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Polymer Technology

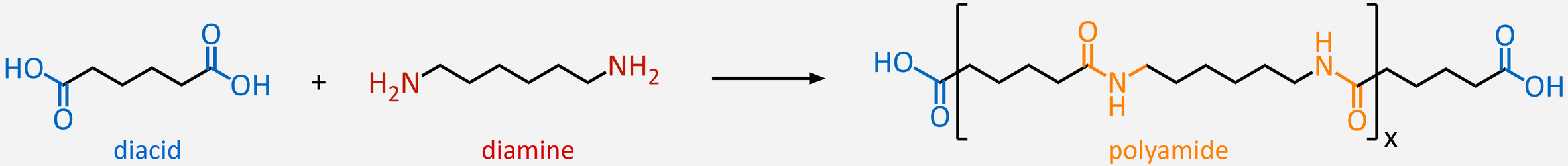
6.1
Polymer Chemistry

6.1.1
Step-Growth Polymerization

Step Growth Reactions

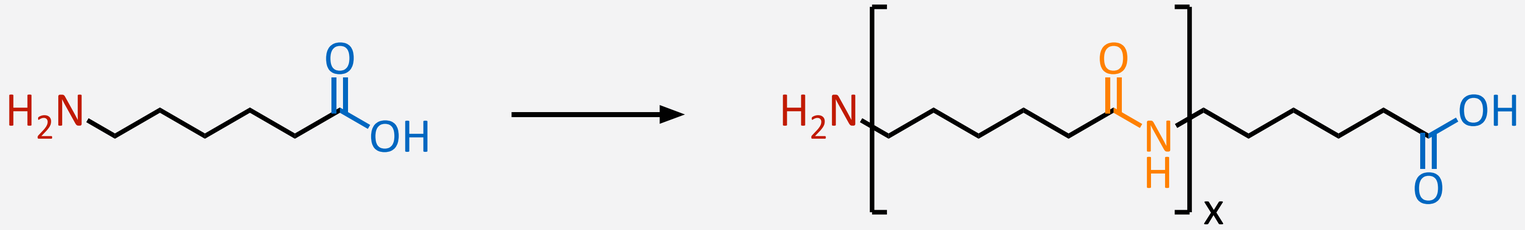
- every step of polymer growth is an independent organic reaction (e.g., esterification)
- requirement for polymer formation: monomers must be difunctional molecules

  - AA/BB-type: two monomers with two identical, complementary functions each



diacid diamine polyamide

  - AB-type: one monomer with two complementary functions

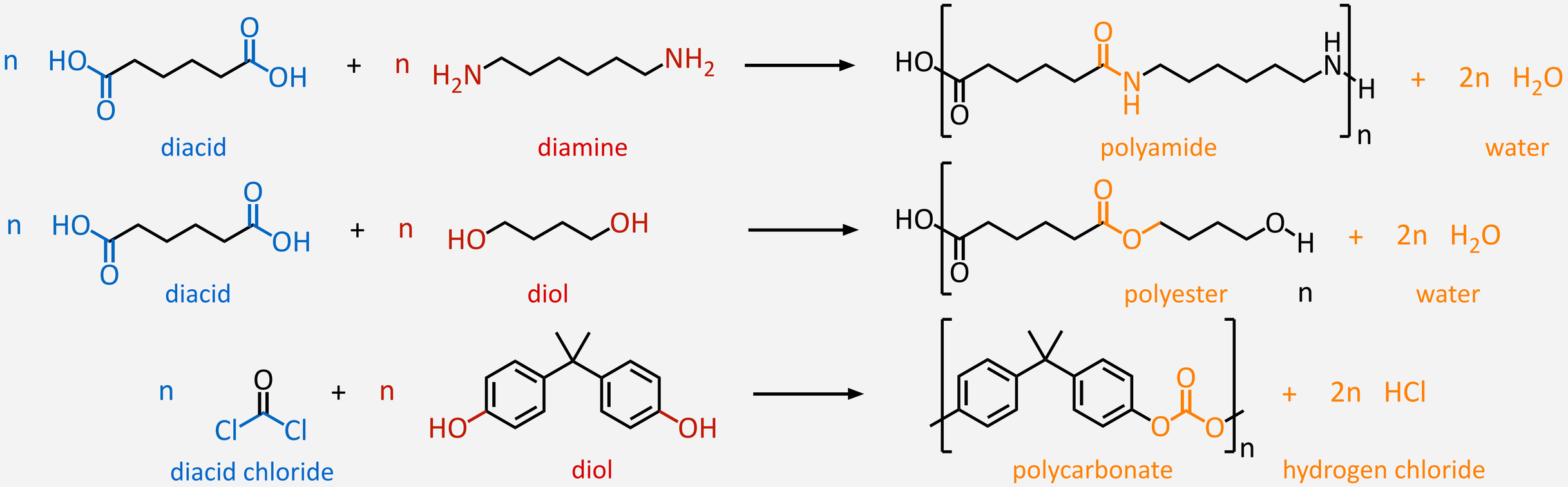


amino carboxylic acid polyamide

- end groups always remain active for further coupling reactions
- degree of polymerization is function of the degree of conversion of functional groups

Polycondensations

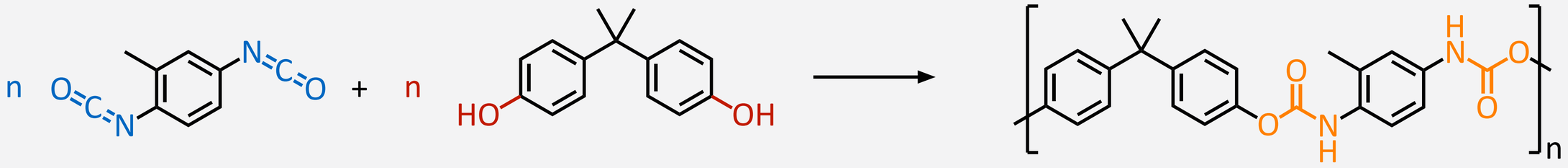
- **polycondensation**: reaction of difunctional molecules by release of small molecule side-product



- **problem: each step is an equilibrium reaction, multiplication results in diminishing polymer yield**
- **relatively “simple” and very efficient coupling reactions are typically employed**
- **typically performed in “open systems”, under removal of the small molecule side product**

Polyadditions

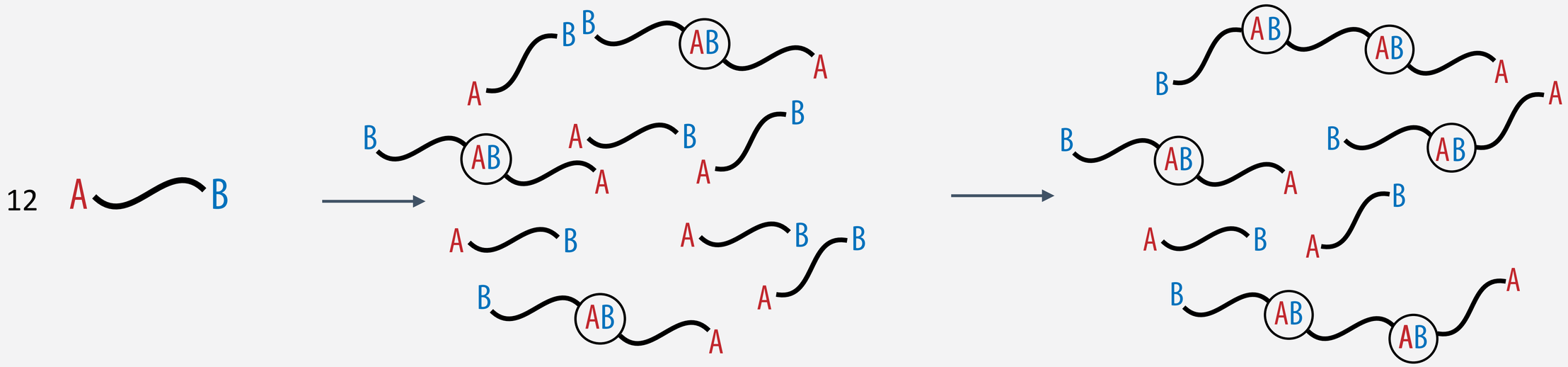
- **polyaddition**: reaction of difunctional molecules **without release of small molecule side-product**



diisocyanate diol polyurethane

- **small molecule elimination already performed during monomer synthesis**
- **high-energy monomers, coupling reactions are inherently efficient**

Origin of Dispersity and Molecular Weight Limitations



0% conversion
$M_n = 1$
$M_w = 1$
$Đ = 1$

25% conversion
$M_n = 1.33$
$M_w = 1.50$
$Đ = 1.13$

50% conversion
$M_n = 2.00$
$M_w = 2.33$
$Đ = 1.16$

- **polymer chain growth is a statistical process, and hence the source of dispersity**
- **dispersity increases with conversion of functional groups**
- **conversion limits molecular weight – high molecular weights require extremely high conversions!**

The Carothers Equation

- in the polymerisation of A-A and B-B type monomers, the resulting number-average degree of polymerization $\overline{X}_n$ relates to the conversion *p* of groups A and B and their stoichiometric ratio *r*

ratio of monomers and functional groups

$$r = \frac{[M_A]}{[M_B]} = \frac{N_{A,0}}{N_{B,0}} \qquad N_{A,0} < N_{B,0}$$

conversion of functional groups

$$p = \frac{N_{A,0} - N_A}{N_{A,0}} = \frac{N_{B,0} - N_B}{N_{B,0}}$$

degree of polymerization

$$\overline{X}_n = \frac{N_0}{N} = \frac{1 + r}{1 + r - 2pr}$$

general Carothers Equation

- **perfect stoichiometry and high degree of conversion required for high molecular weight polymers**

see Reading Recommendation “Step-Growth Polymerizations”

