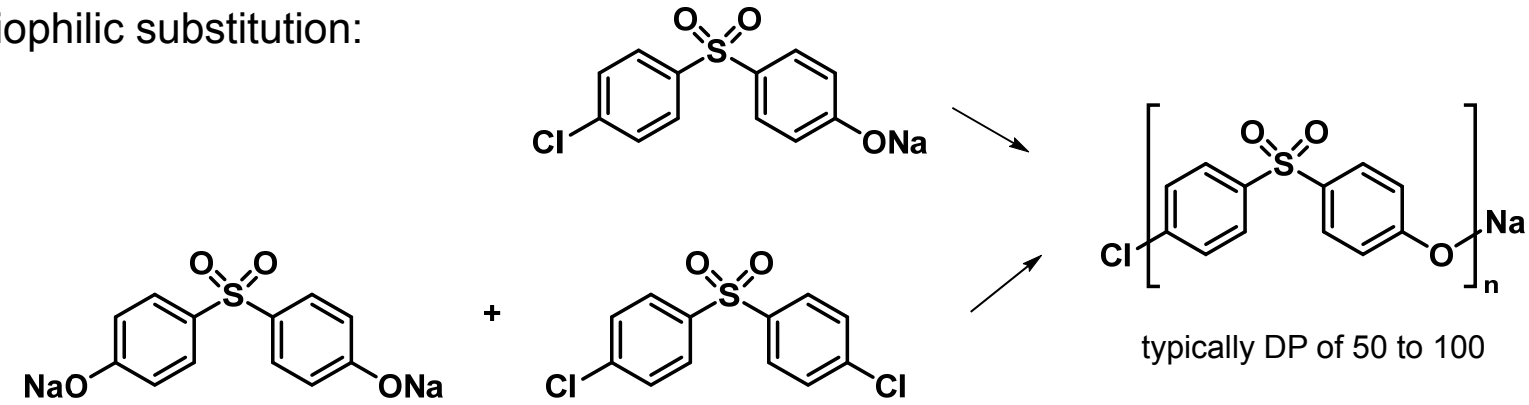
→ allows applications with temperatures up to 140-180°C

Step growth reactions: Industrially relevant 1

Polyethersulfons:

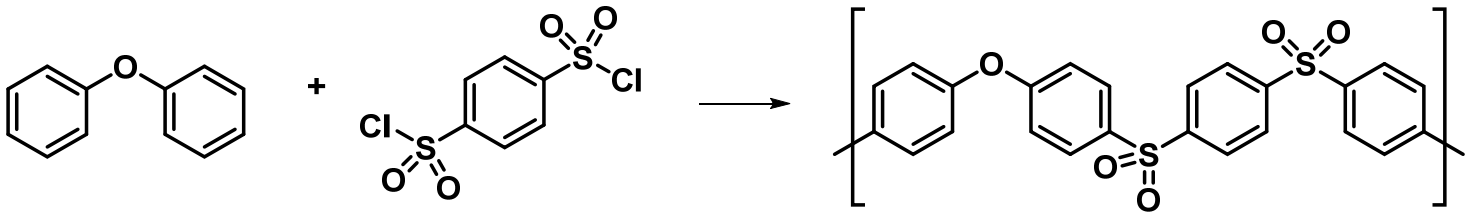
generally amorphous polymers with T_g ~190°C

via nucleiophilic substitution:



typically DP of 50 to 100

via electrophilic substitution:

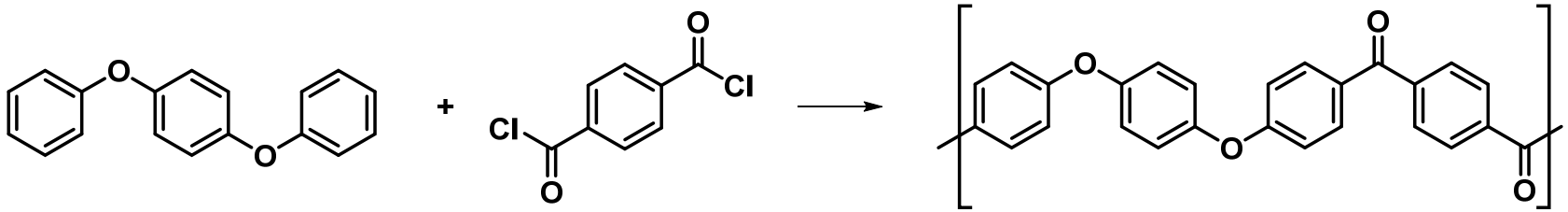


Step growth reactions: Industrially relevant 1

Polyetherketones:

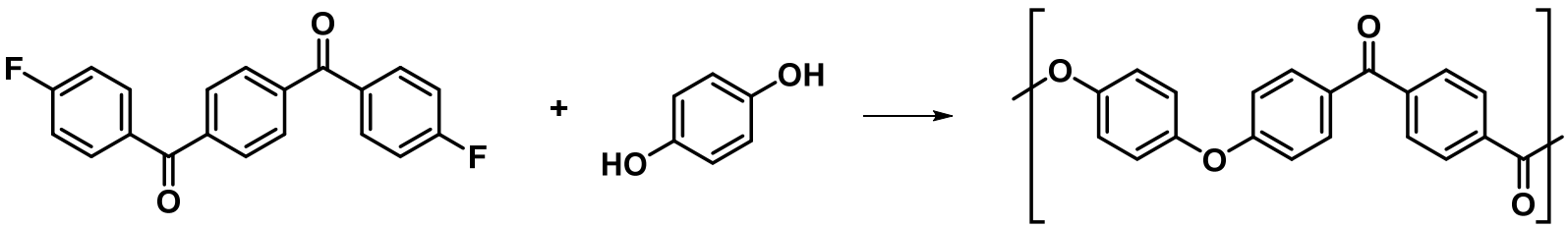
Generally semi-crystalline, T_g ~ 150°C, T_m ~ 330°C; T_g and T_m increase with C=O

via electrophilic substitution (Friedel Crafts acylation):



