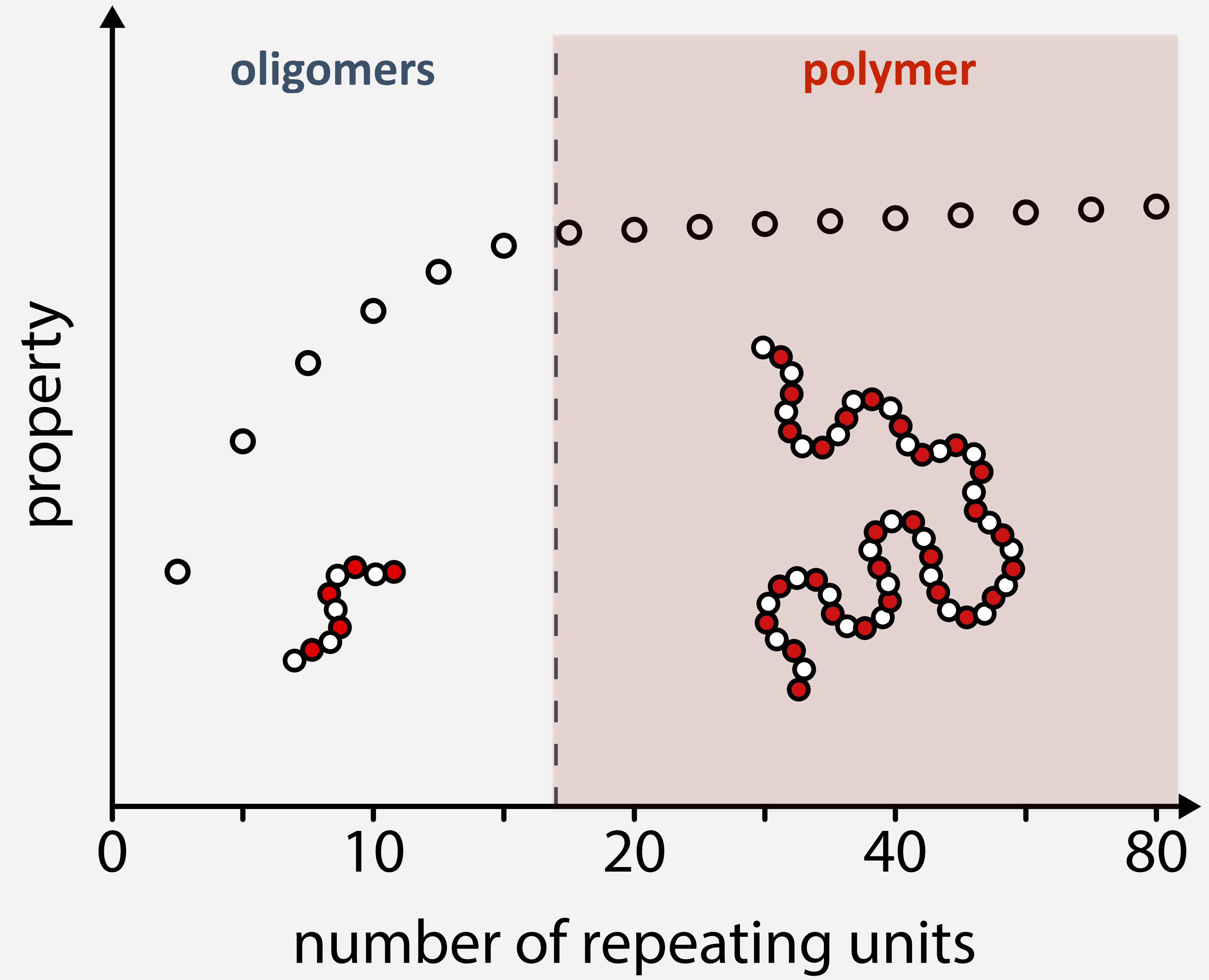
1.2

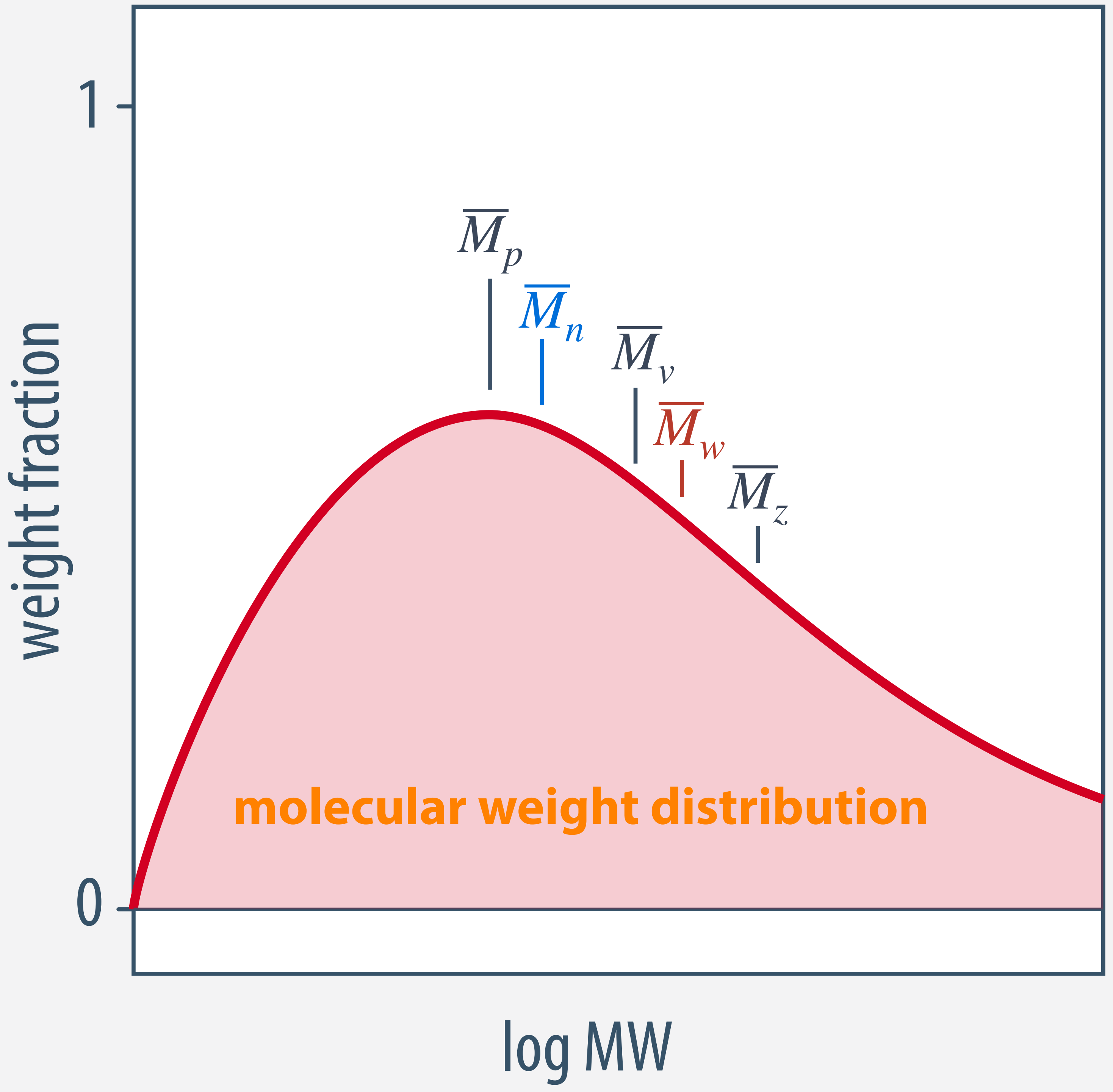
Definition, Synthesis, Basic Properties

Definition of a Polymer

- definition of a polymer according to Hermann Staudinger:

  “A polymer is a large molecule constituted from (identical) smaller structural ‘repeating units’ with a length sufficient such that molecules with n and n+1 repeating units are indistinguishable”





- **different from many natural macromolecules, natural and synthetic polymers are “polydisperse”**
- **since properties are indistinguishable, polymers are also inseparable**

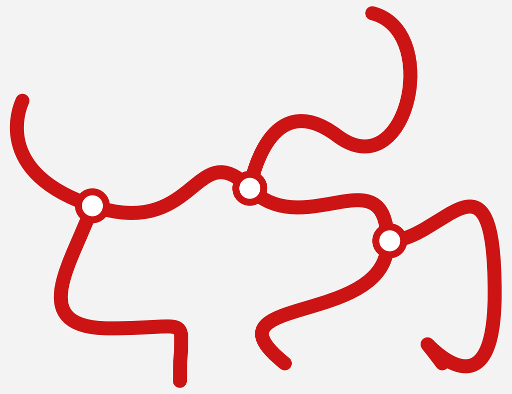
Hermann Staudinger, *Ber. Chem. Ges.* **1920**, *53*, 1073; *Helv. Chim. Acta* **1922**, 5, 785

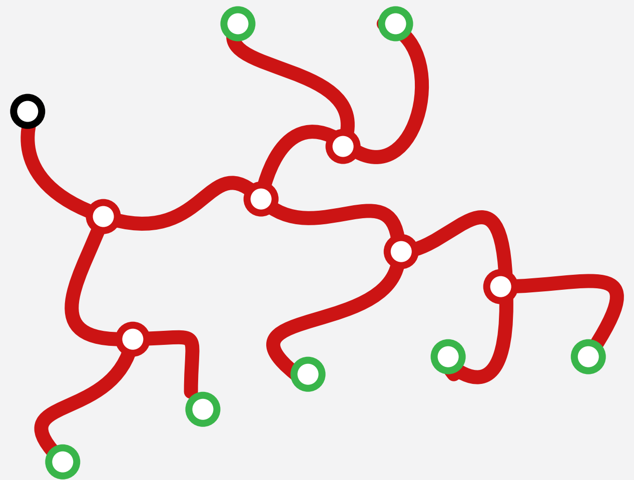
Polymer Types, Architectures, Microstructures

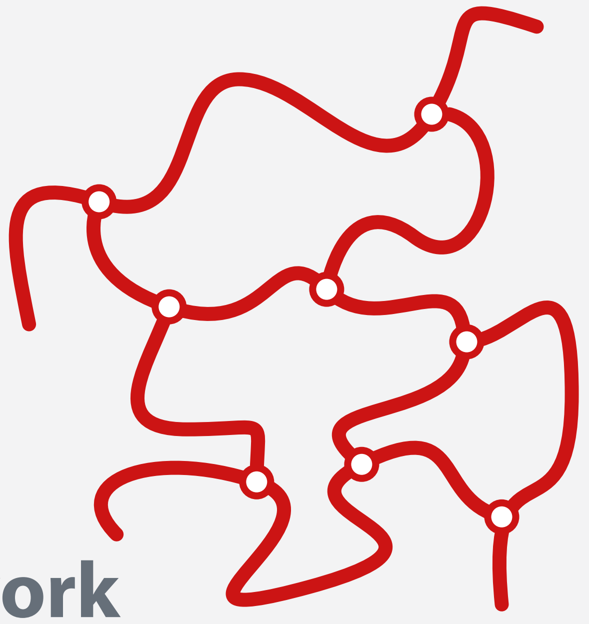
- homopolymers: one type of repeating units (but different architectures)


linear

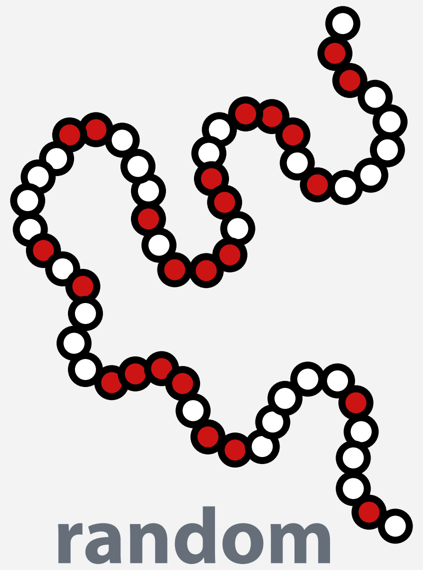

star

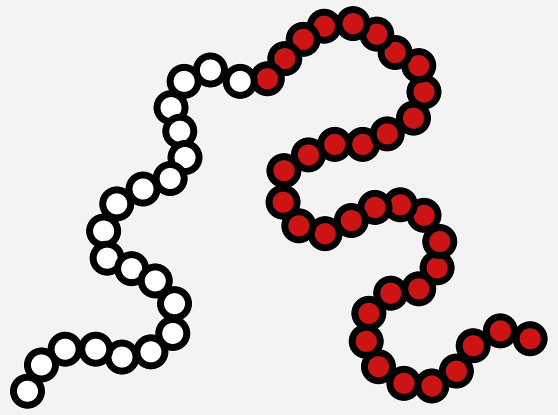

branched

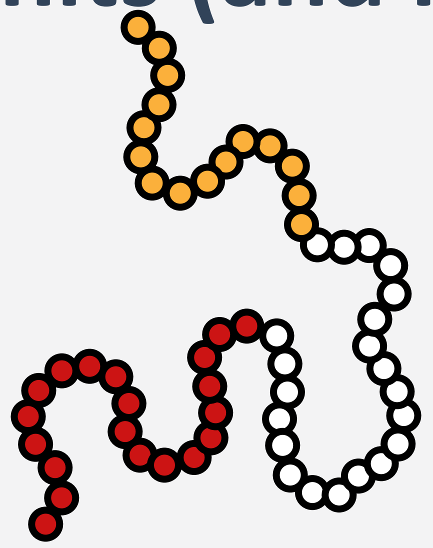

hyperbranched


network

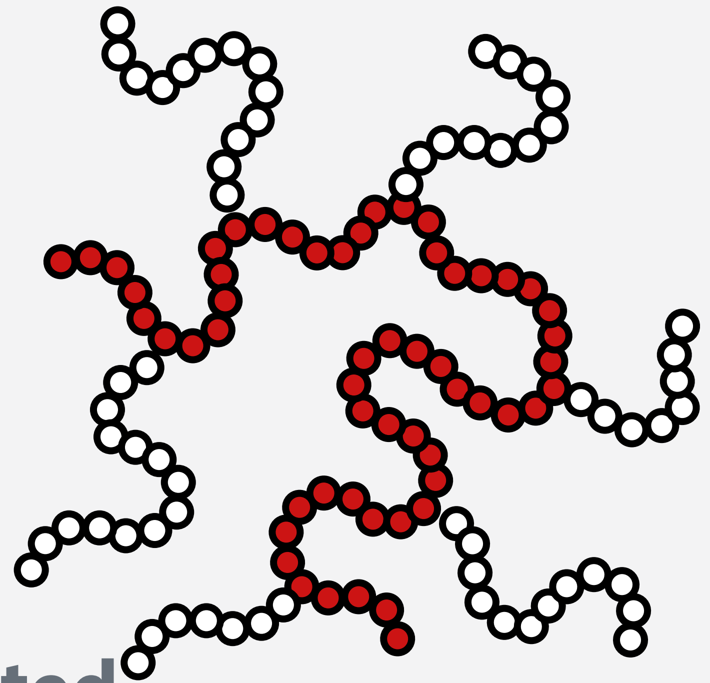
- copolymers: different types of repeating units (and microstructures)

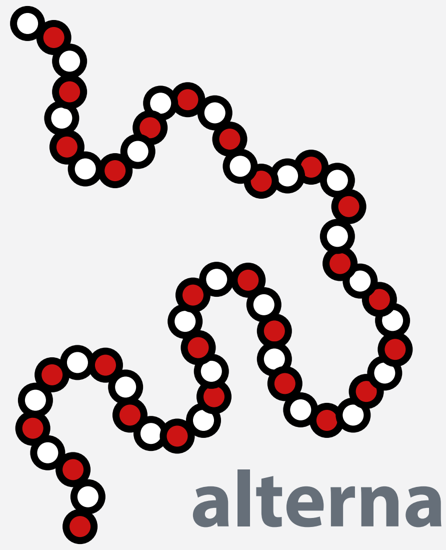

random

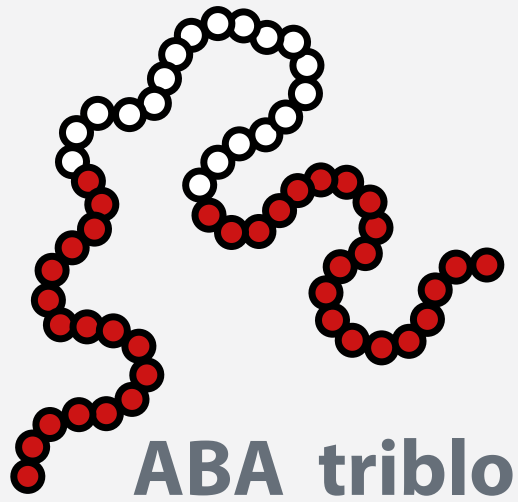

AB diblock


ABC triblock

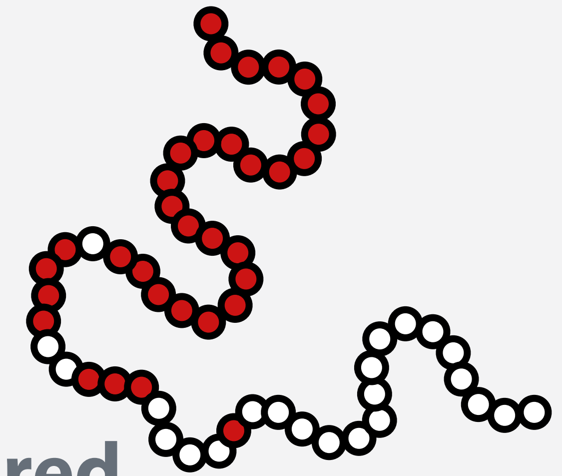

segmented

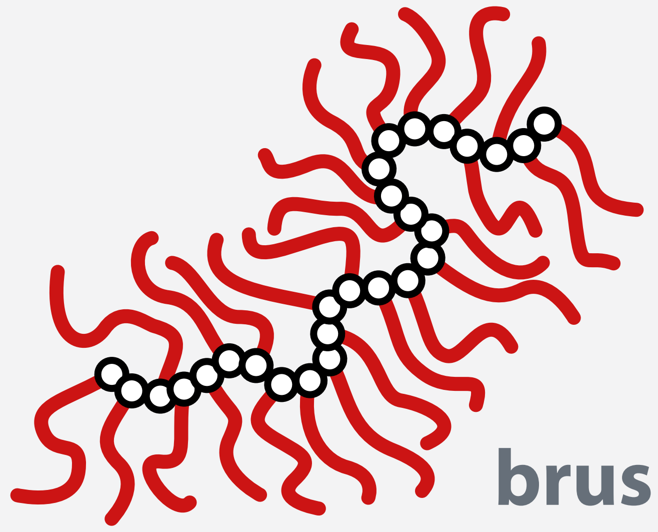

grafted


alternating


ABA triblock


miktoarm star

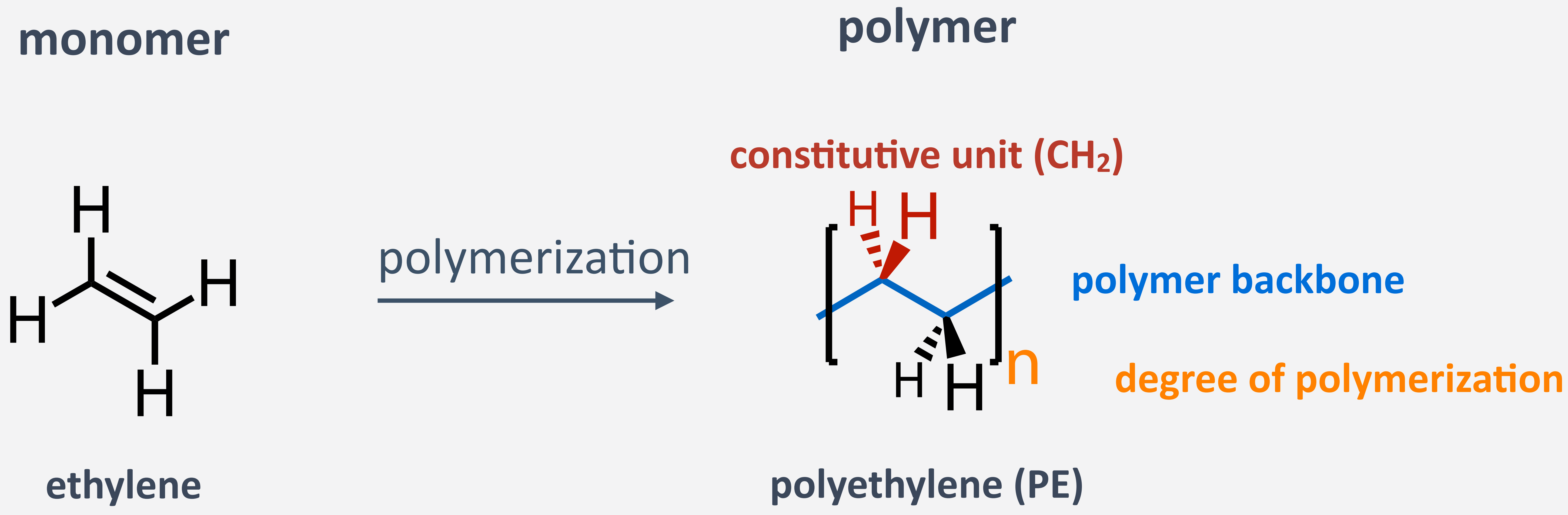

tapered


brush

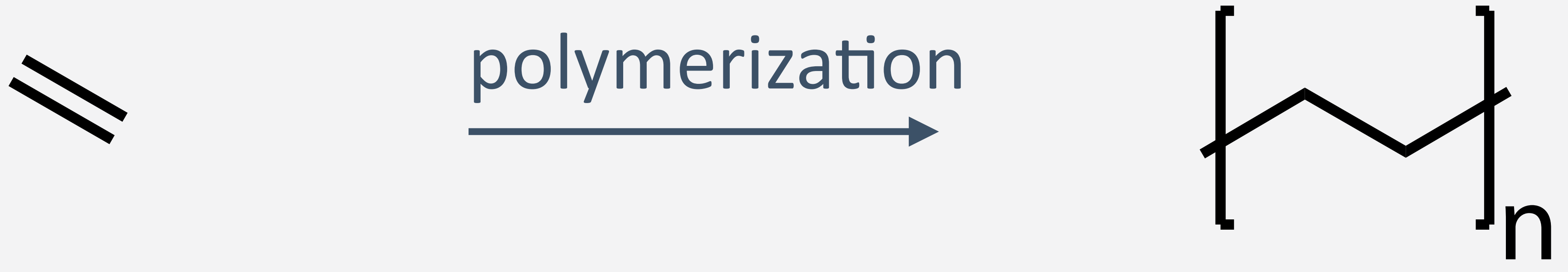
The Polymerization Reaction

- **polymer chain architecture, chemical composition, molecular weight, molecular weight distribution are all generated during the polymerisation reaction**

- chemical formulae: the repeating unit is indicated in brackets.