Dependence of Molecular Weight on Conversion and Functional Group

$$\overline{X}_n = \frac{1 + r}{1 - r}$$

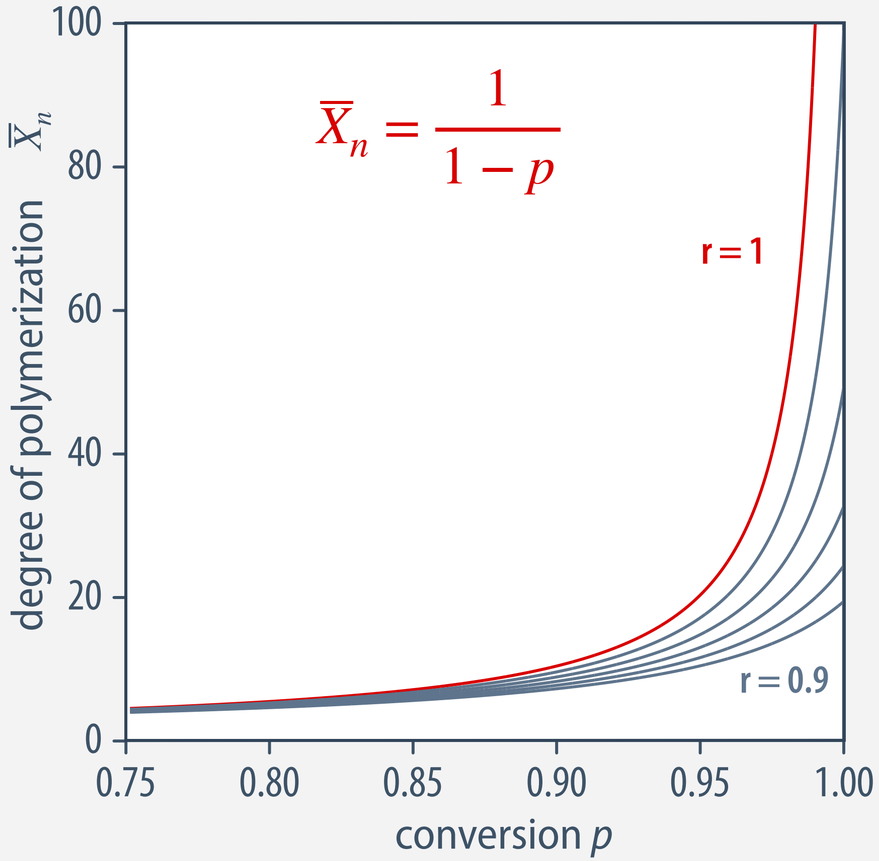
for complete conversion (p = 1)

$$\overline{X}_n = \frac{1 + r}{1 + r - 2pr}$$

general Carothers Equation

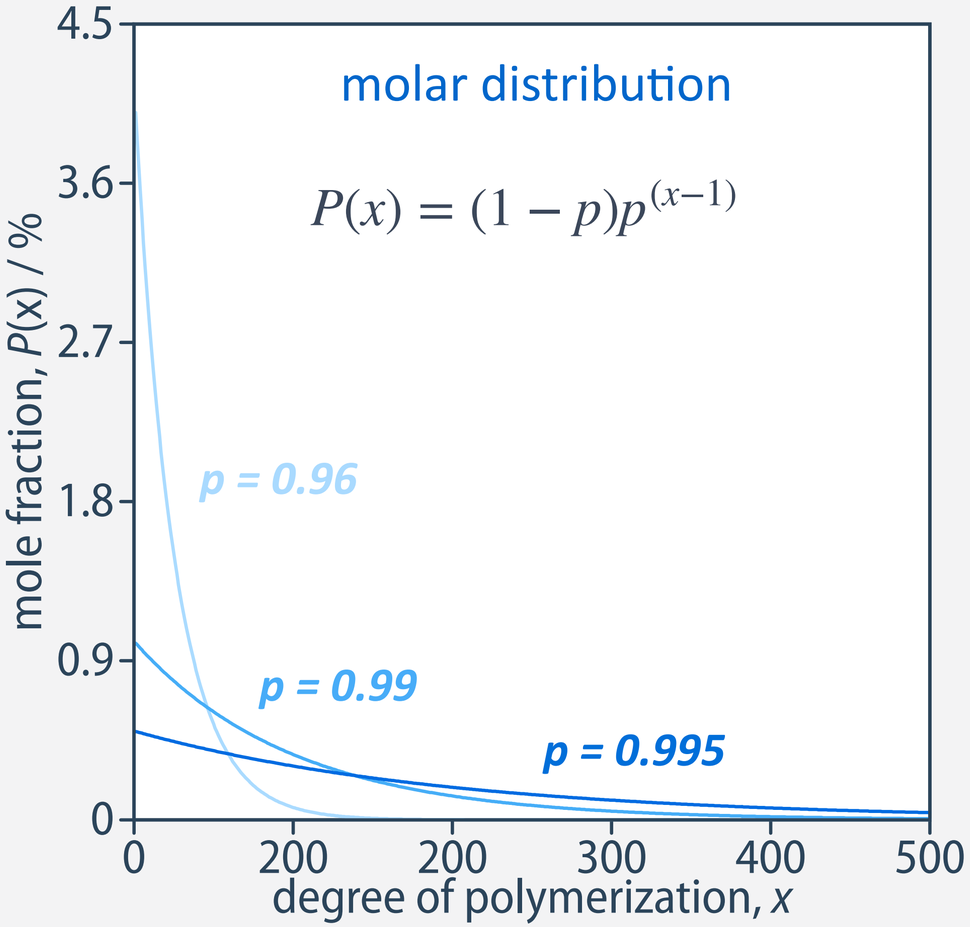
$$\overline{X}_n = \frac{1}{1 - p}$$

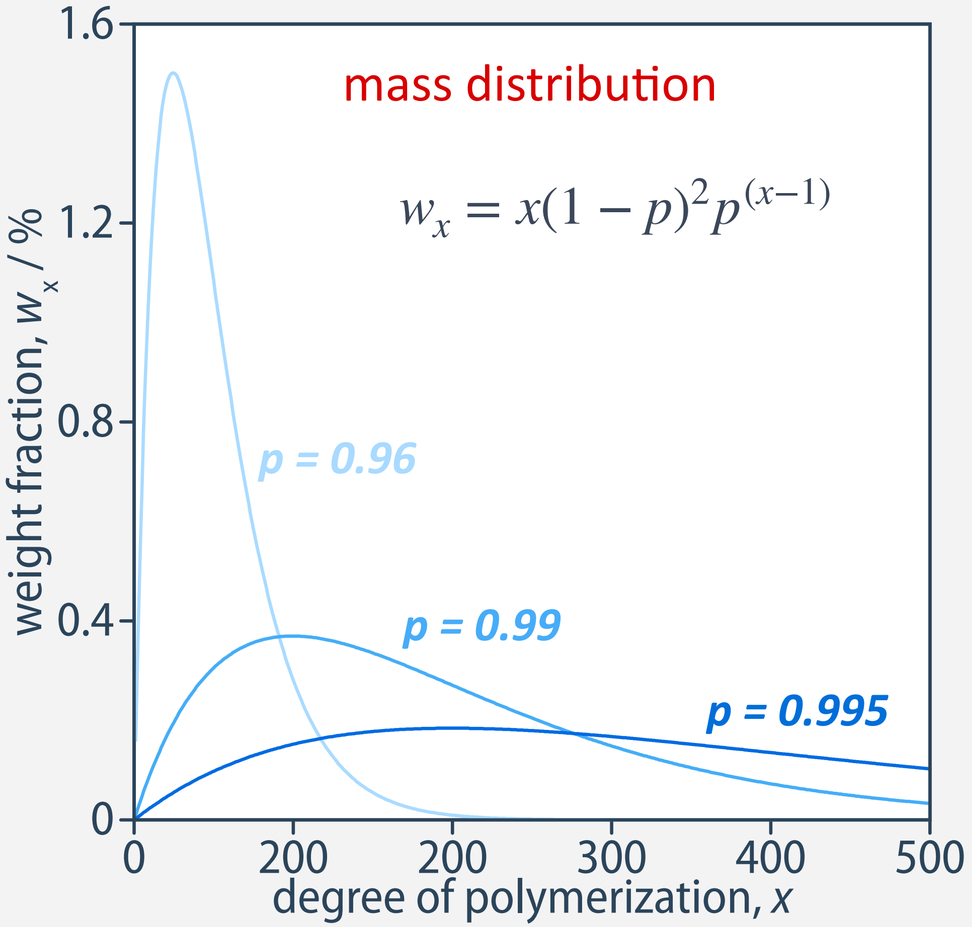
for perfect stoichiometry (r = 1)



- functional group conversions close to unity required for highmolar mass polymers
- significantly reduced molecular weight for any deviation from perfect stoichiometry

Flory-Schulz Distribution





- **at any conversion, the mole fraction of monomer is greater than that of any other species !**
- **mass distribution shows a maximum that moves to higher *x* with increasing conversion *p***

see Reading Recommendation “Step-Growth Polymerizations”

