Introduction to Macromolecular Chemistry

aka polymer chemistry

Mondays, 8.15-9.45 am, NC 02/99

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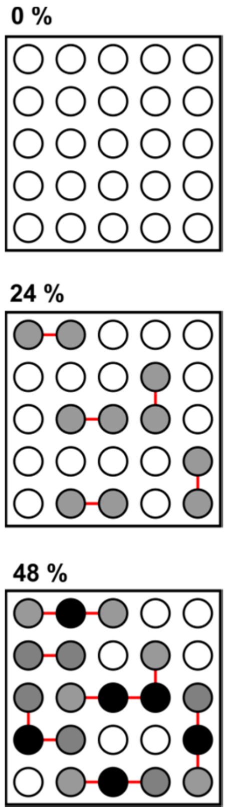
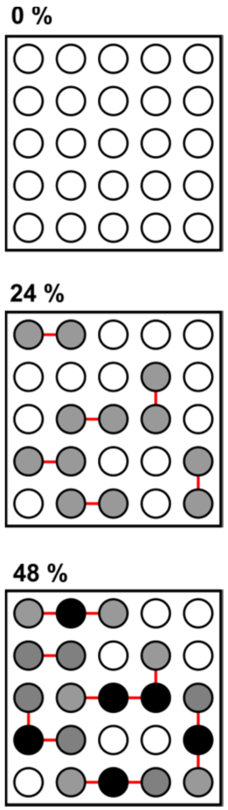
Polymerization reactions: Summary

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

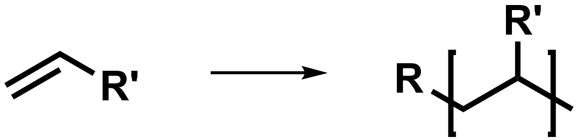


- Monomer has one polymerizable group
- Active chain end, i.e. growth in one direction

Different mechanisms:

- Radical polymerization
- Cationic polymerization
- Anionic polymerization
- Coordinative polym.

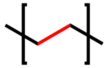
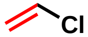
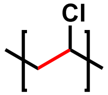
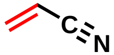
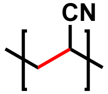
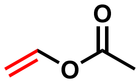
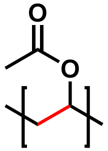
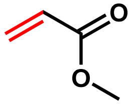
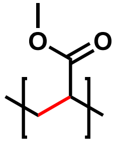
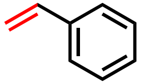
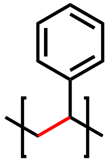
Free radical polymerization



Three step reaction:

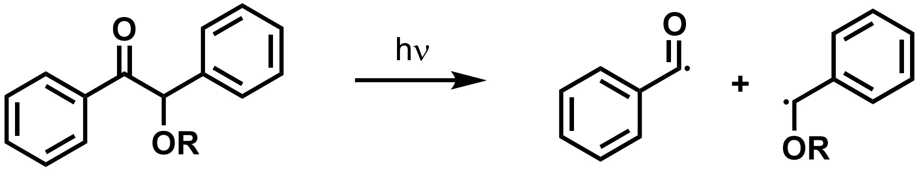
- Initiation
- Chain growth
- Termination

Typical examples

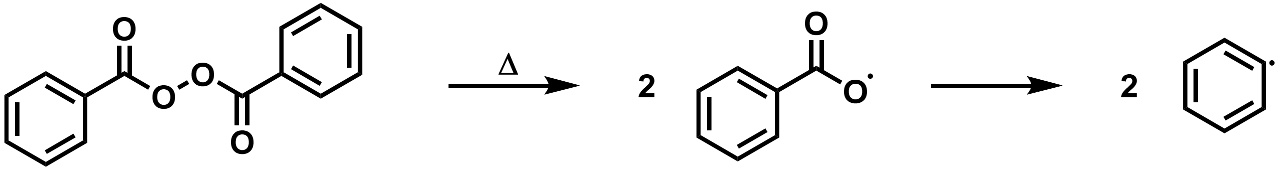
	monomer	**polymer**
Ethylene		
Vinyl chlorid		
Acrylo nitrile		
Vinyl acetate		
Methyl acrylic acid		
Styrene		

