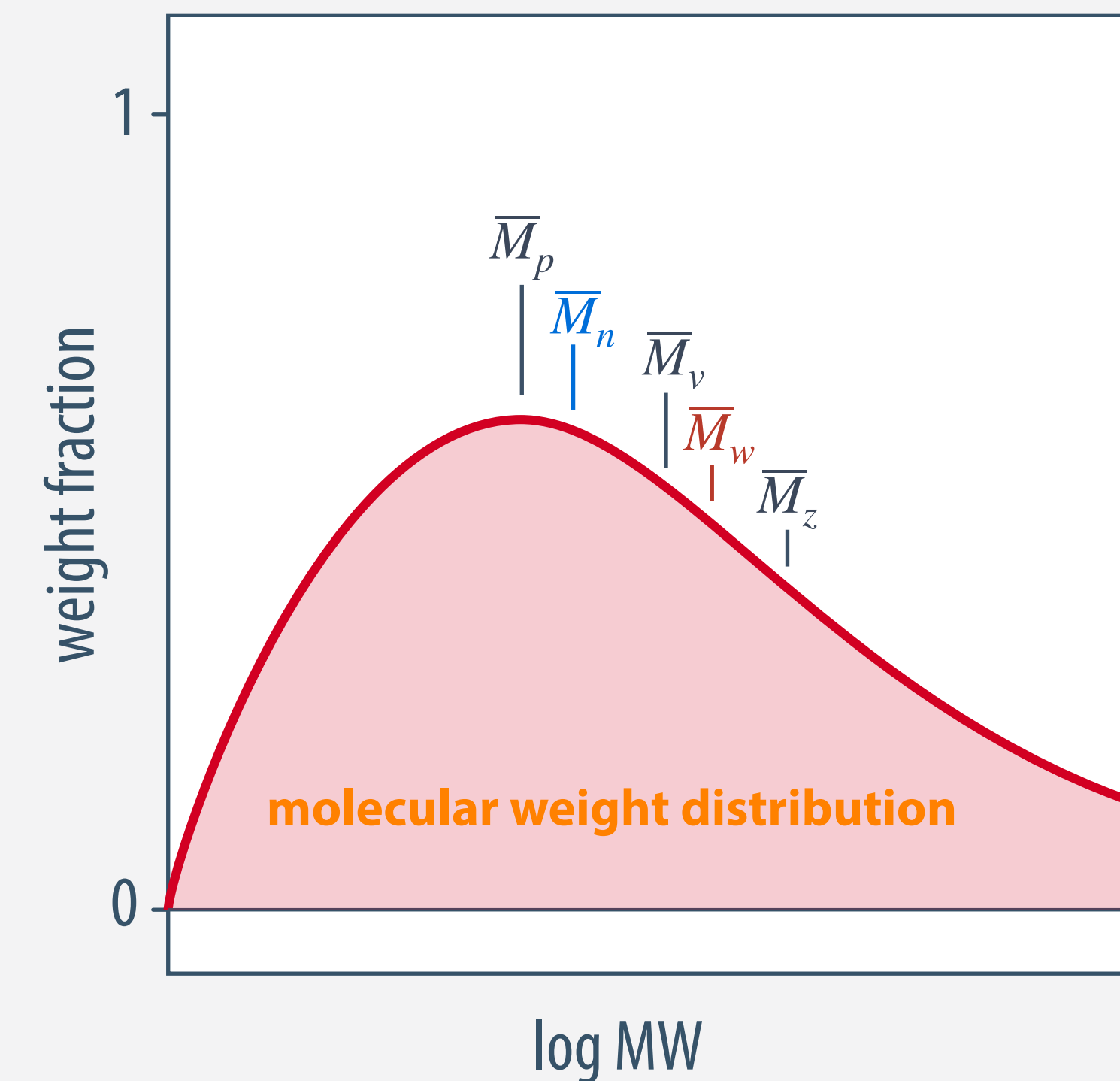
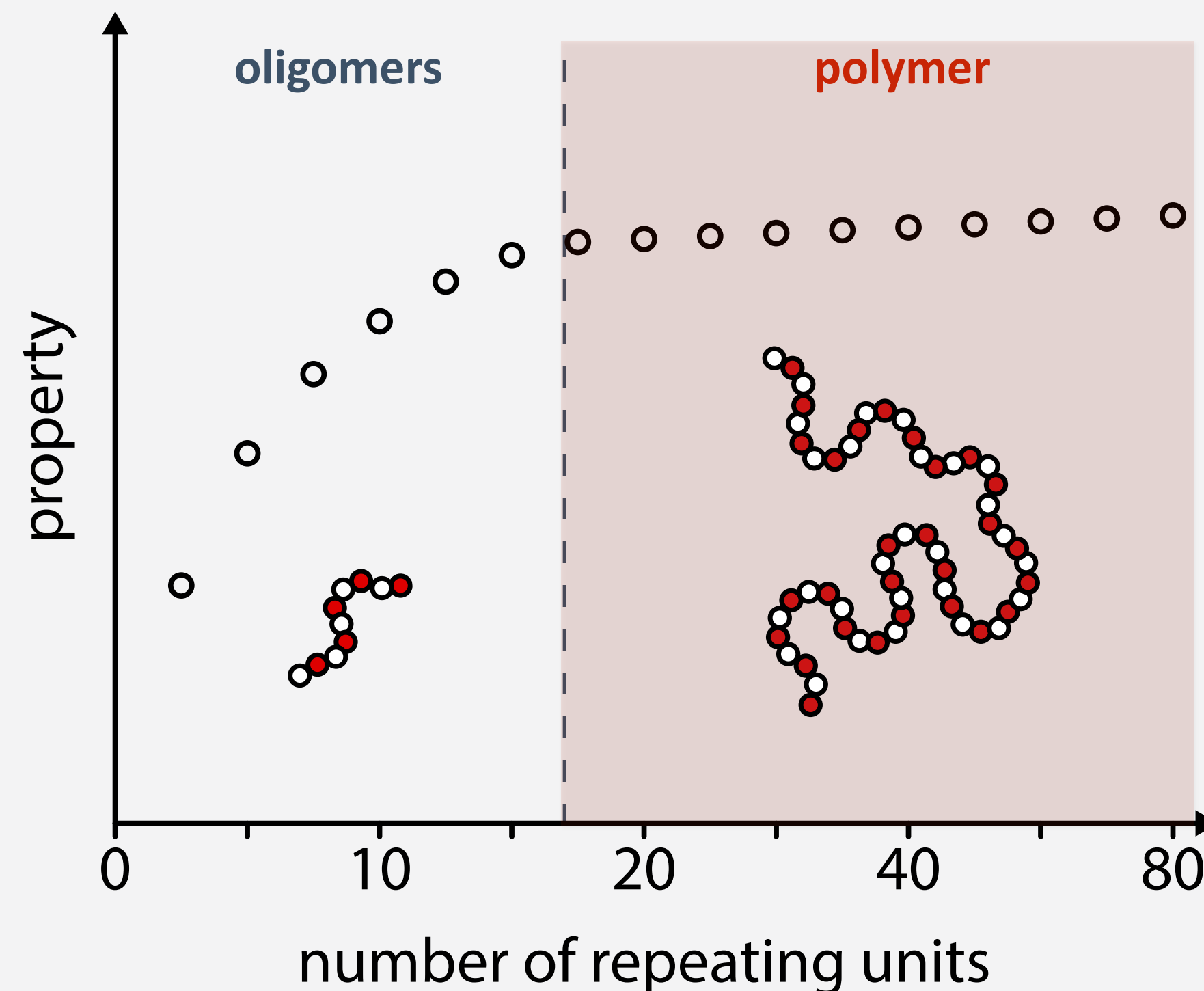


1.2

Definition and Basic Properties

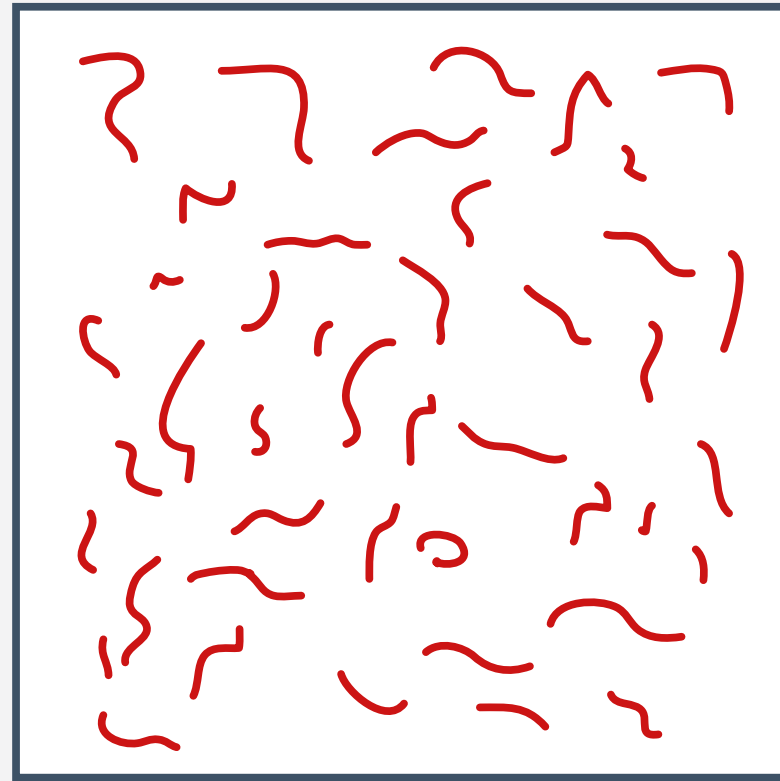
Definition of a Polymer

- 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”