Summary of the Kinetics of Step Growth Polyreactions

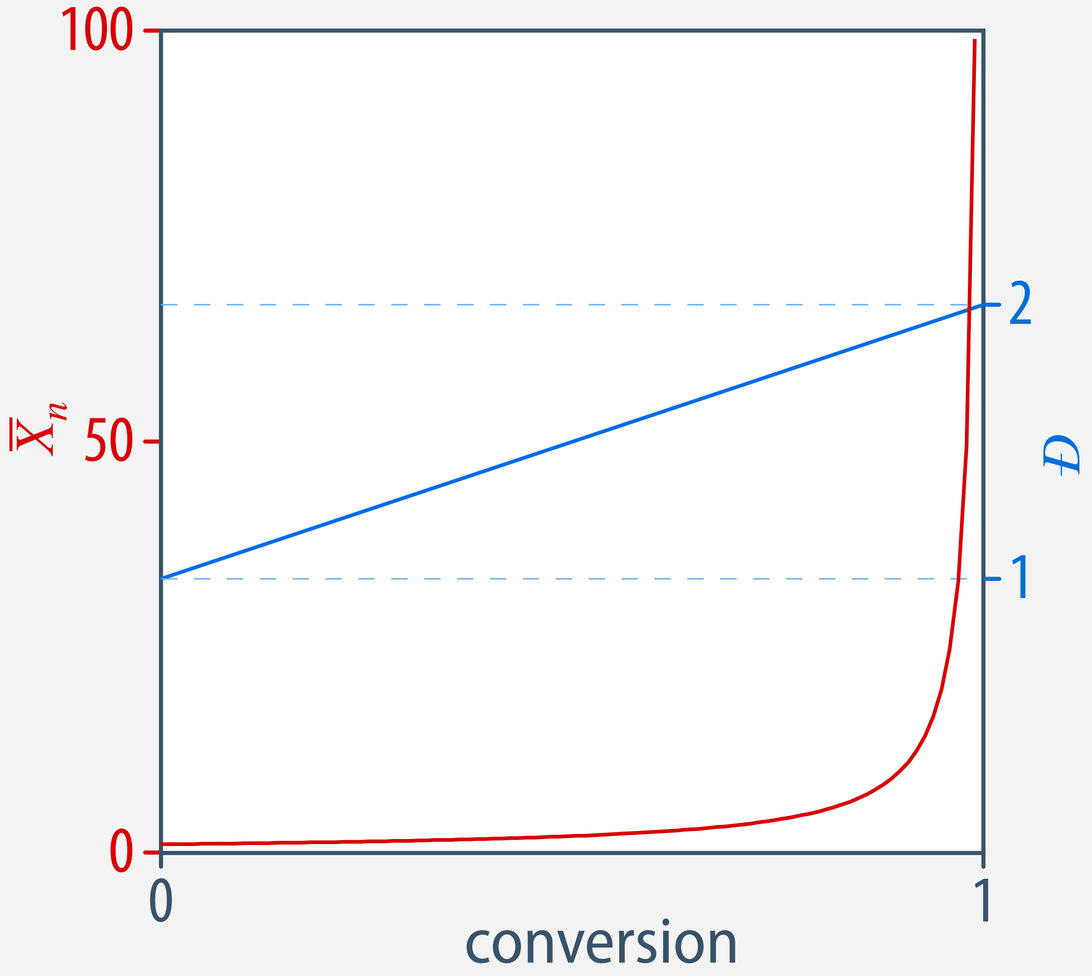
number average degree of polymerization and molar mass

$$\overline{X}_n = \frac{1}{1-p} \qquad \overline{M}_n = M_0\overline{X}_n = \frac{M_0}{(1-p)}$$

weight average degree of polymerization

$$\overline{X}_w = \sum xw_x = \frac{1+p}{1-p} \qquad \overline{M}_w = M_0\overline{X}_w = M_0\frac{(1+p)}{(1-p)}$$

dispersity $\text{Đ} = \dfrac{\overline{X}_n}{\overline{X}_w} = 1+p$

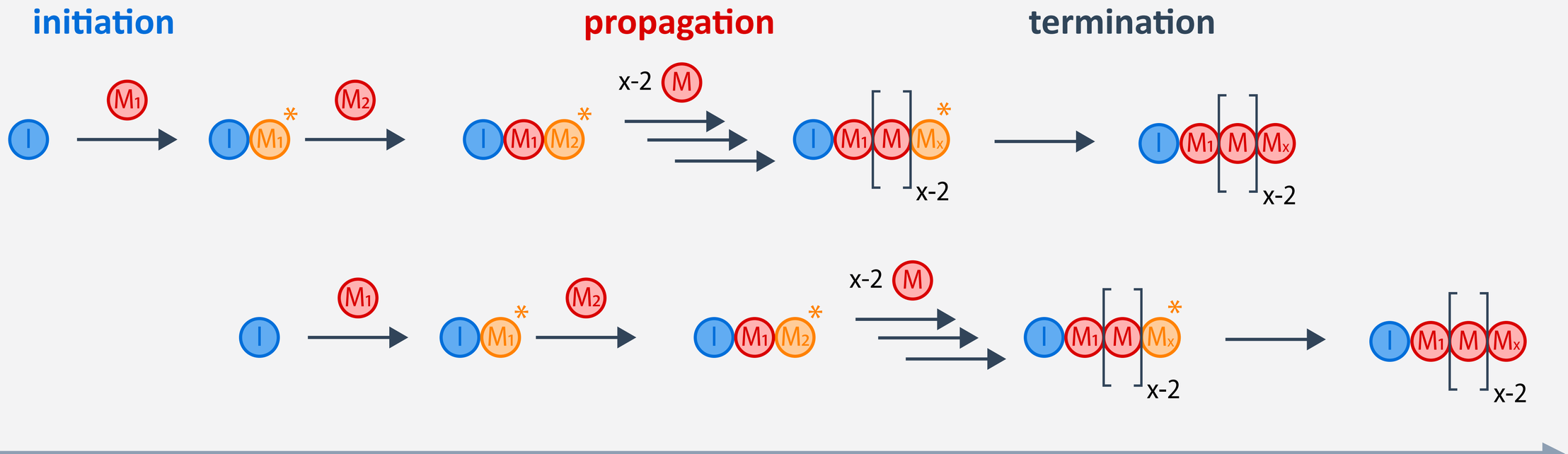


- **convergence to a dispersity of *Đ* = 2 is diagnostic of a well-behaved step-growth polymerization**

6.1.2
Chain-Growth Polymerization

Principal Steps of Chain-Growth Polymerizations

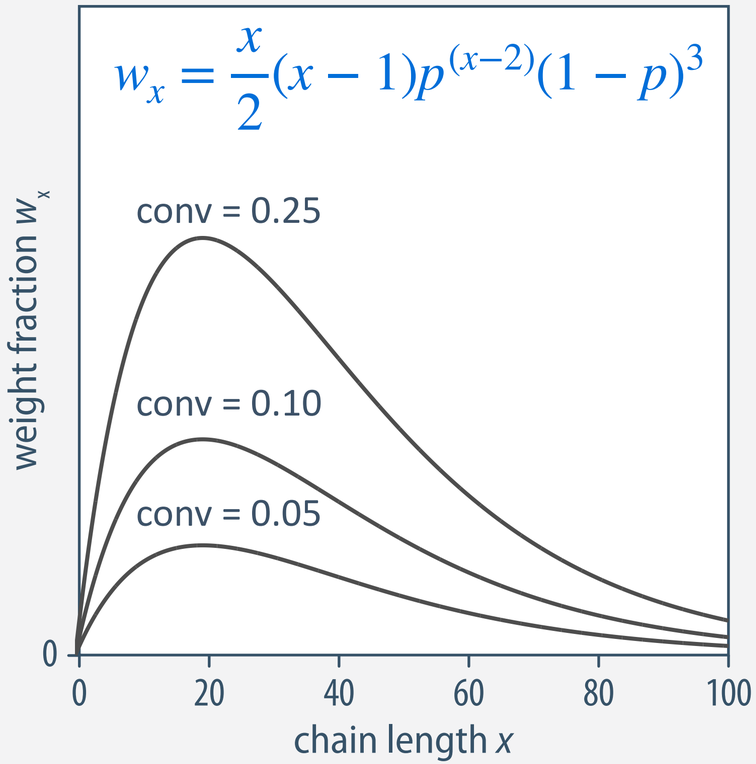
- monomers add rapidly to the active center of a growing chain until that center is deactivated



- **polymerizations require initiation that attacks a first monomer and creates an active center**
- **during propagation, monomers add consecutively to the active center of a growing polymer chain**
- **Initiation continuously occurs during entire polymerization time**
- **termination is a stochastic event, greatly determining the molecular weight distribution**

Molar Mass Distribution in Chain Growth Polymerizations

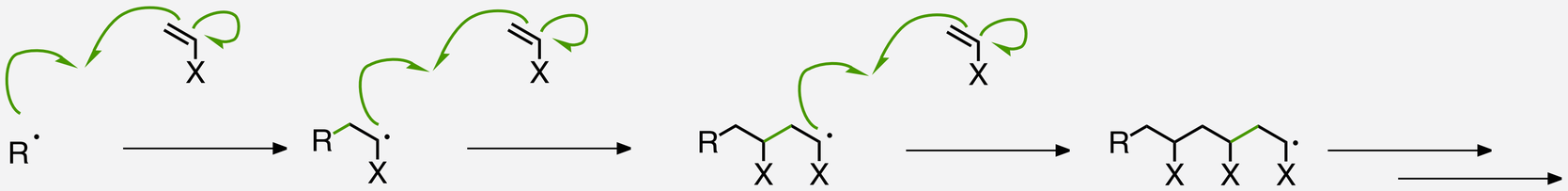
- Flory-Schulz-type distribution is expected to(at least, in the low conversion regime)



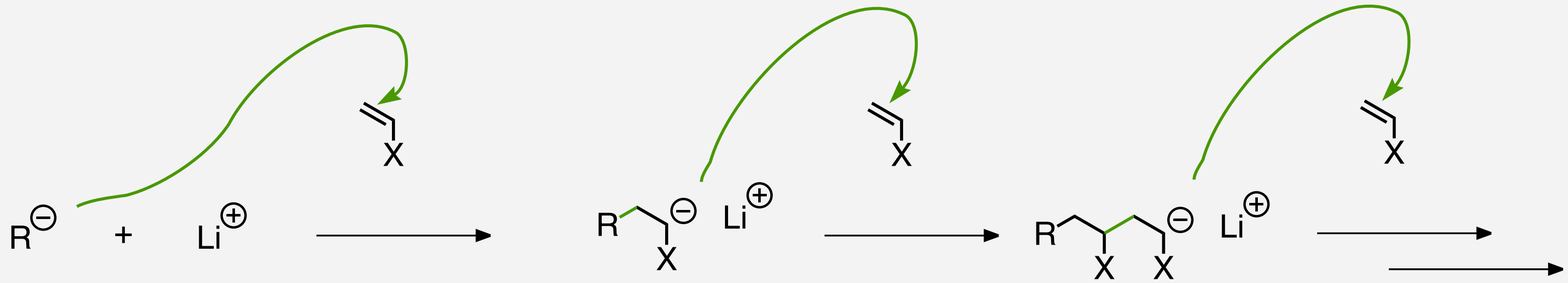
- **wgh molar mass polymer is formed from the beginning in a free radical polymerization**
- **With increasing time and conversion, the number of each species increases continuously**