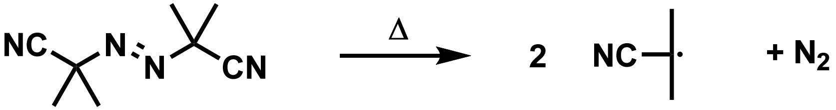
Free radical polymerization: Initiation

Photochemical activation of initiator

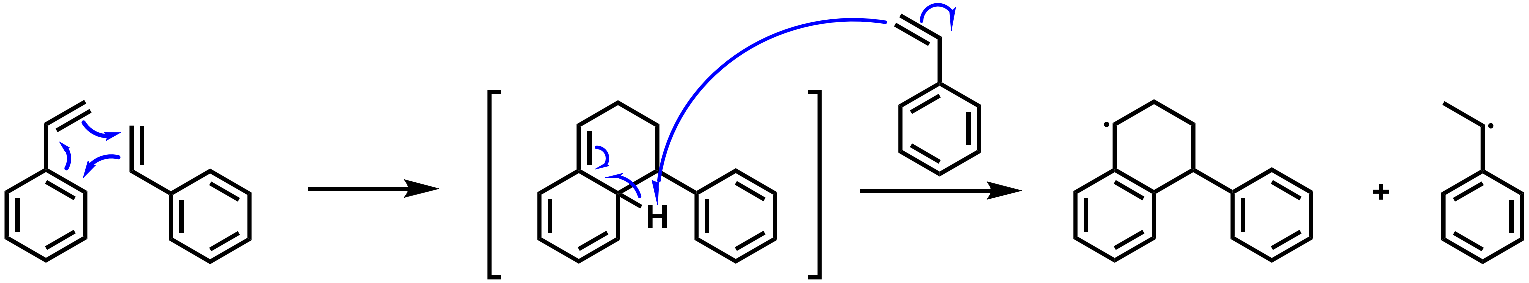


Thermal activation of initiator



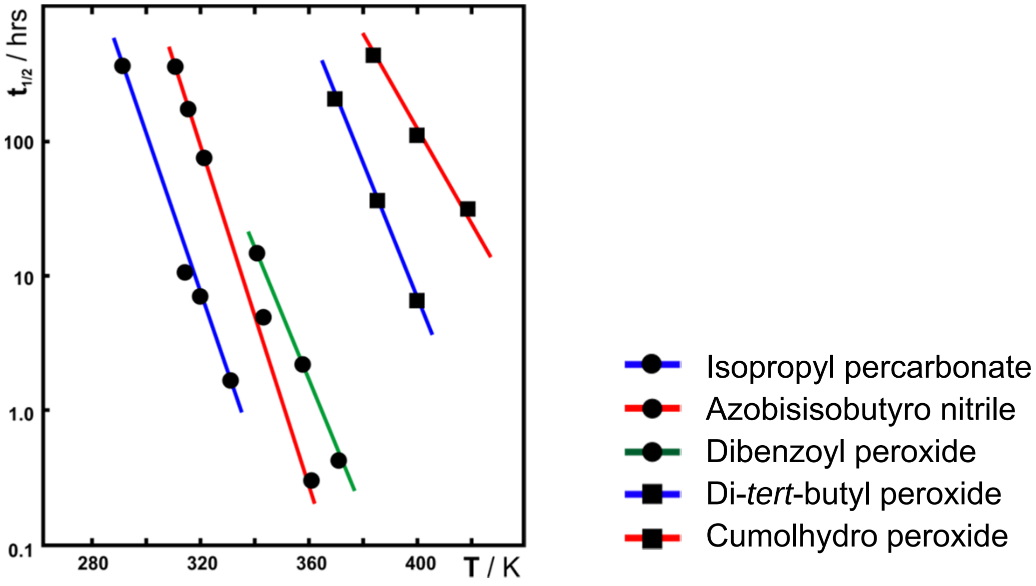


Thermal initiation of polymerization



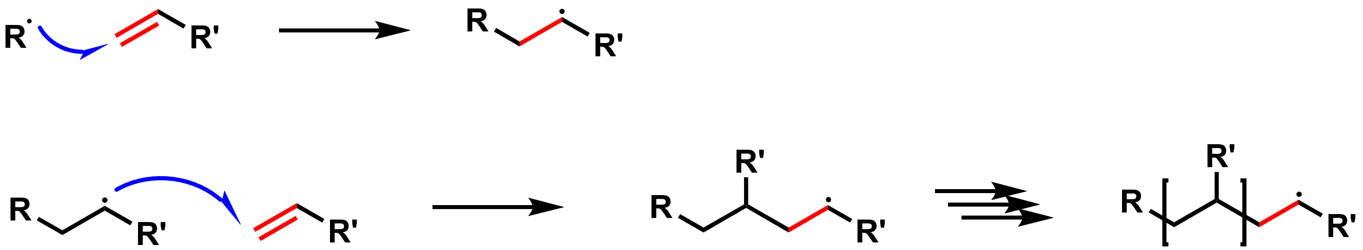
Free radical polymerization: Initiation

Important: **Initiator radical lifetime at polymerization temperature**



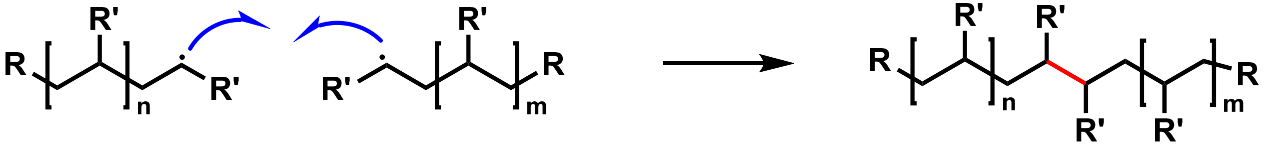
Free radical polymerization: Growths and termination

Chain growths

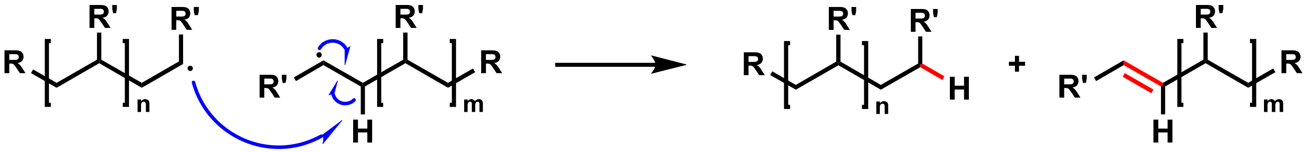


Termination mechanisms

a) Combination



b) Disproportionation



Free radical polymerization: Kinetics

Initiation: In-In $\xrightarrow{k_{in}}$ 2 In•

Chain start: In• + M $\xrightarrow{k_{st}}$ In-M•

Initiation is much slower than chain start: $k_{st} \gg k_{in}$

Reaction kinetics of 1st order in concentration of initiator:

$$-\frac{\mathrm{d}[\mathbf{InIn}]}{\mathrm{d}t} = k_{in}[\mathbf{InIn}]$$

$$\frac{\mathrm{d}[\mathbf{In}^{\cdot}]}{\mathrm{d}t} = 2k_{in}[\mathbf{InIn}]$$

Growth: M_i• + M $\xrightarrow{k_p}$ R-M_{i+1}•

For polymerization rate: $-\frac{\mathrm{d}[\mathbf{M}]}{\mathrm{d}t} = k_p \cdot [\mathbf{M}] \cdot \sum[\mathbf{M_i}^{\cdot}]$