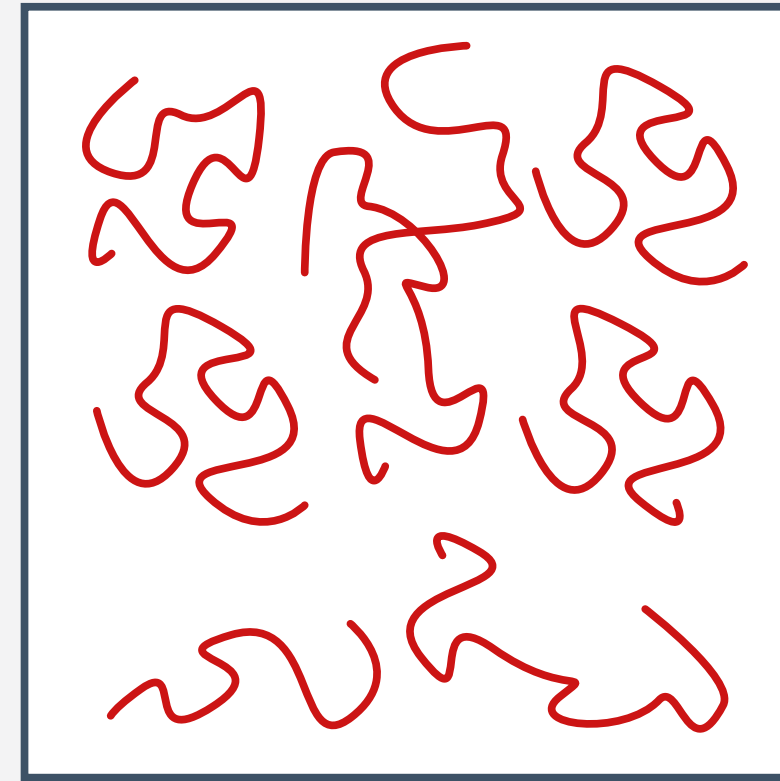


- different from many natural macromolecules, natural and synthetic polymers are “polydisperse”
- since properties are indistinguishable, polymers are also inseparable

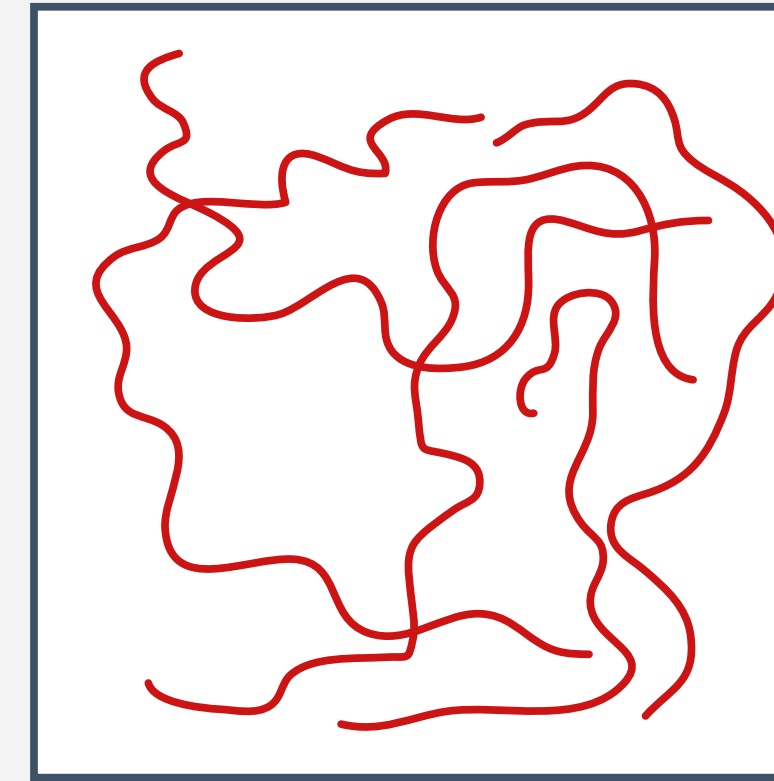
Influence of Chain Length on Physical Properties



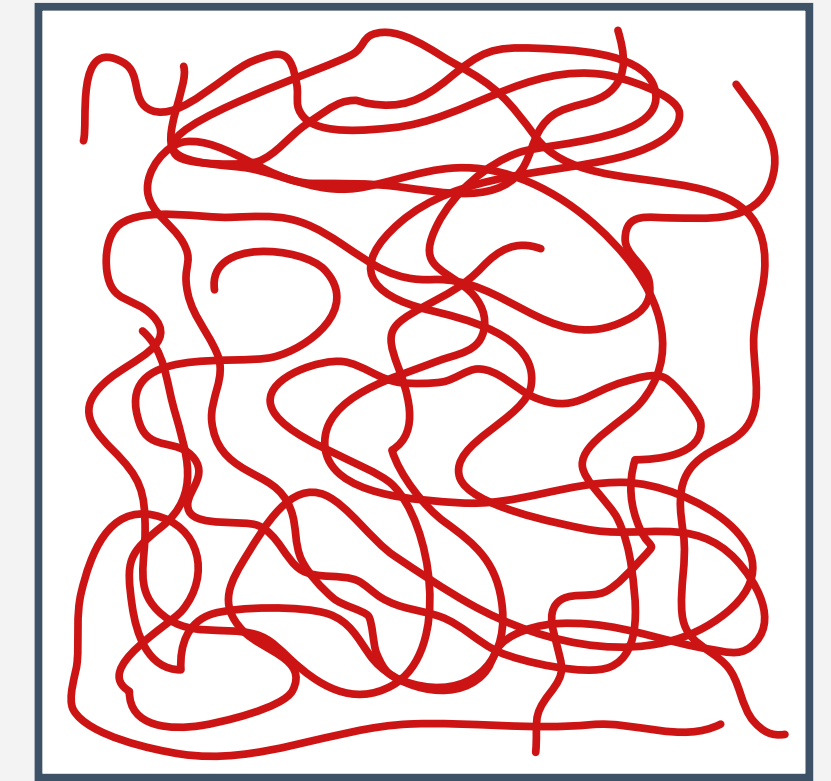
liquid



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 with increasing molecular weight (**Chapter 4.1**)

Polymer Types, Architectures, Microstructures

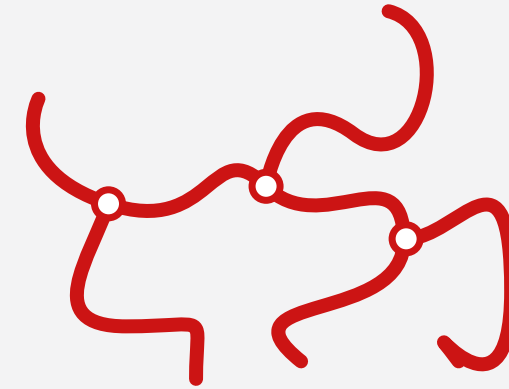
- homopolymers: one type of repeating units (but different architectures)