- usually, hydrogen atoms are omitted for clarity:

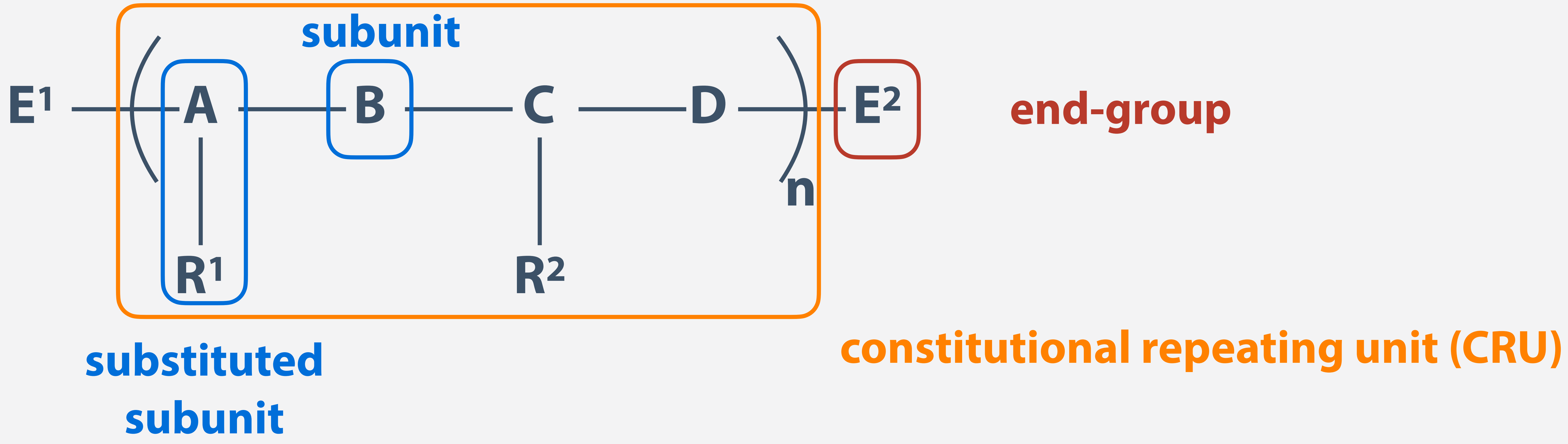


Nomenclature of Single-Strand Polymers

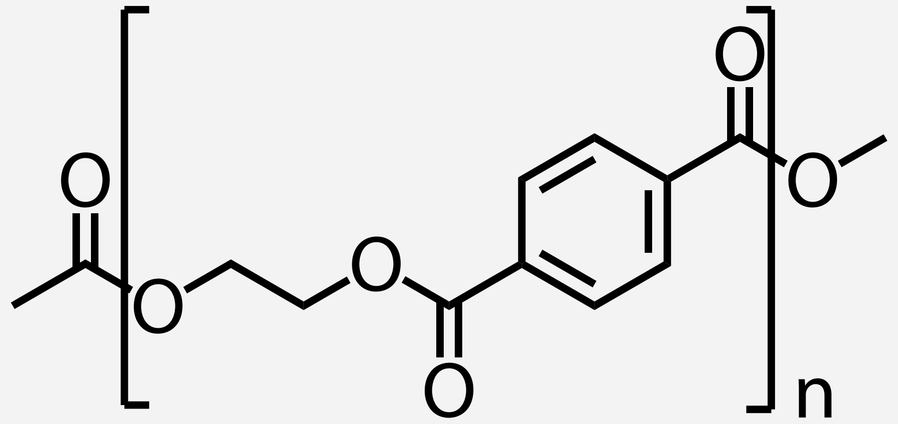
- **attachement of the prefix “poly” to the name of the monomer**

  examples: polystyrene (PS), poly(vinyl chloride) (PVC), poly(etyhelene terephthalate) (PET)

- **systematic nomenclature** as defined by the *International Union of Pure and Applied Chemistry* (IUPAC) based on the identification of a preferred repeating unit.

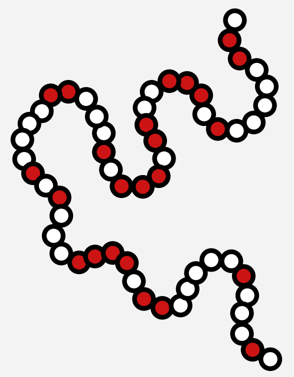


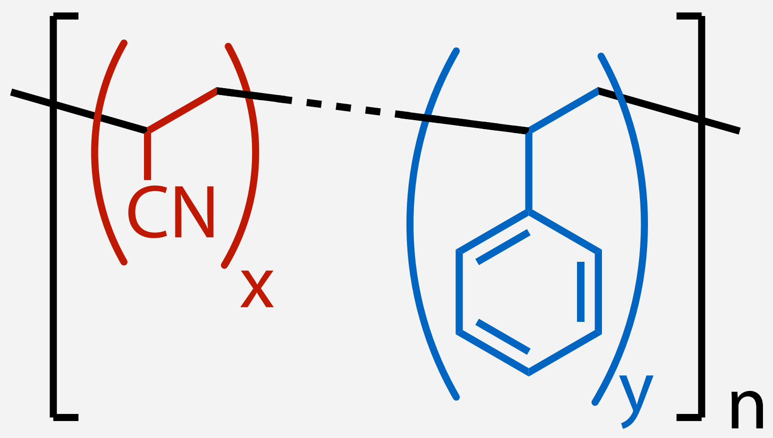
example: α-acetyl-ω-methoxy-poly(oxyethyleneoxyterephthaloyl)



Nomenclature of Copolymers

- **random copolymer**

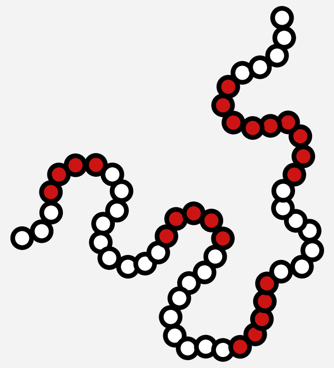


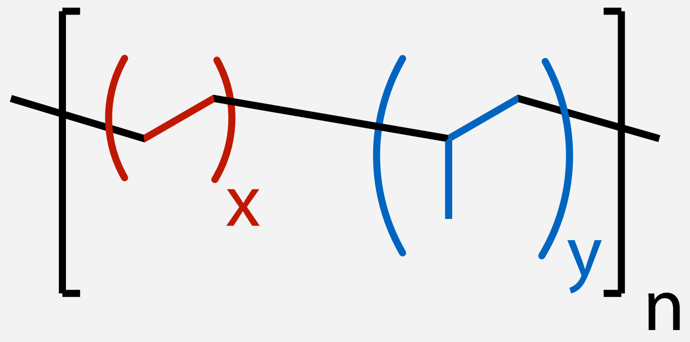


poly(acrylonitrile-*co*-styrene)

SAN

- **multiblock copolymer**

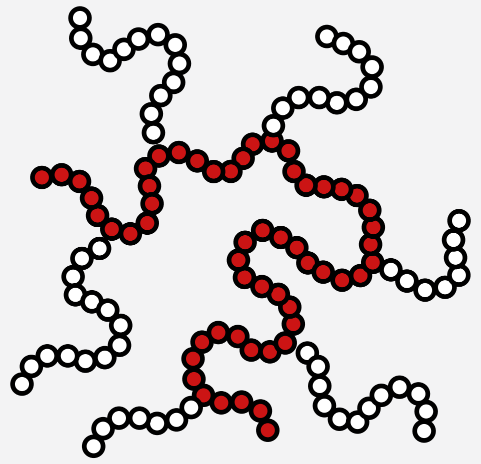


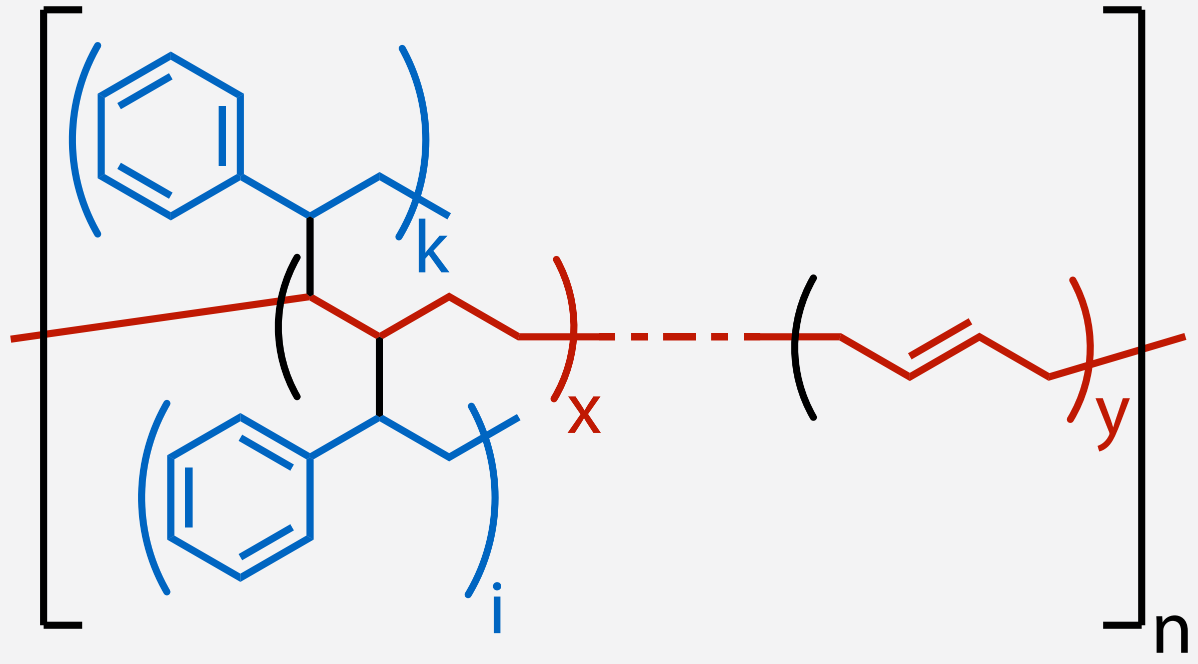


poly(polyethylene-*b*-polypropylene)

PP-b

- **branched copolymer**





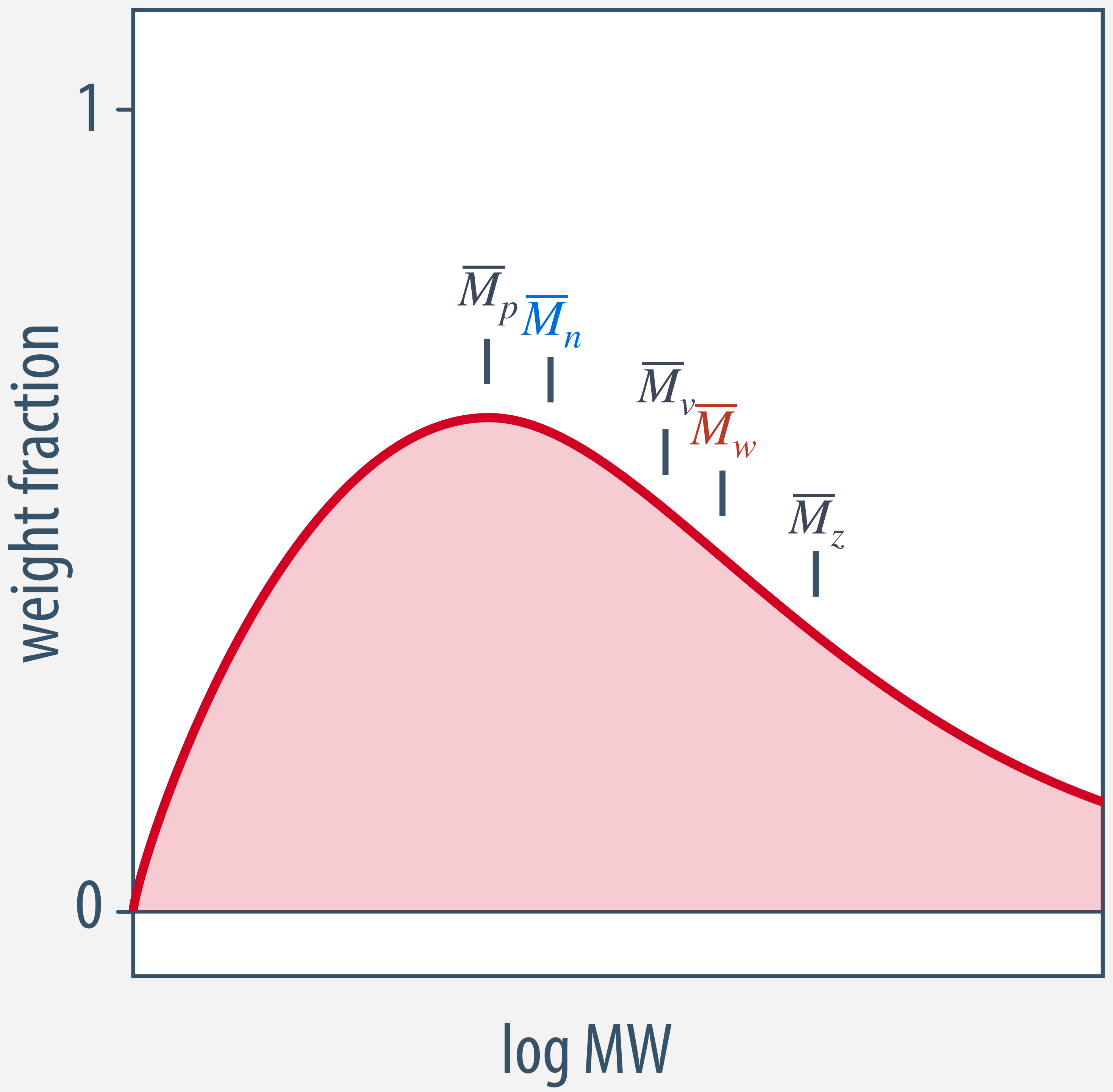
poly(butadiene-*g*-polystyrene)

component of
“high-impact polystyrene” (HIPS)

1.2.1 Polymer Synthesis

Average Molar Masses and Molar Mass Distribution

- stochastic process in polymer synthesis give mixtures of molecules of different molar masses



molar mass distribution

number average molar mass

$$\overline{M}_n = \frac{\mu_1'}{\mu_0'} = \frac{\sum n_x M_x}{\sum n_x}$$

weight average molar mass

$$\overline{M}_w = \frac{\mu_2'}{\mu_1'} = \frac{\sum n_x M_x^2}{\sum n_x M_x}$$

dispersity (formerly, polydispersity index)

$$Đ = \frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{\sigma^2}{\overline{M}_n{}^2}$$

- **polymers do not have defined molar masses but molar mass distributions**
- **different molar mass averages based on "moments" (μ') of the molar mass distribution**

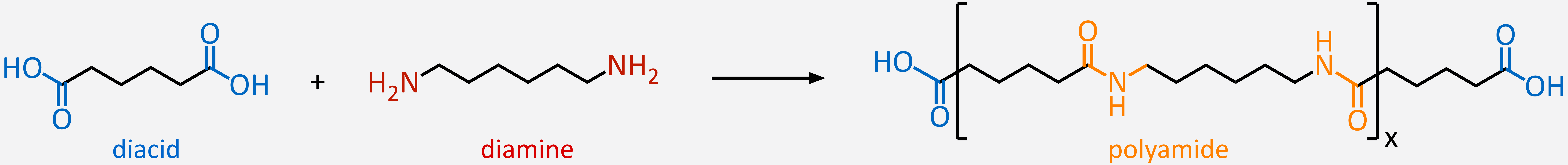
Key concept: See reader on *Molar Masses*

Number Average and Weight Average Molar Mass

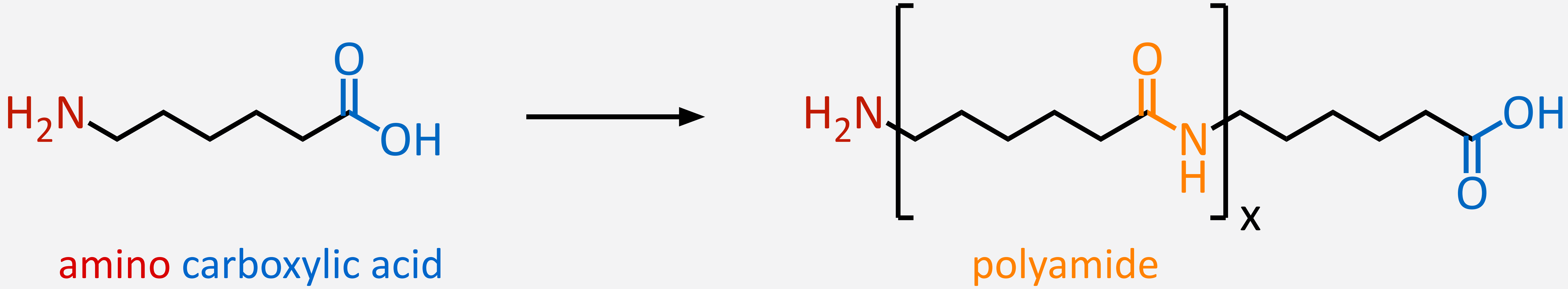
Step-Growth Polymerization

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



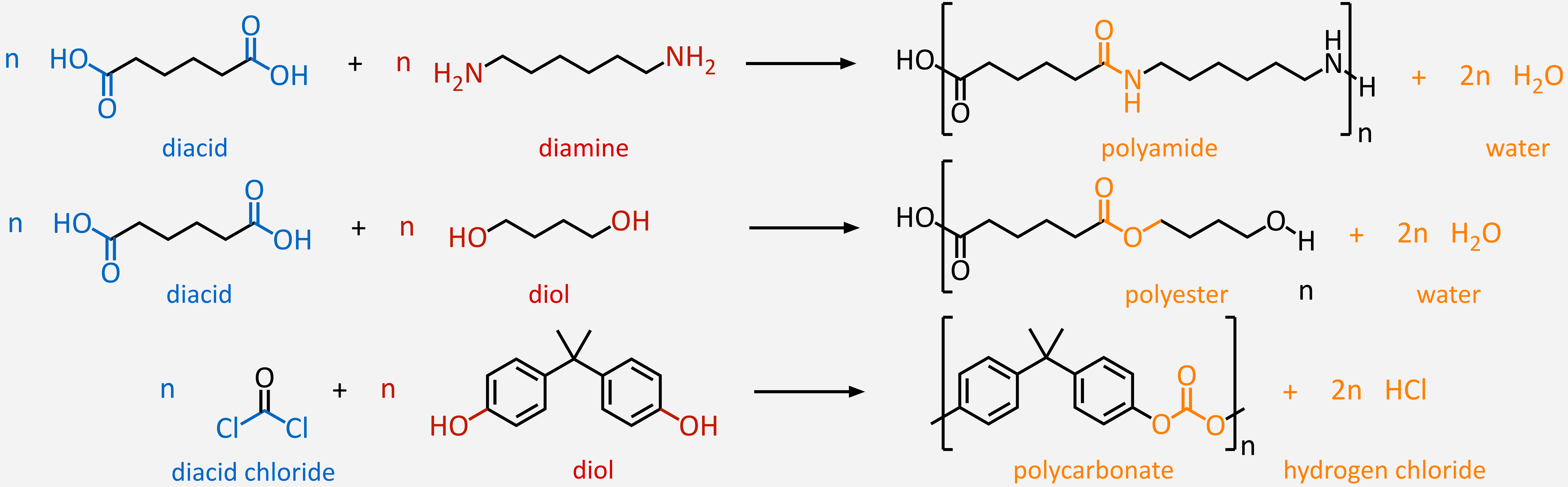
  - AB-type: one monomer with two complementary functions



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

Polycondensations

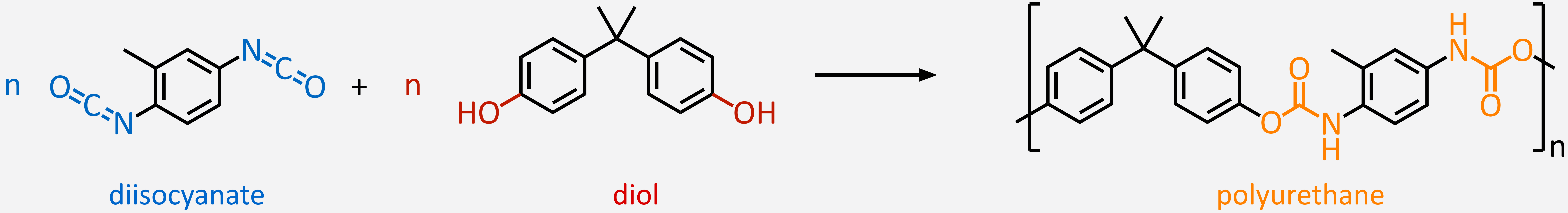
- **polycondensations are reactions of difunctional molecules under release of a small molecule**
- **AA/BB-type and AB-type polycondensations are both possible**



- **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 moleciule side product**

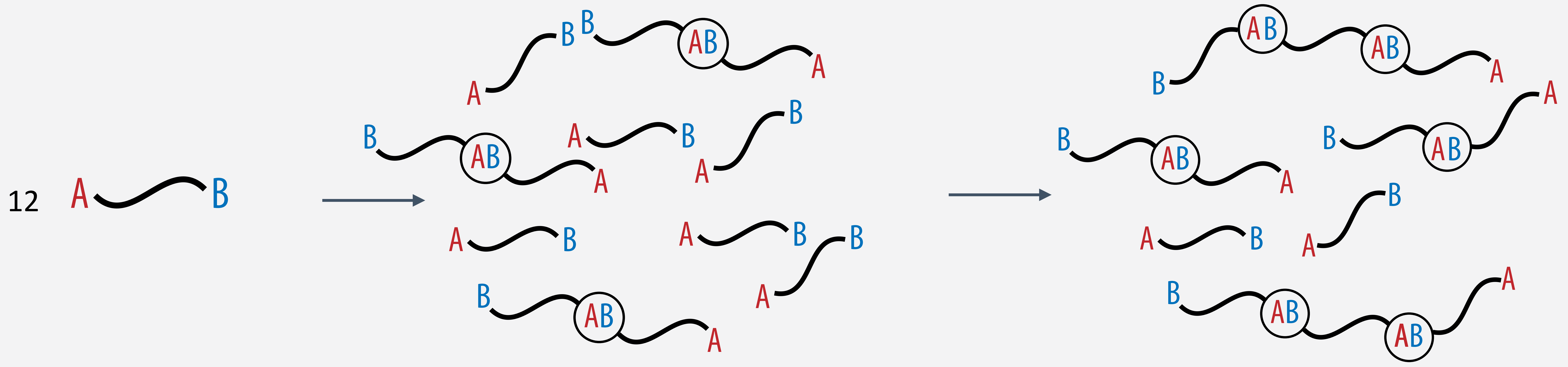
Polyadditions

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



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

Origin of Dispersity and Molar Mass 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: source of molar mass distribution and dispersity**
- **dispersity increases with conversion of functional groups**
- **conversion limits molecular weight – high molecular weights require extremely high conversions!**

Dependence of Molecular Weight on Conversion and Functional Group Ratio

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

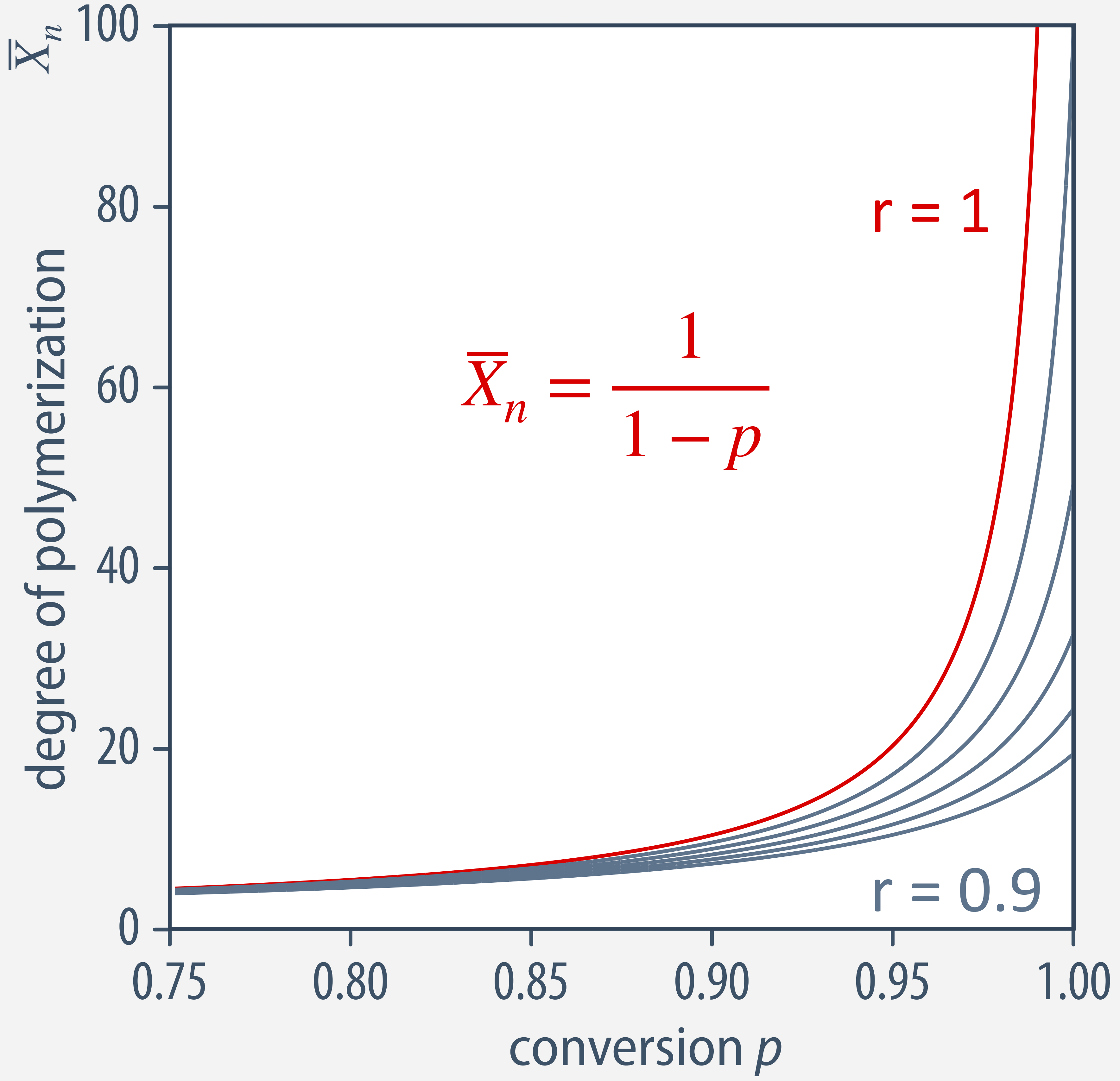
general Carothers Equation

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

for complete conversion (*p* = 1)