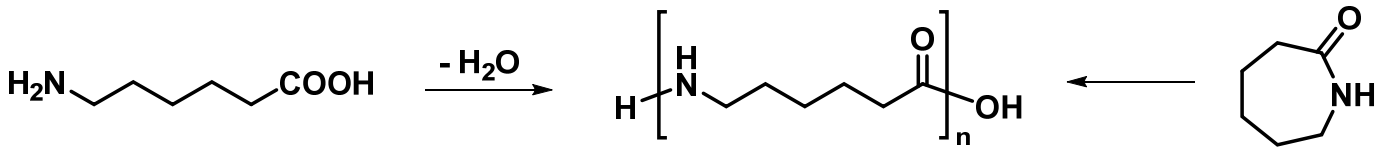
***P*olye*ther*e*ther*keton*keton**
(PEEKK)

via nucleophilic substitution



Step growth reactions: Industrially relevant 1

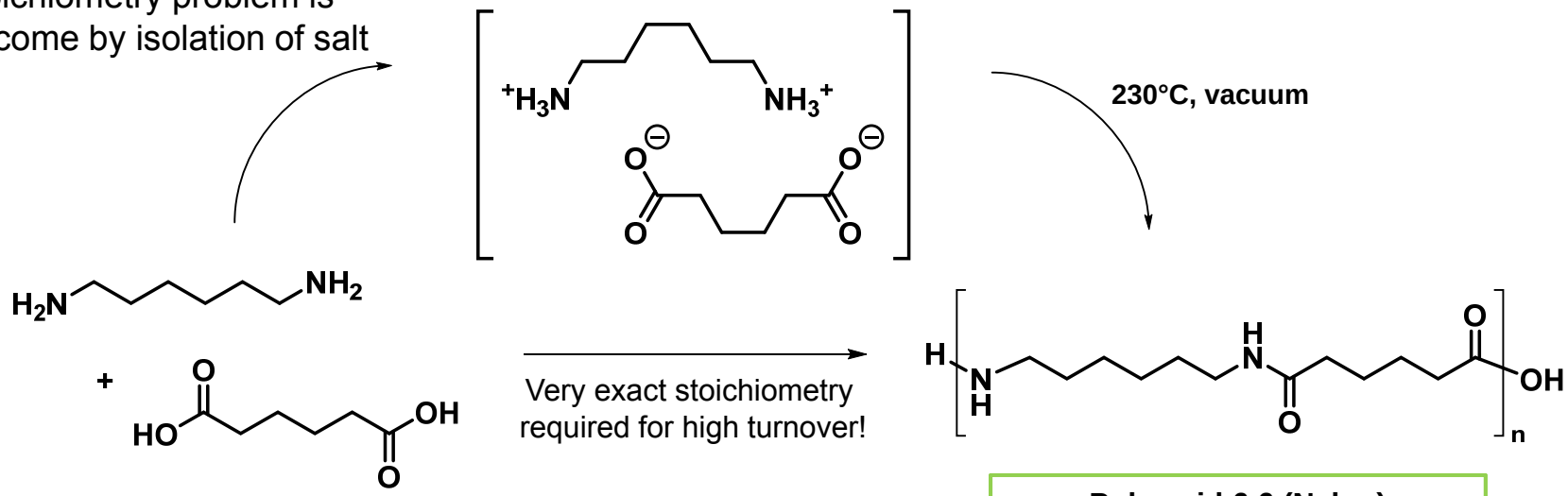
Aliphatic polyamides (PA):



Polyamid 6

1) AH-salt condensation (**A**dipinic acid / 1,6-**H**examethylen diamine)

Stoichiometry problem is overcome by isolation of salt

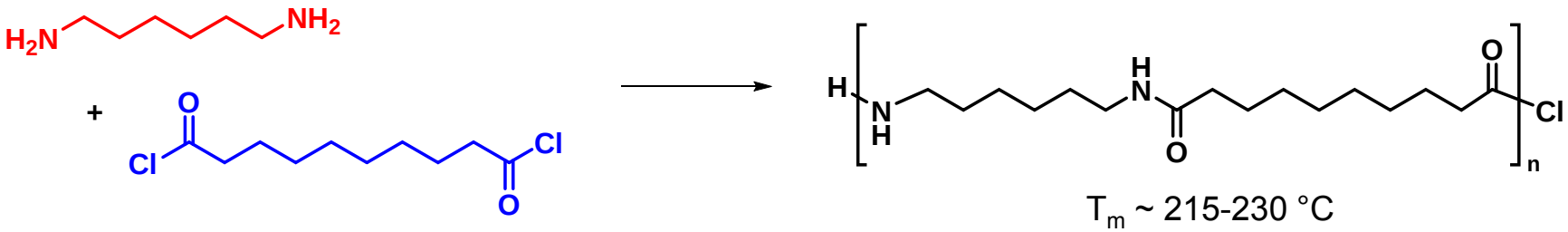


Polyamid 6,6 (Nylon)
T_m ~ 260 °C, 30-50% crystallinity,
$\bar{M}_n$ 1.5 to 5 x 10^4, PDI = 2

Step growth reactions: Industrially relevant 1

Aliphatic polyamides (PA):

2) Interfacial polymerization (Schotten-Baumann reaction)



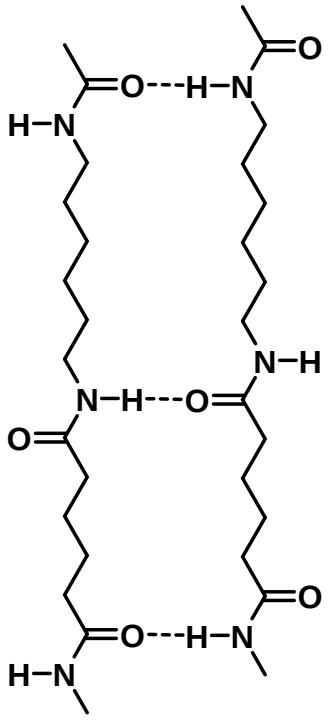
No strict stoichiometry required, as reaction is carrier out at interface of aqueous phase (diamine) and organic phase (acid chloride)

Step growth reactions: Industrially relevant 1

Aliphatic polyamides (PA):