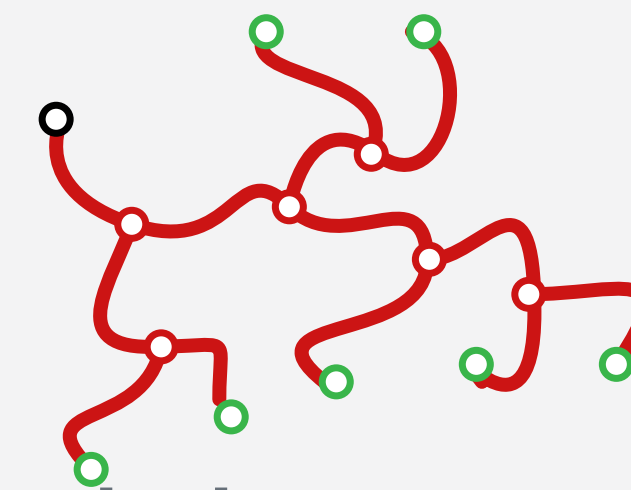
linear



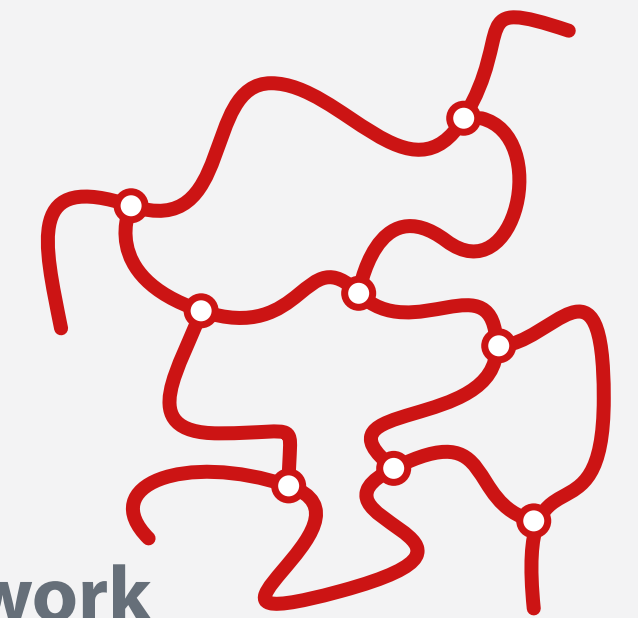
star



branched

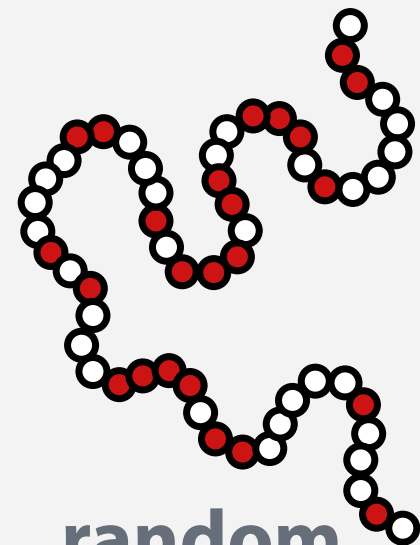


hyperbranched

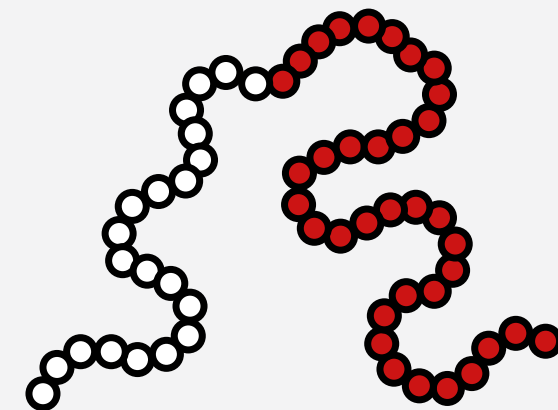


network

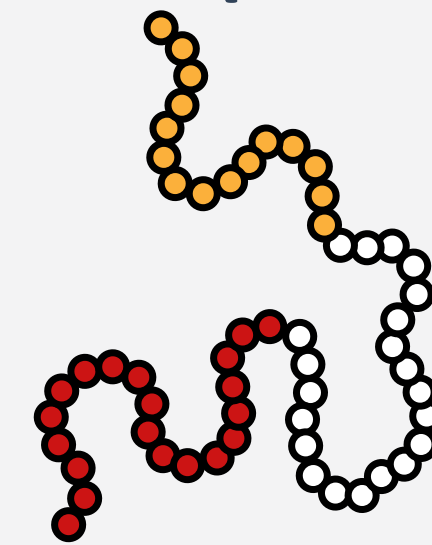
- copolymers: different types of repeating units (and microstructures)