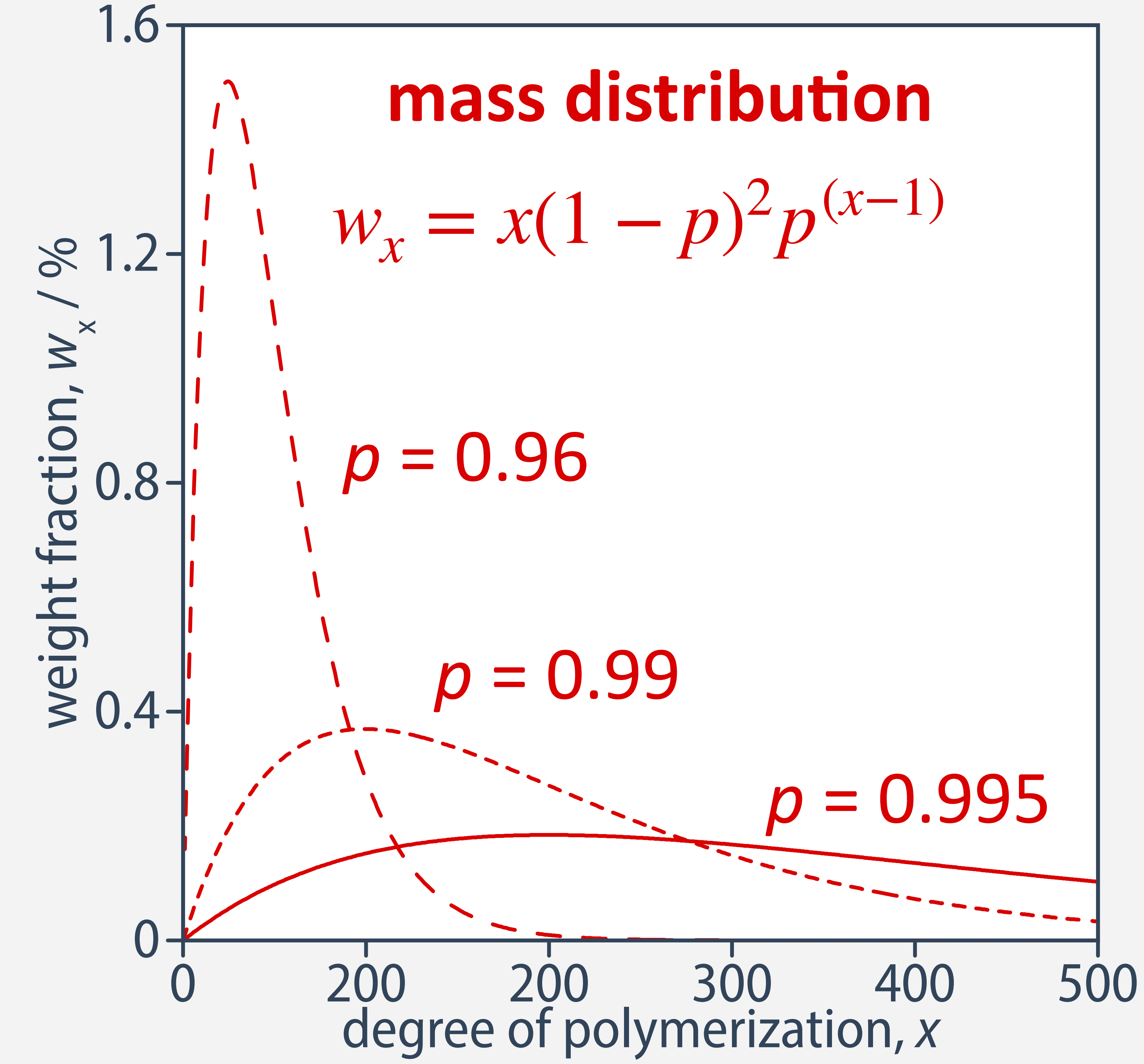
$$\overline{X}_n = \frac{1}{1-p}$$

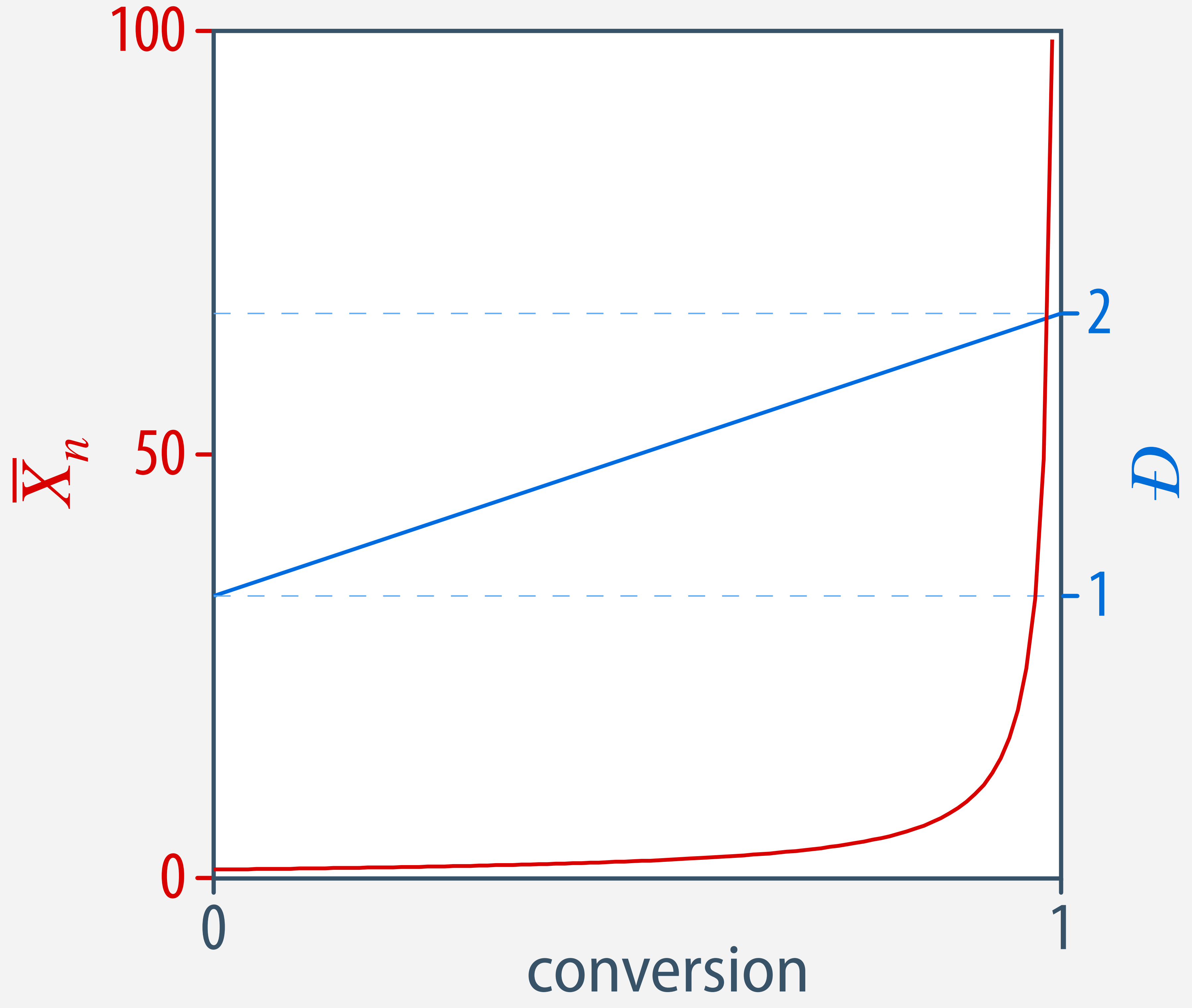
for perfect stoichiometry (*r* = 1)



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

Flory-Schulz Distribution





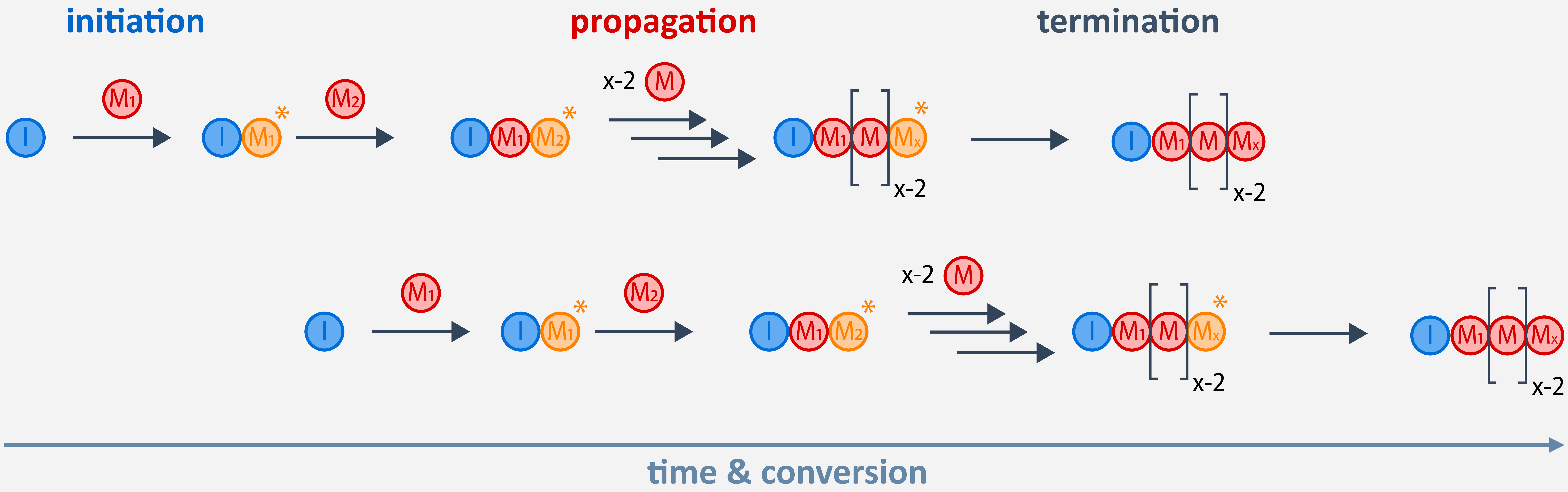
- **mass distribution shows a maximum that moves to higher *x* with increasing conversion *p***
- **convergence to a dispersity of *Đ* = 2 is diagnostic of a well-behaved step-growth polymerization**

see reader on *Step-Growth Polymerizations*

Chain-Growth Polymerization

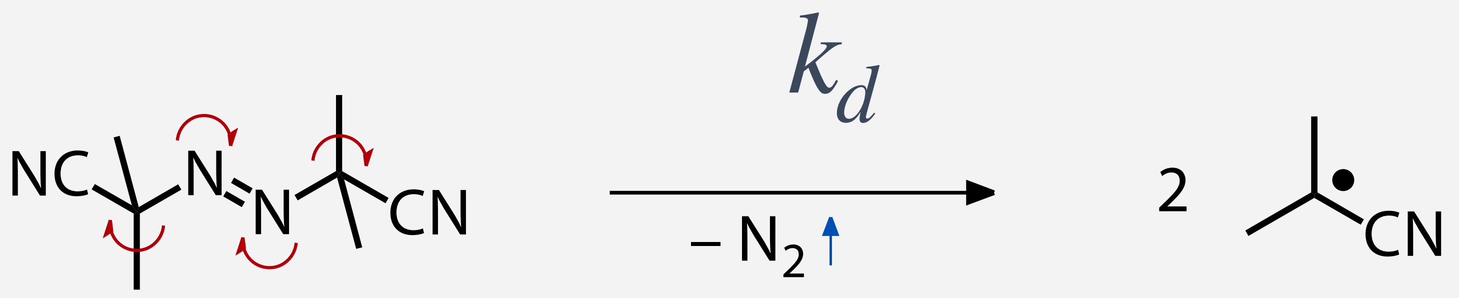
Principal Steps of Chain-Growth Polymerizations

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

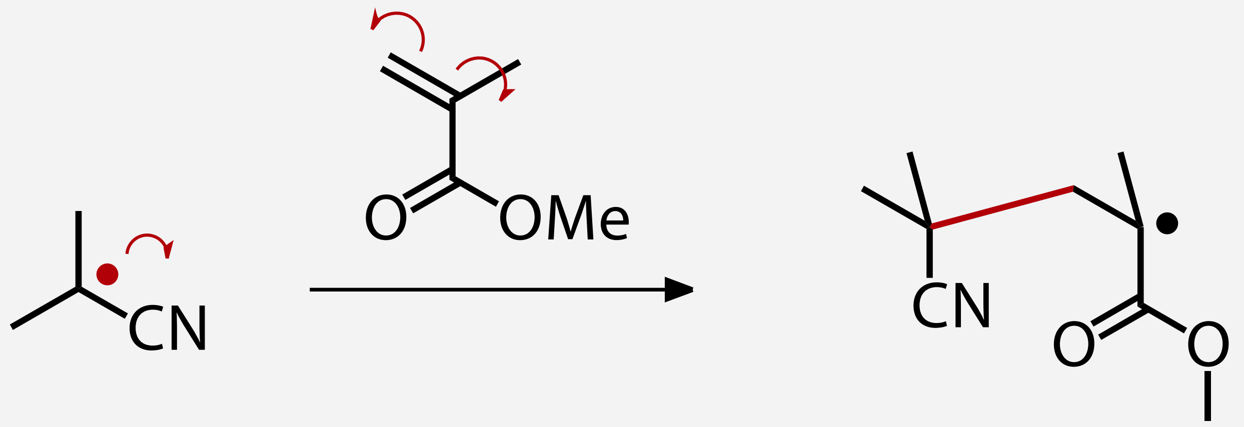


- **polymerizations require an initiator that attacks a first monomer and creates an active center**
- **during propagation, monomers add consecutively to the active center of a growing polymer chain**
- **initiation continuously occurs during entire polymerization time**
- **termination is a stochastic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

Elementary Steps of Free Radical Polymerizations

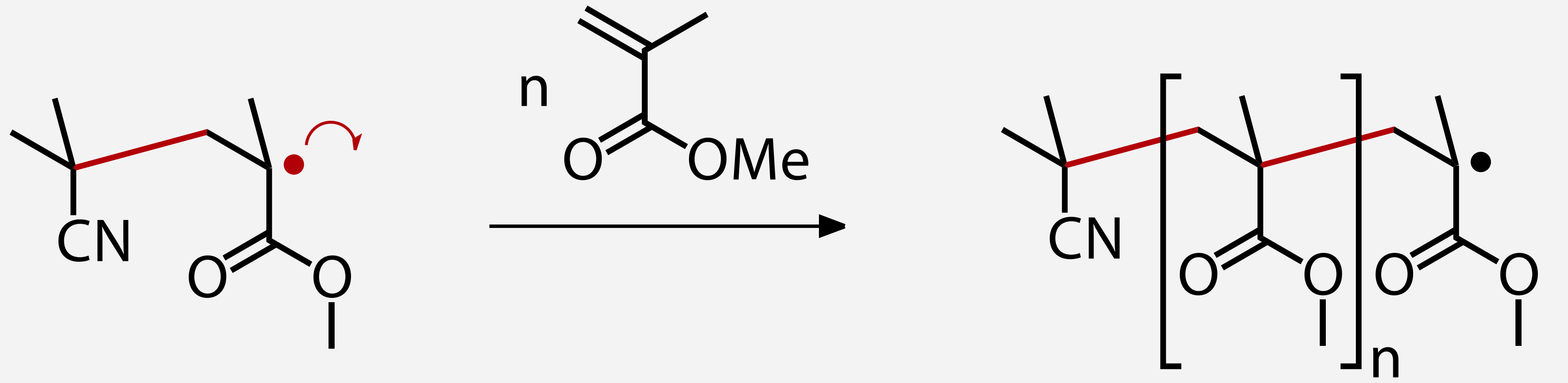


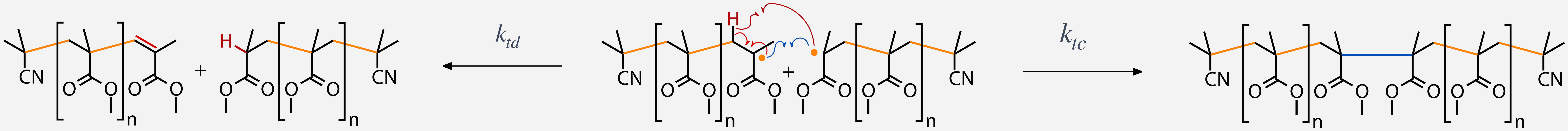
initiator decomposition (slow)



initiation (fast)

propagation (chain growth)



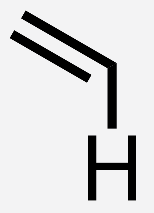


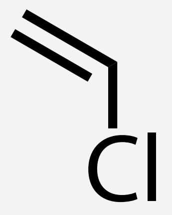
disproportionation

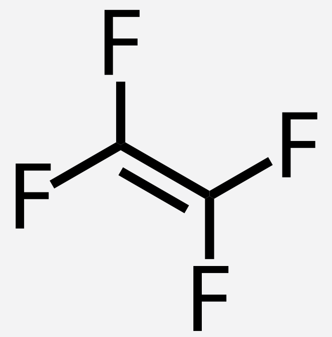
radical combination

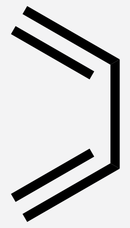
- **termination by combination and disproportionation often occur both and are stochastic processes**

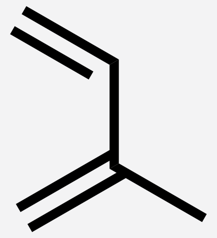
Important Vinyl Monomers in Radical Polymerization

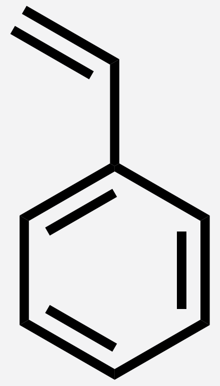

ethene
ethylene (PE)

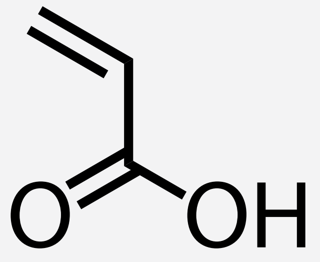

chloroethene
vinyl chloride (PVC)

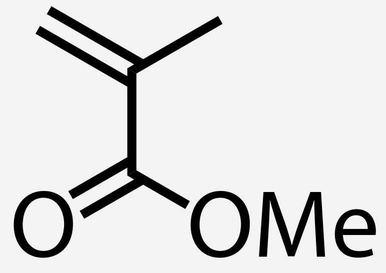

tetrafluoroethene
(PTFE, Teflon)

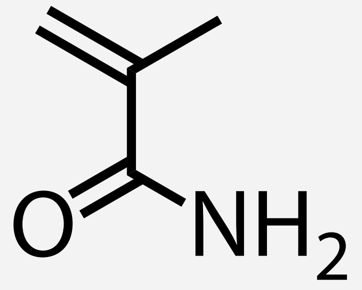

butadiene
(PB)


2-methylbutadiene
isoprene (PI)


phenylethene
styrene (PS)


propenoic acid
acrylic acid (PAA)


methyl 2-methylpropenoate
methyl methacrylate (PMMA)


2-methylpropenoic amide
methacrylamide (for PMAAm)

- **vinyl monomers mostly with +M or –M substituents used for technologically relevant polymers**

Kinetics of Chain Growth Polymerization

rate of initiation

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

rate of propagation

$$R_p = -\frac{d[\mathrm{M}]}{dt} = \sum k_p[\mathrm{M}_i^\bullet][\mathrm{M}]$$

rate of termination

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

- **steady-state-conditions:** $R_i = R_t$ $\quad R_p = k_p\sqrt{\frac{fk_d}{k_t}}\sqrt{[\mathrm{M}][\mathrm{I}]}$ $\quad$ with $k_t = k_{tc} + k_{td}$

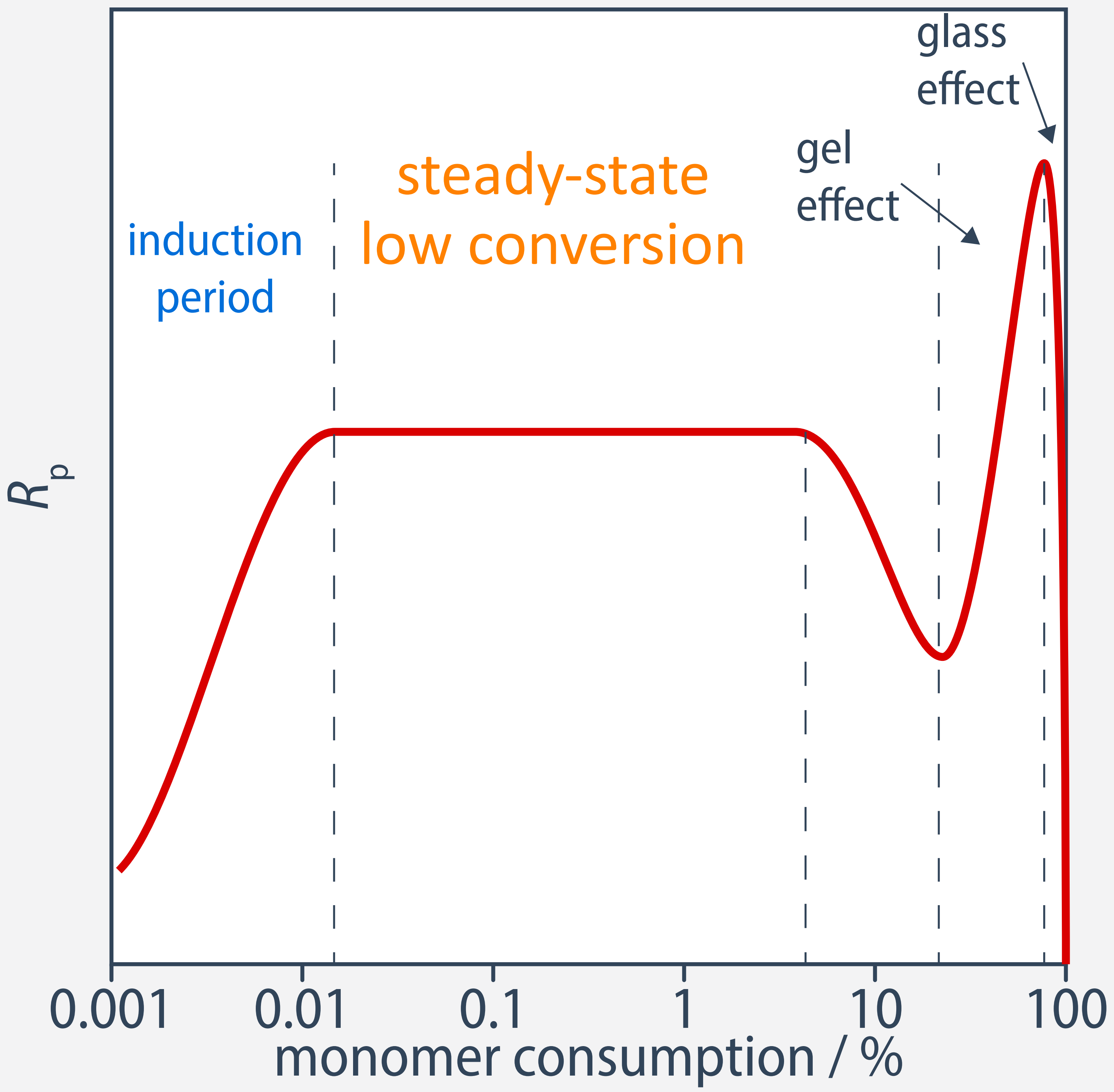
- **kinetic chain length:** $\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}]}{2(fk_dk_t[\mathrm{I}])^{1/2}} \propto \frac{[M]}{\sqrt{[\mathrm{I}]}}$