3 General Types of Chain-Growth Reactions

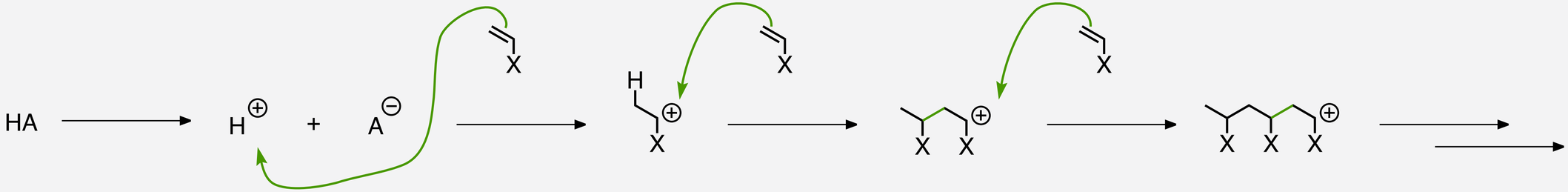
radical
(most common)



anionic



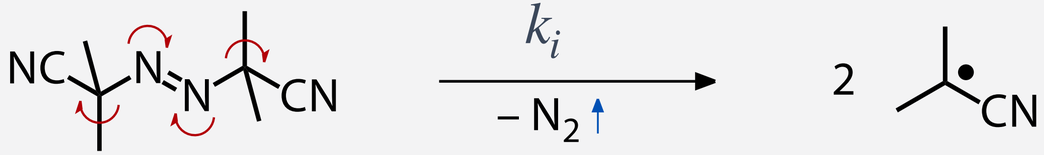
cationic



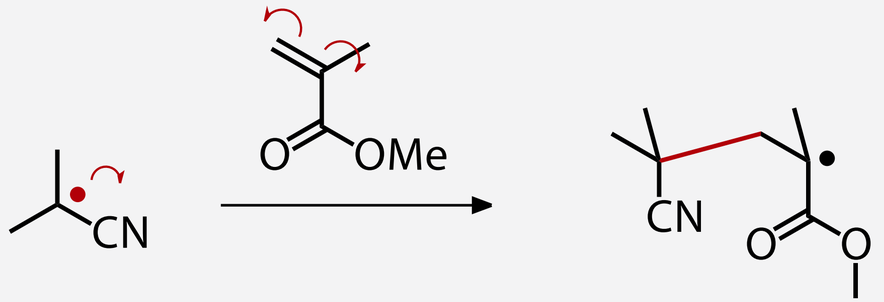
Free Radical Polymerization

General Reaction Stages in the Example of Free Radical Polymerizations

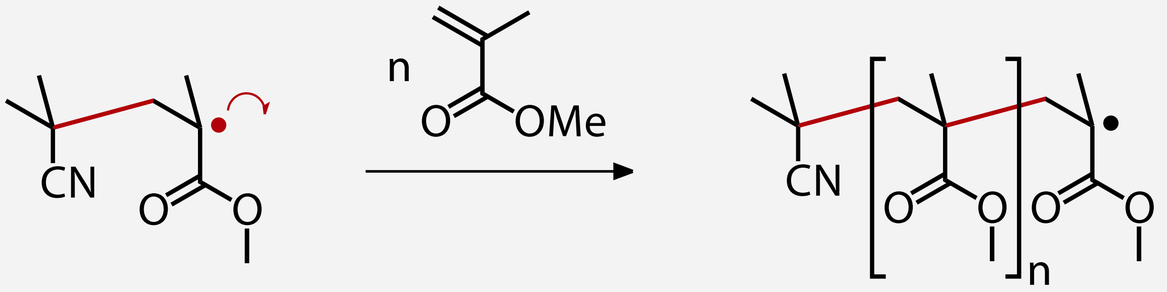
- initiator decomposition (slow)



- initiation (fast)



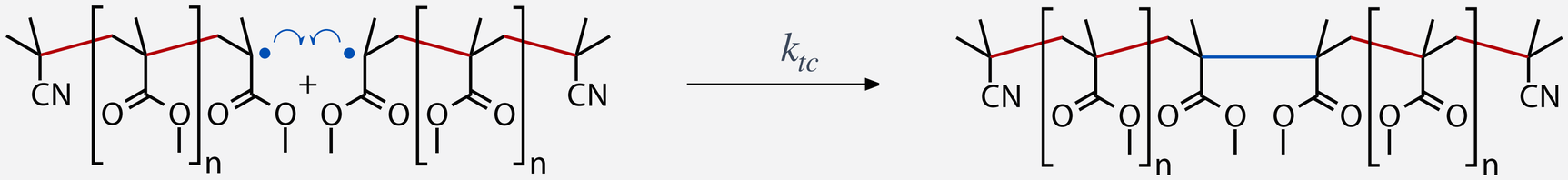
- propagation (chain growth)



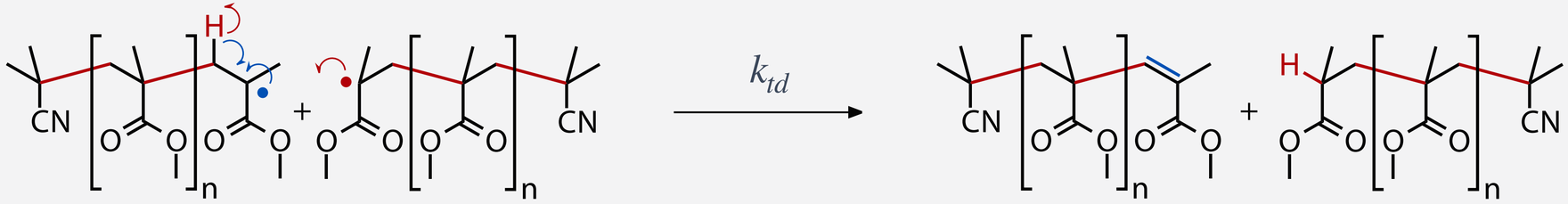
- **efficiency factor for initiation of a polymer by a radical $f \approx 0.3–0.8$**
- **initiator decomposition is a statistical process, occurring slowly throughout polymerization process**
- **radical life time τ = 0.1–10 s, about 100–10’000 propagation steps before chain terminates**

Termination Reactions in Radical Polymerizations

termination (combination)

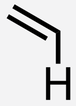


termination (disproportionation)

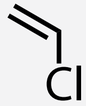


- termination by combination and disproportionation often occur both and are stochastic processes

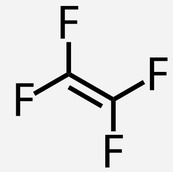
Important Vinyl Monomers in Radical Polymerization



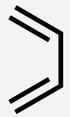
ethene
ethylene (for PE)



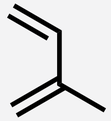
chloroethene
vinyl chloride (for PVC)



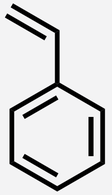
tetrafluoroethene
(for PTFE)



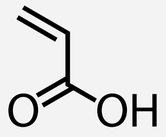
butadiene
(for PB)



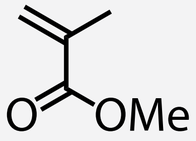
isoprene (for PI)
2-methylbutadiene



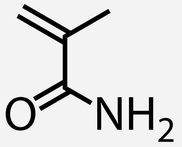
styrene (for PS)
phenylethene



propenoic acid
acrylic acid (for PAA)



methyl 2-methylpropenoate
methyl methacrylate (for PMMA)

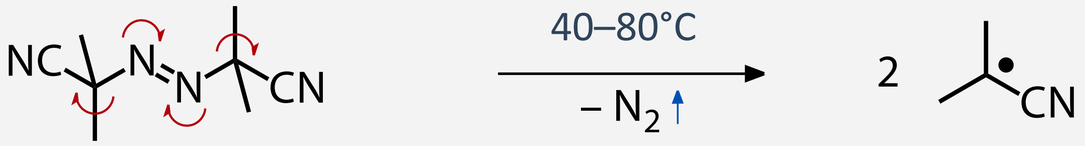


2-methylpropenoic amide
methacrylamide (for PMAAm)

- **unsaturated monomers used for technologically relevant polymers (in brackets)**

Examples of Radical Initiators

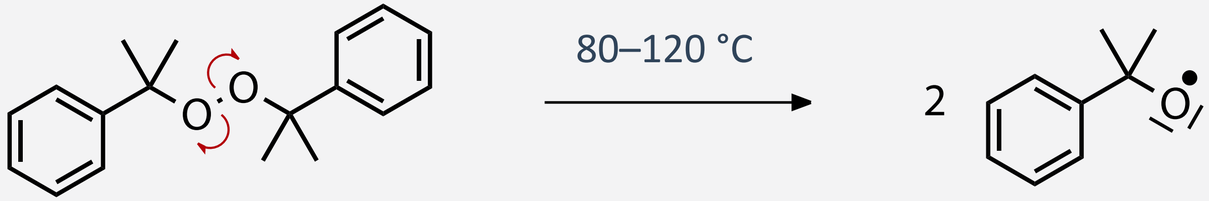
- azobis(isobutyronitrile) (AIBN)