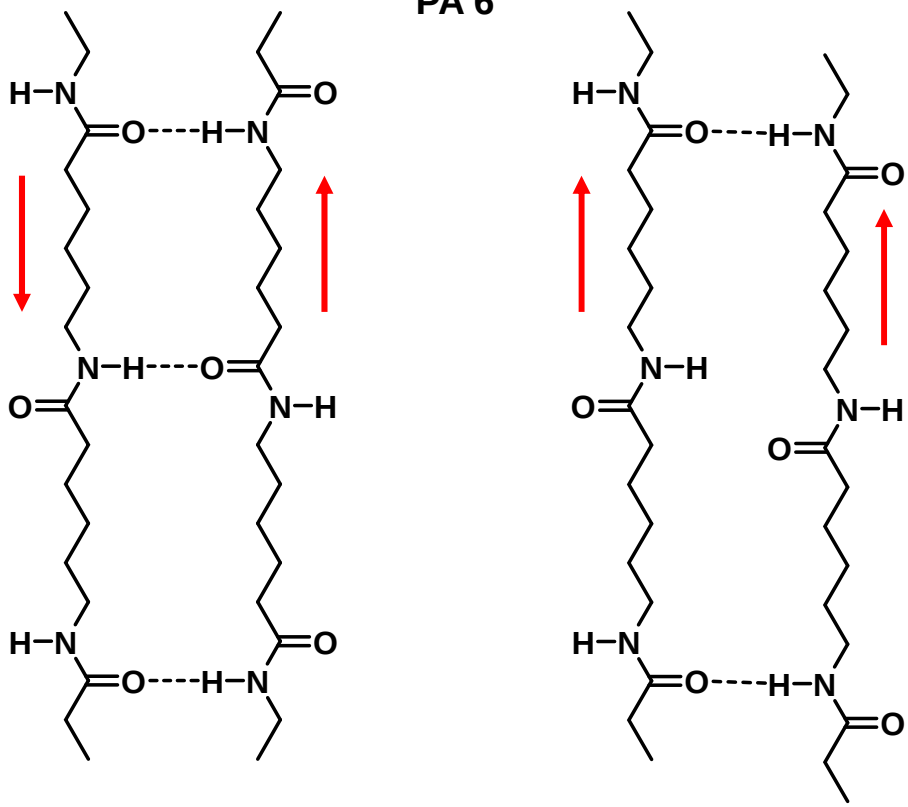
!! Properties of PA mainly determined by hydrogen bonding interactions between amid bonds !!

PA 6,6



T_m ~260°C

PA 6



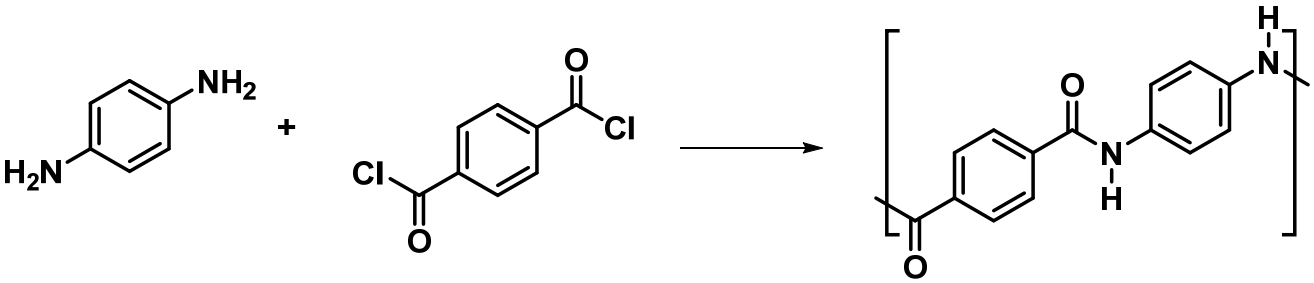
T_m ~220°C

Step growth reactions: Industrially relevant 1

Aromatic polyamides:

1) Nomex (high temperature stability, flame-resistant)