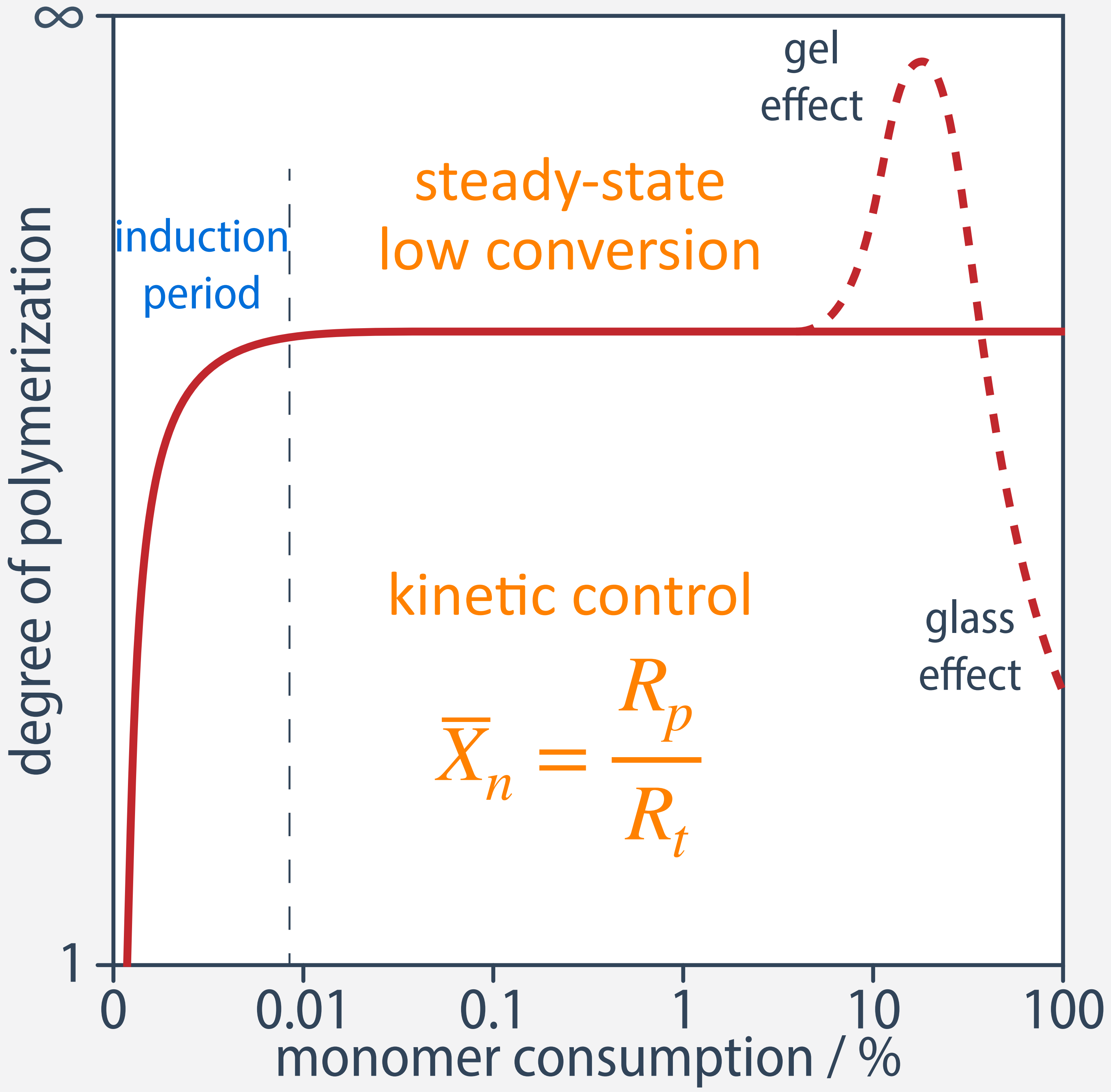
- **steady state conditions required for stable polymerization, results in reaction order 0.5 for initiator**
- **increasing initiator concentration increases polymerization rate but results in decreased molar mass**

see reader “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**



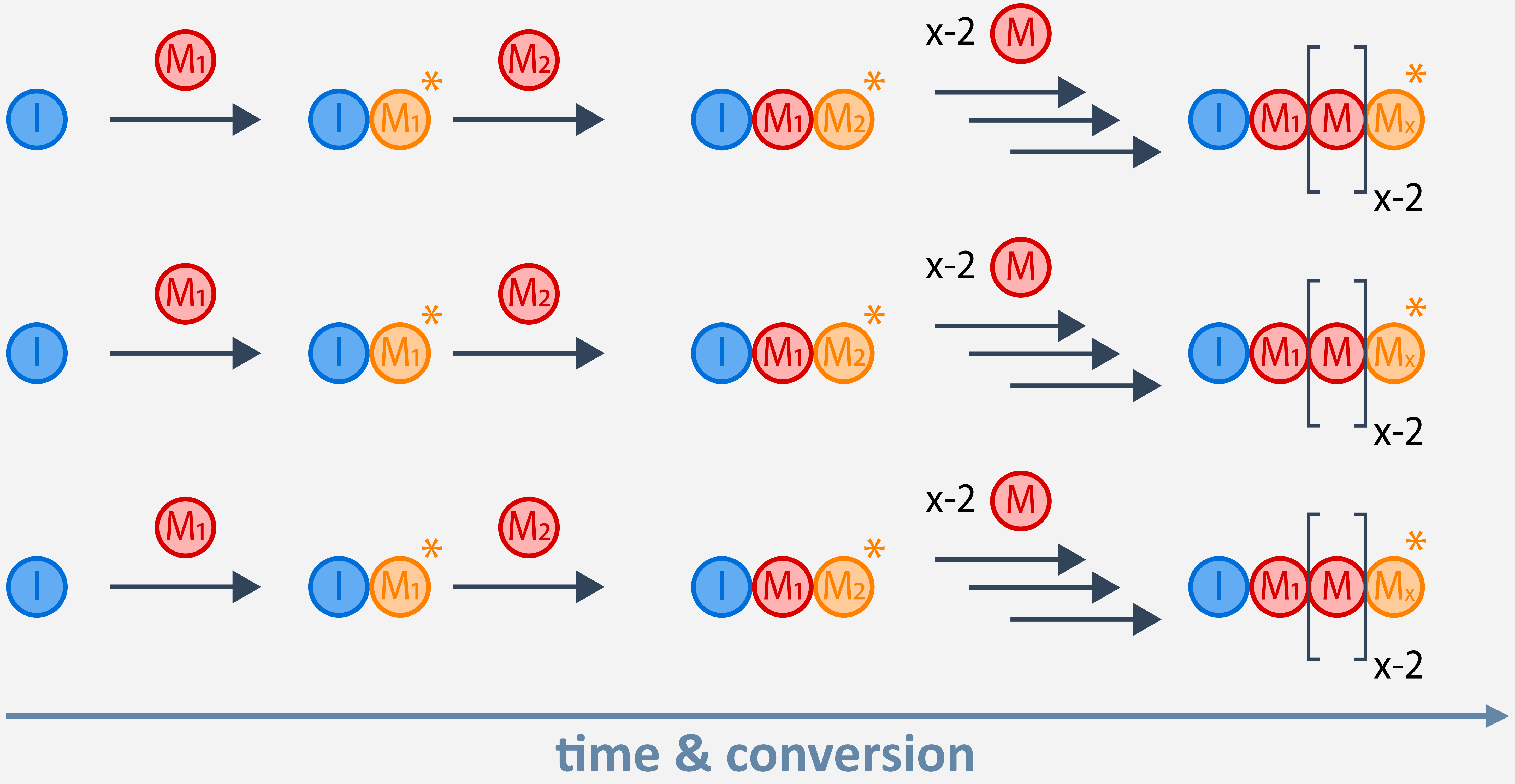


- **steady-state conditions are not maintained at medium to high conversions, causing a loss of control over polymerization rate and molar mass distribution**

Living and Controlled Polymerization

The Living Nature

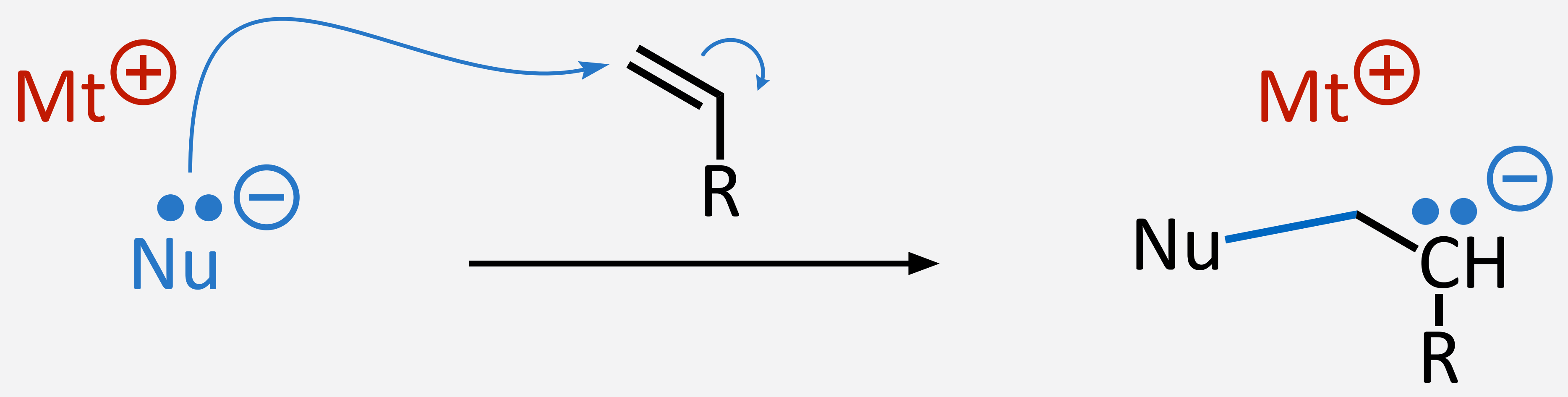
- **absence of termination (no mechanism & strong electronic repulsion between active chain ends!)**



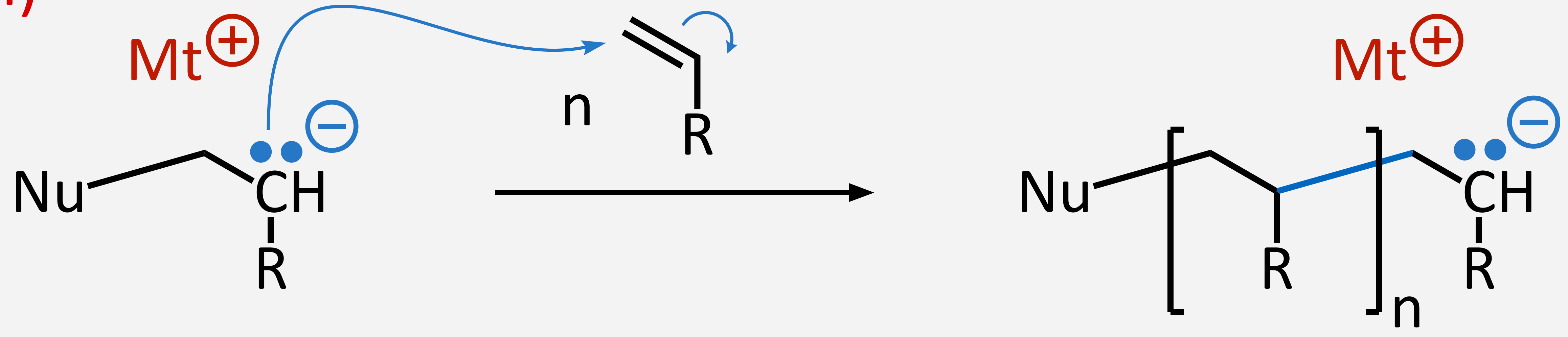
- **polymers are all initiated fast and at approximately the same time; origin of (small) dispersity**
- **chain ends remain active after full monomer consumption (absence of impurities!)**
- **the polymerization can be continued with an additional feedstock of monomers (same or different)**

Living Anionic Polymerization of Vinyl Monomers

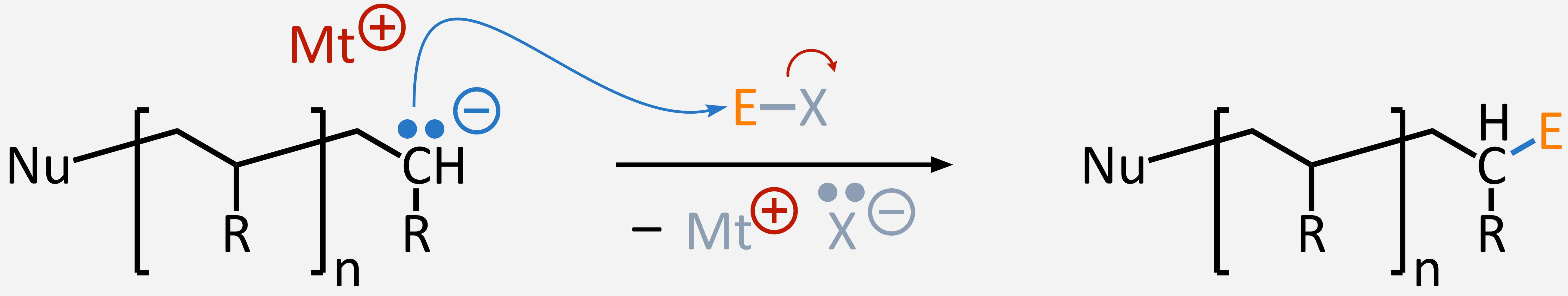
- initiation (very fast)

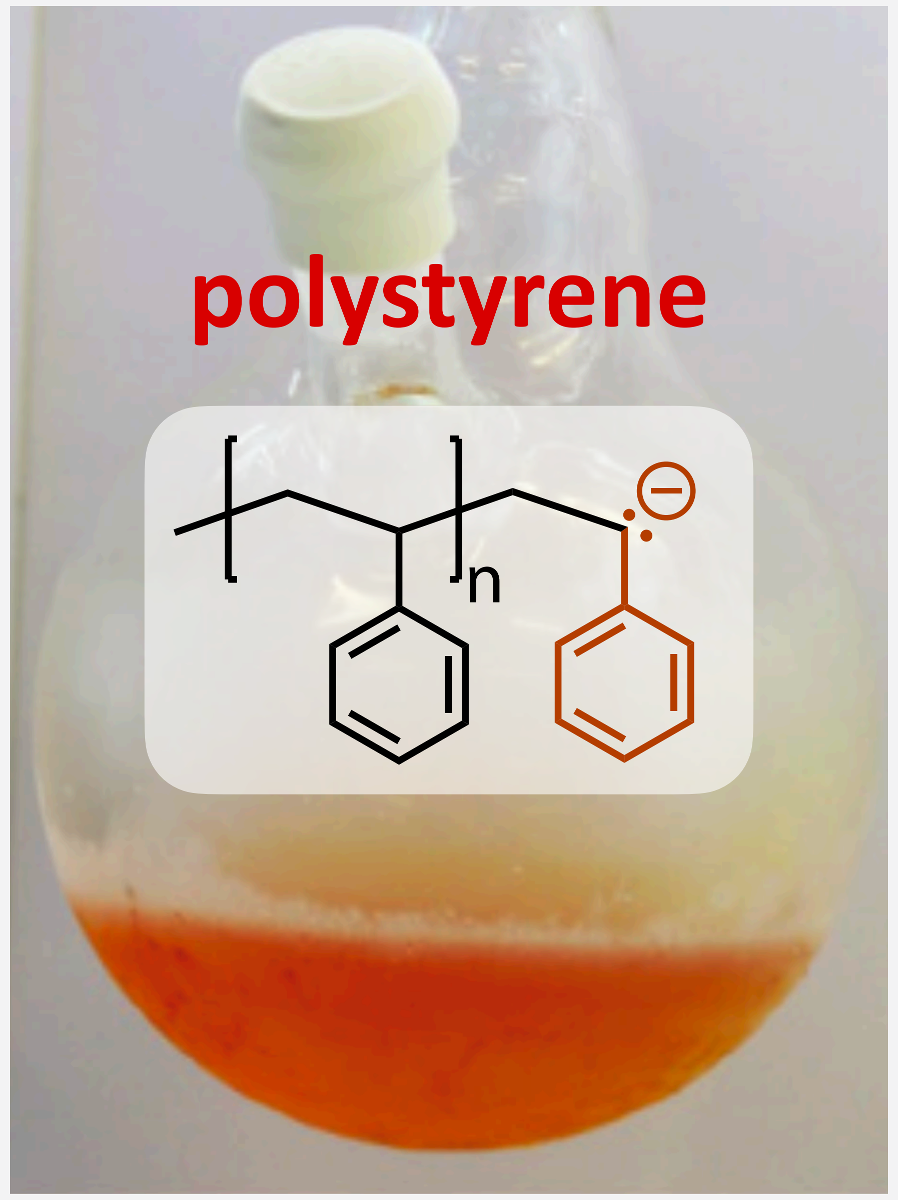


- propagation (chain growth)



- quenching



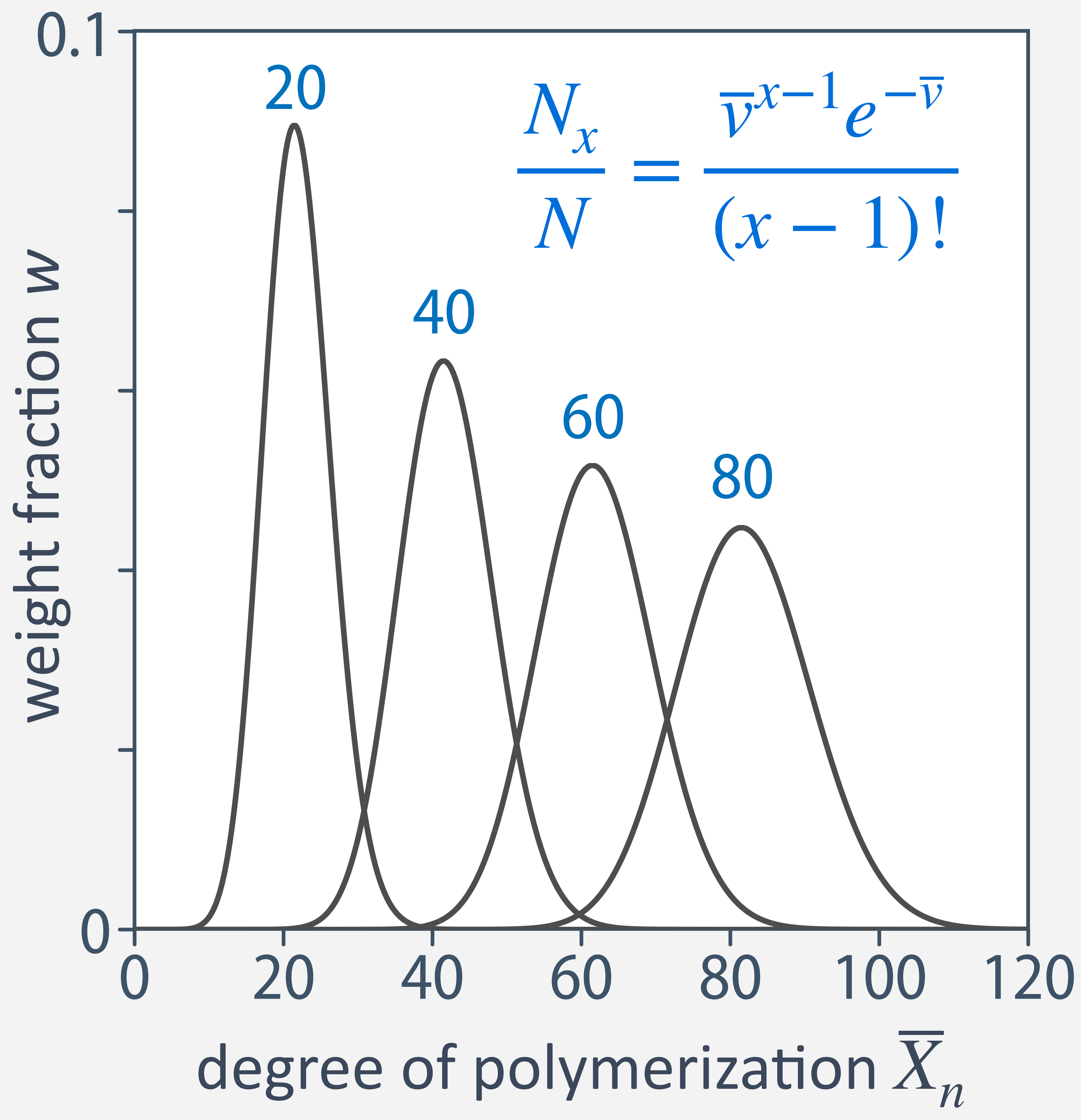


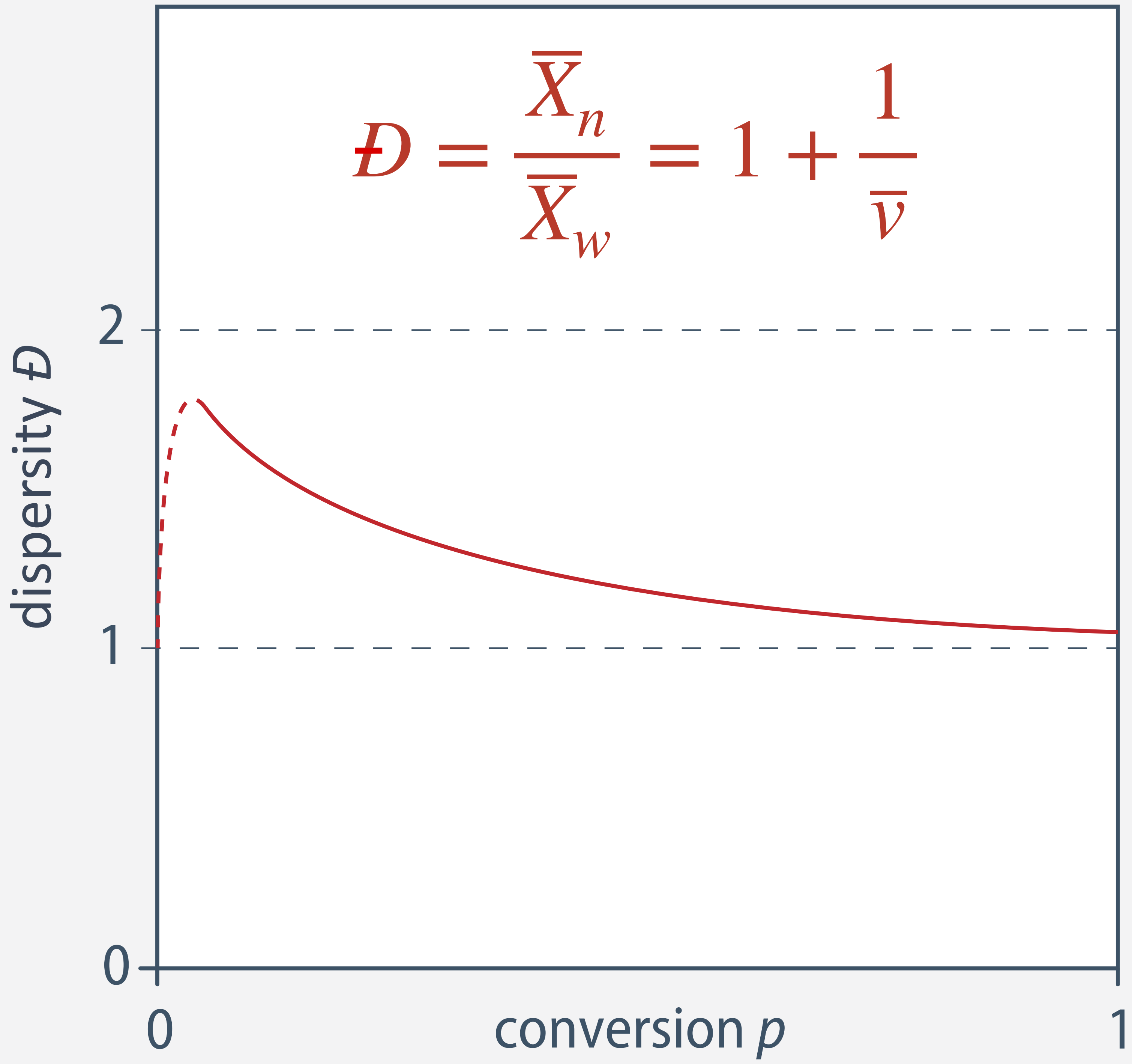
characteristic color as evidence of the presence and non-terminating character of living chains