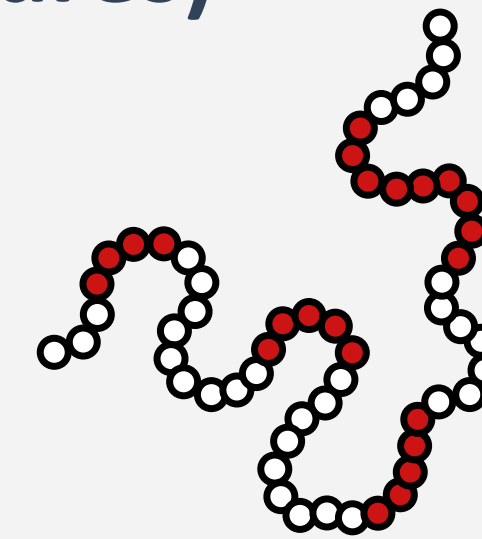
random



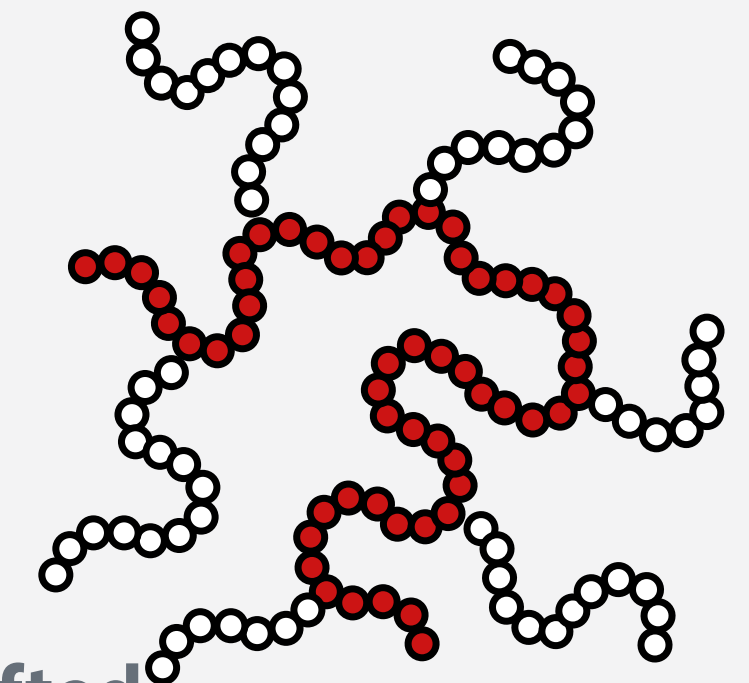
AB diblock



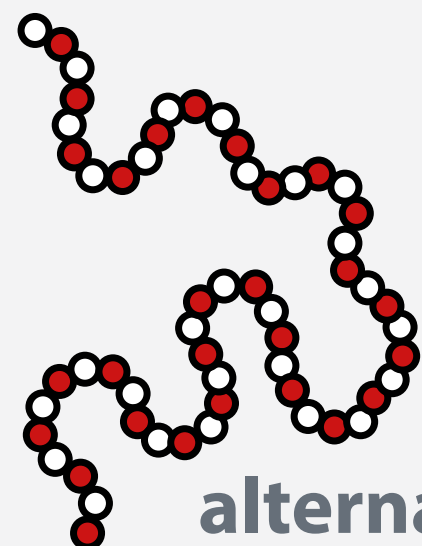
ABC triblock



segmented



grafted



alternating



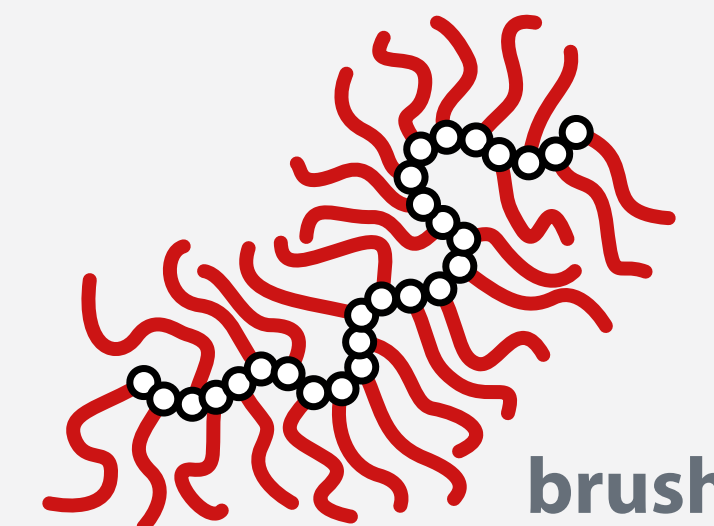
ABA triblock



miktoarm star

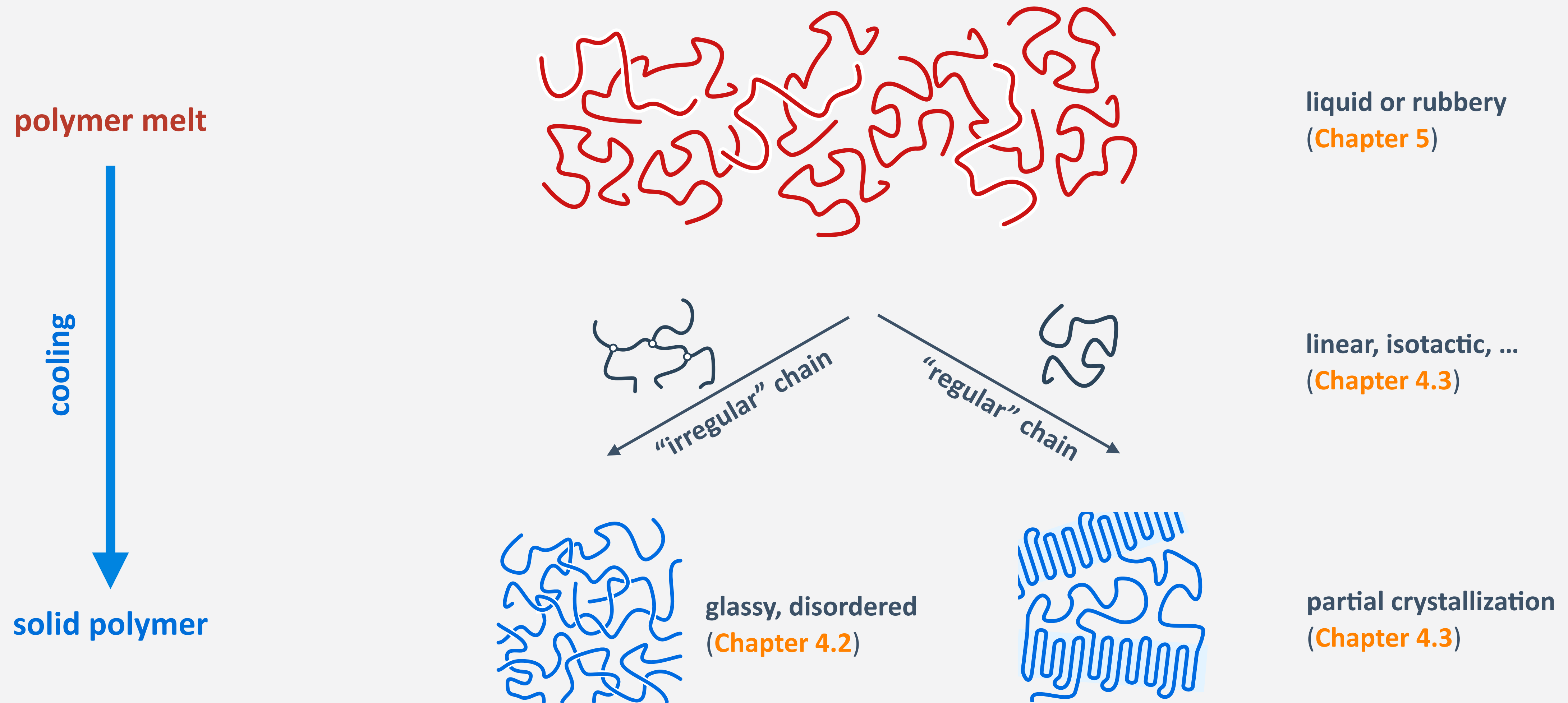


tapered



brush

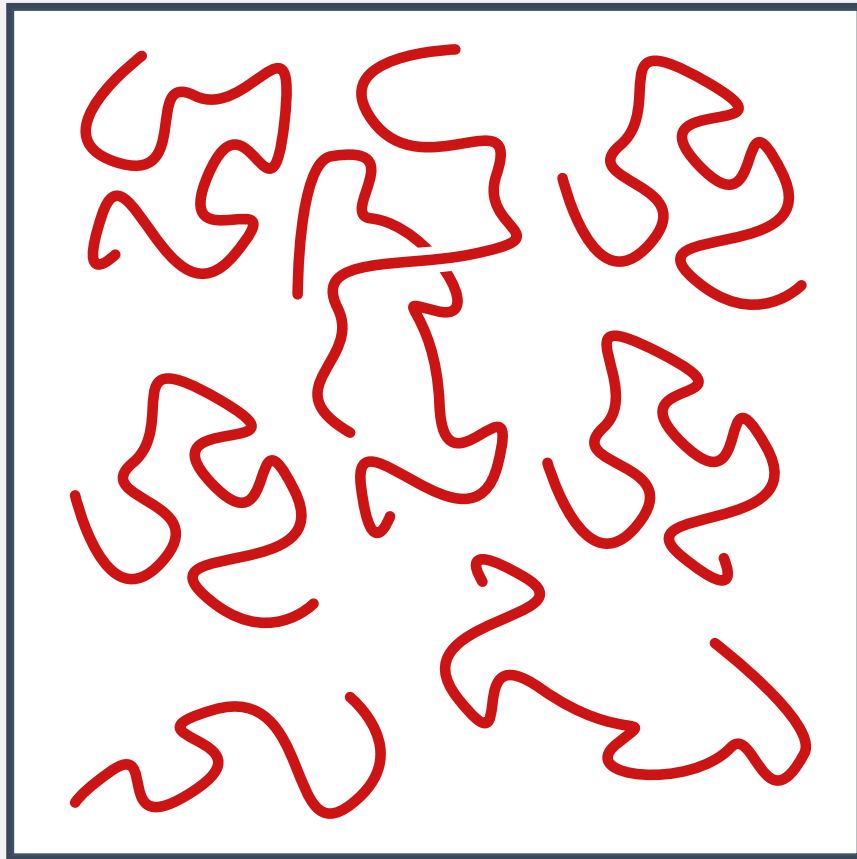
Importance of Polymer Chain Architecture



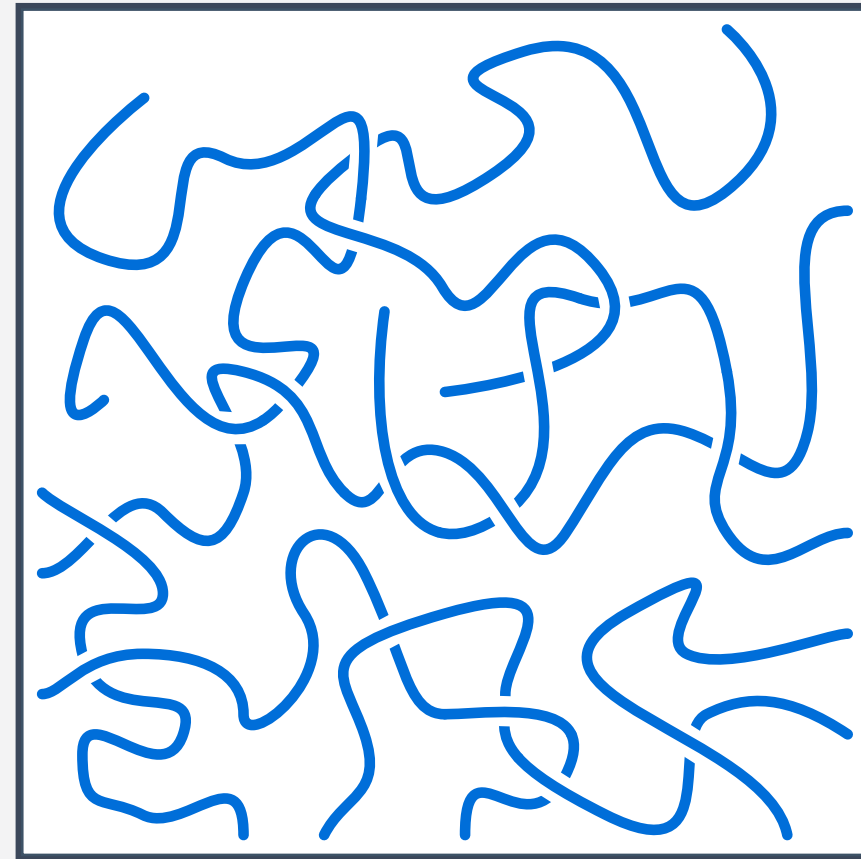
- the polymer chain architecture affects the solidification of the polymers