2) Kevlar

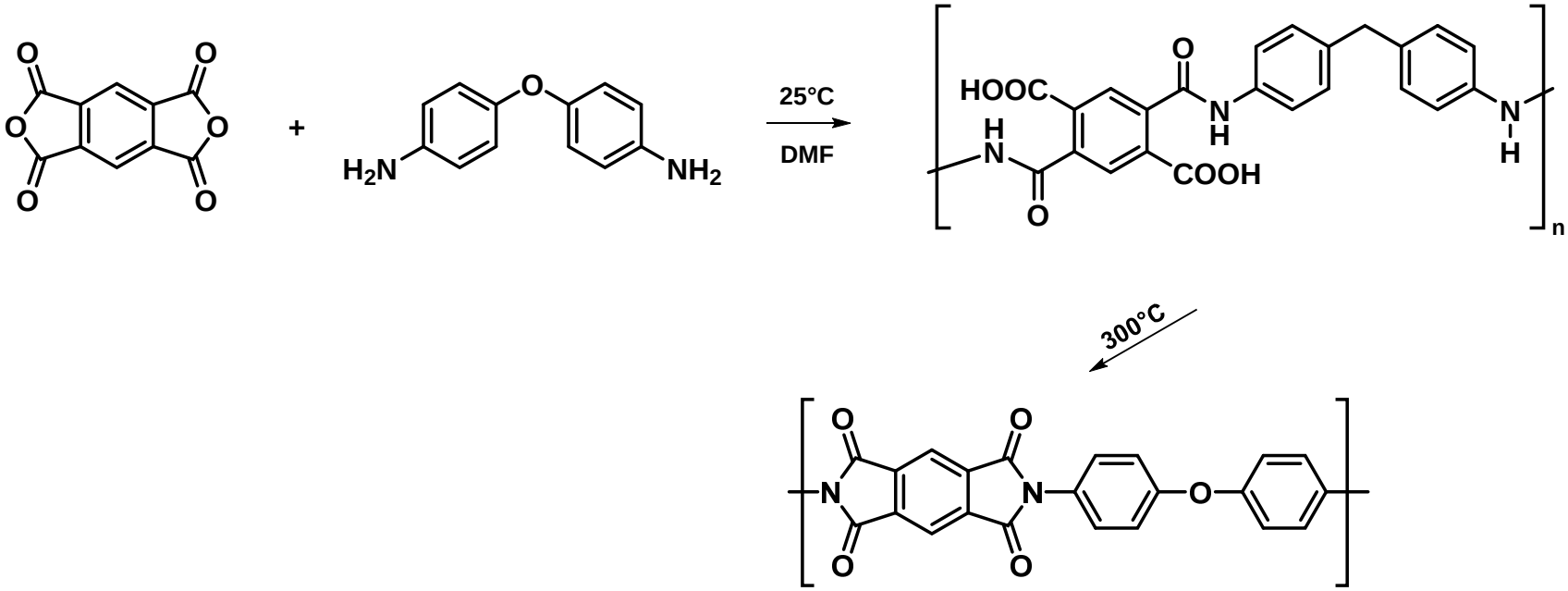


- Strong tendency to formation of hydrogen bonding network
- Only soluble in conc. H_2SO_4, which is also solvent for prepartion of fibres
- Degradation temperature ~ 550°C (carbonizes!)

Step growth reactions: Industrially relevant 1

Polyimides:

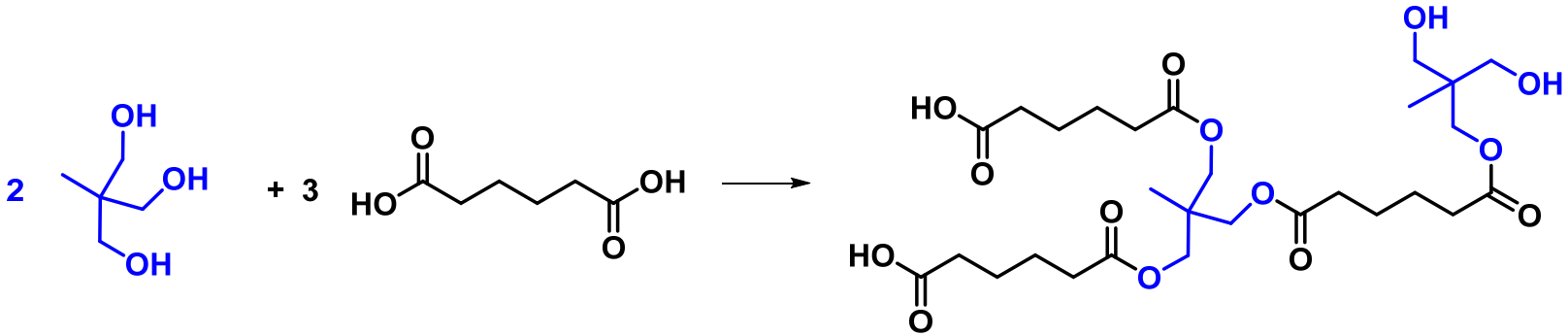
… via dianhydride and diamine



Typical applications:
Flame retarding insulators
Decomposition T >420 °C (in vaccum > 500°C)

Step growth reactions: Branching

What happens when a polyester formation is carried out with triol?:



→ Network formation

→ Steep increase in viscosity and finally gelation

→ Leads to highly branched polymer, insoluble and not meltable

Step growth reactions: Prediction of gel point

Modification of the Carother equation

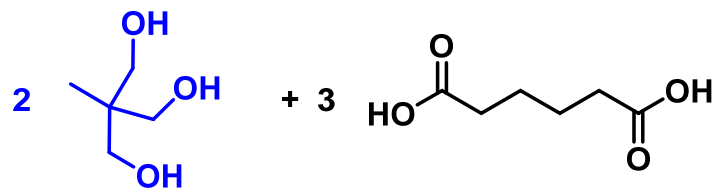
Let us first define an average functionality $\bar{f}$ of all monomer units:

- $\bar{f} = \frac{\sum n_j f_j}{\sum n_j}$

n_j: number of monomers j
f_j: functionality (integer number)
$\sum n_j$: sum of all monomer molecules

… and understand this with an example:

2 mol triol + 3 mol adipinic acid:



$$\bar{f} = \frac{\sum n_j f_j}{\sum n_j} = \frac{(2\times3)+(3\times2)}{5} = \frac{12}{5} = 2.4$$

Step growth reactions: Prediction of gel point

Modification of the Carother equation

Let us first define an average functionality $\bar{f}$ of all monomer units:

- $\bar{f} = \frac{\sum n_j f_j}{\sum n_j}$

n_j: number of monomers j
f_j: functionality (integer number)
$\sum n_j$: sum of all monomer molecules

If n_0 molecules are present at the start of the polymerization, the number of functional groups is $n_0 \cdot \bar{f}$

After time *t*, n_t molecules are present, and $2(n_0 - n_t)$ groups have reacted.

The probability for group to react (turnover) is then: $p = \frac{2(n_0 - n_t)}{n_0 \cdot \bar{f}} = \frac{2}{\bar{f}} - \frac{2n_t}{n_0 \cdot \bar{f}}$

With the average degree of polymerization $\bar{P}_n = \frac{n_0}{n_t}$

$$\Rightarrow p = \frac{2}{\bar{f}} - \frac{2}{\bar{P}_n \cdot \bar{f}}$$

Step growth reactions: Prediction of gel point

Modification of the Carother equation

With the average degree of polymerization $\overline{P}_n = \frac{n_0}{n_t}$

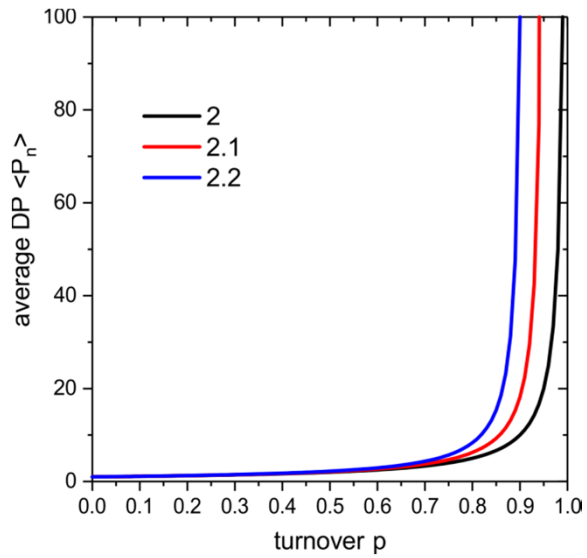
$$\Rightarrow p = \frac{2}{\overline{f}} - \frac{2}{\overline{P}_n \cdot \overline{f}}$$

At gel point, $\overline{P}_n \rightarrow \infty$, so that $\frac{2}{\overline{P}_n \cdot \overline{f}} \rightarrow 0$.