Free radical polymerization: Kinetics

Termination: $M_i^{\bullet} + M_j^{\bullet} \xrightarrow{k_{tc}} M_{(i+j)}$ for recombination

$\xrightarrow{k_{td}} M_i + M_j$ for disproportioning

The rates of determination thus are:

$$-\frac{\mathrm{d}[\mathrm{M_i^{\cdot}}]}{\mathrm{d}t} = 2k_{tc}\sum[\mathrm{M_i^{\cdot}}][\mathrm{M_j^{\cdot}}]$$

$$-\frac{\mathrm{d}[\mathrm{M_i^{\cdot}}]}{\mathrm{d}t} = 2k_{td}\sum[\mathrm{M_i^{\cdot}}][\mathrm{M_j^{\cdot}}]$$

with $k_t = k_{tc} + k_{td}$ and assuming that $M_i^{\bullet}$ and $M_j^{\bullet}$ are indistinguishable it follows that

$$-\frac{\mathrm{d}[\mathrm{M_i^{\cdot}}]}{\mathrm{d}t} = 2k_t\left(\sum[\mathrm{M_i^{\cdot}}]\right)^2$$

Simplification: **steady state** in which number of radicals formed and consumed are equal

$$\frac{\mathrm{d}[\mathrm{In^{\cdot}}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{M_i^{\cdot}}]}{\mathrm{d}t} \quad \Rightarrow \quad 2k_{in}[\mathrm{InIn}] = 2k_t\left(\sum[\mathrm{M_i^{\cdot}}]\right)^2 \quad \Rightarrow \quad \sum[\mathrm{M_i^{\cdot}}] = \sqrt{\frac{k_{in}[\mathrm{InIn}]}{k_t}}$$

Free radical polymerization: Kinetics

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We can thus write for the rate of polymerization:

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_p \cdot [\mathrm{M}] \cdot \sum[\mathrm{M_i}^{\cdot}] = \frac{k_p\sqrt{k_i}}{\sqrt{k_t}} \cdot [\mathrm{M}] \cdot [\mathrm{InIn}]^{1/2}$$

but, as $\boldsymbol{k_i}$ is small, [InIn] remains approximately constant

during the reactions, so that the rate of polymerization becomes 1st order in [M]!

Free radical polymerization: Degree of polymerization

Kinetic chain length: How many monomers are added to each started radical chain before termination?:

$$\bar{\nu} = \frac{\text{Rate of monomer addition to chain}}{\text{Rate of new chain formation}} \quad \widehat{=} \quad \bar{\nu} = \frac{\text{growth rate}}{\text{initiator rate}} = \frac{-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t}}{\frac{\mathrm{d}[\mathrm{In}^{\cdot}]}{\mathrm{d}t}}$$

Substituting the equations from above gives in case of steady state:

$$\bar{\nu} = \frac{k_p[\mathrm{M}] \cdot \sum[\mathrm{M_i^{\cdot}}]}{2k_i[\mathrm{InIn}]} = \frac{k_p[\mathrm{M}]}{2\sqrt{(k_i k_t[\mathrm{InIn}])}}$$

The degree of polymerization is linked with the kinetic chain length by

$$\boldsymbol{\bar{P}_n = a \cdot \bar{\nu}}$$

where a is a factor which depends on the mechanisms of termination

($a = 1$ for disproportionation, $a = 2$ for recombination)

Free radical polymerization: Degree of polymerization

The degree of polymerization is linked with the kinetic chain length by

$$\boldsymbol{\bar{P}_n = a \cdot \bar{v}}$$

where a is a factor which depends on the mechanisms of termination

($a = 1$ for disproportionation, $a = 2$ for recombination)

So we end up with

$$\bar{P}_n = a \cdot \frac{k_p[\mathrm{M}]}{2 \cdot \sqrt{(k_i k_t[\mathrm{InIn}])}}$$

For the number average molecular mass, $\bar{M}_n = M_0 \cdot \bar{P}_n$, and by simplifying $\mathrm{b} = \frac{a k_p M_0}{2\sqrt{k_i k_t}} = constant$,

we get

$$\boxed{\bar{M}_n = \frac{b[\mathrm{M}]}{\sqrt{[\mathrm{InIn}]}}}$$

Free radical polymerization: Mass distribution

Mass distribution of radical polymerizations depend on kinetic chain length:

$$\bar{\nu} = \frac{\text{Rate of monomer addition to chain}}{\text{Rate of new chain formation}} \quad \widehat{=} \quad \bar{\nu} = \frac{\text{growth rate}}{\text{initiator rate}}$$

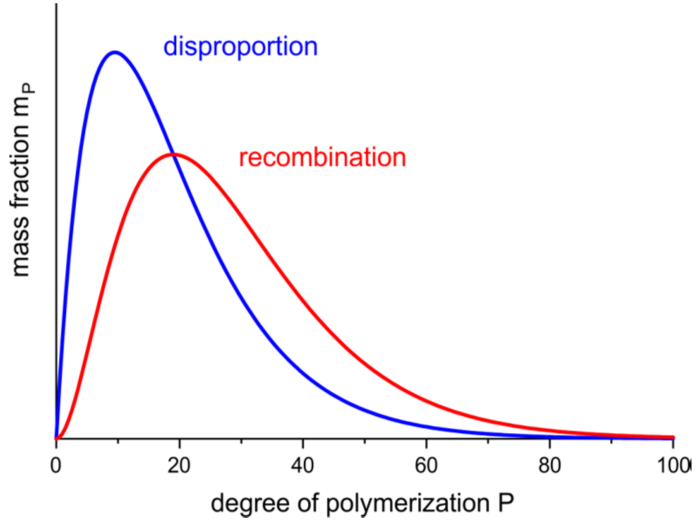
and on the mechanism of termination – disproportion or recombination:

For disproportion:

$$m_P = \ln^2(1-\tfrac{1}{\bar{\nu}}) \cdot P \cdot \left(1-\tfrac{1}{\bar{\nu}}\right)^P$$

For recombination:

$$m_P = -\tfrac{1}{2}\ln^3(1-\tfrac{1}{\bar{\nu}}) \cdot P^2 \cdot \left(1-\tfrac{1}{\bar{\nu}}\right)^P$$



m_P represents mass fraction of polymers with certain degree of polymerization.

Free radical polymerization: Temperature effects

Temperature dependence can be described with Arrhenius equations:

$$k_i = A_i \cdot \exp\left(-\frac{E_i}{RT}\right) \qquad k_p = A_p \cdot \exp\left(-\frac{E_p}{RT}\right) \qquad k_t = A_t \cdot \exp\left(-\frac{E_t}{RT}\right)$$

For the T-dependence of the rate of polymerization we get:

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = \frac{k_p\sqrt{k_i}}{\sqrt{k_t}} \cdot [\mathrm{M}] \cdot [\mathrm{InIn}]^{\frac{1}{2}} \quad \Rightarrow \quad -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = \frac{A_p\sqrt{A_i}}{\sqrt{A_t}} \cdot \exp\left(\frac{\frac{E_t}{2} - \frac{E_i}{2} - E_p}{RT}\right) \cdot [\mathrm{M}] \cdot [\mathrm{InIn}]^{\frac{1}{2}}$$

Generally, the exponential term is negative ➢➢ reaction rate goes up, if T is raised.

But:

$$\bar{M}_n = \frac{a k_p M_0}{2\sqrt{k_i k_t}} \cdot \frac{[\mathrm{M}]}{\sqrt{[\mathrm{InIn}]}} \quad \Rightarrow \quad \bar{M}_n = \frac{a A_p M_0}{2\sqrt{A_i A_t}} \cdot \exp\left(\frac{\frac{E_t}{2} + \frac{E_i}{2} - E_p}{RT}\right) \cdot \frac{[\mathrm{M}]}{\sqrt{[\mathrm{InIn}]}}$$

Here the exponential term is often positive ➢➢ average molecule weight decreases!

Free radical polymerization: Thermodynamic aspects

A reaction takes place, if $\boldsymbol{\Delta G = \Delta H - T\Delta S < 0}$.

This is the case, if $\Delta H < 0$ and $\Delta S > 0$

$\Delta H > 0$ and $T\Delta S > \Delta H$

$\Delta H \ll 0$ even with $\Delta S < 0$

typical for polymerizations!

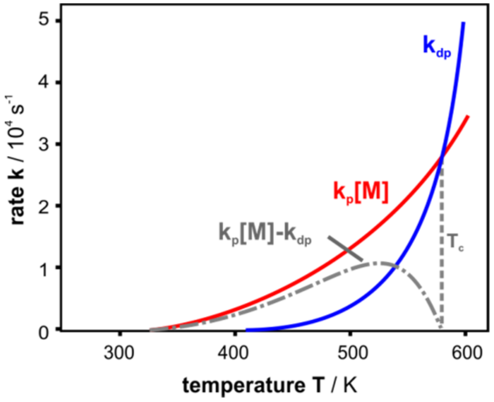
Ceiling-temperature T_c: $\Delta H = T_c \Delta S$

At T_c, polymerization and depolymerization are equally likely:

$$M_i^{\cdot} + M \xrightarrow{k_p} M_{i+1}^{\cdot}$$

$$M_{i+1}^{\cdot} \xrightarrow{k_{dp}} M_i^{\cdot} + M$$

If T_c is reached, the reaction stops ($k_p[M] = k_{dp}$).



examples:
MMA 493 K
styrene 583 K

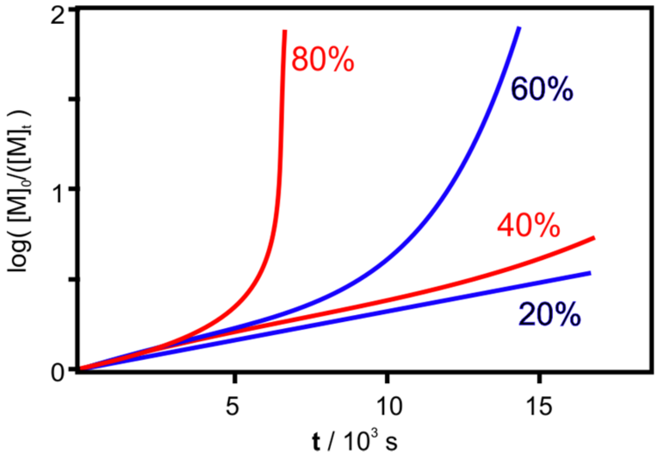
(Diagram redrawn based on Tieke, „Markomolekulare Chemie“)

Free radical polymerization: Autoacceleration

For bulk polymerization or in concentrated solutions, strong deviations from steady state kinetics are possible:

- increased viscosity prevents termination mechanisms.
- termination rate decreases significantly
- decrease in reaction rate once glass temperature is reached

➢➢ gel effect (**Trommsdorf Norrish effect**)