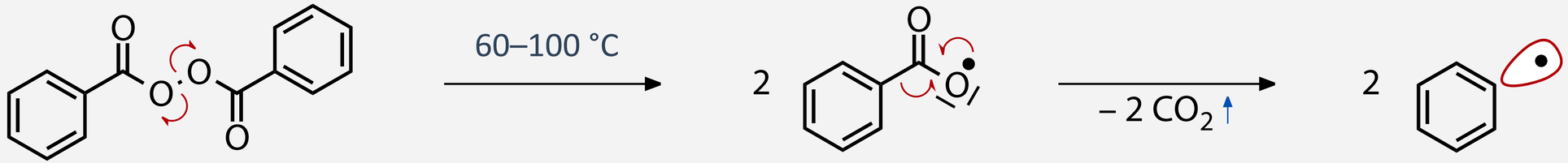
(or photolysis at 366 nm)

- di(tert.-butyl peroxide) (DTPO)

- dicumyl peroxide (DCPO)



- dibenzoyl peroxide (DBPO)



- **suitable decomposition rates (k_d: 10^{-7}–10^{-6} M s^{-1}) for different temperature regimes**
- **goal is to balance initiation and termination reaction rates to reach “steady state” conditions**

Steady-State Kinetics

rate of initiation

$$R_i = \frac{d[R^\cdot]}{dt} = 2fk_d[I]$$

rate of propagation

$$R_p = -\frac{d[M]}{dt} = \sum k_p[M_i^\cdot][M]$$

rate of termination

$$R_t = -\frac{d[M^\cdot]}{dt} = 2k_t[M^\cdot]^2$$

- **steady-state-conditions:** $R_i = R_t$

$$R_p = k_p \left(\frac{fk_d}{k_t}\right)^{1/2} [M][I]^{1/2} \quad \text{with} \quad k_t = k_{tc} + k_{td}$$

- **kinetic chain length:**

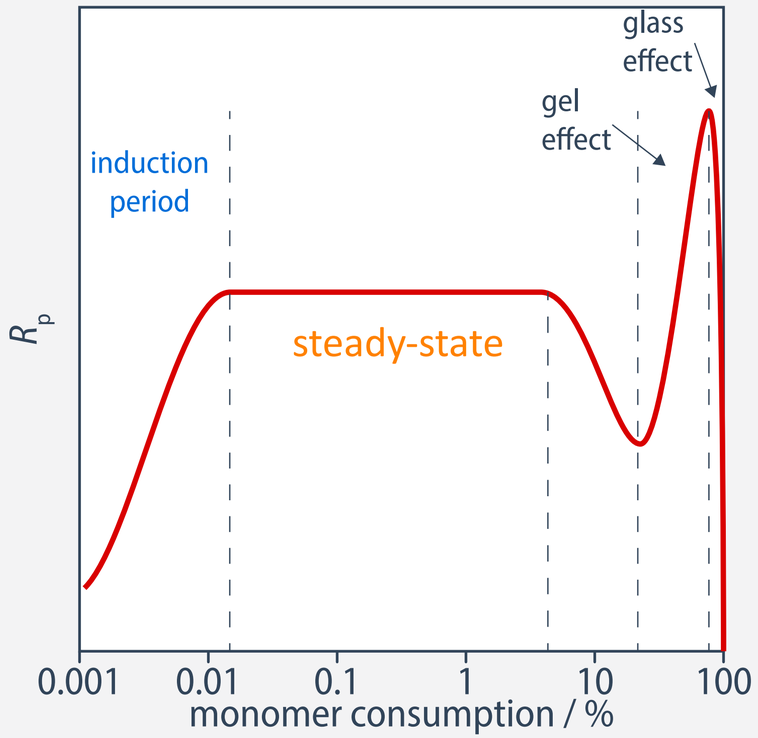
$$\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[M]}{2(fk_ik_t[I])^{1/2}} \propto \frac{[M]}{\sqrt{I}}$$

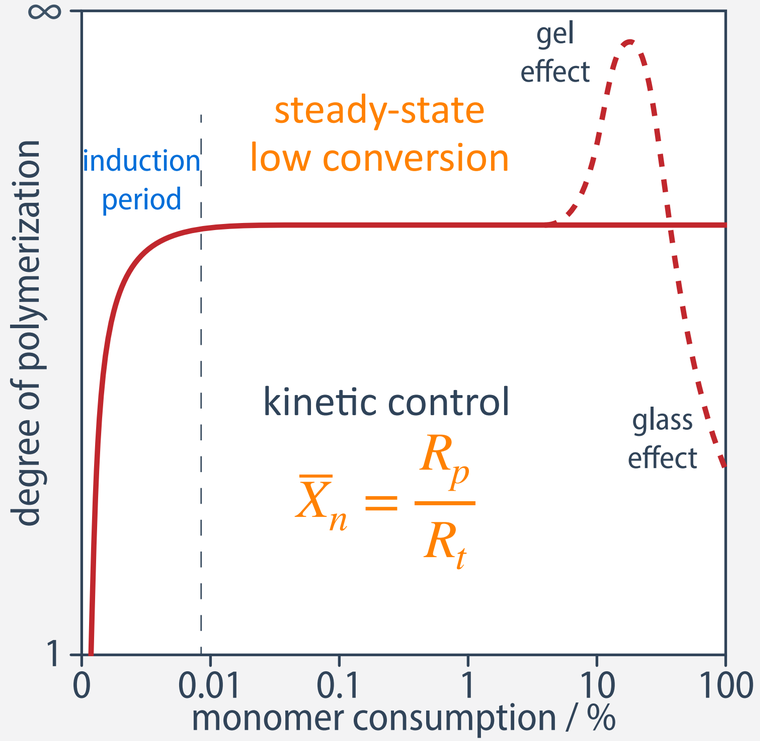
- steady state conditions required for stable polymerization, results in reaction order 0.5 for initiator
- increasing iniator concentration **increases polymerisation rate** but results in **decreased molar mass**

see Reading Recommendation “Chain-Growth Polymerizations”

High Conversion Effects

- gel effect: diffusion-controlled termination (auto-acceleration of propagation)
- glass effect: monomers get trapped, if the matrix becomes increasingly glassy

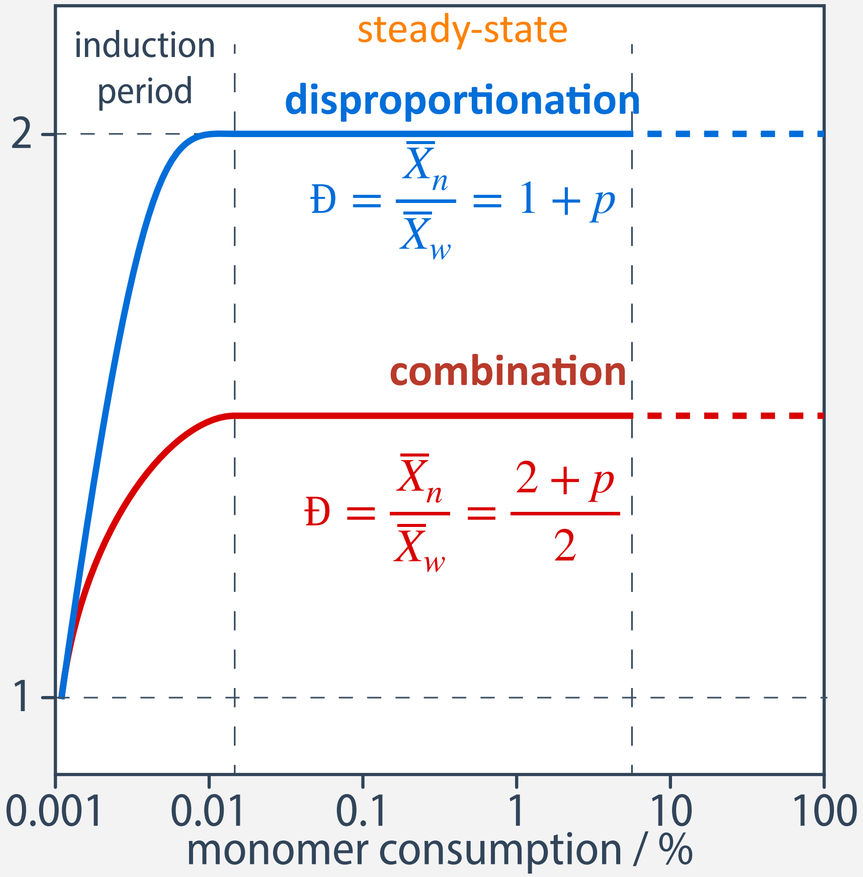


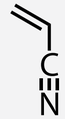
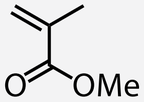
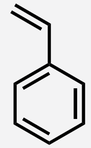


- steady-state conditions are not maintained at medium to high conversions, causing a loss of the control over polymerization rate and molar mass distribution

Dispersity in the Low Conversion Regime

- in reality, termination may occur via both pathways
- transfer reactions and side-reactions are not taken into consideration



	disproportionation	combination
	0%	100%
	79%	21%
	23%	77%

- **molecular weight distribution and dispersity depend on termination mechanism**