For turnover at gel point, we get:

$$p_{gel} = \frac{2}{\overline{f}}$$

Average functionality has dramatic effect on average DP

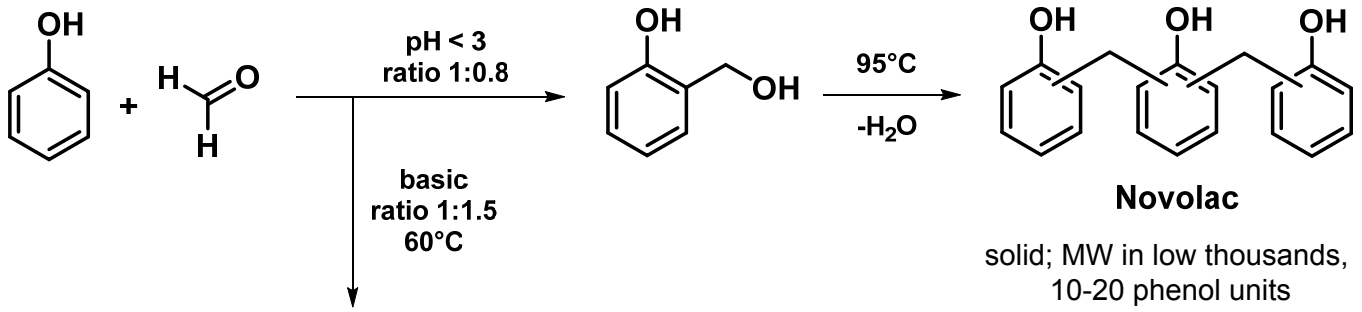


Step growth reactions: Industrially relevant 2

Phenol formaldehyde (PF) resins or phenolic resins

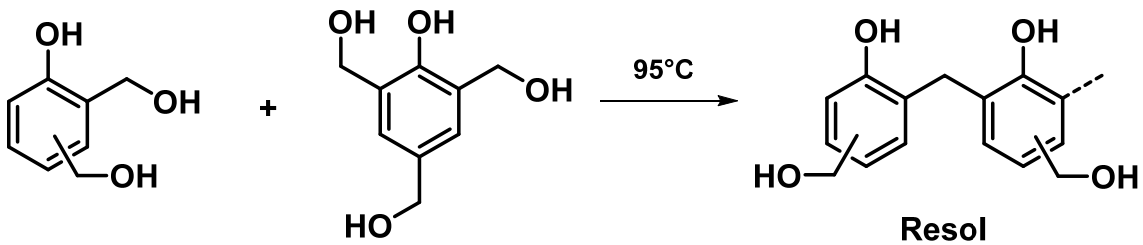
first commercial synthetic resin, introduced 1910, two-stage preparation: ***precondensation*** and ***curing***

1) Precondensation = *preparation of a prepolymer*



Novolac

solid; MW in low thousands,
10-20 phenol units



Resol

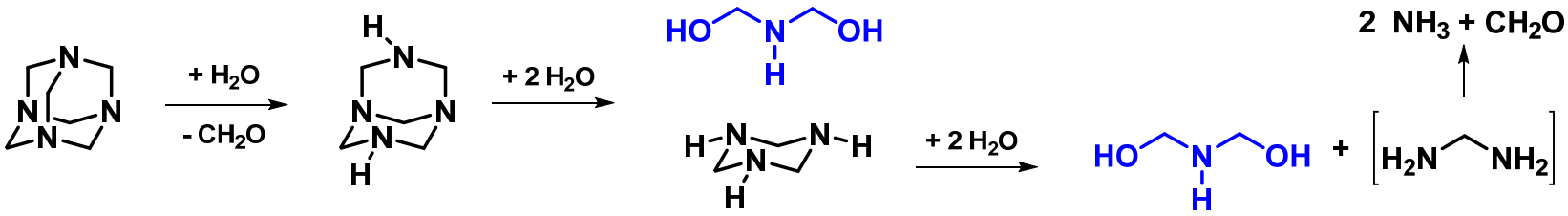
liquid, sold as ethanolic solution;
curing with high temperture

Step growth reactions: Industrially relevant 2

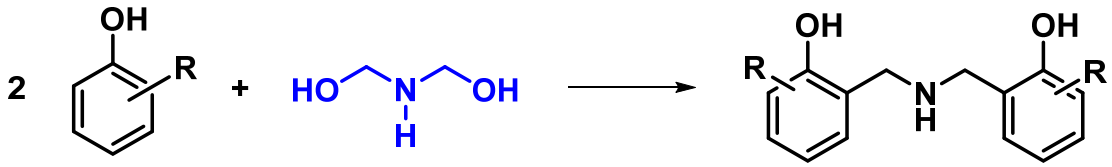
Phenol formaldehyde (PF) resins or phenolic resins

***2a) Curing / hardening of* novolacs**

Thermal hardening in presence of 8-15% hexamethylene tetramine:



DMA reacts with novolacs:



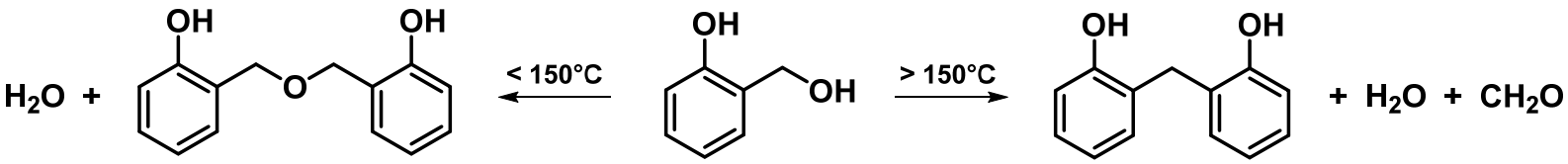
Step growth reactions: Industrially relevant 2