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

The Poisson Distribution of the Molecular Weight

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



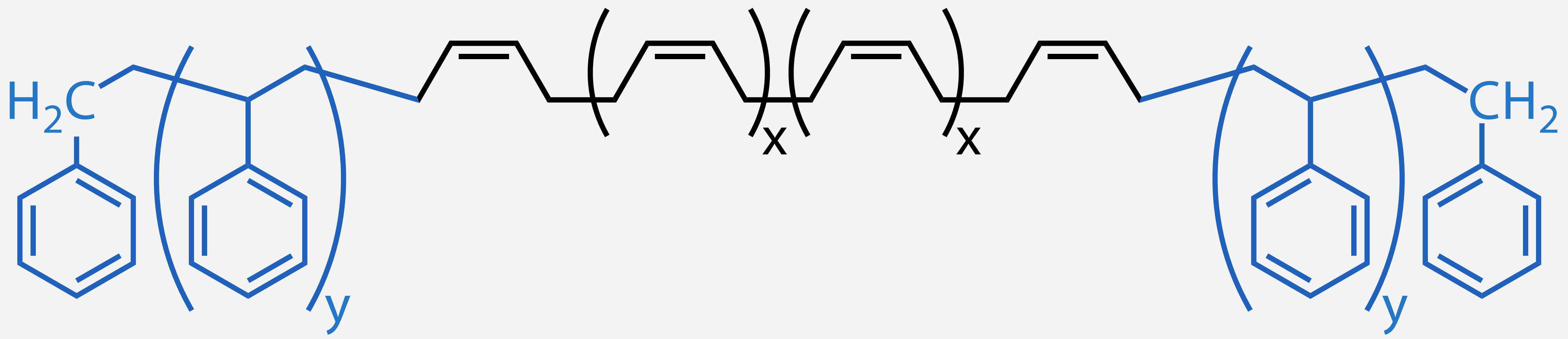


- **number-average degree of polymerization $\overline{X}_n \approx p \frac{[M]_0}{[I]_0}$ controlled by monomer/initiator ratio**

Key concept: see reader “Living & Controlled Polymerizations”

Thermoplastic Elastomers from BAB Triblock Copolymers

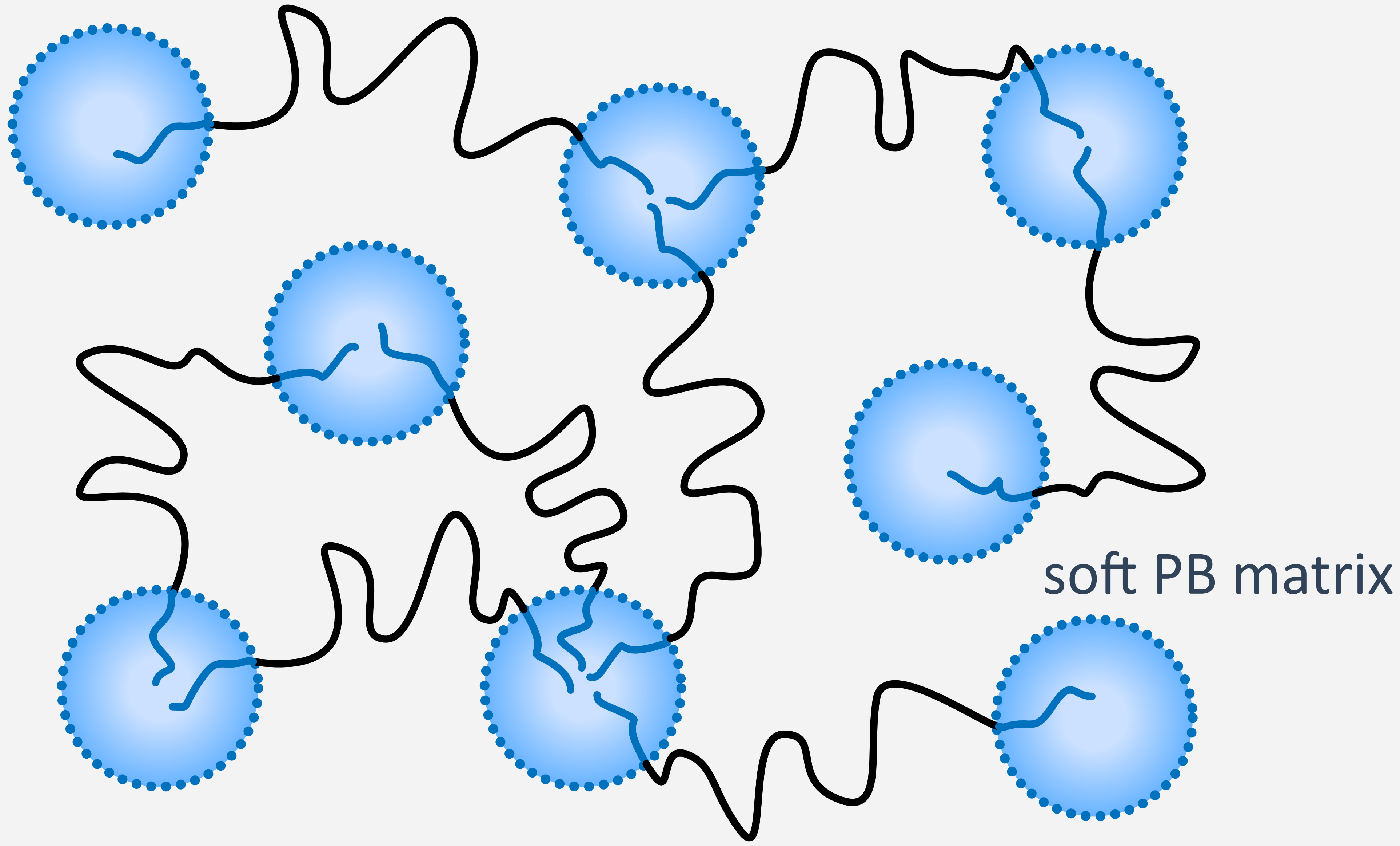
- SBCs (styrene-butadiene block copolymers) are relevant elastomer materials (like some TPUs)



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

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 (see 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

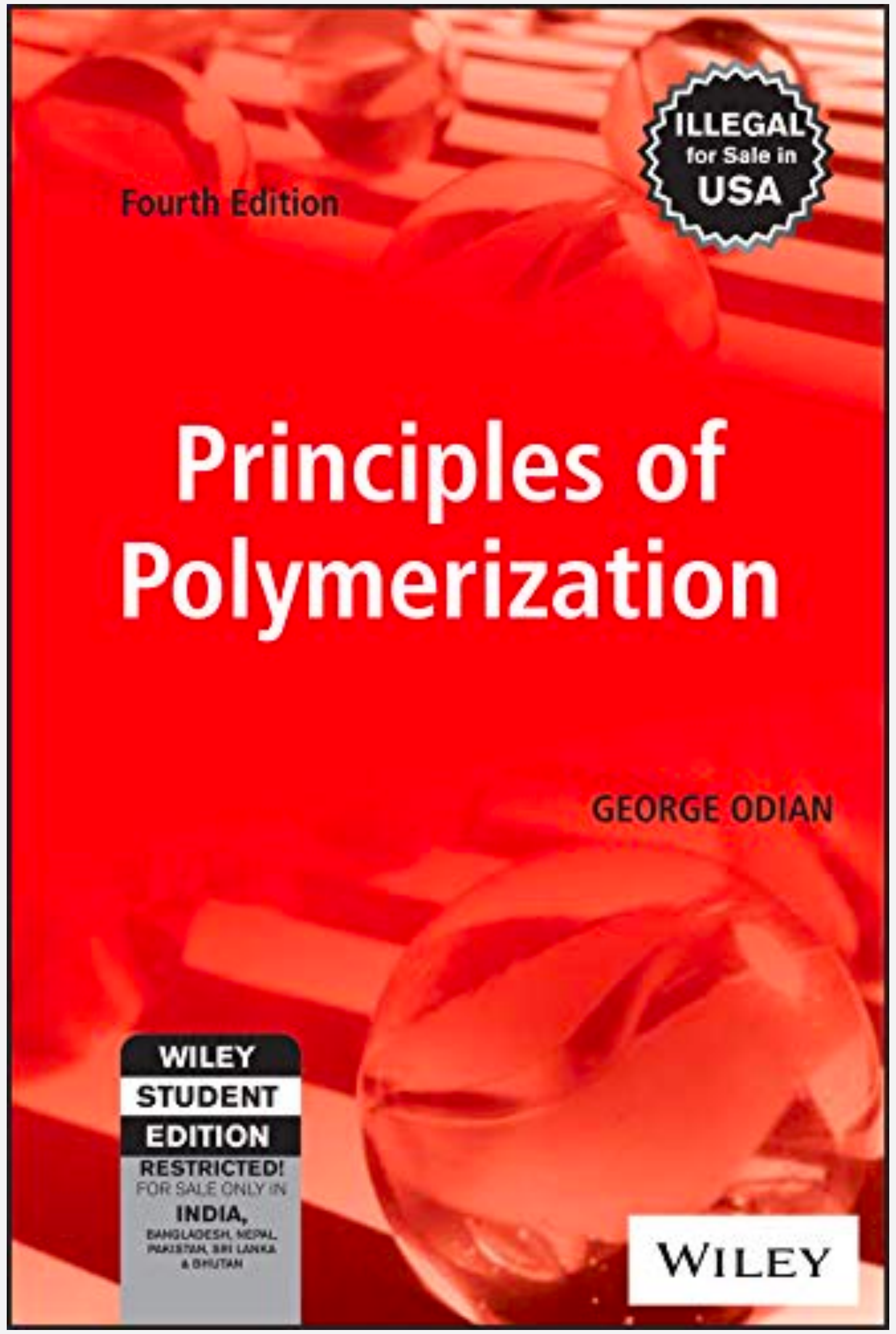
- radical polymerization generates polymers of similar molecular weights up to 10% conversion, above which the molecular weight can either decrease or increase (due to exhaustion of reagents, transfer reactions, gel effect)

- for living polymerization, polymer chains start growing at the same time and are not terminated by stochastic events.

- 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

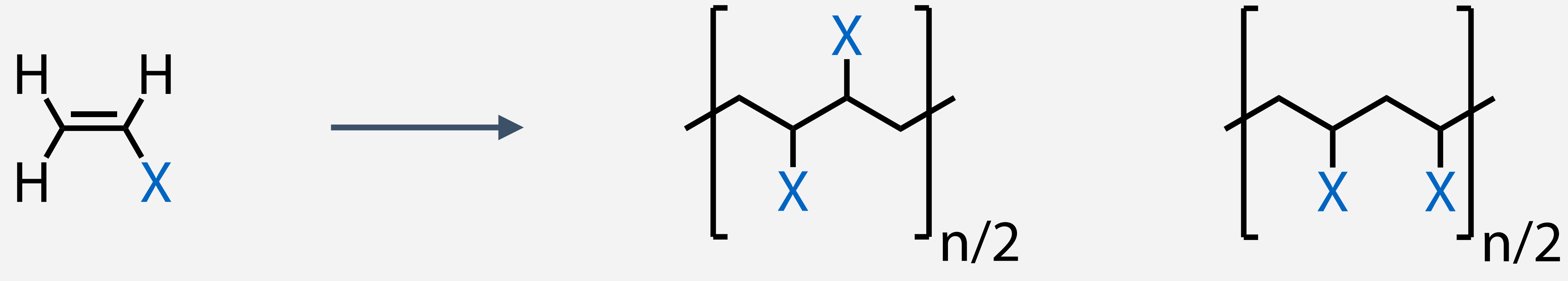


George Odian: *Principles of Polymerization*

1.2.2 Isomerism

Chain Configuration and Isomerism: Sequence Isomerism

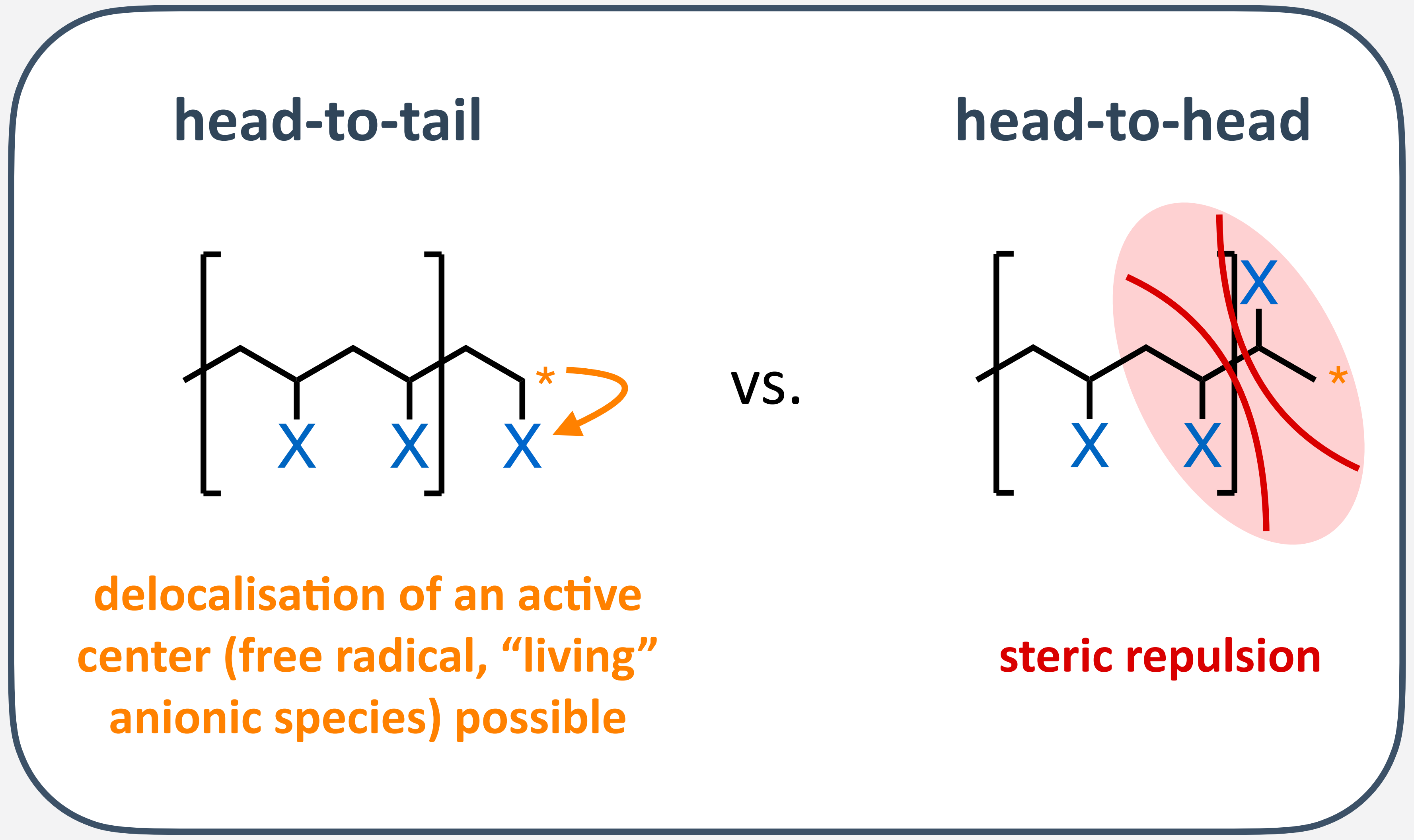
- physical properties of polymeric systems are strongly affected by chain configuration and different forms of isomerism, i.e. the exact 3D arrangement of atoms or groups bound to a central atom
- **built-in properties during polymerisation: no interconversion of isomers possible for a polymer chain**



unsymmetric monomer

head-to-head polymer

head-to-tail polymer (predominant)



head-to-tail

head-to-head

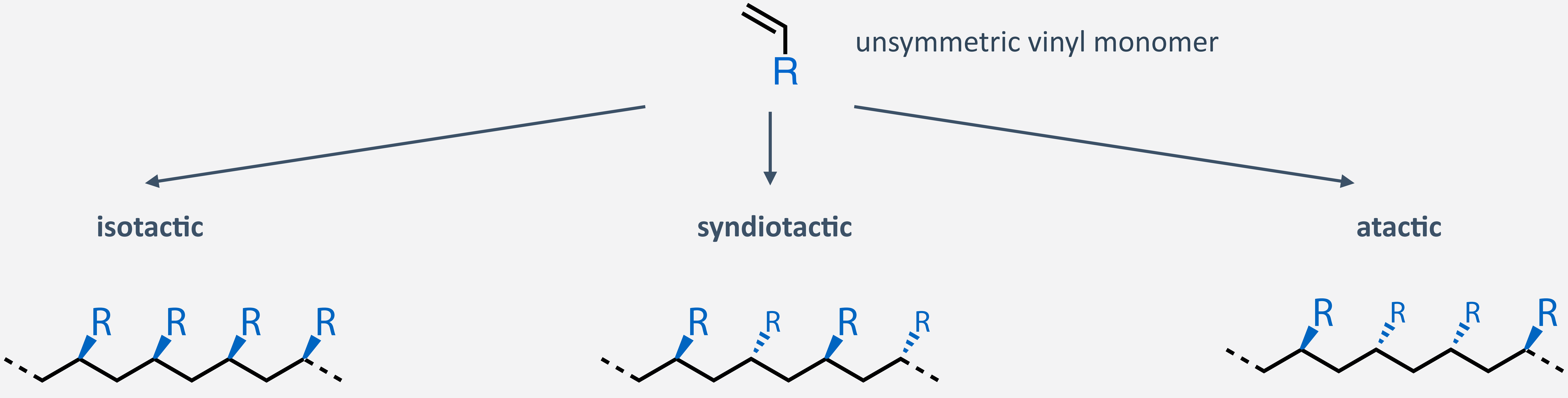
delocalisation of an active center (free radical, “living” anionic species) possible

steric repulsion

- examples: polystyrene, polypropylene, poly(methyl methacrylate), poly(vinyl chloride), …
- **head-to-tail addition is the predominant mode of propagation in chain growth polymerisations**

Stereoisomerism / Tacticity

- tacticity refers to the stereoregularity of the substituted backbone atoms, i.e. to the manner of how the pendant groups (R) are arranged along the polymer chain backbone



unsymmetric vinyl monomer

isotactic

(same side of the chain)

usually semi-crystalline

syndiotactic

(regular alternation)

usually semi-crystalline

atactic

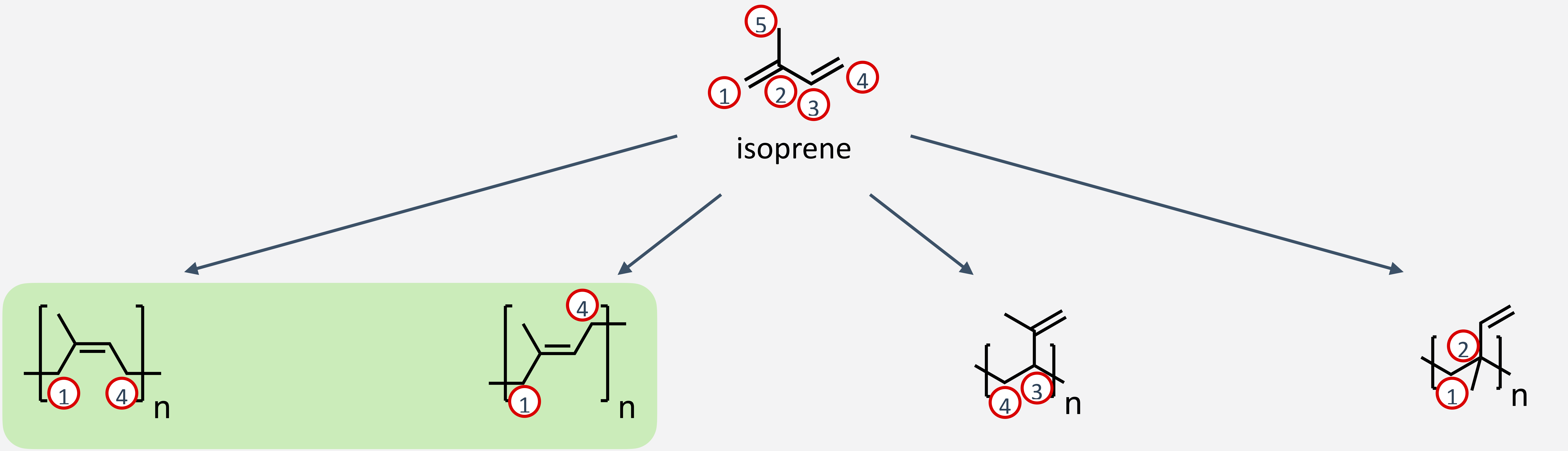
(irregular alternation)

amorphous

- **tacticity has huge impact on the physical properties of polymer materials** (see crystallization, Chapter 3.3)

Constitutional (Structural) Isomerism in Polyisoprene

- polyisoprene (PI) is obtained in different forms depending on the polymerisation conditions



***cis*-1,4-PI**	***trans*-1,4-PI**	**3,4-PI**	**1,2-PI**
soft, highly elastic (when vulcanised) used in tires	hard, semi-crystalline thermoplastic	of no practical importance	

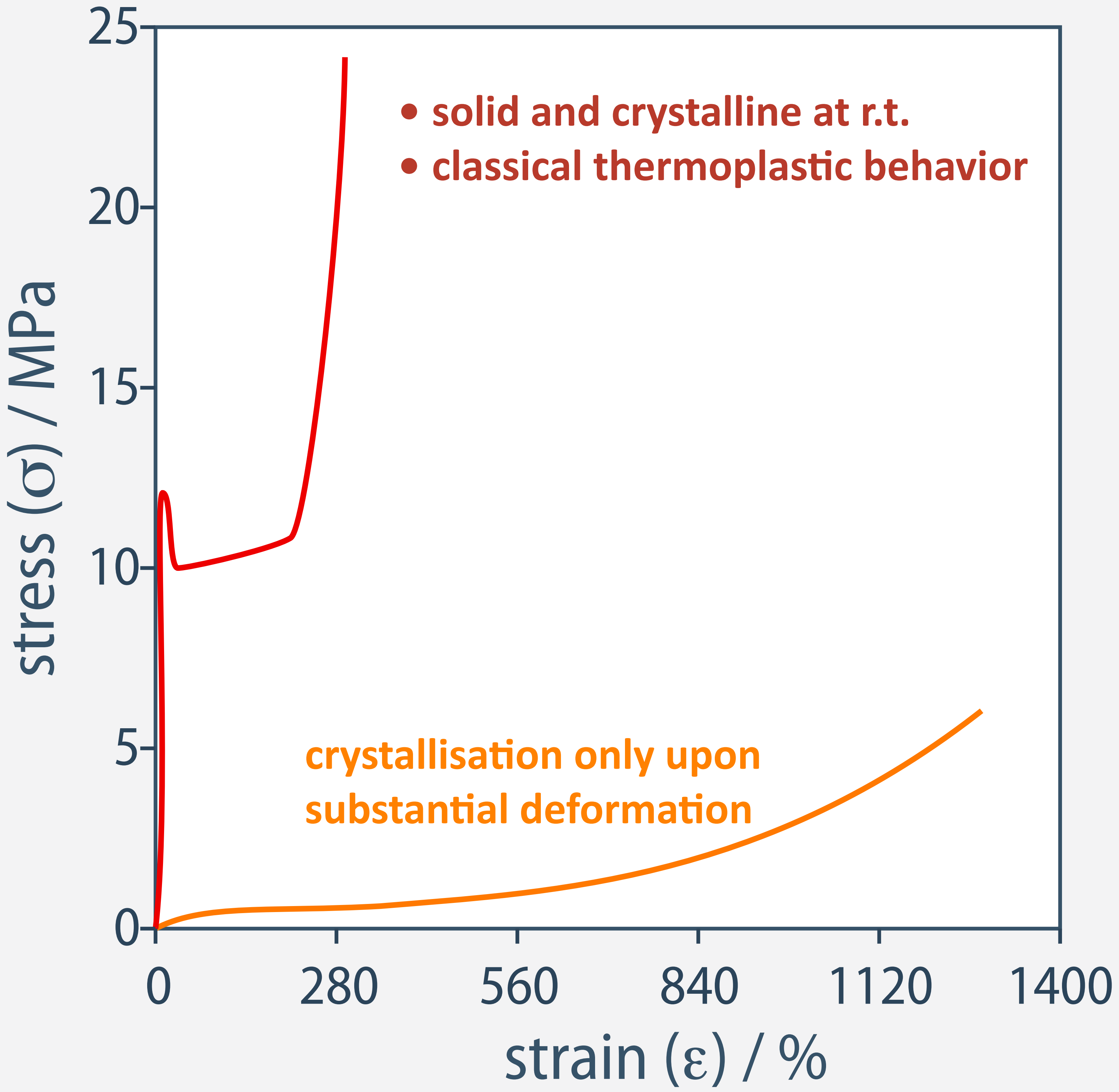
- **only *cis*-1,4-polyisoprene is produced at large scale with major application in tires**