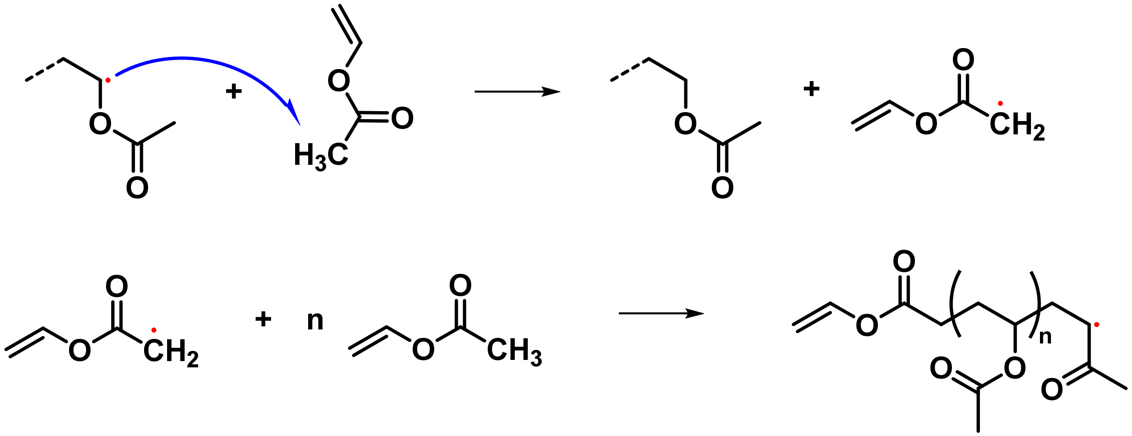
$$-\frac{\mathrm{d[M]}}{\mathrm{d}t} = \frac{k_p\sqrt{k_i}}{\sqrt{k_t}} \cdot [\mathrm{M}] \cdot [\mathrm{InIn}]^{\frac{1}{2}} \quad \Rightarrow \quad \ln\left(\frac{[M]_o}{[M]_t}\right) = \frac{k_p\sqrt{k_i}}{\sqrt{k_t}} \cdot t$$

Schematic change in $\log\left(\frac{[M]_o}{[M]_t}\right)$ with time at different concentrations of MMA in benzene: **A linear correlation is only observed for low concentrations.** (Diagram redrawn based on Tieke, „Markomolekulare Chemie“)

Free radical polymerization: Chain transfer

Chain transfer: Transfer of radical from growing chain to other species, from which the growth can continue ➢ kind of termination reaction

(a) Chain transfer to monomer (≠ regular polymerization step)



Competition with polymerization:

$$\left.\begin{aligned} P^\bullet + M &\xrightarrow{k_{transfer}} P + M^\bullet \\ M^\bullet + n\,M &\xrightarrow{k_{growth}} P^\bullet \end{aligned}\right\}$$

transfer constant

$$C_M = k_{transfer}/k_{growth}$$

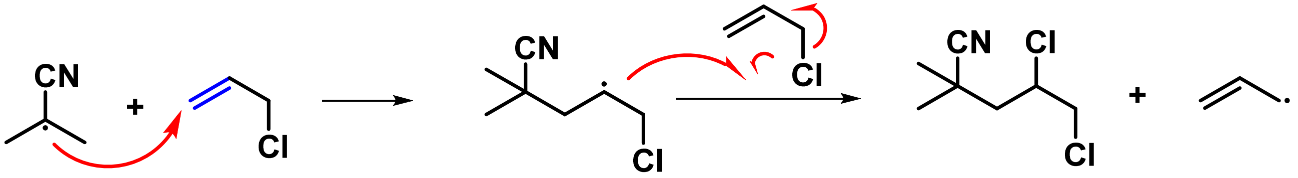
Free radical polymerization: Chain transfer

Consequence of chain transfer: **Autoinhibition**

Allyl compounds , propene, isobutylene, vinyl ether cannot be polymerized via radical polymerization.

Formation of resonance stablized monomer radical is thermodynamically favored over polymer radical!

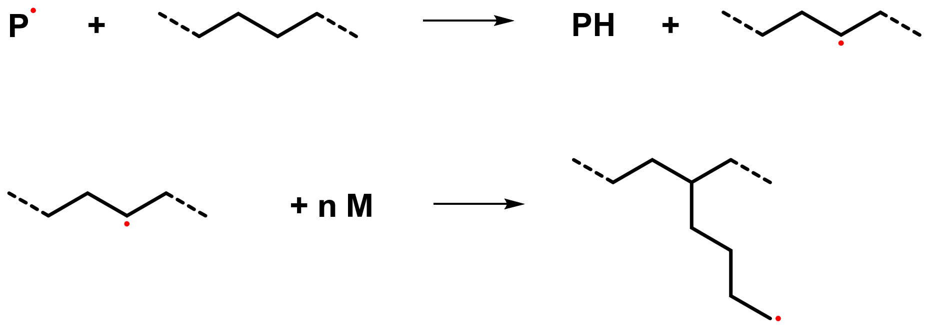
Monomer	**C_M / 10^4**
Acrylamide	0.5
Acrylonitrile	0.26
Ethene	0.4 - 4.2
Styrene	0.3 - 0.6
Vinyl acetate	1.75 - 2.8
Vinyl chloride	10.8 – 16



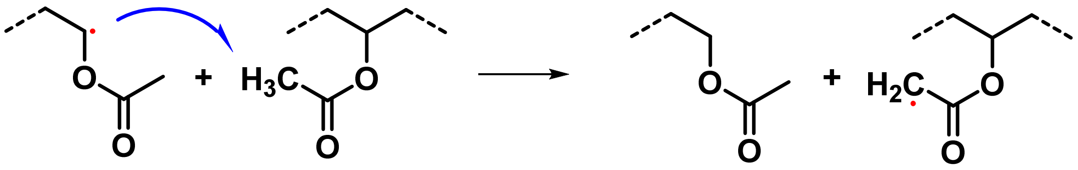
Free radical polymerization: Chain transfer