Phenol formaldehyde (PF) resins or phenolic resions

***2b) Curing / hardening of* resoles**

Themal hardening in neutral to weakly acidic medium

at 130-200°C (<150°C benzyl bridges, >150°C methylene):



Typical applications of PF resins (today) are, for instance, billiards balls, laminates, synthetic resin bounded paper (countertops), and also:

Novolacs: photoresist (in photolitography)

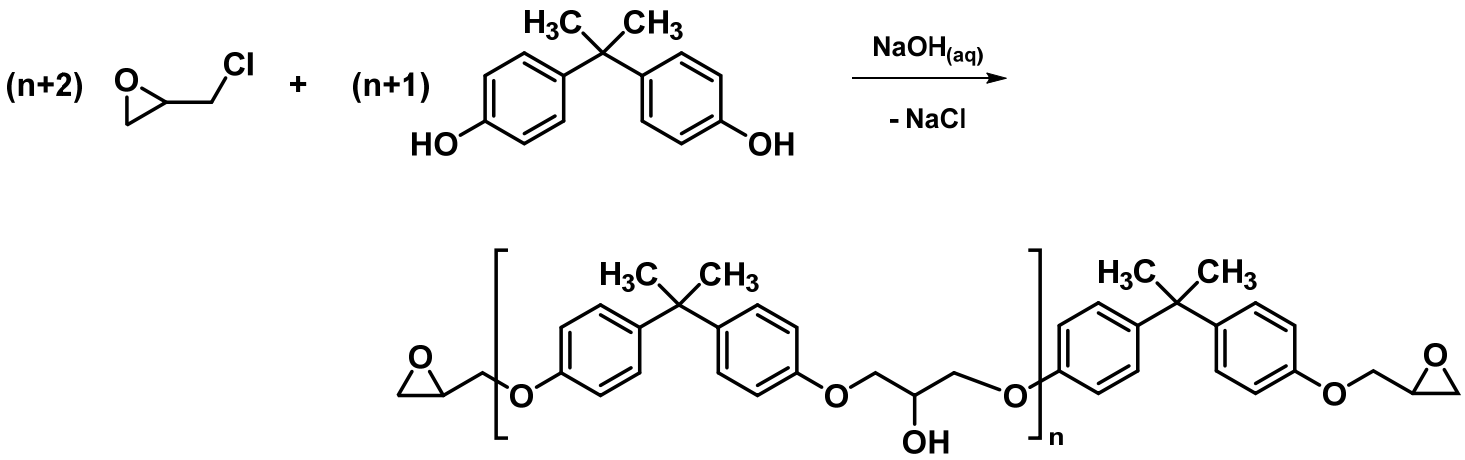
Resoles: plywood, oriented strand boards, laminated composite lumber

Step growth reactions: Industrially relevant 2

Epoxid resins

- Epoxid-compounds are highly reactive towards amines and acid anhydrides
- Relevant for technical application in branched polymer networks

Most important resin of epoxid networks: **Bisphenol-A-diglycidylether**

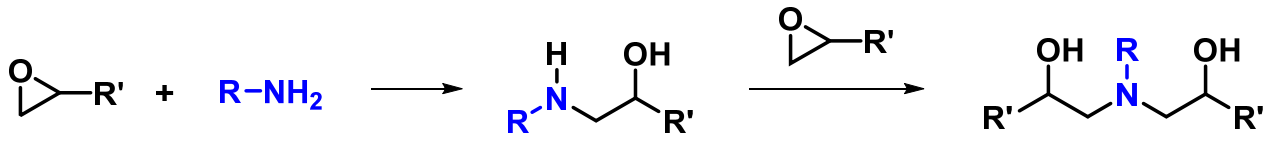


Oligomers from n = 0 to 30 with T_m from 9°C to 112 °C (M_n=1420)

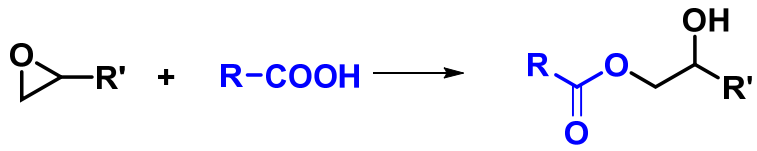
Step growth reactions: Industrially relevant 2

Epoxid resins – Crosslinking mechanisms

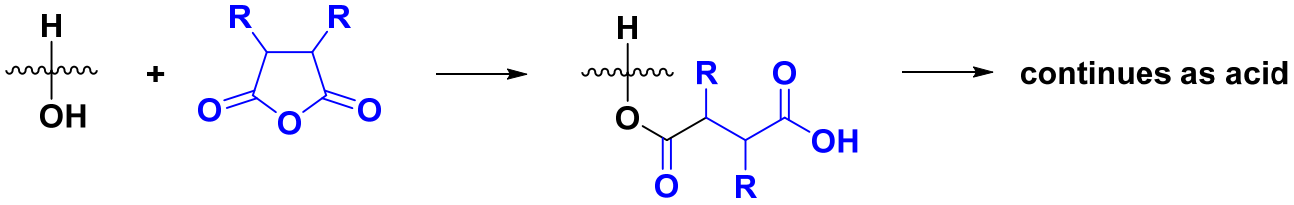
A) Crosslinking with primary amines



B) Crosslinking with carboxylic acids



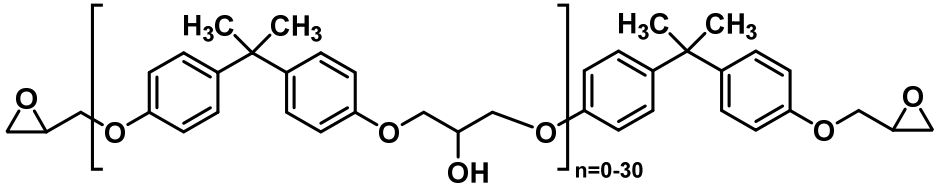
C) Crosslinking with acid anhydrides



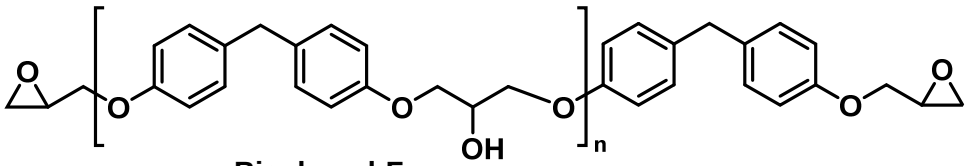
Step growth reactions: Industrially relevant 2