Influence of Constitutional Isomerism on Materials Properties

cis-1,4-polyisoprene
(natural rubber)

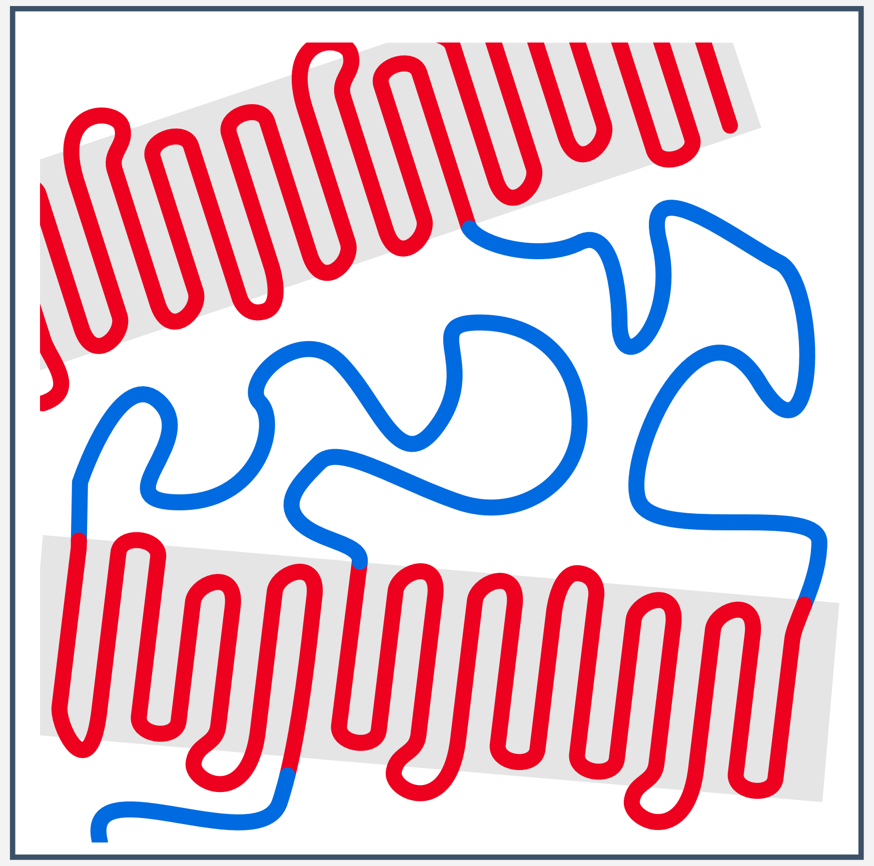
trans-1,4-polyisoprene

elastomers



- solid and crystalline at r.t.
- classical thermoplastic behavior

crystallisation only upon substantial deformation

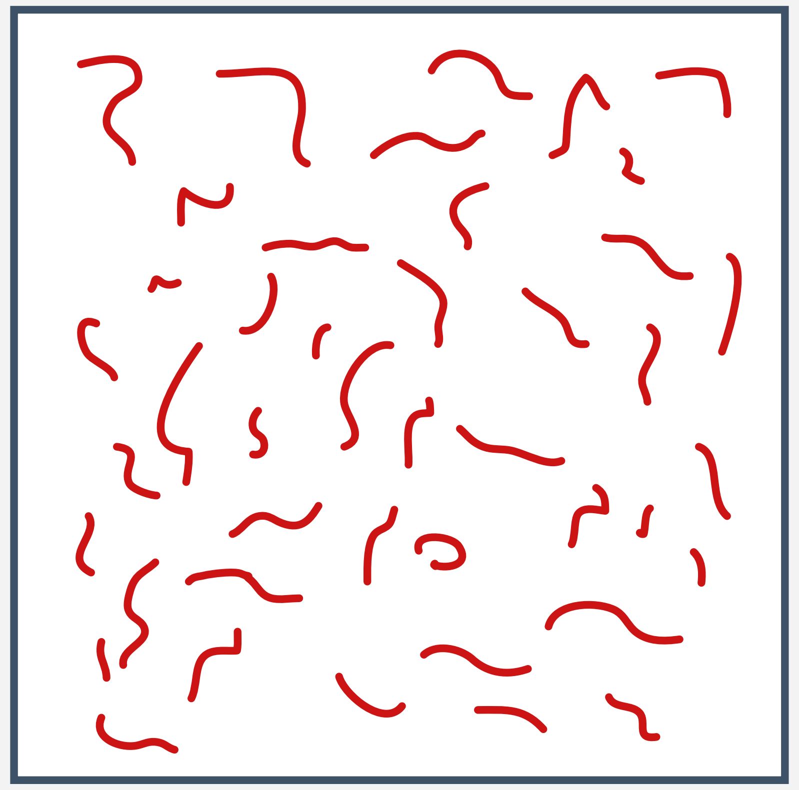


semi-crystalline

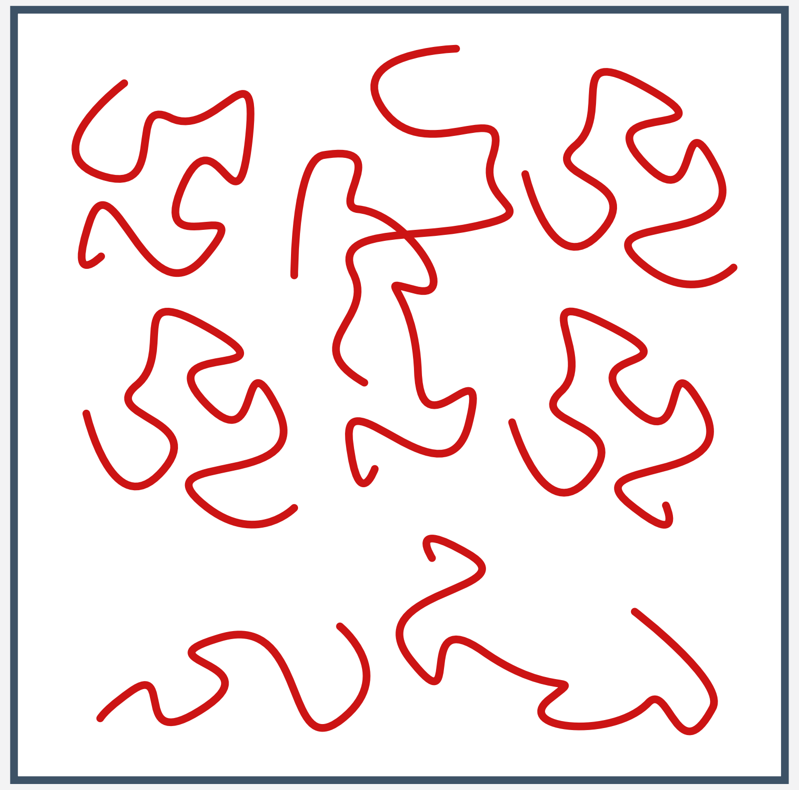
- two naturally occurring polyisoprenes, but two very different materials!

1.2.3 Structure and Properties

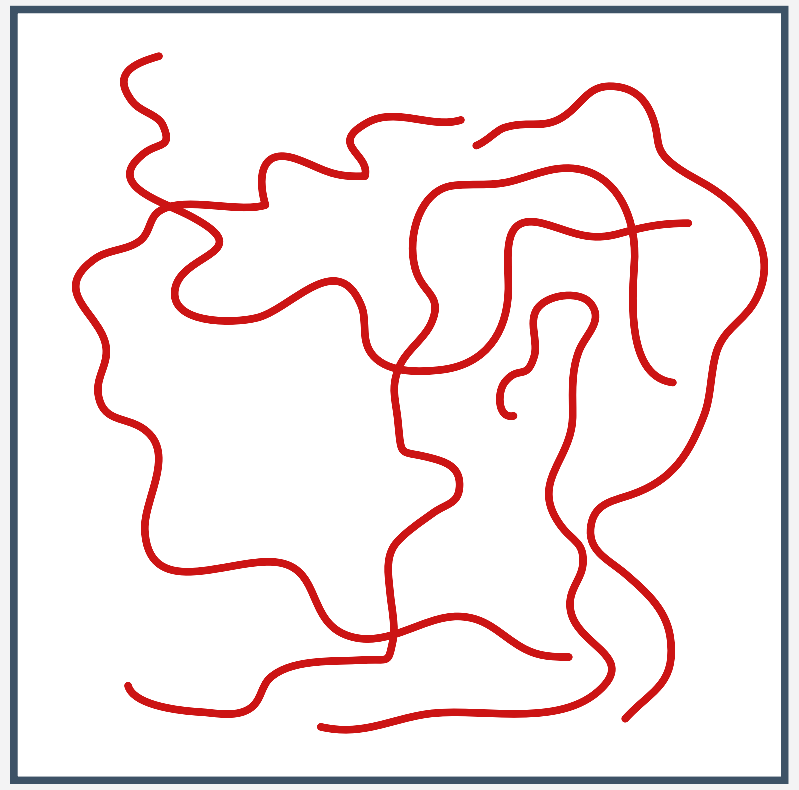
Influence of Chain Length on Physical Properties



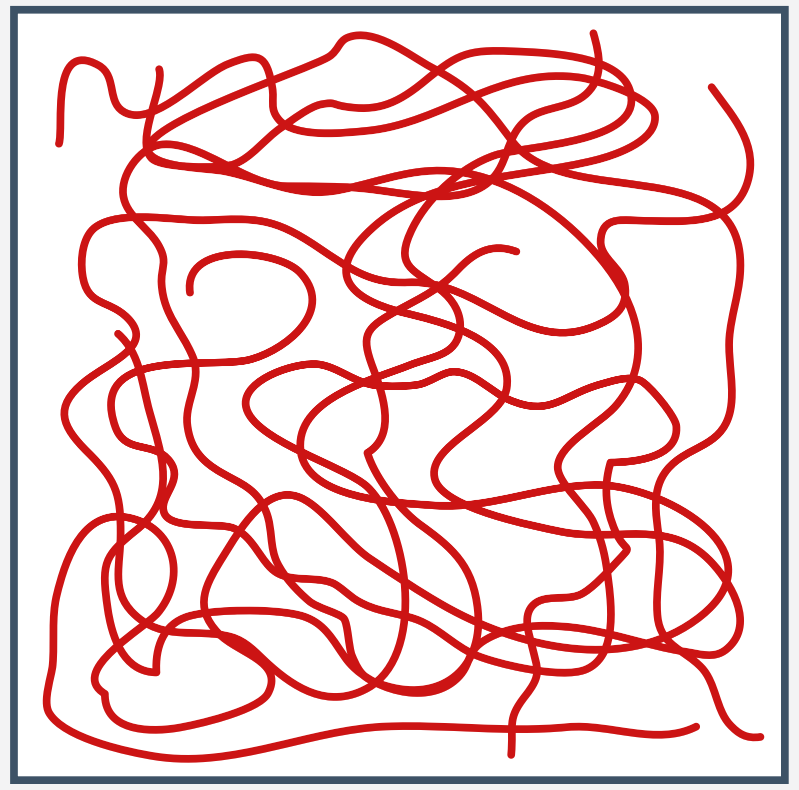
liquid



oil



wax



solid

number of C atoms	aggregation state (25 °C)	example	usecase
1-4	gas	propane	gaseous fuel
5-15	low-viscosity liquid	gasoline	liquid fuel
16-25	high-viscosity liquid	motor oil	oils and greases
20-50	soft solid	paraffin wax	candles and coatings
> 1000	tough plastic material	polyethylene	bottles and toys

- **increasing cohesive energy and entanglement give rise to “typical” polymer properties (Chapters 3 & 4)**

Polymer Chain Entanglement

Video by Sophia Thiele

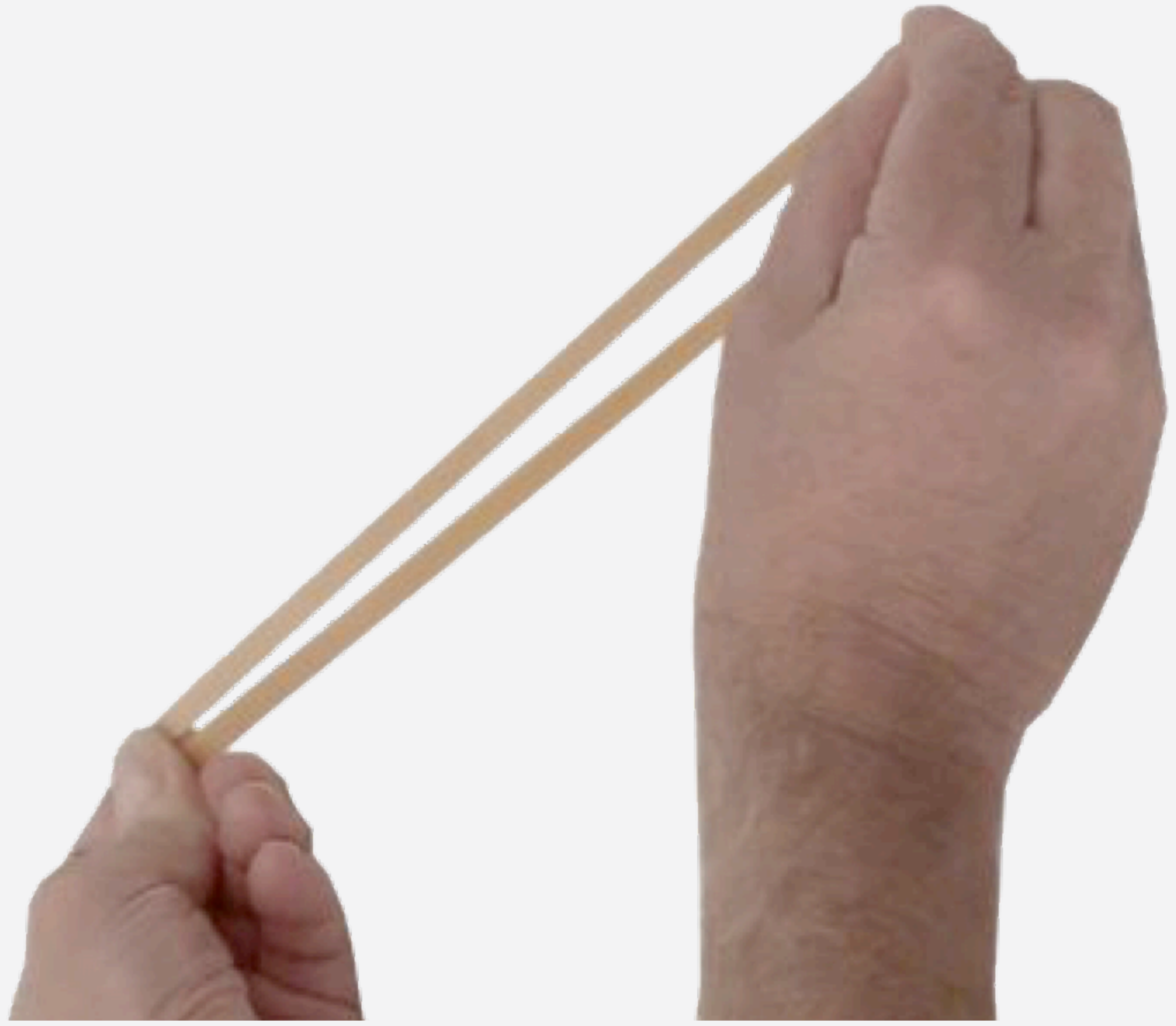
Unique Mechanical Properties

- polymers show unique mechanical properties not shown by other materials classes (see **Chapter 4**)

rubber elasticity

viscoelasticity

plasticity



large elastic deformation
specific to elastomers

viscoelastic in the melt state
important for processing

ductile behaviour, plastic deformation
important for processing

- **strength, toughness, impact resistance, ductility, melt elasticity increase with molecular weight**

Important Consequences of High Molar Mass

1. Physicochemical Properties

- absence of a precise relation between T_m and M (Chapter 3.3)
- absence of a gaseous phase (Chapter 3.1)
- dominant chain entropy impacting both thermodynamics and mechanics (Chapter 4.1)

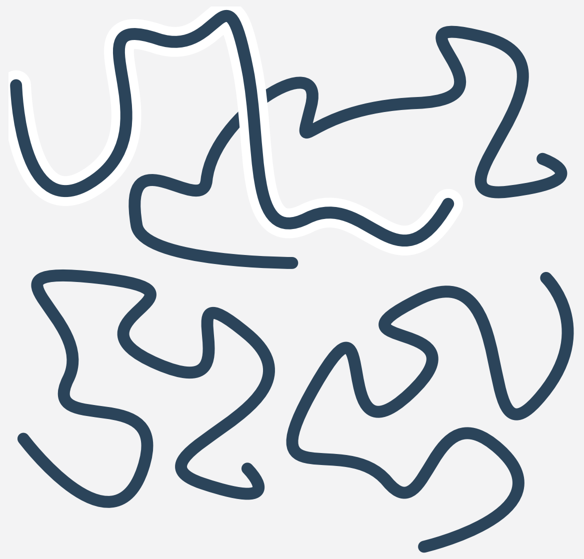
2. Processing

- high viscosity (in solution and in the molten state) (Chapter 4.2)
- energy storage capacity in the molten state (viscoelasticity) (Chapter 4.2)
- capability of film and fiber formation from the molten state (viscoelasticity) (Chapter 6)

3. Viscoelastic and Mechanical Properties

- spectrum of relaxation times (Chapter 4.2)
- vitrification (Chapter 3.2)
- elongation at break and high strength (Chapter 4.3)

Thermal Transitions of Polymers



polymer melt (**Chapter 4**)

- liquid or rubbery

glass transition

vitrification ↔ softening

- exact nature not known
- onset of segmental motion
- change in heat capacity

(**Chapter 3.2**)

$\rightleftarrows T_g$

$\upharpoonleft\downharpoonright T_g, T_m$

$\rightleftarrows T_m$

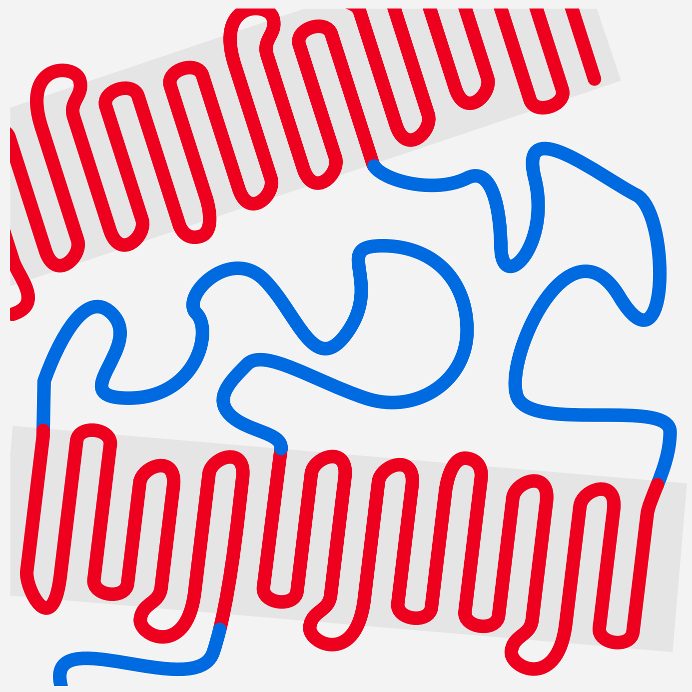
melting temperature

crystallization ↔ melting

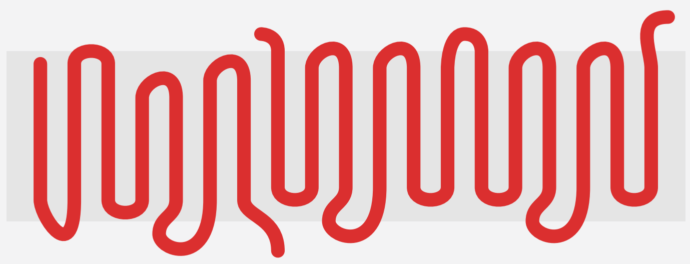
- first order thermodynamic transition
- slow formation of ordered domains
- exothermic

(**Chapter 3.3**)

amorphous, glassy



semi-crystalline

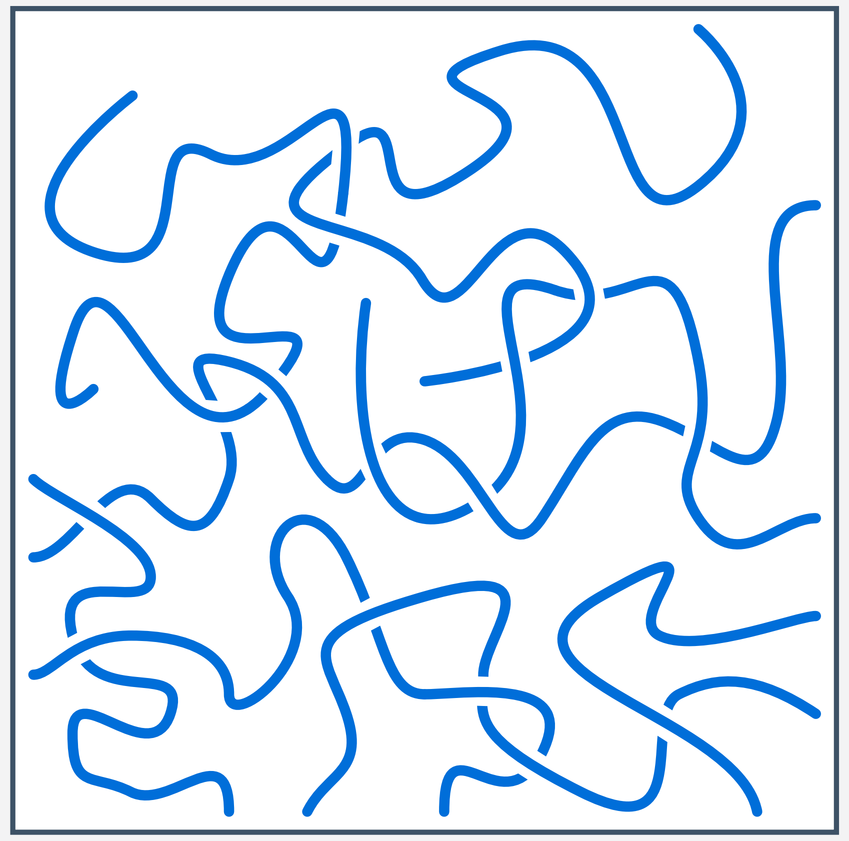


monocrystalline

- **T_m and T_g are important intrinsic materials parameters; crystallization strongly dependent on kinetics**
- **high molar mass, dispersity, and polymer chain architecture affect the solidification of polymers**