Step-Growth vs. Chain-Growth Polymerization

step(-growth) polymerizations

- *usually no initiator necessary*
- *same reaction mechanism throughout*
- *rapid loss of monomer species*
- *a wide range of species present at any stage*
- *growth by the reaction of any monomers, oligomers, polymers*
- *DP of growing polymer chains increases slowly*
- *no termination, chain ends remain reactive*
- *typically yields polymers with relatively low molar masses (15–30 kg/mol)*

chain(-growth) polymerizations

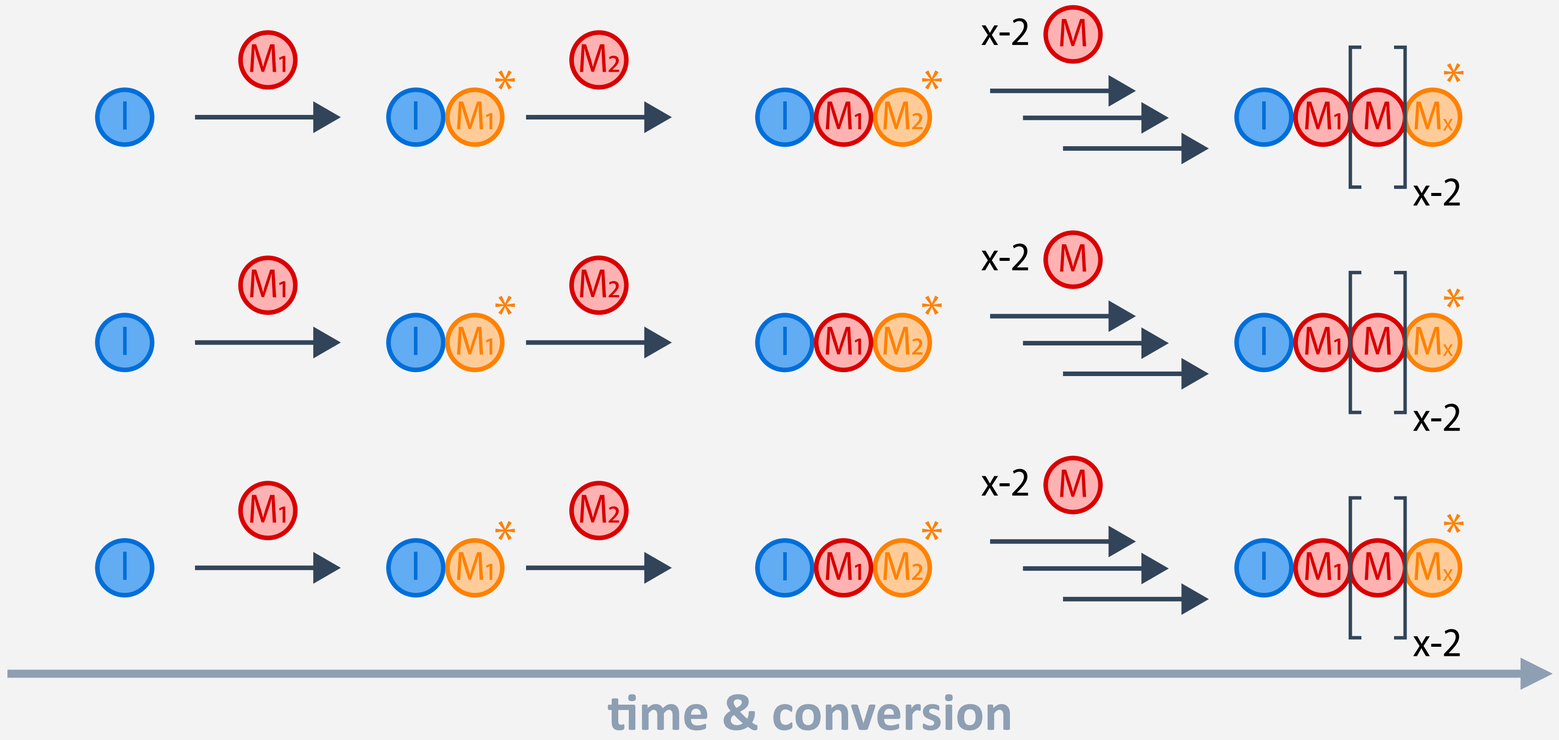
- *initiator required*
- *different mechanisms for initiation/propagation*
- *monomer remains present throughout*
- *mixture contains only monomer, high polymer, and very small amount of growing chains*
- *successive addition of monomers*
- *DP of growing polymer chains stays the same*
- *termination step involved, chains are inert after*
- *typical molar masses of polymers can get very high (50–1000 kg/mol)*

- **key variables are stoichiometry of monomers vs. initiator concentration**

6.1.3
Living and Controlled Chain Growth Polymerizations

The Living Nature

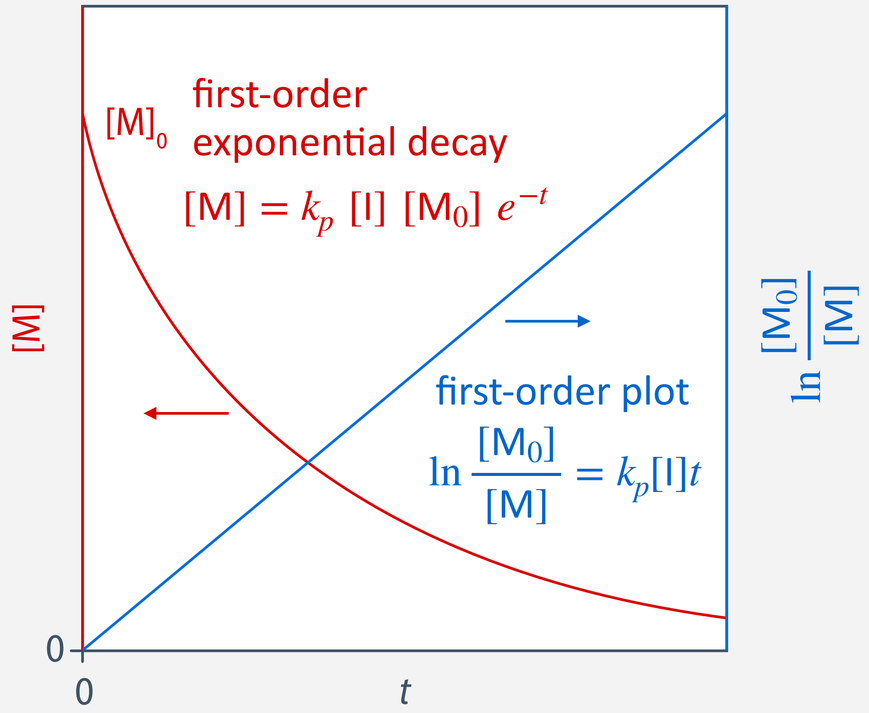
- absence of termination (strong electronic repulsion between active chain ends!)



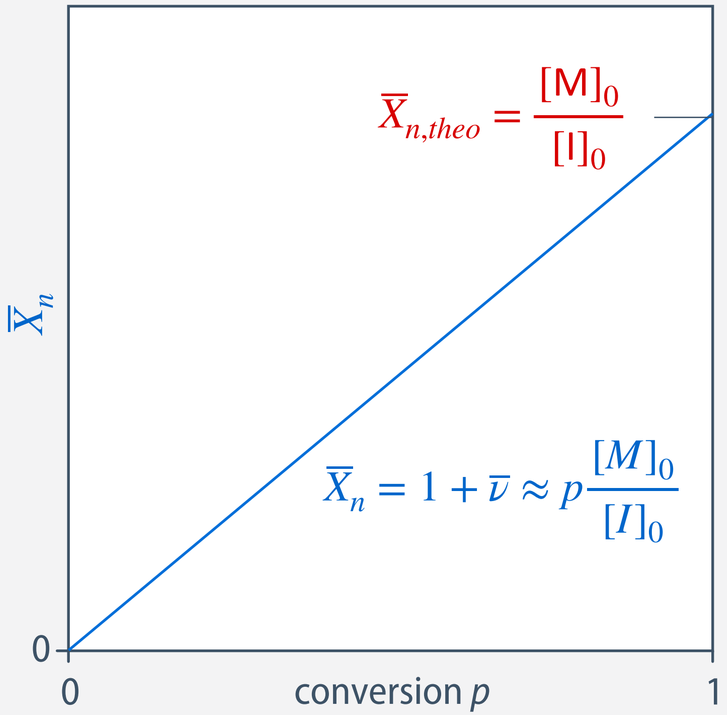
- polymers are all approximately initiated at the same time; origin of (small) dispersity
- chain ends remain active after full monomer consumption (absence of impurities!)
- the polymerization can be continued with an additional feedstock of monomers (same or different)