Condensed States of Polymers

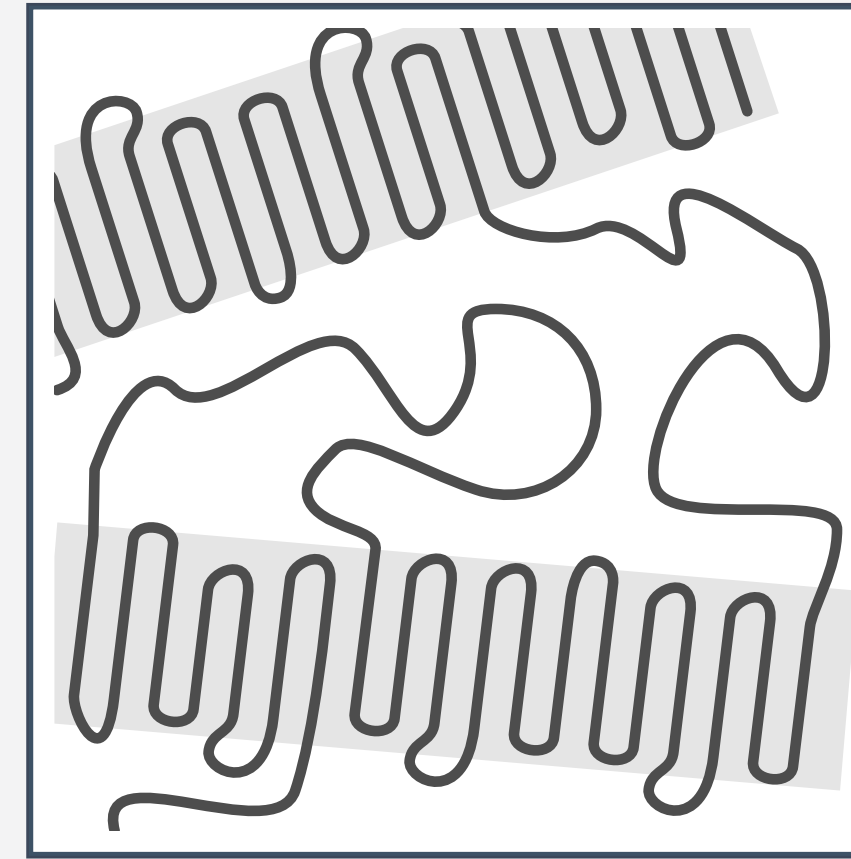
viscous liquids



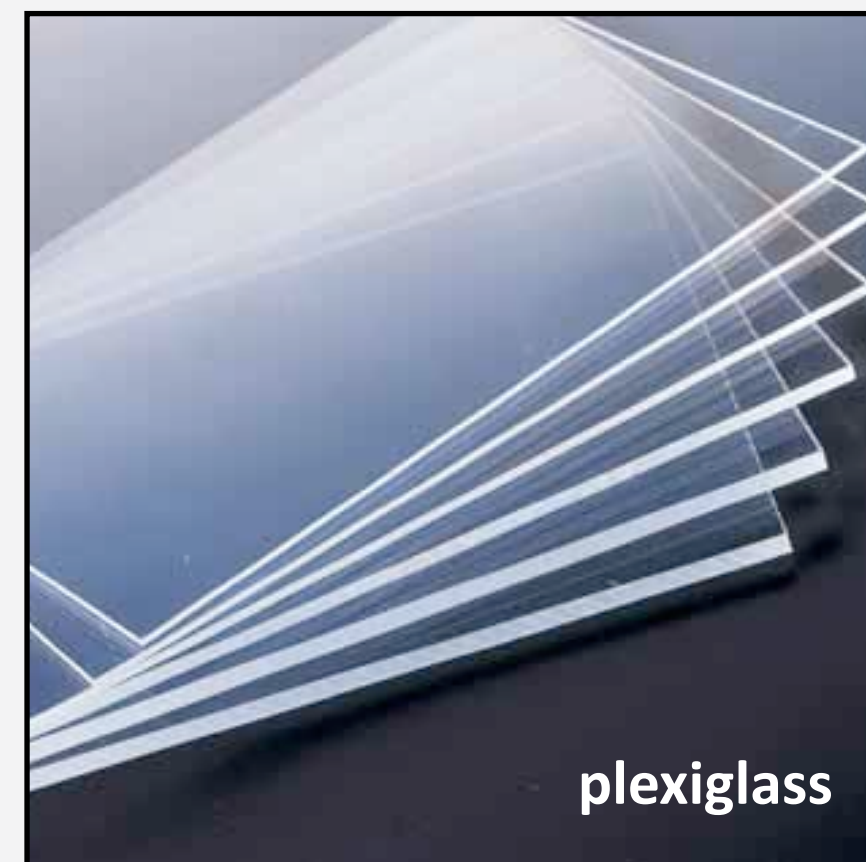
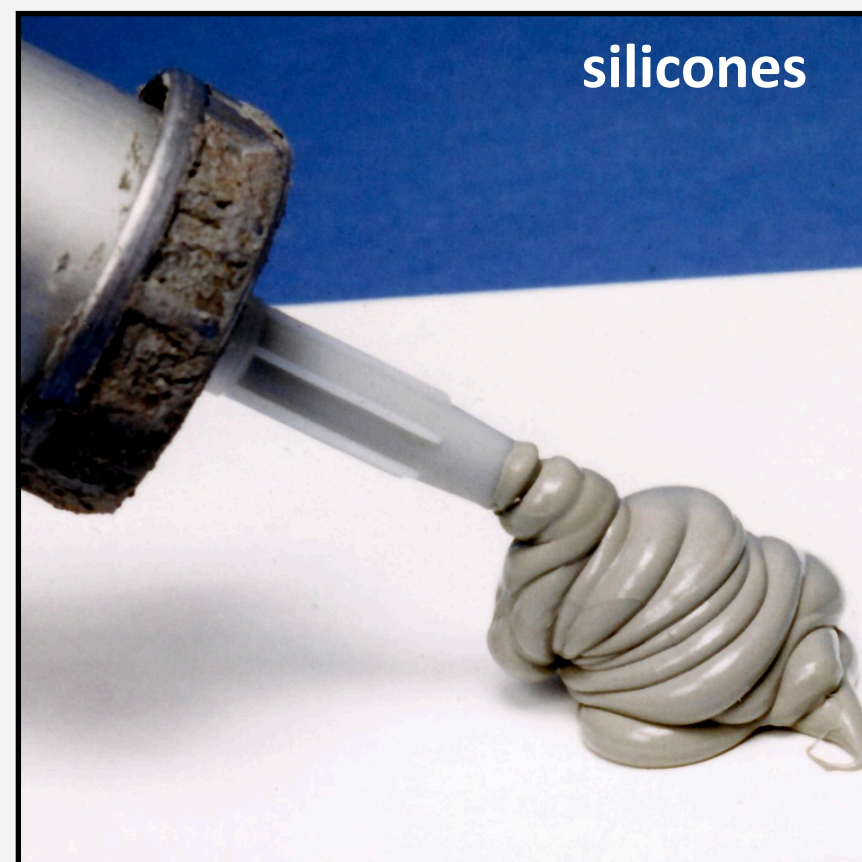
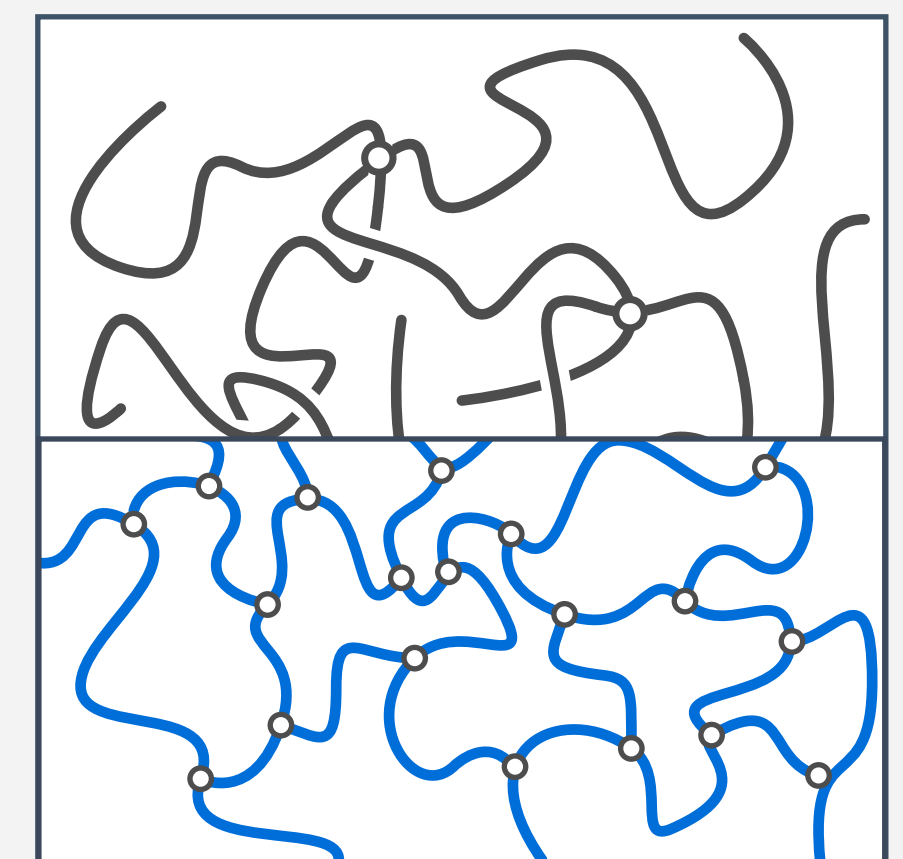
amorphous glasses



semi-crystalline



elastomers
or thermosets



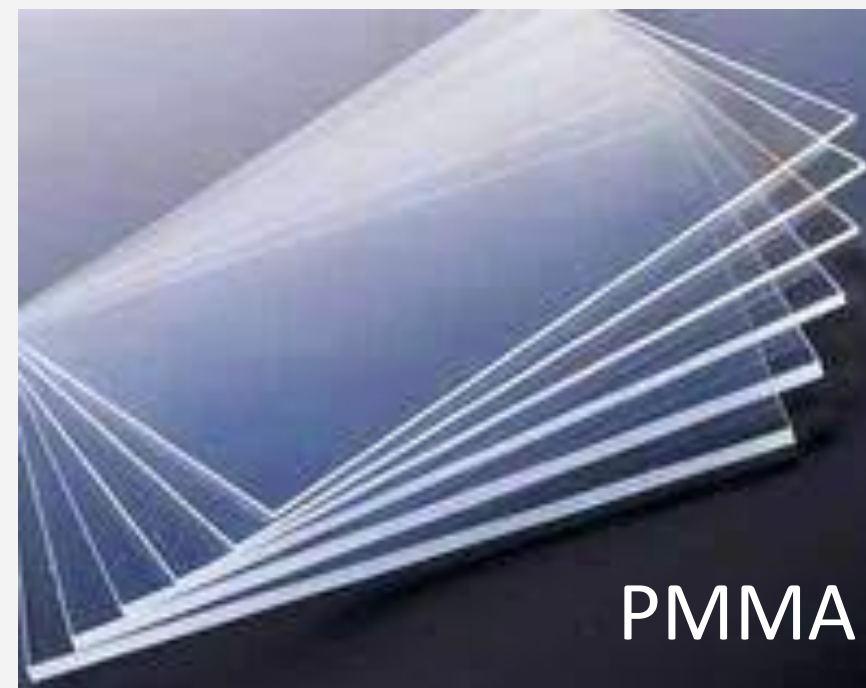
- polymers are versatile materials with unique mechanical properties not shown by other materials classes