(b) Chain transfer to polymer

Example: polyethylene:



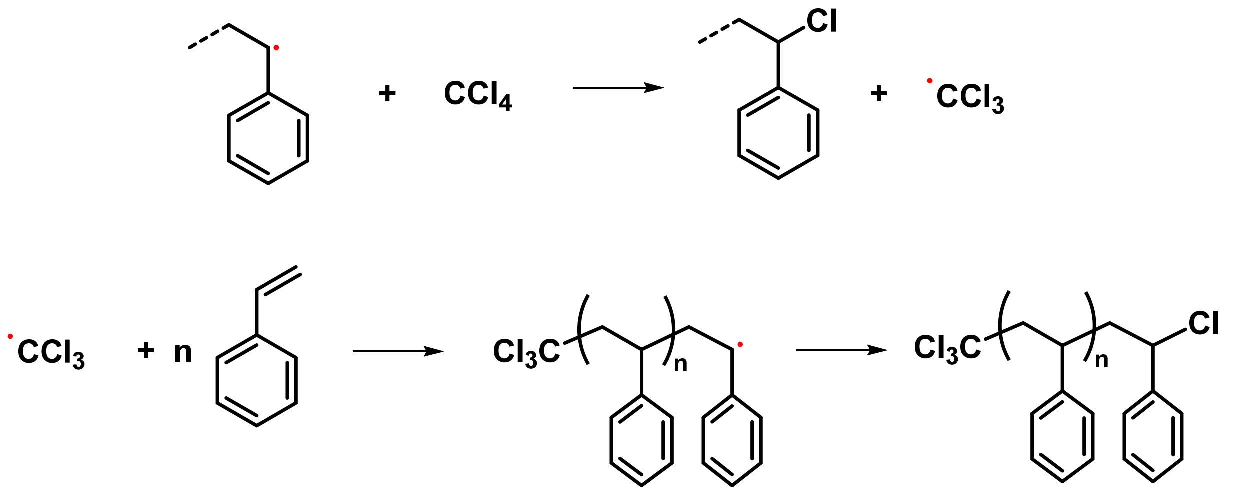
Example: Poly vinylacetate



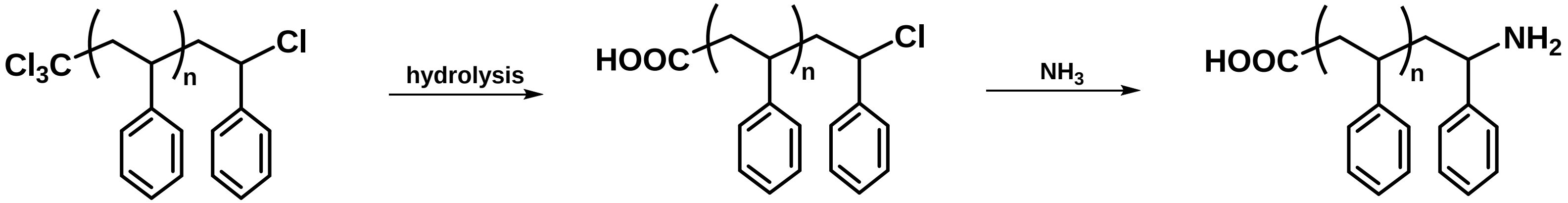
➢➢➢ Crosslinking of polymer chains

Free radical polymerization: Chain transfer

(c) Chain transfer to solvent



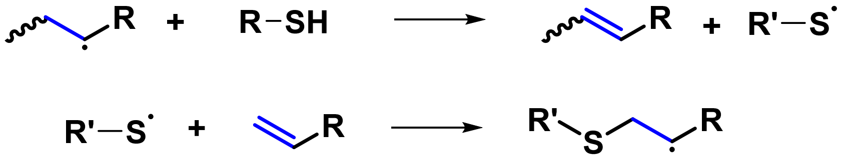
- Can be utilized for end group functionalization:



Free radical polymerization: Chain transfer

(d) Chain transfer to regulators

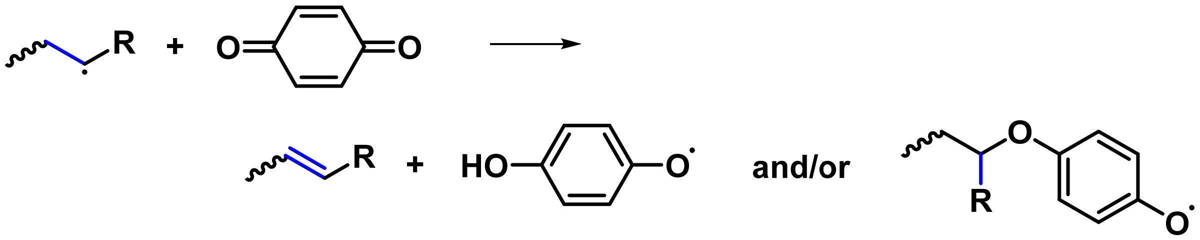
e.g. to mercaptanes

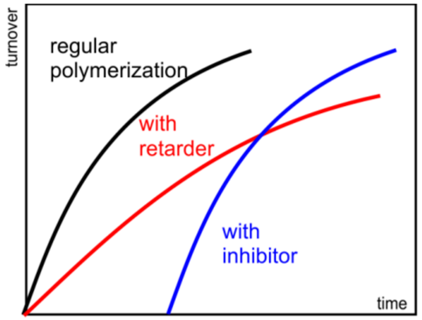


… allows control of molecular mass

(e) Chain transfer to retarders and inhibitors

example: chinone as inhibitor





Free radical polymerization: Industrially relevant polymers and processes

Emulsion polymerization

An important process for polyacrylates, poly(vinvyl chloride), poly(vinyl acetate)