Epoxid resins – Typical resins and hardeners

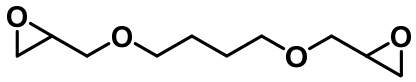
Resins:



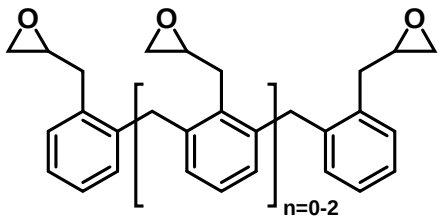
Bisphenol-A



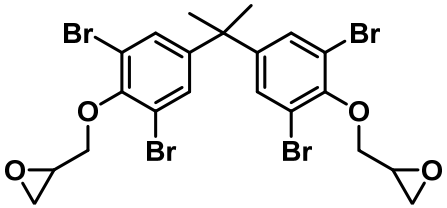
Bisphenol-F
(lower viscosity, often used as mixture with bisphenol-A)



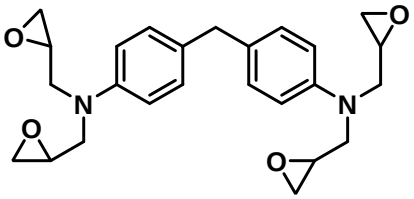
Butan-diol-1,4-diglycidyl ether
(reactive dilutant)



Glycidyl novolacs



Tetrabromo bisphenol-A digylcidyl ether



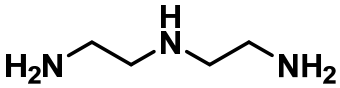
Tetraglycidyl-diamine diphenyl methan
(often as binder in fiber reinf. materials)

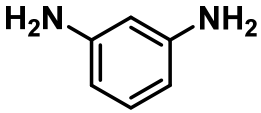
Step growth reactions: Industrially relevant 2

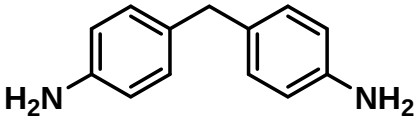
Epoxid resins – Typical resins and hardeners

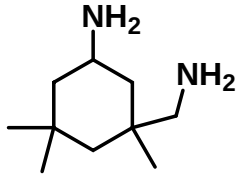
Hardeners:

Amines



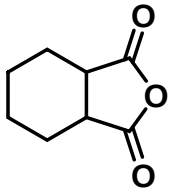


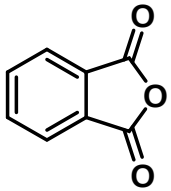


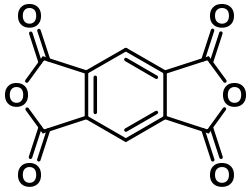


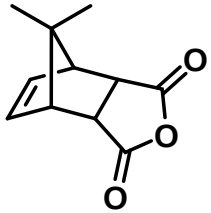
Isophorone diamine

Acid anhydrides







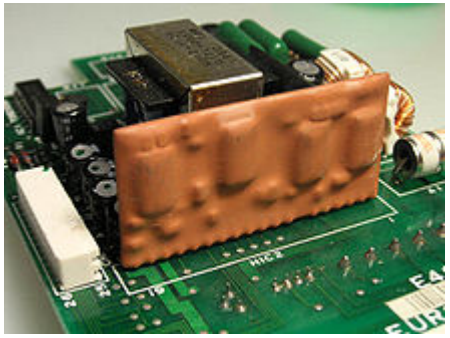


Step growth reactions: Industrially relevant 2

Epoxid resins

Important note on crosslinking of epoxides:

- No formation of volatile products
- Small volume change



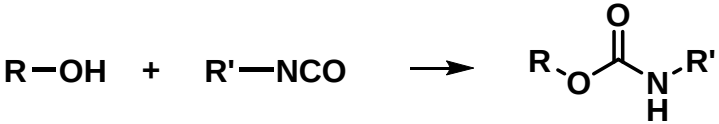
Applications:

- Matrix for fiber reinforced materials
- moulding material in electronics
- Weather resistant coatings
- 1K and 2K adhesives, lacquer, …

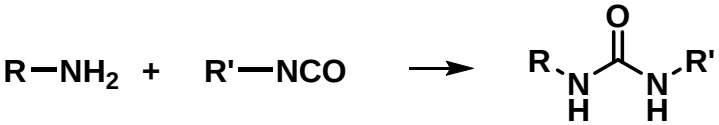
Step growth reactions: Industrially relevant polymers 2

Polymers based on isocyanates

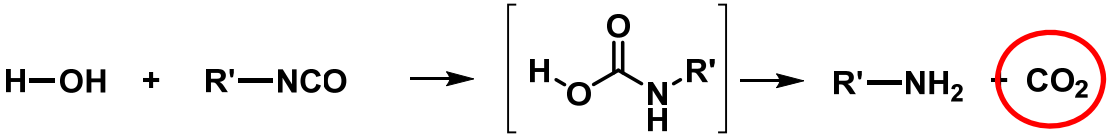
Fast(er)



Urethanes (25-50 °C)

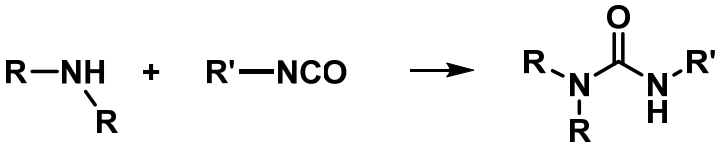


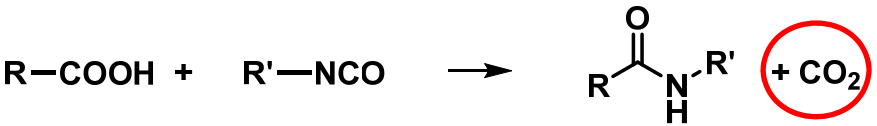
Ureas (25 °C)



Hydrolysis

Slow(er)

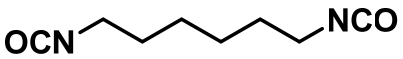




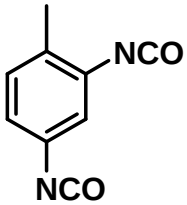
CO_2 can be used as foaming agent!