Amorphous, Glassy Polymers

- hard solids, rigid (typical Young's modulus of 2-3 GPa)
- plastic behaviour, i.e. polycarbonate (PC), or more brittle behaviour, i.e. PS or PMMA
- generally transparent, amorphous (no structure that can scatter or absorb light)
- opaque, if fillers or pigments are added



amorphous, glassy



PMMA



PC



PVC



PS



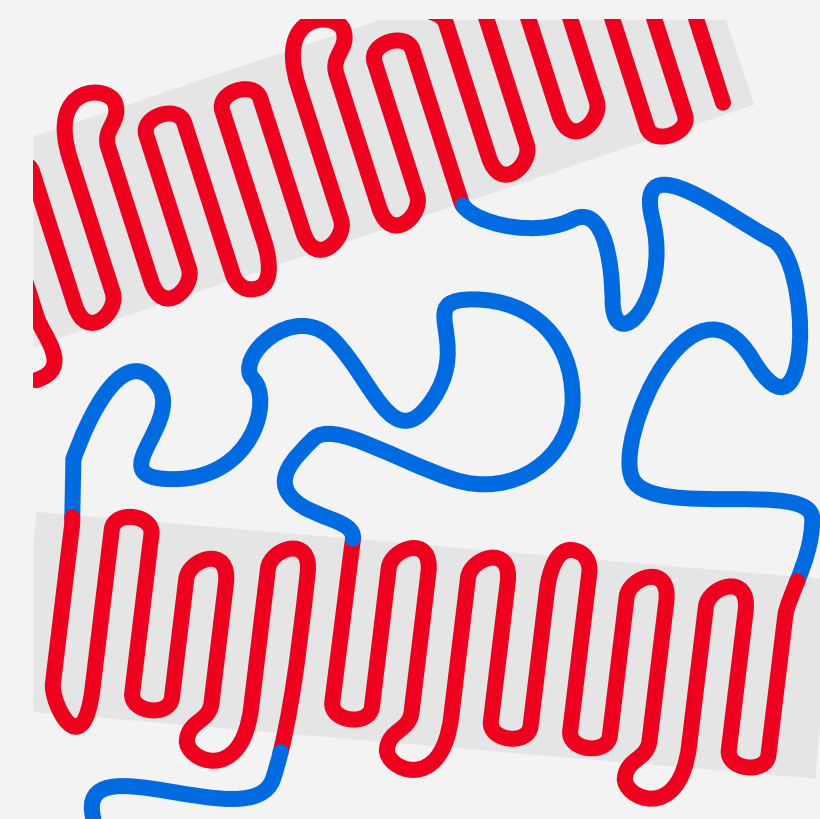
HIPS



ABS

Semi-Crystalline Polymers

- more or less rigid solids (Young's modulus can range from 0.1 to > 5 GPa depending on crystallinity, orientation and T_g of the amorphous phase)
- resistance to rupture, resistance to solvents
- generally opaque, depending on the microstructure



semi-crystalline



PET



Nylons



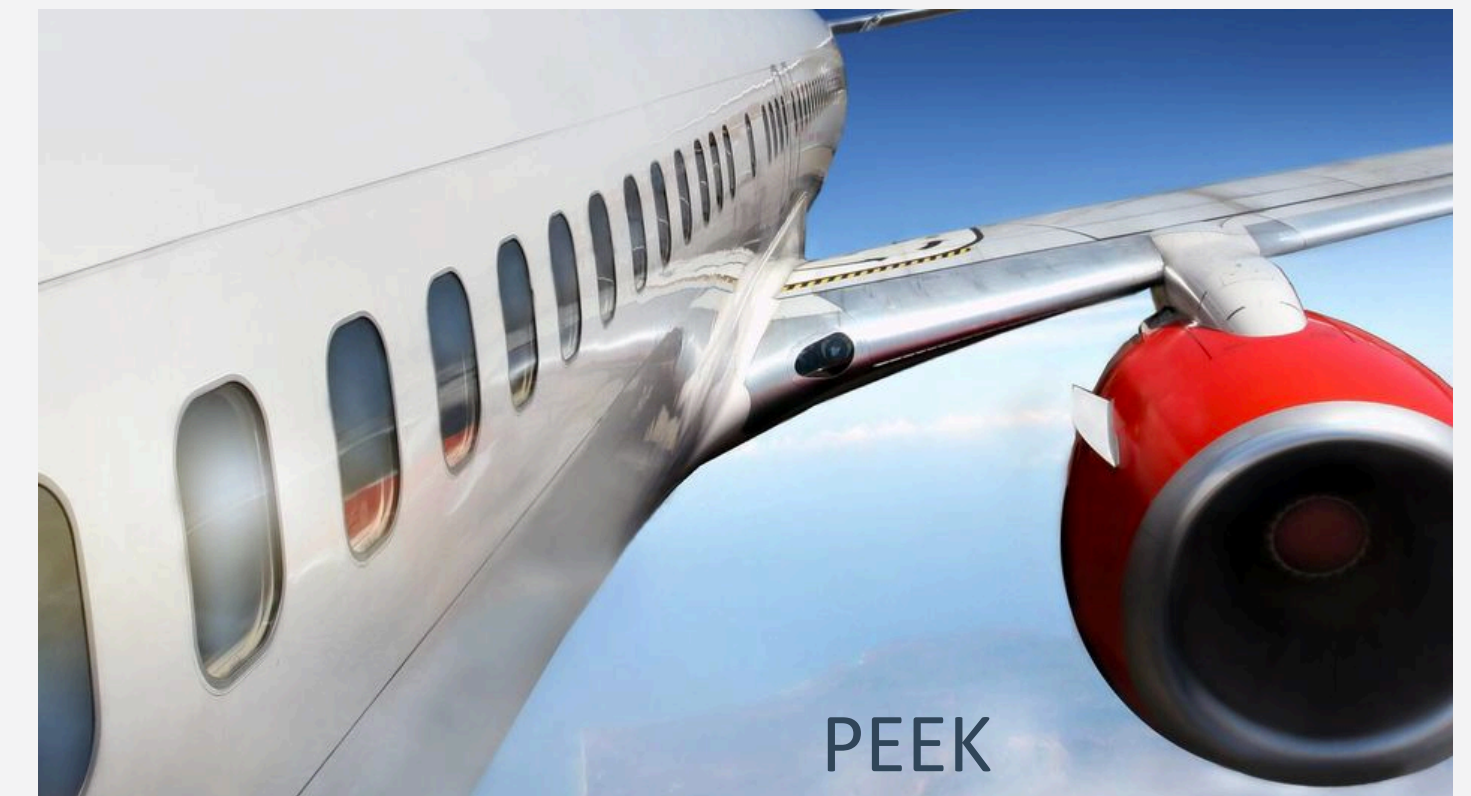
PP



LDPE



HDPE

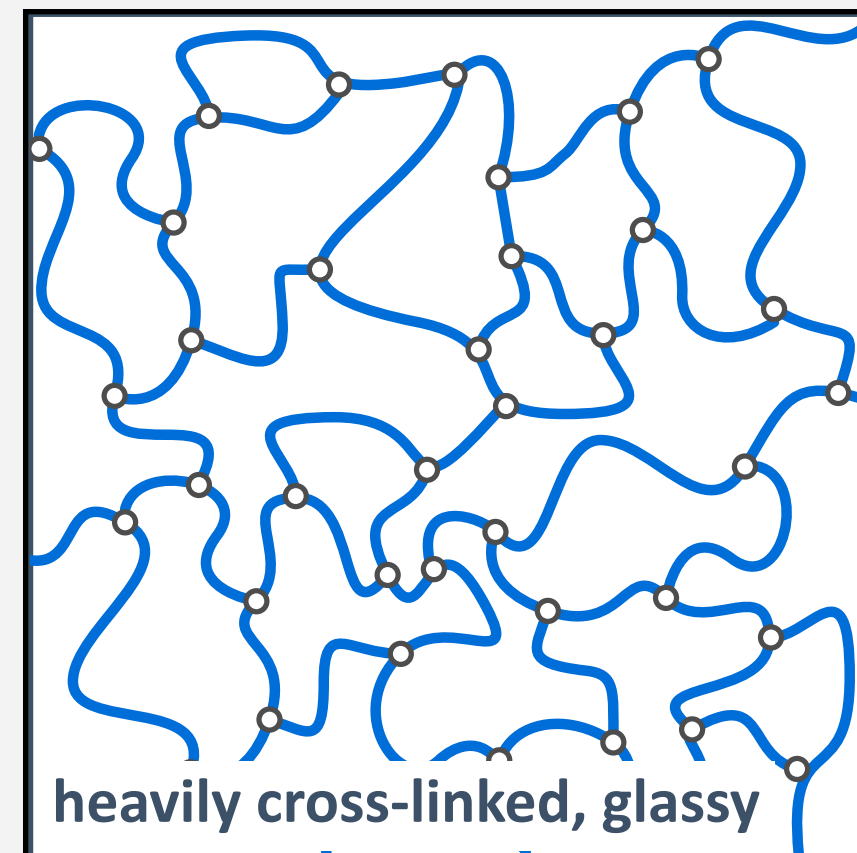


PEEK

Examples of Thermosets

- resins typically low in molecular weight and low in viscosity
- cross-linked during processing by applying heat or irradiation (e.g. UV)

Thermosets



epoxy resins, unsaturated polyesters (composites)



phenolic resins



melamine



PUR

- often good chemical and thermal resistance

One Example of an Elastomer

- amorphous polymers with low glass transition temperatures
- slightly cross-linked into a network structure

elastomers



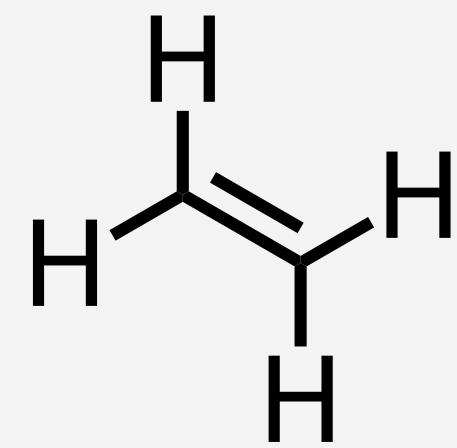
- soft, elastic materials (**Chapter 5.1**)