Advantages over homogeneous (bulk) polymerization:

- No heat formation (respectively good discipation)
- No increase in viscosity
- No organic solvents

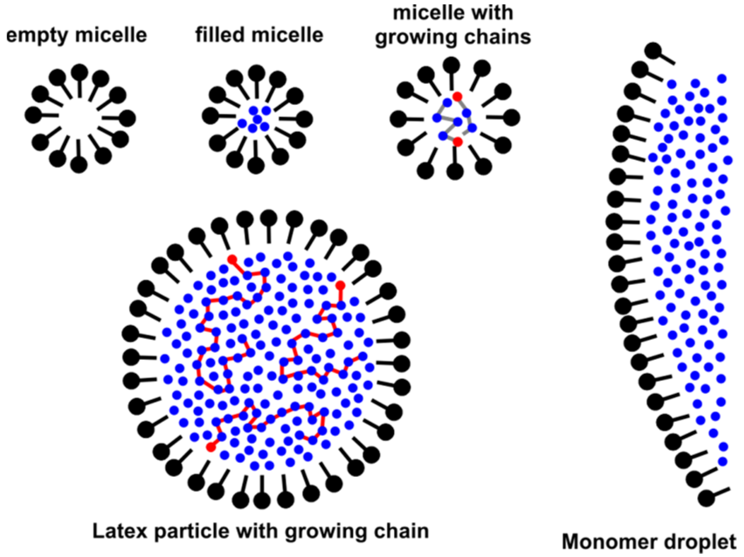
Reaction mixture:

Monomers, emulsifier, water, water-soluble initiator

Polymerization almost exclusively in the micelles,

new monomer molecules are provided from droplets

Technically relevant for instance for wall paint



Free radical polymerization: Industrially relevant polymers

Polystyrene (PS)

- Commerciallized by BASF in 1930s
- Polymerization either in
  - highly concentrated solution (5-25% ethylbenzene) with thermal initiation
  - Suspension with peroxid initiation
- In both cases, preparation of granules/pellets, which can be molten for further processing

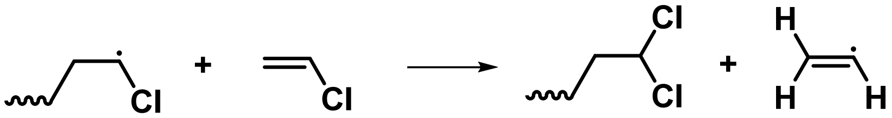
Polyethylene (PE)

- High pressure PE = LDPE: commerciallized by ICI in 1939
- Radical polymerization in bulk at 1400-3500 bar, 130-330 °C
- Initiation: oxygen, organic peroxides
- Characteristic: short crosslinks (butyl/ethyl) through chain transfer

Free radical polymerization: Industrially relevant polymers

Polyvinylchloride (PVC)

- Commerciallized by IG Farben in 1931
- Polymerization either in suspension (75%), emulsion (15%), or bulk (10%)
- In each case, atactic polymers with short syndiotactic sequences; crystallinity of 3-10%
- Monomer with tendency for chain transfer, therefore polymerization at low temperatures



- Suspension polymerization: 10-200 µm particles, $\bar{M}_w$ between 30-130 kg/mol

Commerically relevant:

- Rigid PVC („Hart-PVC"): T_m ~ 150-200°C, processed > 220°C
- Flexible PVC („Weich-PVC"): up to 50% softener added

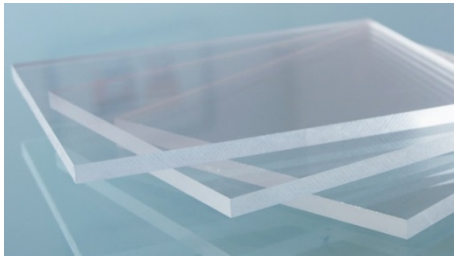
  (e.g. diisopropyl phthalate)

Both used for foils, flooring, cable insulation, tubing …

Free radical polymerization: Industrially relevant polymers

Polymethylmethacrylate (PMMA)

- Radical polymerization in bulk, usually processed by molding
- Often preparation of prepolymer, polymerized up to 20%, then filled in form
- Shrinkage of ~ 20% during curing, therefore polymerization at lower temperatures
- Polymer is fully optically transparent (known usually as Plexiglas)

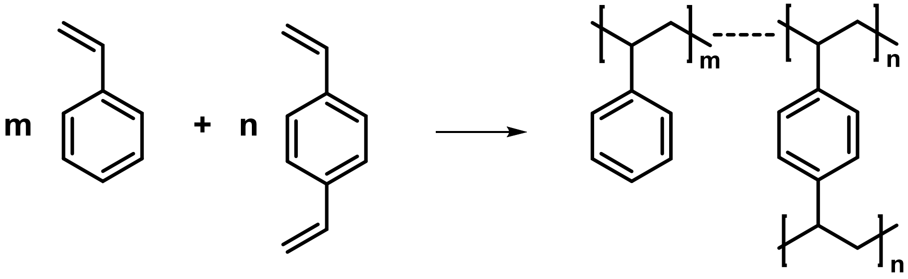


Polytetrafluoroethylene (PTFE)

- Commerciallized 1940 by DuPont
- Polymerized via emulsion or suspension polymerization in aqueous solution
- Initator: ammonium persulfate – $NaHSO_3$ – Cu^{2+} mixture
- Stabilizer: perfluoro octyl carboxylic acid
- Particles of 0.1-0.3 µm (emulsion) and 2-4mm (suspension)
- Processing: Sintering (compacting without melting) or coating with emulsion
- Crystallinity ~ 50-70%