Criteria for the Experimental Verification of Living Polymerizations

conversion over time



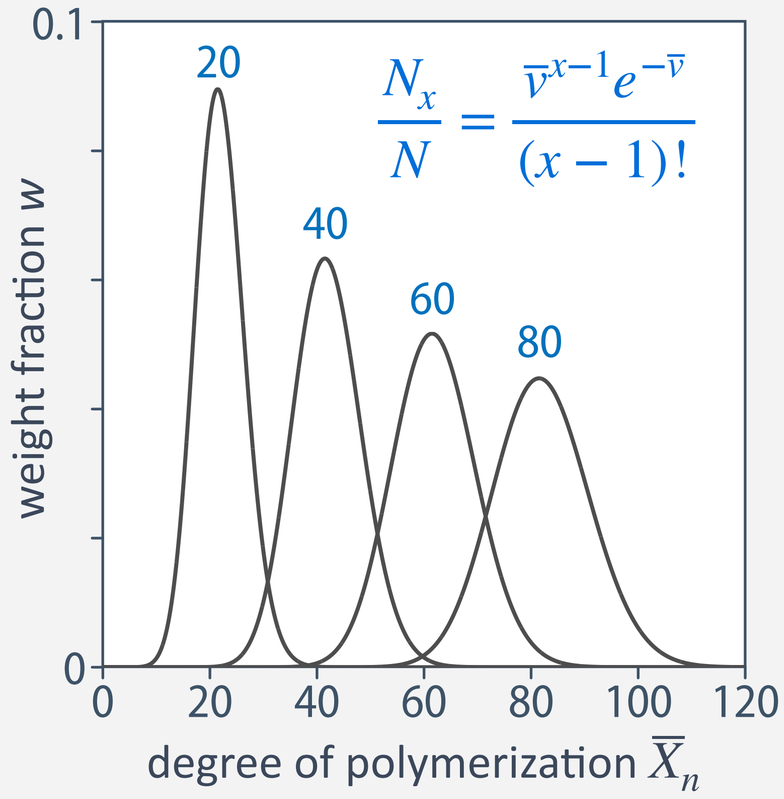
molar mass over conversion

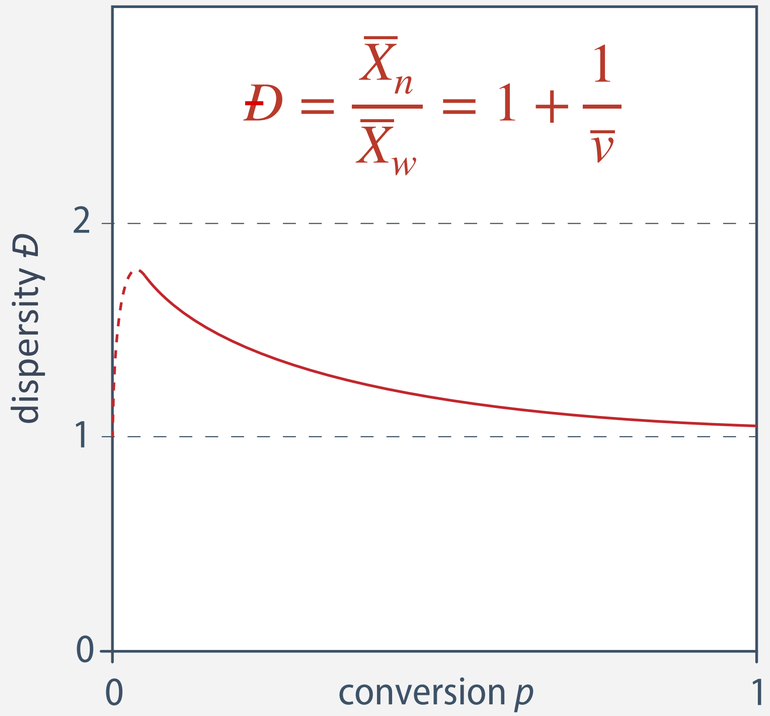


- **conversion over time plot: polymerization reaction is first order in monomer concentration**
- **molar mass over conversion plot: number-average molar mass $\overline{X}_n = 1 + \overline{\nu}$ linear with conversion**

The Poisson Distribution of the Molecular Weight

- **kinetic analysis leads to a Poisson distribution for the molecular weight distribution:**

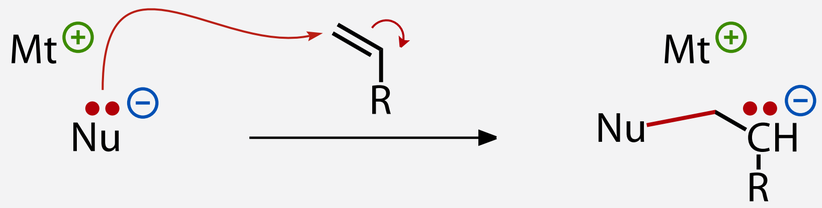




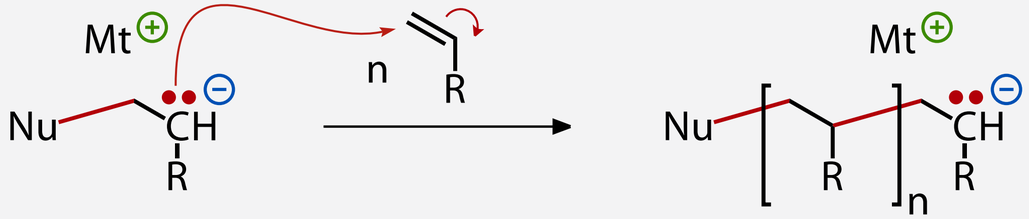
- **number-average degree of polymerization $\overline{X}_n \approx p \frac{[M]_0}{[I]_0}$ controlled by monomer/initiator ratio**

Living Anionic Polymerization of Vinyl Monomers

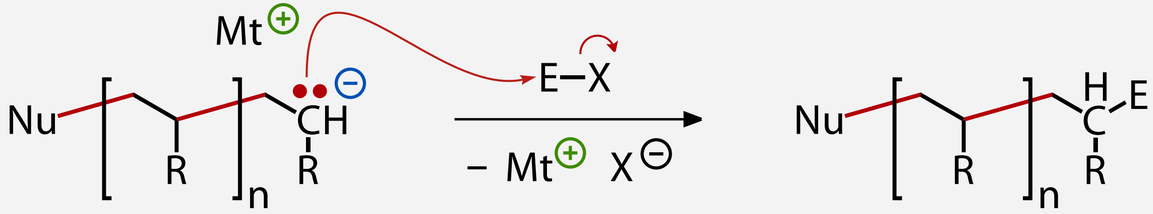
- initiation



- propagation (chain growth)



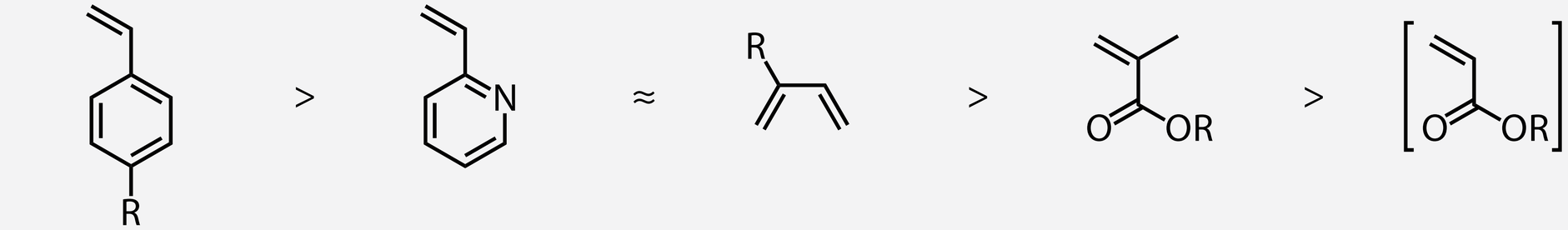
- quenching



- **anionic polymerisations of vinyl monomers are initiated by strong nucleophiles**
- **termination reactions are absent, except for electrophilic impurities (H_2O, CO_2)**
- **electrophiles serve as quenching reagents, deliberately end the reaction, introduce end groups**

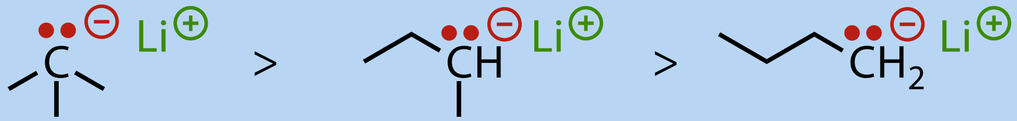
Vinyl Monomers and Initiators

- **monomers with possibility for anion delocalisation**, ideally with electron-withdrawing side groups



styrene derivatives (R = H, Me, COOR') | 2-vinylpyridine | butadiene (R = H) isoprene (R = Me) | methacrylates (R = Me, Bu, tBu) | acrylates (R = Me, Bu, tBu)

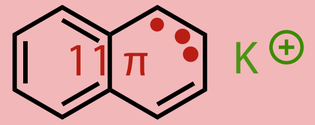
- **initiators are organoalkaline compounds or alkaline metals.**



t-BuLi *tert.*-butyl lithium | s-BuLi *sec.*-butyl lithium | n-BuLi butyl lithium

strong nucleophiles

for monodirectional chain growth



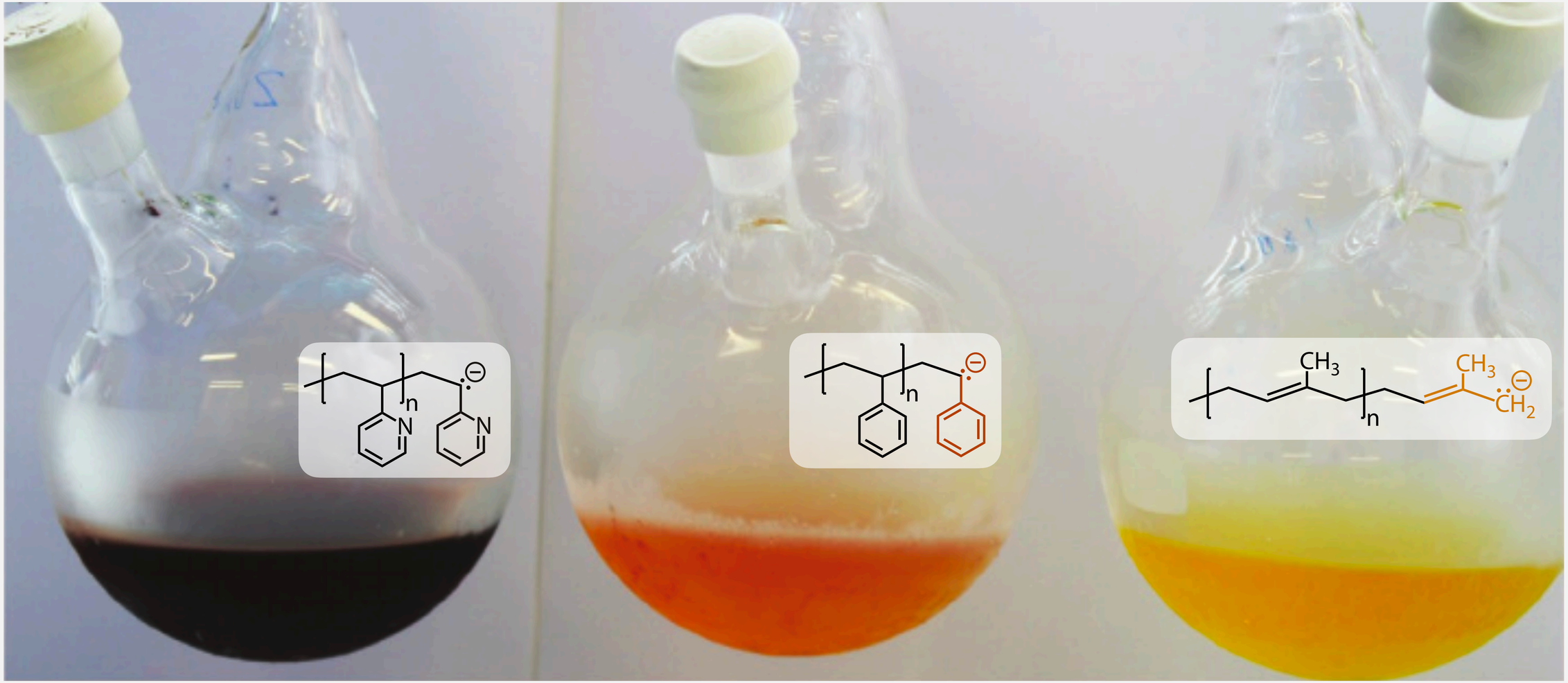
KNaph potassium naphthalide | K, Na, Li alkaline metals