The Polymerization Reaction

- polymer chain architecture, chemical composition, molecular weight, molecular weight distribution are all generated during the polymerisation reaction (**Chapter 6.1**)

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

monomer

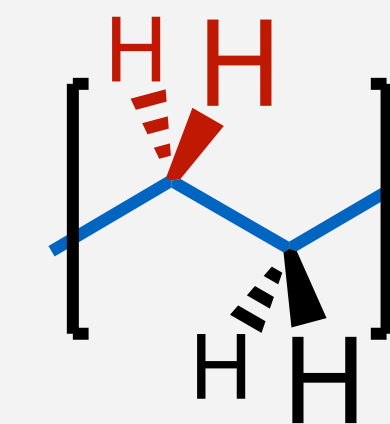


ethylene

polymerization
→

polymer

constitutive unit (CH₂)



polymer backbone

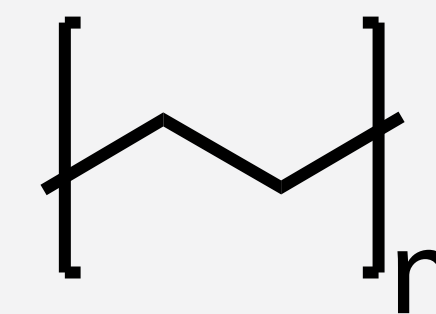
degree of polymerization

polyethylene (PE)

- usually, hydrogen atoms are omitted for clarity:

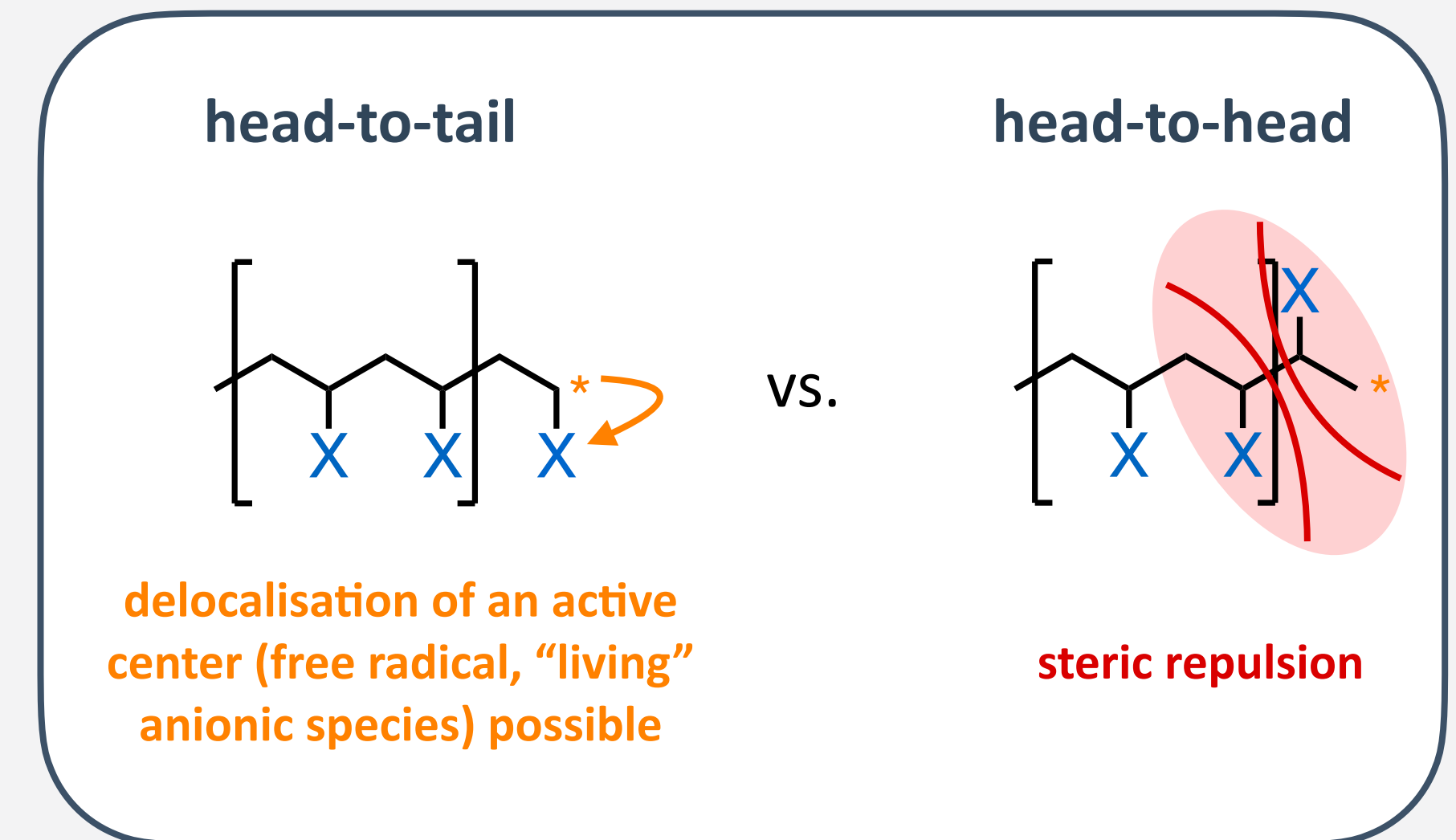
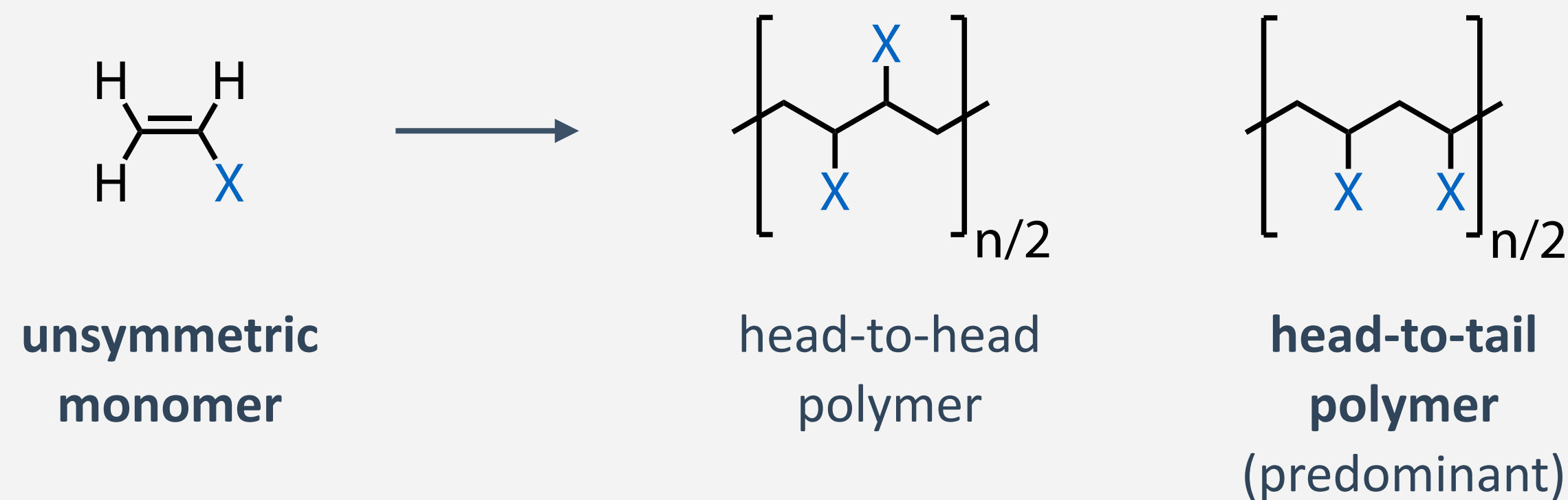