Step growth reactions: Industrially relevant network polymers

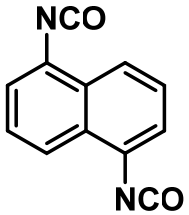
Typical isocyanates



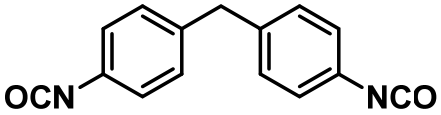
HDI



TDI

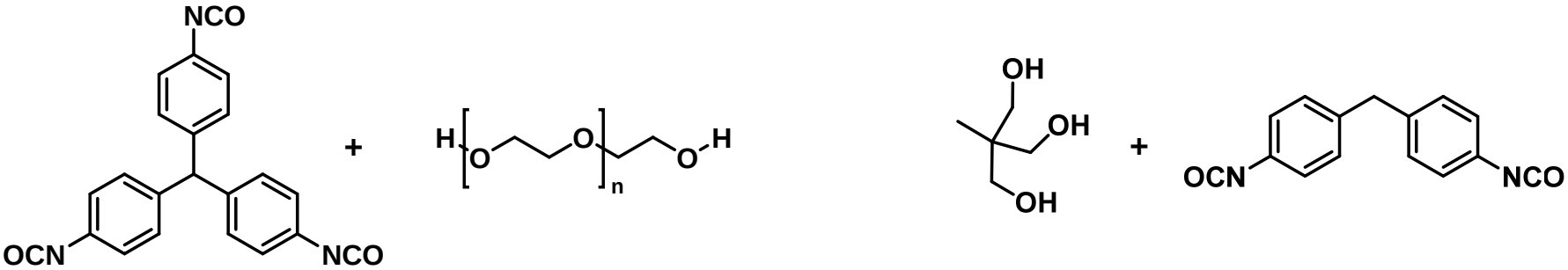


NDI



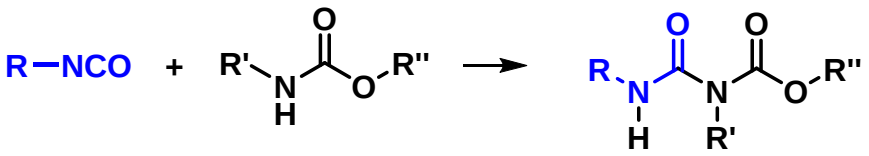
MDI

Crosslinked network structures often with addition of DABCO as catalyst

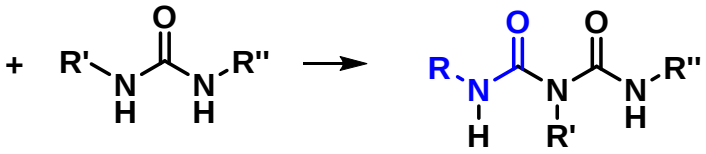


Step growth reactions: Industrially relevant network polymers

Crosslinking via side reactions



Allophanate formation
(>120-140 °C)



Biuret formation
(>100 °C)

Technical usage

1) One-shot process: mixing of polyfunctional components, and direct curing

2) Formation of prepolymer : non-stoichiometric mixture of components, leaves unreacted side groups

Step growth reactions: Polyurethane foams

Controlling foaming behaviour

- Addition of foaming agents:

  Viscosity increases during polymerization → gas bubbles get stuck

- Possible foaming agents:

  CO_2 (from reaction with water)

  chlorofluoroalkanes (not allowed anymore) } evaporate due to heat of polymerization

  pentane

Controlling foam properties

- Long chain polyoles, trifunctional monomers

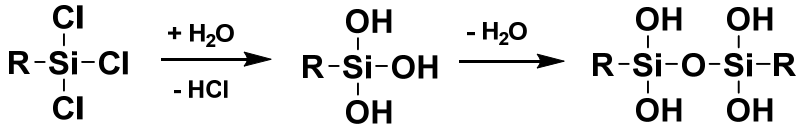
  → soft, flexible foam

- Short chain polyoles, higher degree of crosslinking

  → stiff foams

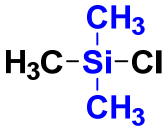
Step growth reactions: Industrially relevant network polymers

Silicones

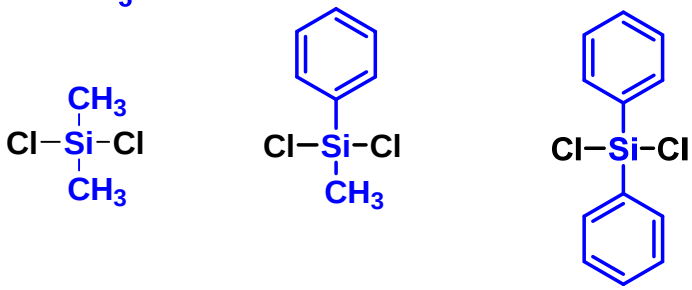


Regulation of crosslinking density using

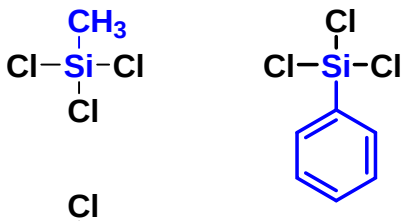
- monofunctional building blocks



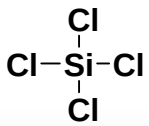
- bifunction building blocks



- trifunctional building blocks



- tetrafunctional building blocks



For consumer products:

Acetates instead of chlorides!