single-electron transfer agents

for bidirectional growth

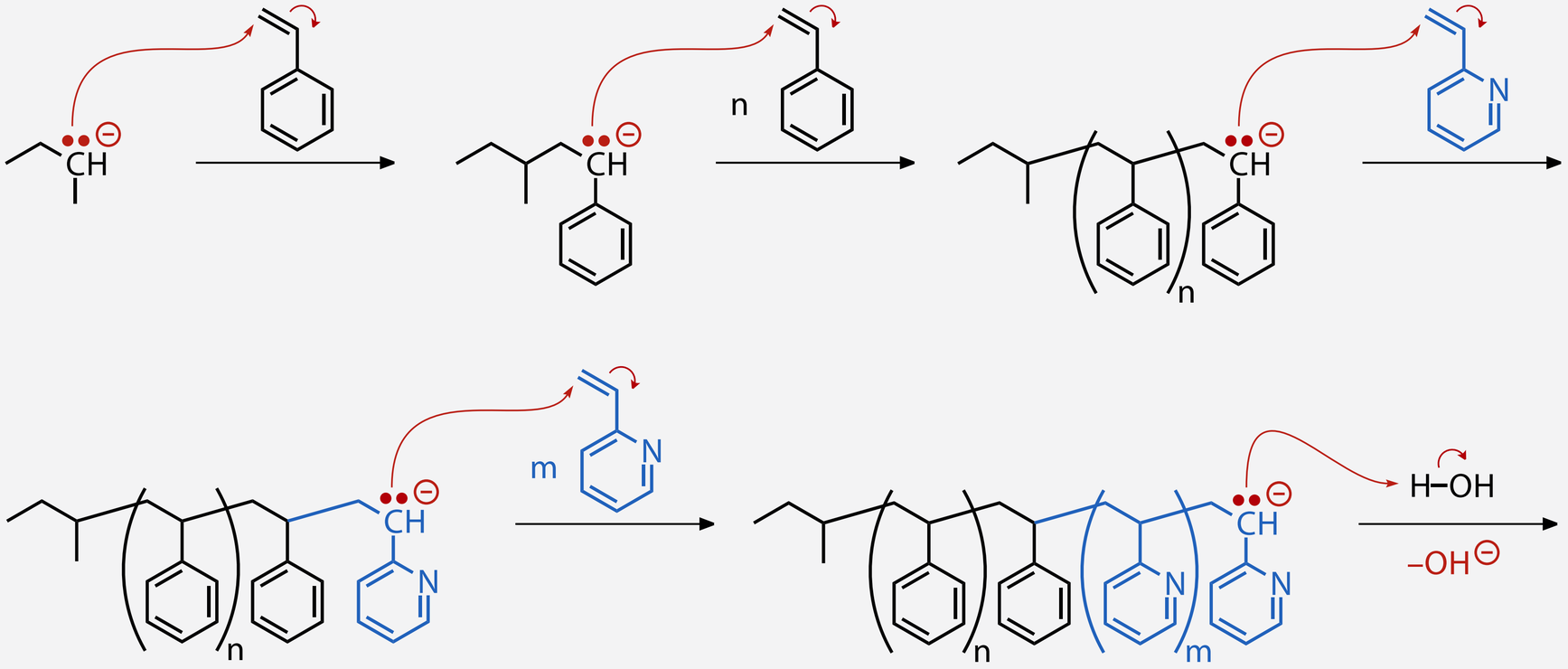
Living Anionic Polymerization of Vinyl Monomers

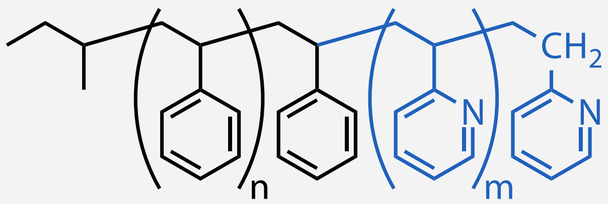
poly(2-vinylpyridine) | polystyrene | polyisoprene



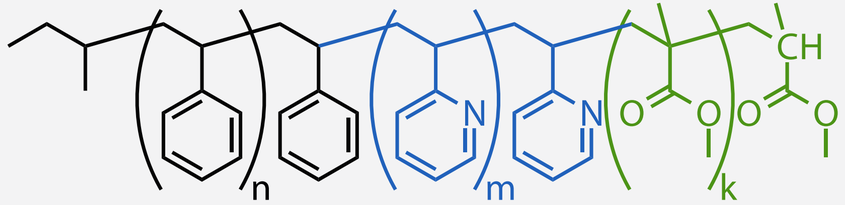
- appearance of color is an evidence of the presence and non-terminating character of living chains

Block Copolymers via Sequential Monomer Addition





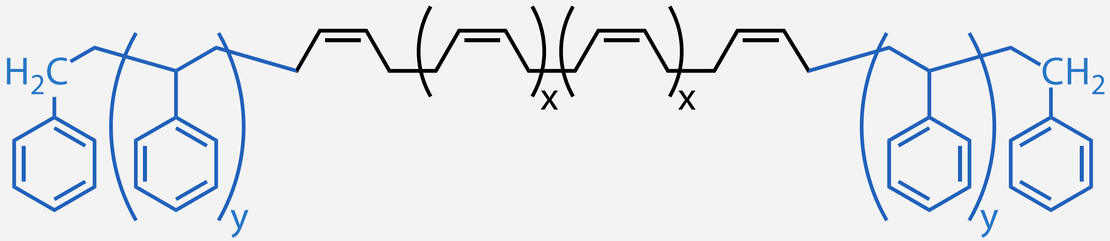
PS–P2VP



PS–P2VP–PMMA

Thermoplastic Elastomers from BAB Triblock Copolymers

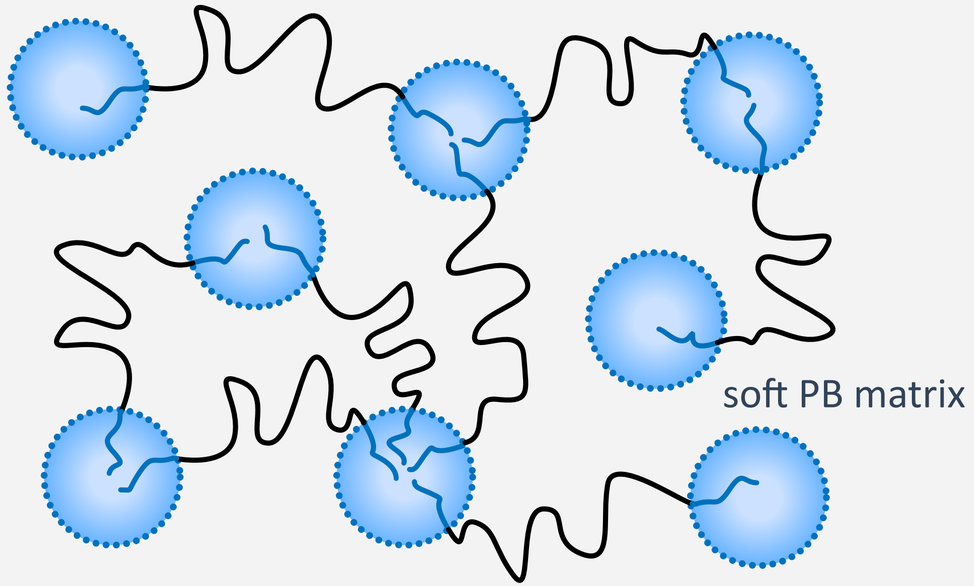
- SBCs (styrene-butadiene block copolymers) are relevant elastomer materials (like some TPUs)



$T_g \approx 100°C$ **$T_g \approx -60°C$** **$T_g \approx 100°C$**

SBS rubber (Kraton™, BASF)

poly(styrene-*block*-butadiene-*block*-styrene)



glassy, hard, physical cross-links

$\varnothing$ 10^{-8}–10^{-7} m

- **phase segregation (demixing) of different polymer segments in bulk material (Chapter 5)**
- **hard PS domains serve as physical cross-links: they melt above their T_g (reprocessable materials)**

Learning Outcome

- **step-growth polymerization** generate polymers of high molecular weight only at very high conversions.

- **chain-growth polymerization** yield high molecular weights at early conversions

- **radical polymerization** generates polymers of similar molecular weights up to 10% conversion, above which the molecular weight can either decrease or increase (due to exhaustion of reagents, transfer reactions, gel effect)

- for **living polymerization**, polymer chains grow linearly with conversion

- dispersities are large for **step-growth (2.0 at the end)** and **chain-growth (1.5 < Đ < 20)**, while **for living polymerization, the polymer chains become less and less disperse with progress of the polymerization**.

Many, Many More Polymerization Mechanisms…

- Atom Transfer Radical Polymerization (ATRP)
- Radical Addition Fragmentation Transfer (RAFT)
- Stable Free Radical Polymerization (SFRP)
- Living Radical Polymerization
- Cationic Polymerization of the C=C double bond
- Living cationic polymerizations
- Emulsion Polymerizations
- Ring Opening Polymerizations
- Carbonyl Carbon Polymerizations
- “Supramolecular” Polymerizations
- various copolymerizations