Free radical polymerization: Crosslinked polymers

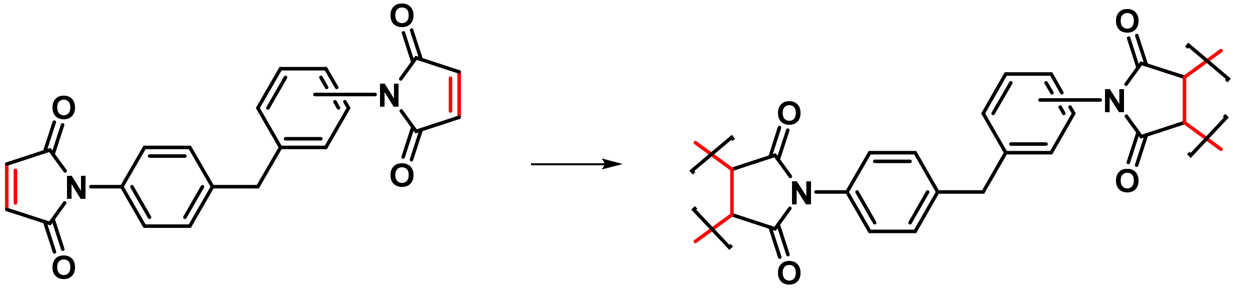
(a) Styrene-divinylbenzene resins



Further chemical modification leads to ion exchanger resins

(b) Bismaleimide resins

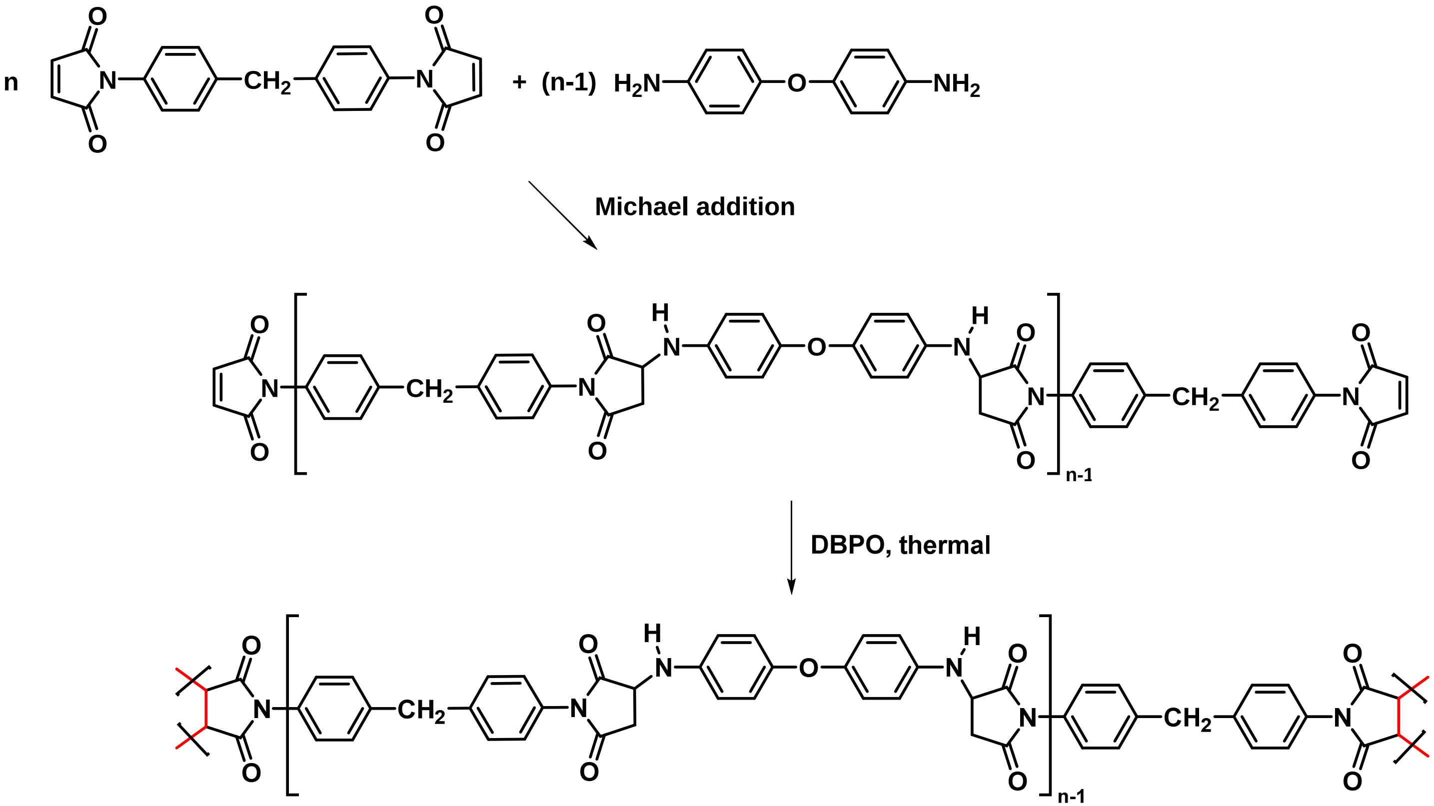
Easily prepared from bismaleimido diphenyl methane, but yielding very brittle networks



Free radical polymerization: Crosslinked polymers

(c) Bismaleimide resins

More flexible materials are obtained when monomer mixtures are used (example Kerimid®)



Kerimid is high performance thermosetting polymer for applications requiring exceptional thermal stability and performance properties like advanced composites, high-temperature electrical laminates and adhesives.