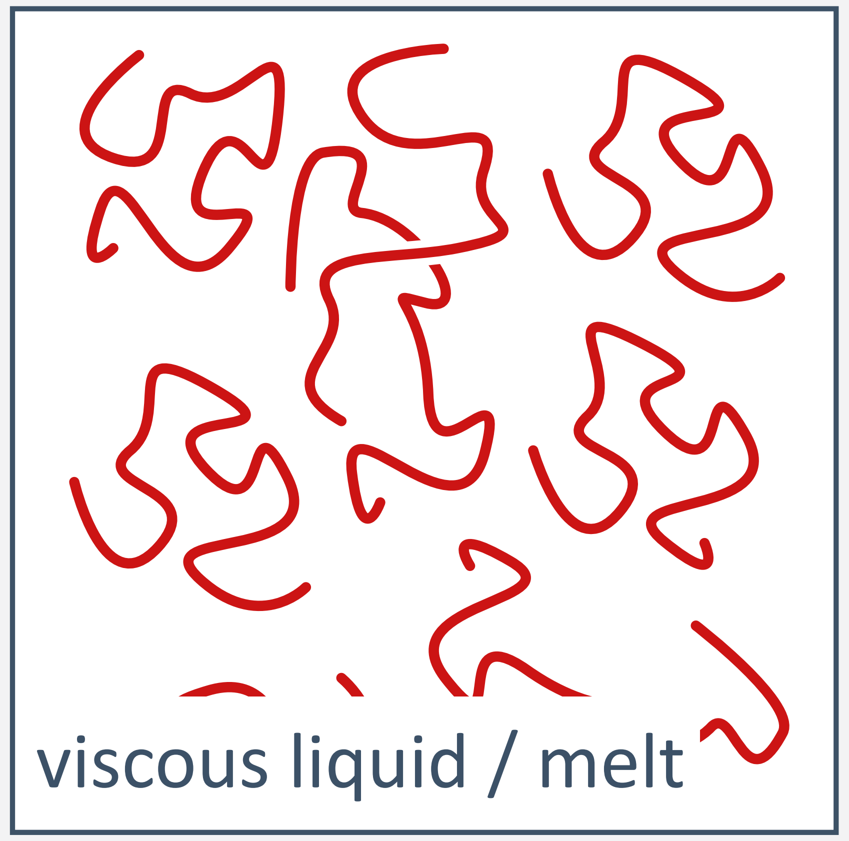
Classification of Polymers According to Structure

Thermoplastics

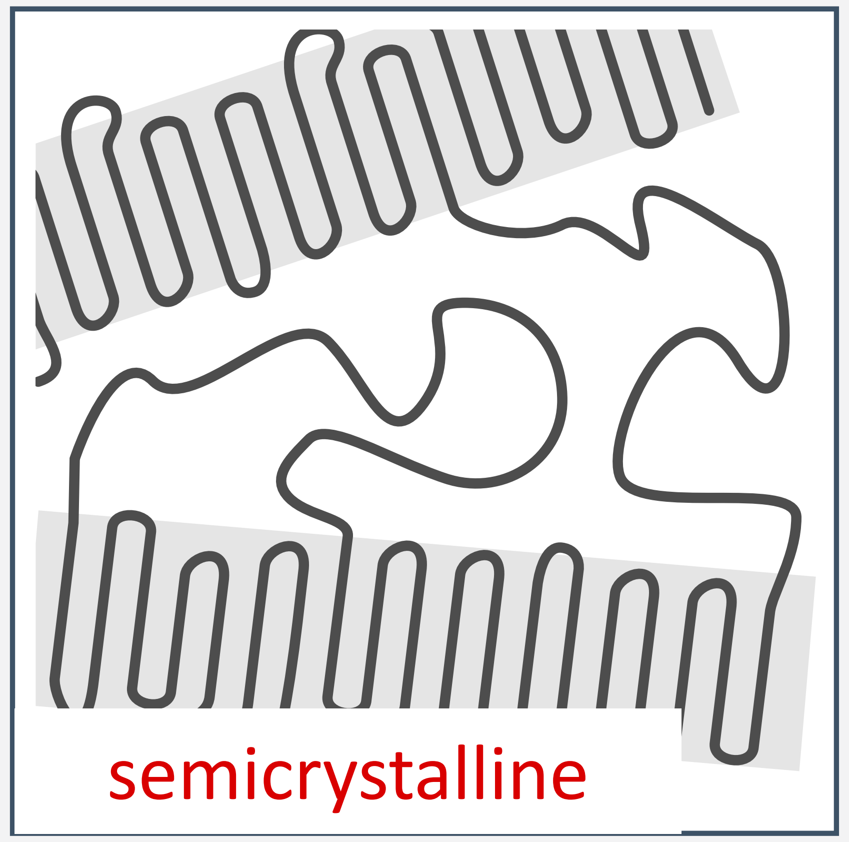


polystyrene
T_g = 100 °C

$\xrightleftharpoons{T_g, T_m}$



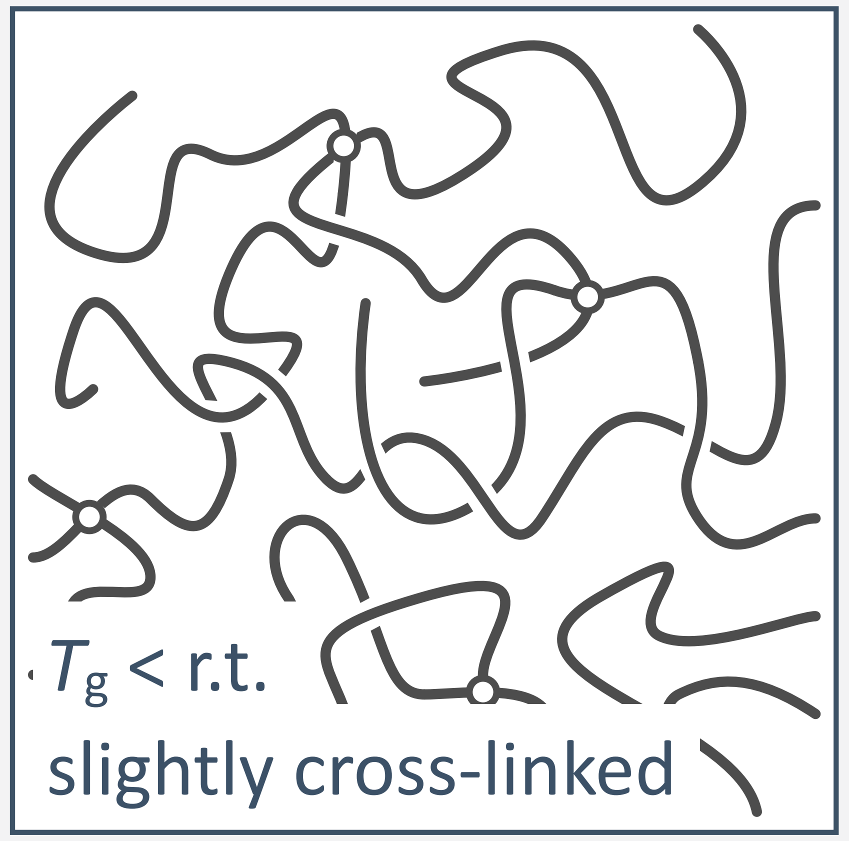
silicones
T_g = –123 °C
T_m = –40 °C



polyethylene
T_g = –50 °C
T_m = 140 °C

liquid, processable, recyclable at high temperatures

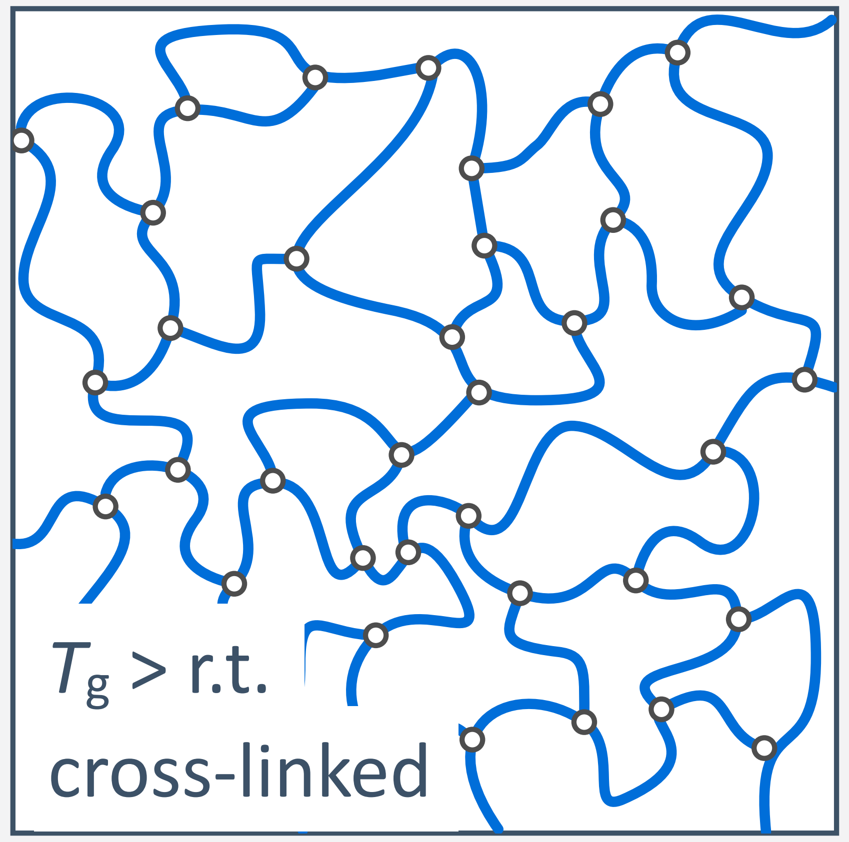
Elastomers



polyisoprene
T_g = –73 °C

rubber elasticity

Thermosets

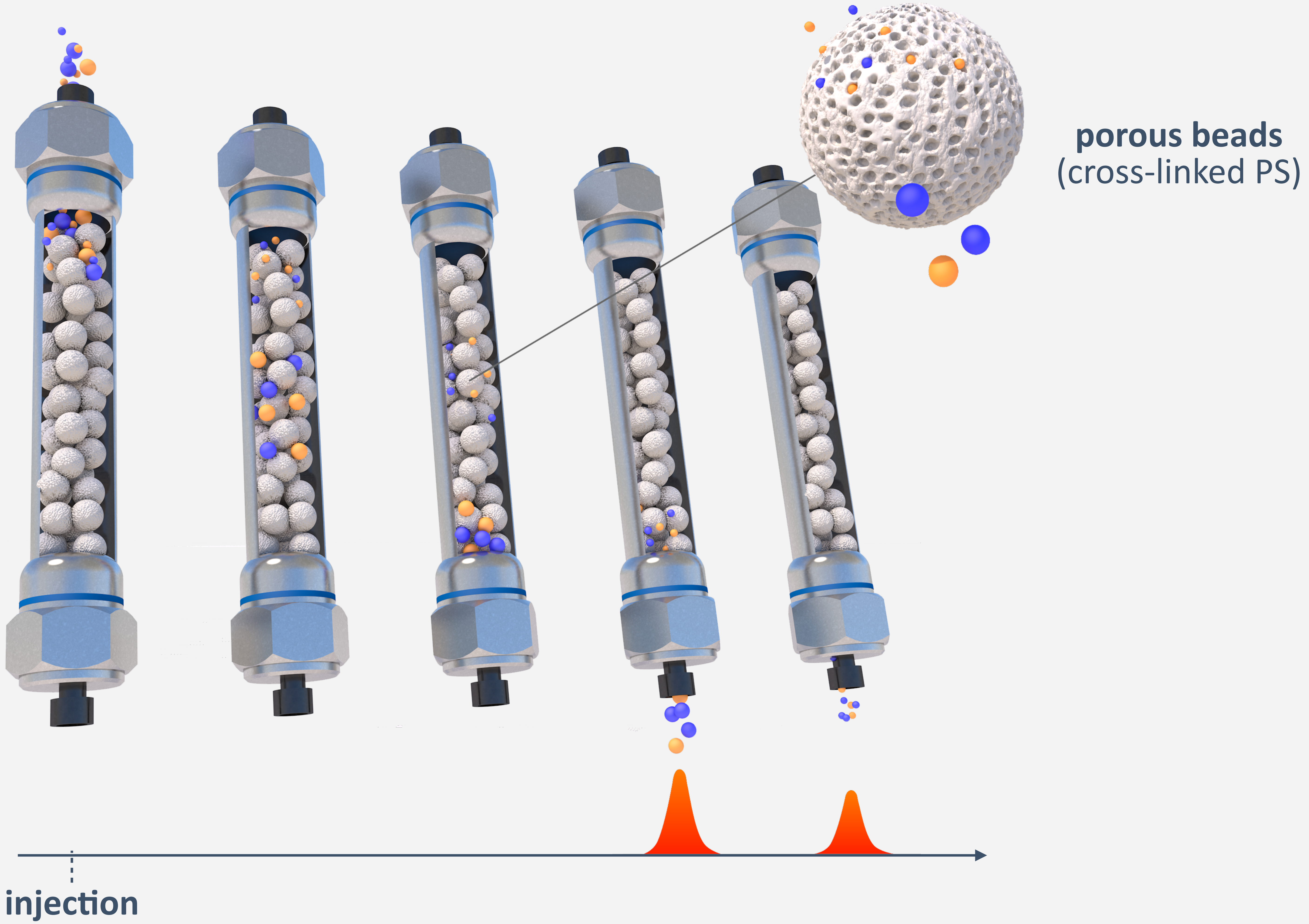


epoxy resin

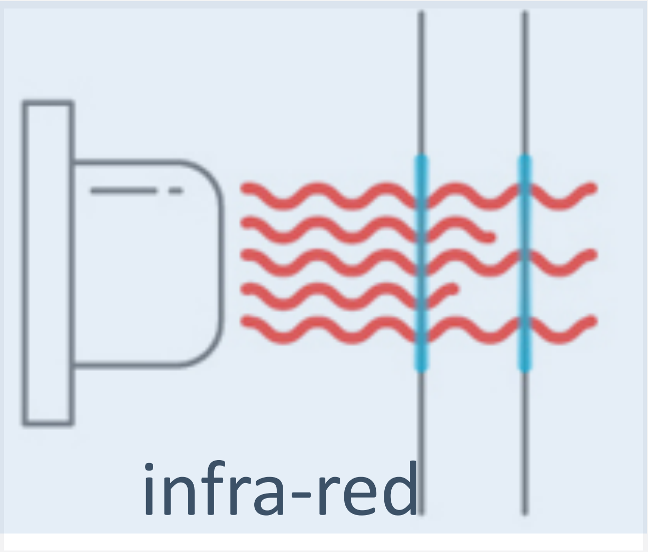
rigid, intractable

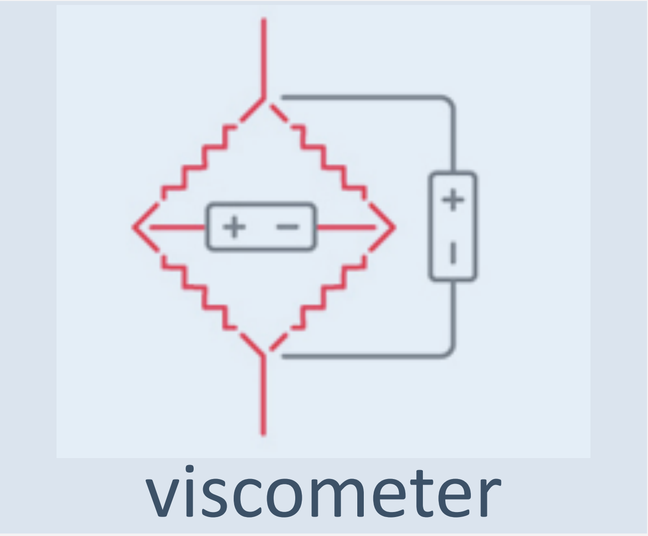
1.2.4 Characterization

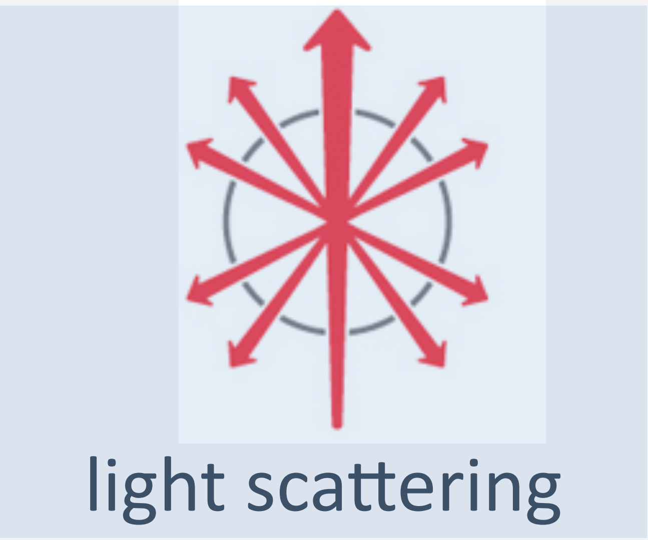
Gel Permeation/Size Exclusion Chromatography (GPC)



detection

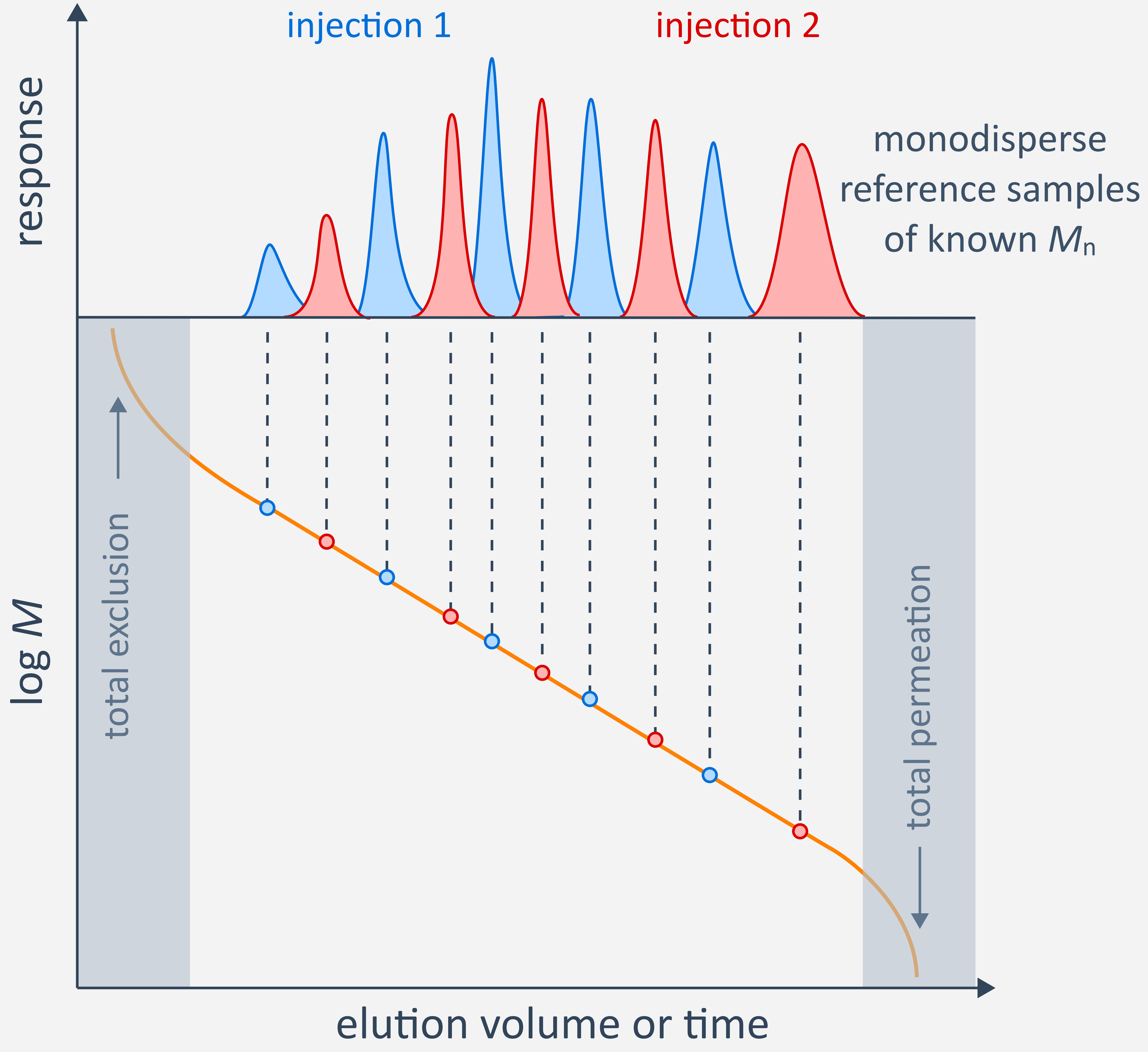


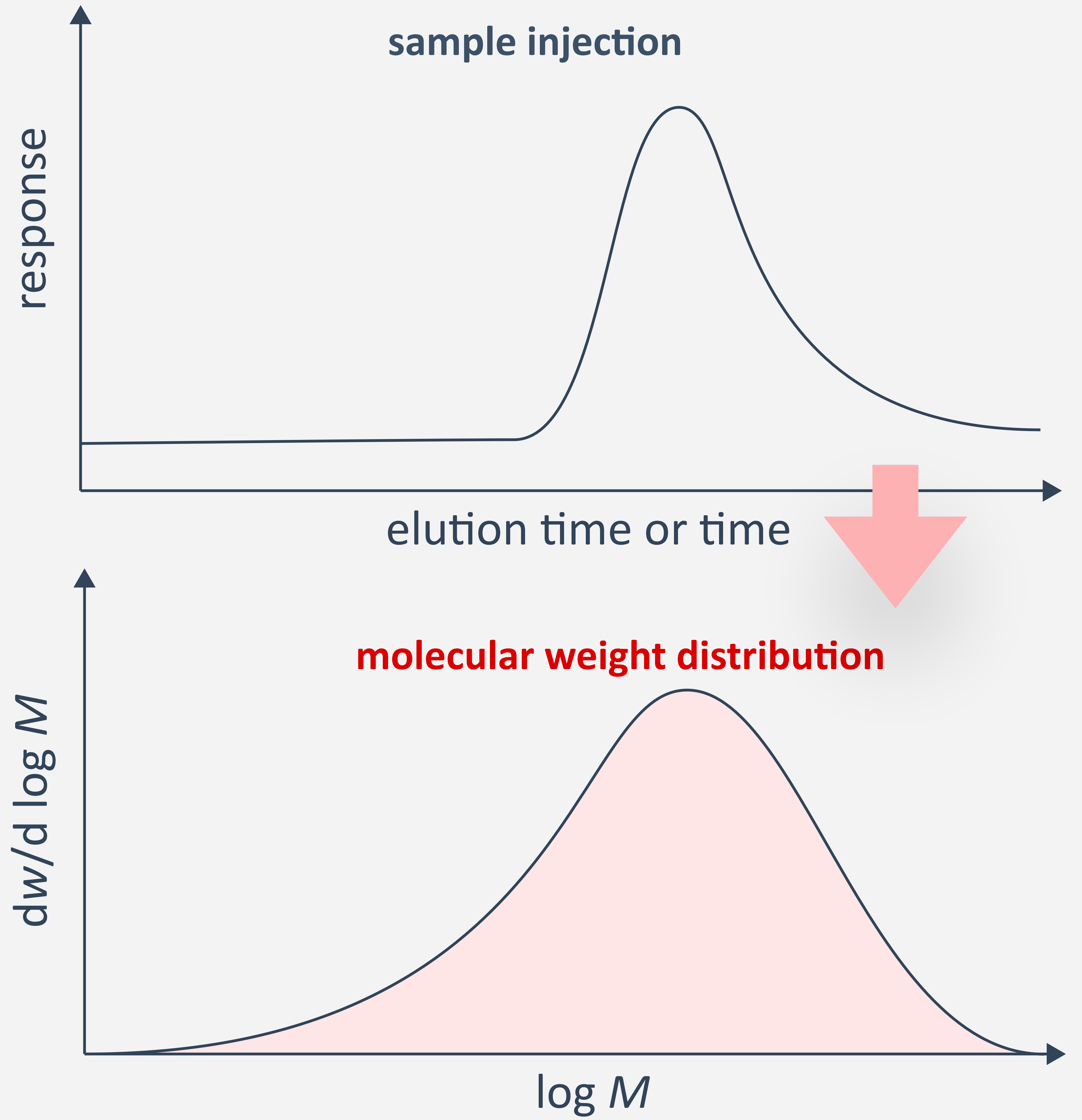




- **separation by polymer size and permeation time (see Chapter 2.1): radius of gyration $R_g \propto M_n^{1/2}$ vs. R_{pore}**

GPC Calibration





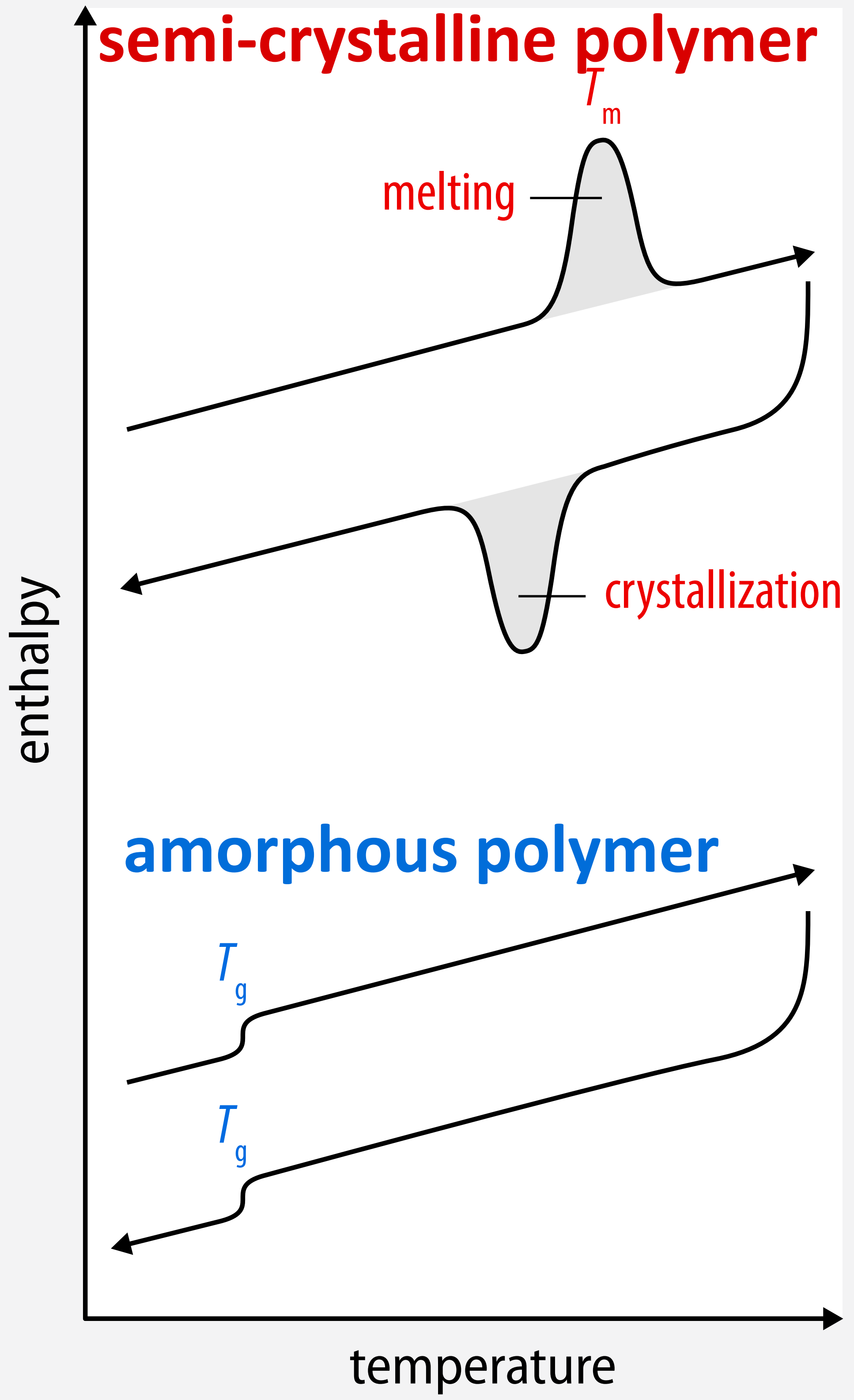
- **determination of molecular weight distribution and average molecular weights using standard samples**

Thermal Transitions of Polymers

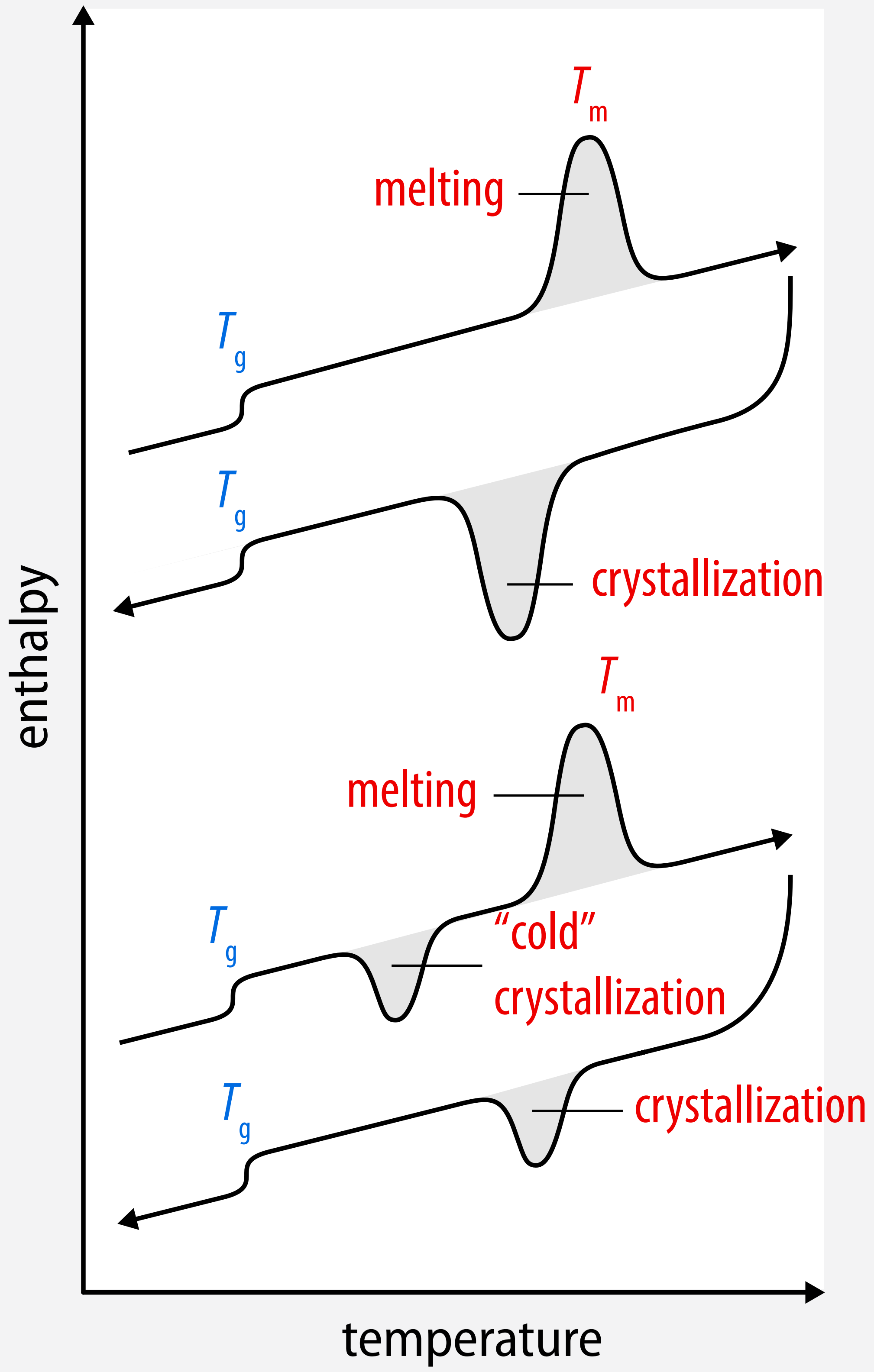
- analysis of thermal transitions with Differential Scanning Calorimetry (DSC)

cifferential scanning calorimeter

melting and glass transition



processing dependence



sufficiently slow cooling

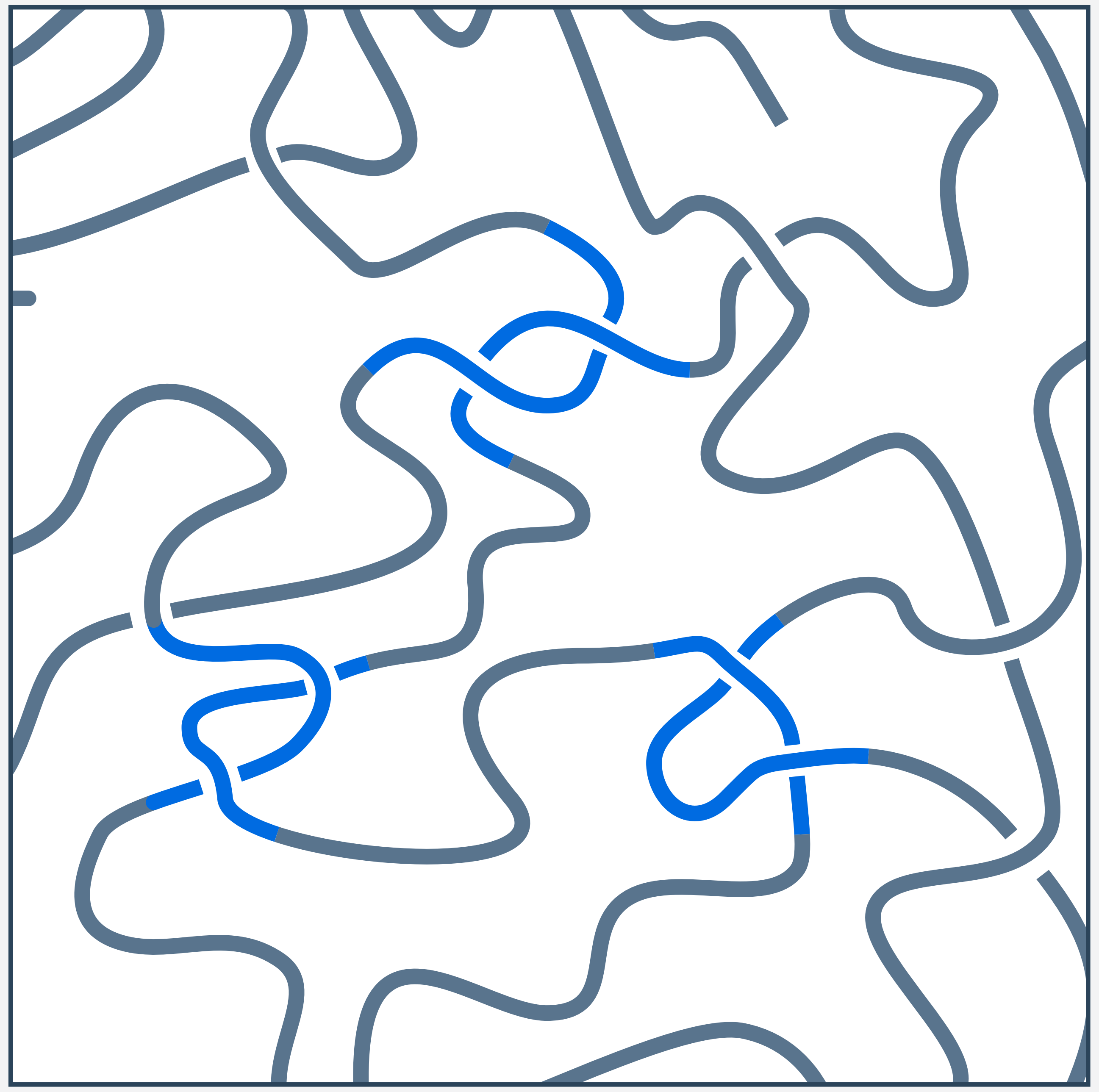
too fast cooling
(potential incomplete crystallisation)

- **both T_m and T_g are important parameters that characterise a given polymer**

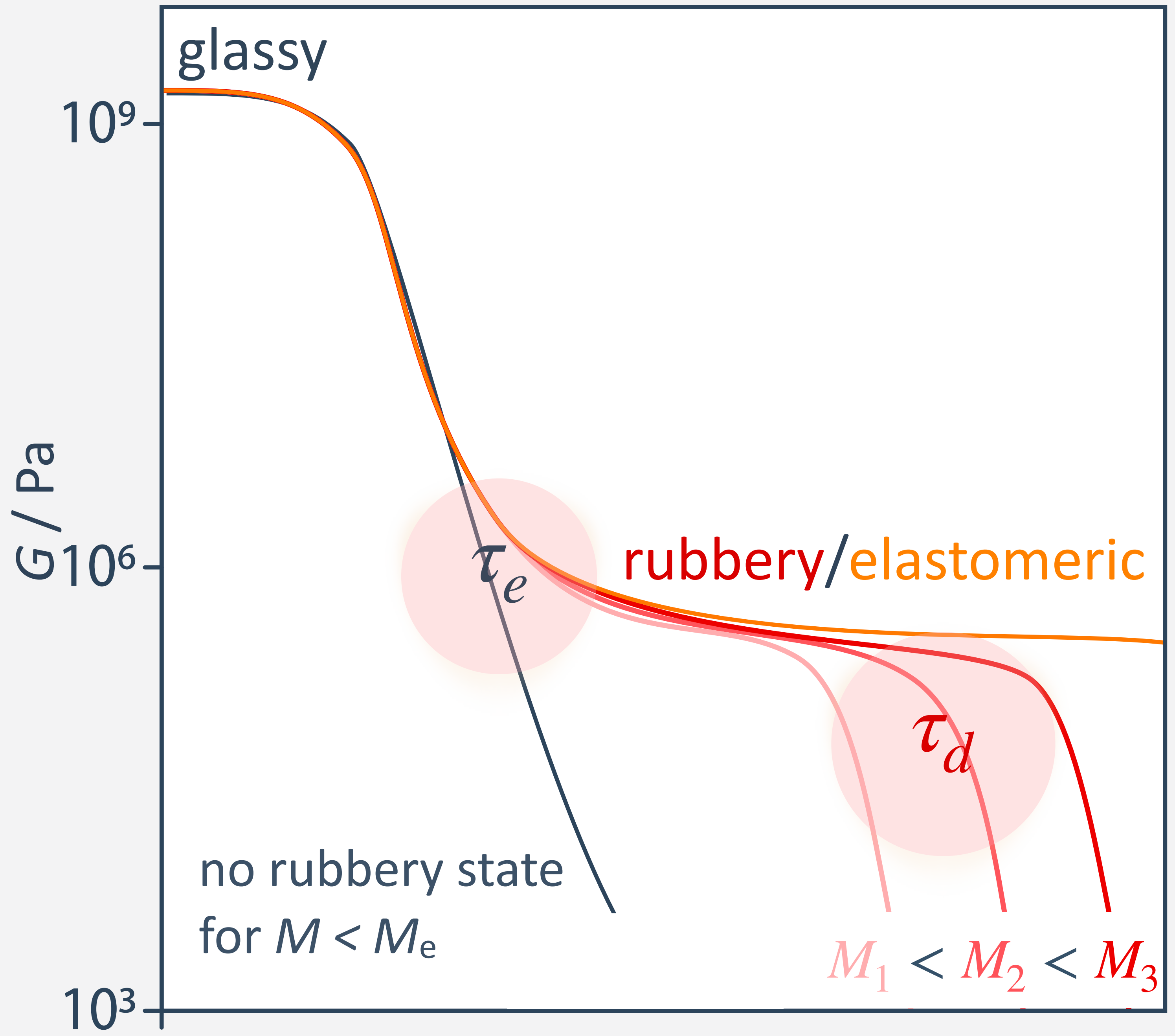
Entanglement and Viscoelasticity

- above entanglement molar mass, M_e, polymer chains cannot pass by one another by simple translational motion but have to “reptate” around other chains

static scheme of entanglements



rubbery state above T_g

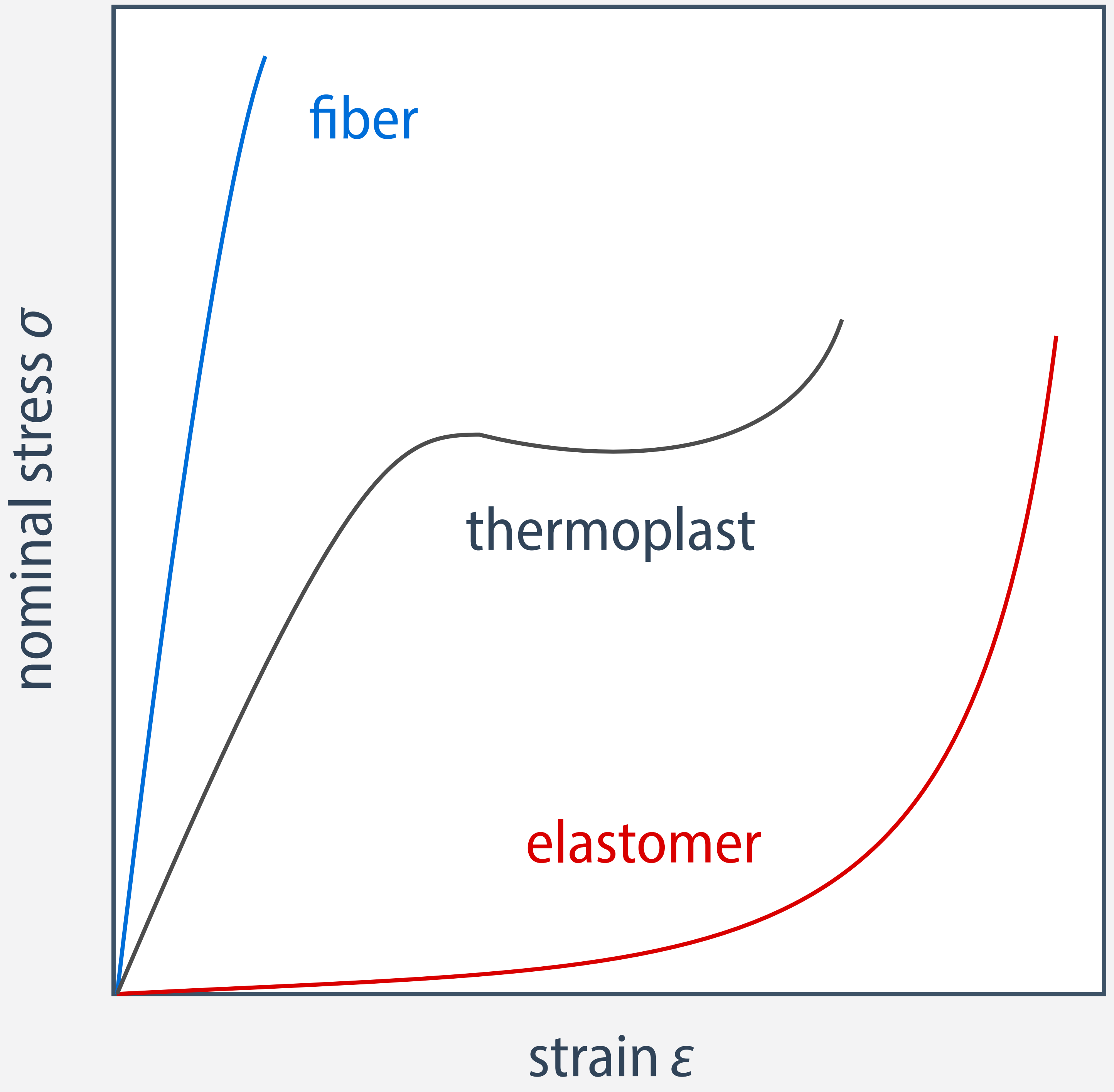


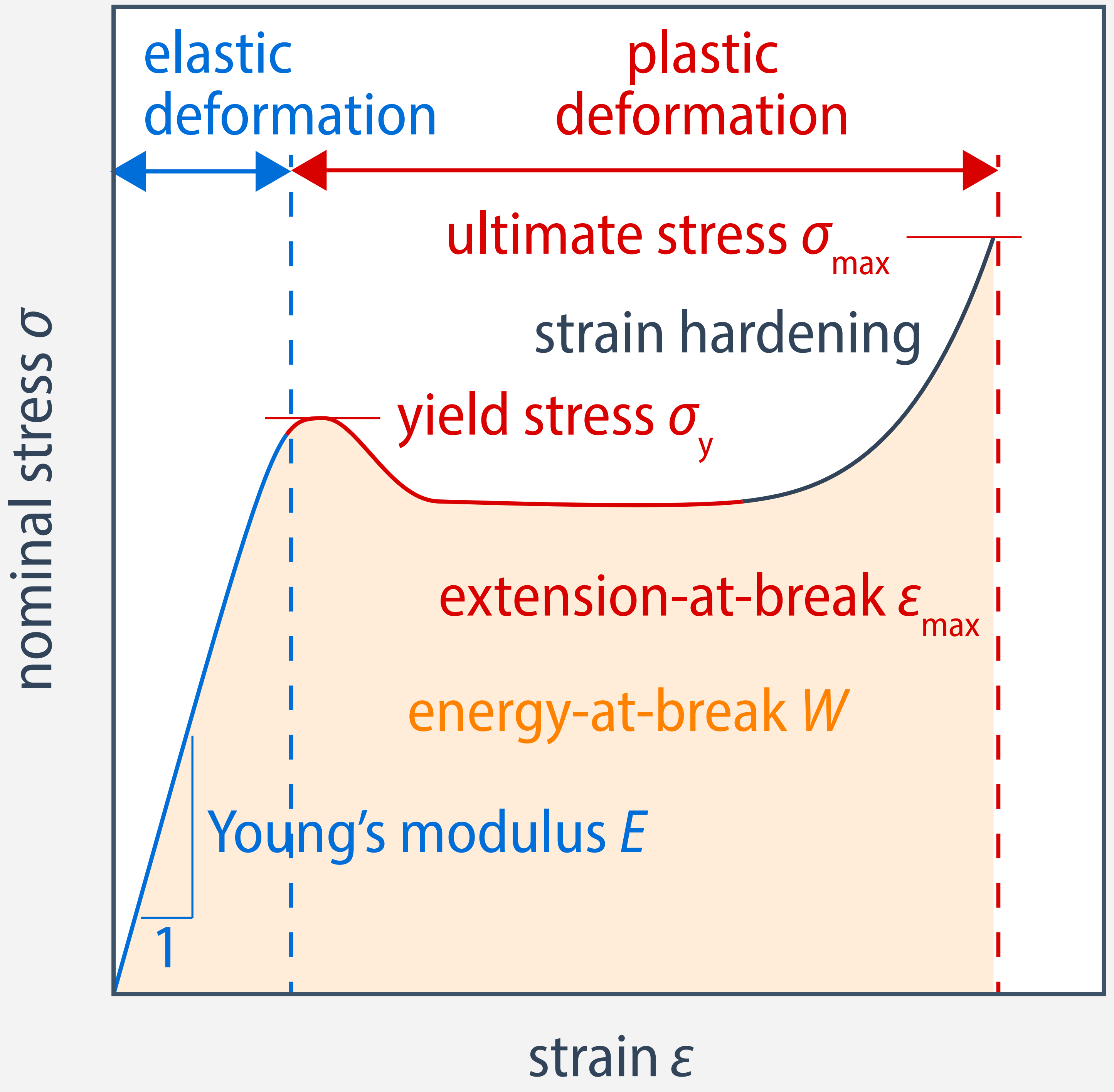
temperature (or time)

dynamic shear rheology

- **entanglement network is at the origin of the rubbery state formed by amorphous polymers**
- **viscoelasticity: rubbery state is frequency-dependent (polymer can flow on long time scales)**

Determination of Mechanical Properties of Polymers by Tensile Testing





- **Young's modulus *E*** (slope in the elastic deformation region) is a measure for **stiffness**
- **yield strength σ_y** is stress at the end of the elastic deformation region
- **ultimate strength σ_{max}** is absolutely highest stress (typically before rupture)
- **energy-at-break *W*** (area under stress-strain curve) is a rough measure for **toughness**

Summary

- **History and Fundamentals:**
  - 1920s: polymers recognized as macromolecules consisting of covalently bonded repeat units
  - 1938: first commercial synthetic polymer (Nylon 6,6)
- **Molecular Characteristics:**
  - polymers are characterised by a **molar mass distribution**, and not by a defined molar mass.
  - main synthesis mechanisms: **step-growth**, **chain-growth**, **living/controlled polymerisation**
  - chemical structure defined by **composition, configuration (isomers), architecture, copolymer types**
- **Thermal and Mechanical Behavior:**
  - notion of **glass transition temperature** and **melting temperature**
  - **chain entanglement** determining the unique mechanical properties of polymers
  - classes: **thermoplastics**, **elastomers**, and **thermosets**
- **Characterization:**
  - gel permeation chromatography (GPC), differential scanning calorimetry (DSC), rheology, tensile testing