polymerization
→



Chain Configuration and Isomerism: Sequence Isomerism

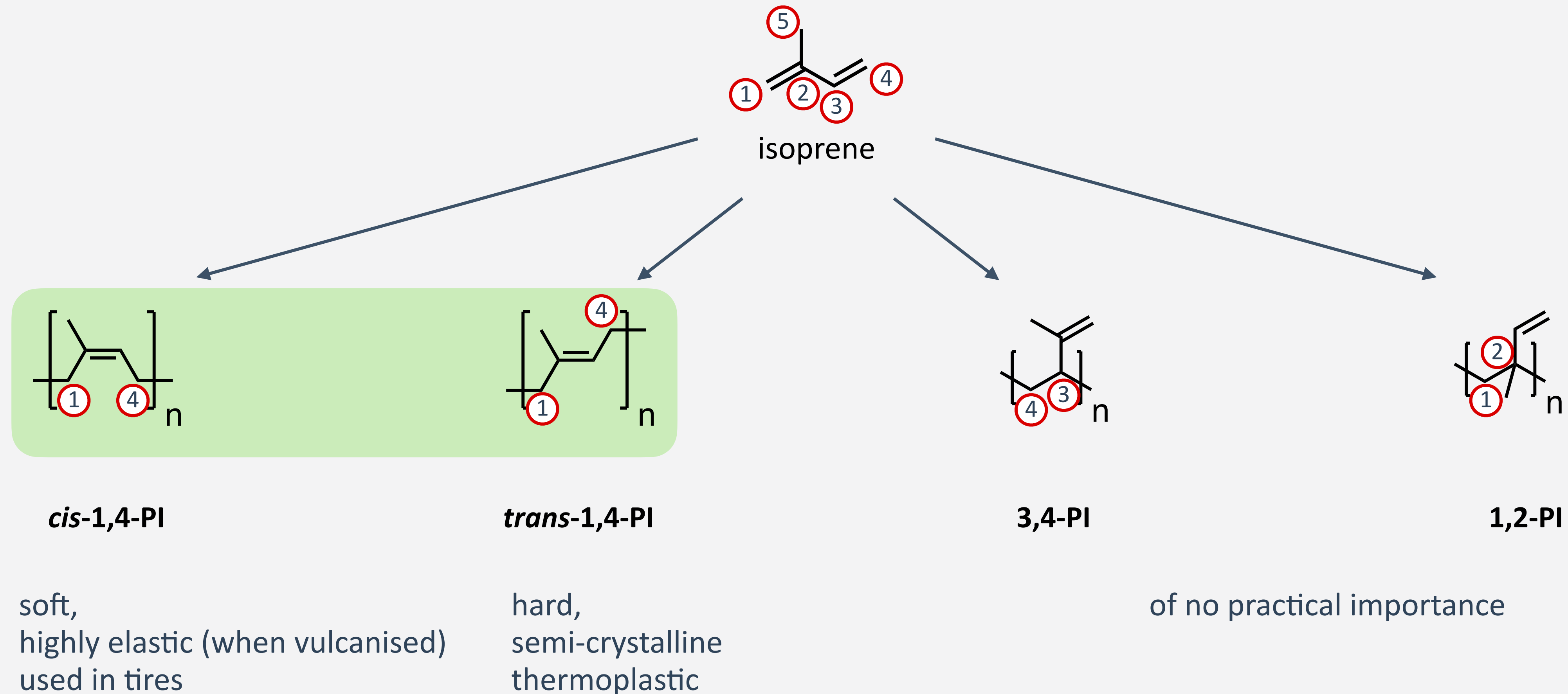
- physical properties of polymeric systems are strongly affected by chain configuration and different forms of isomerism, i.e. the exact 3D arrangement of atoms or groups bound to a central atom
- built-in properties during polymerisation: no interconversion of isomers possible for a polymer chain**



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

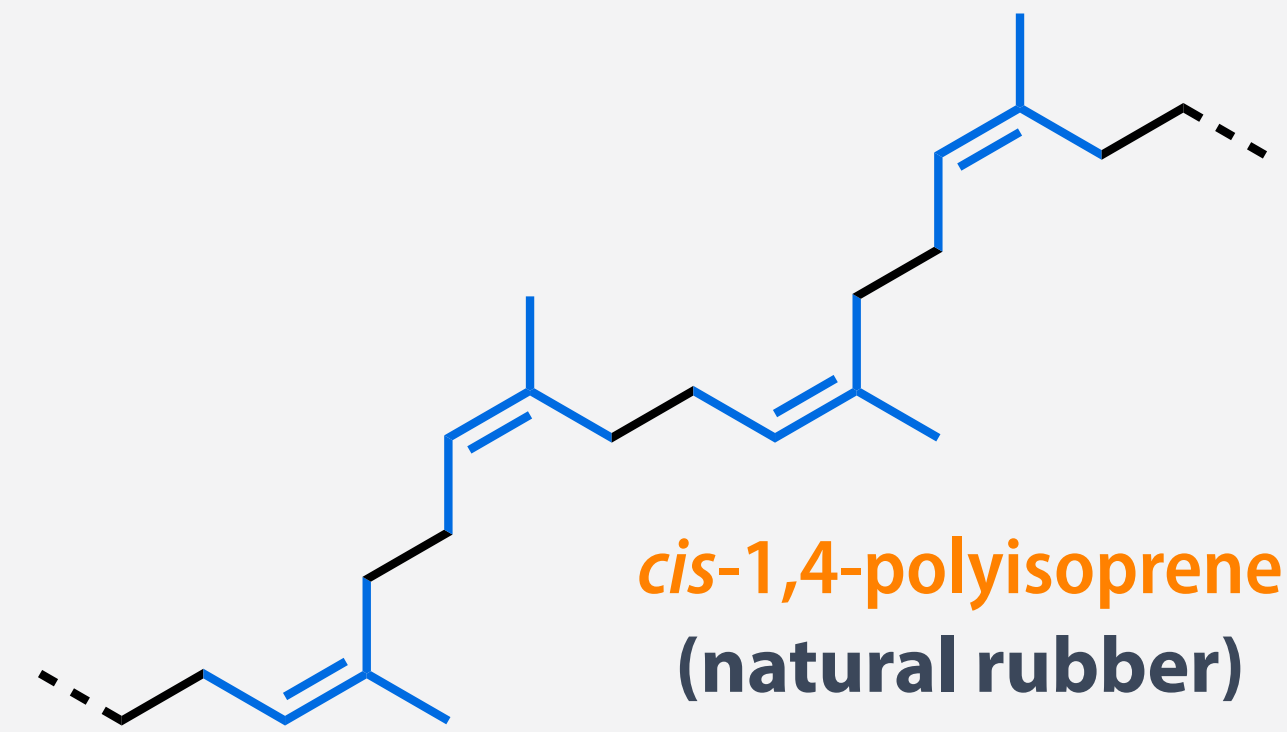
Constitutional (Structural) Isomerism in Polyisoprene

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

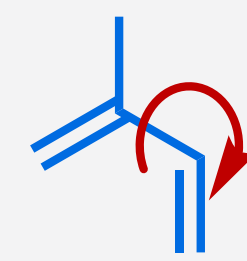


- only *cis*-1,4-polyisoprene is produced at large scale with major application in tires

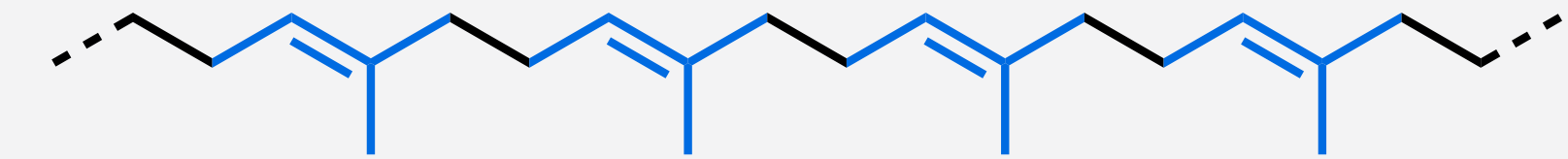
One Example of an Elastomer



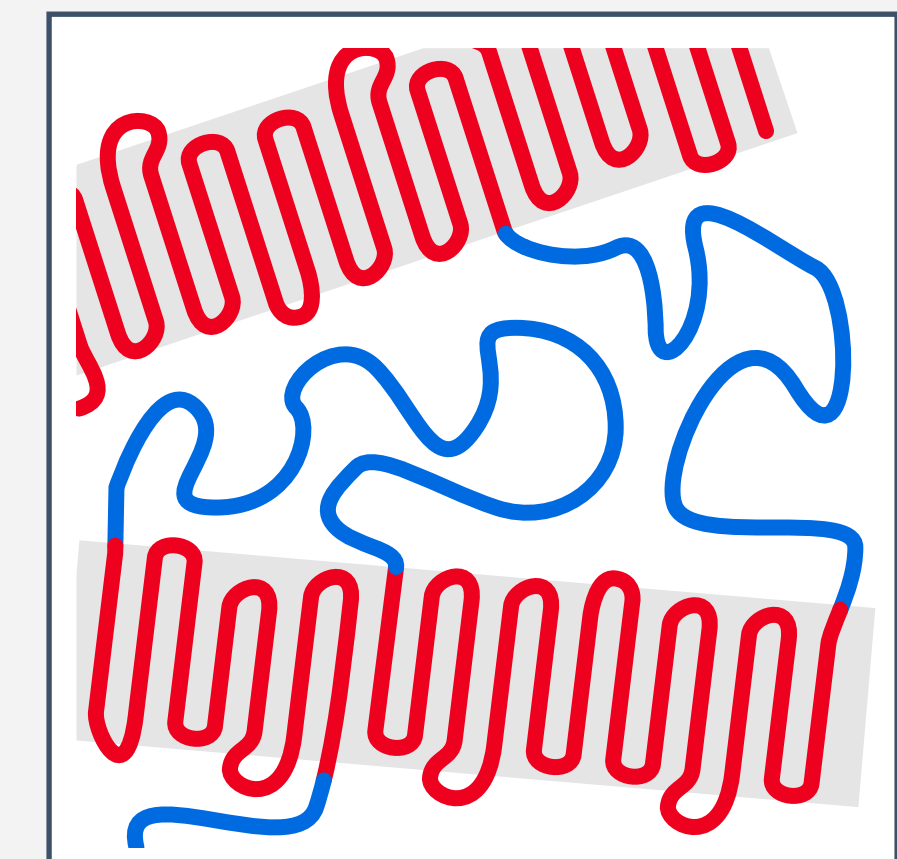
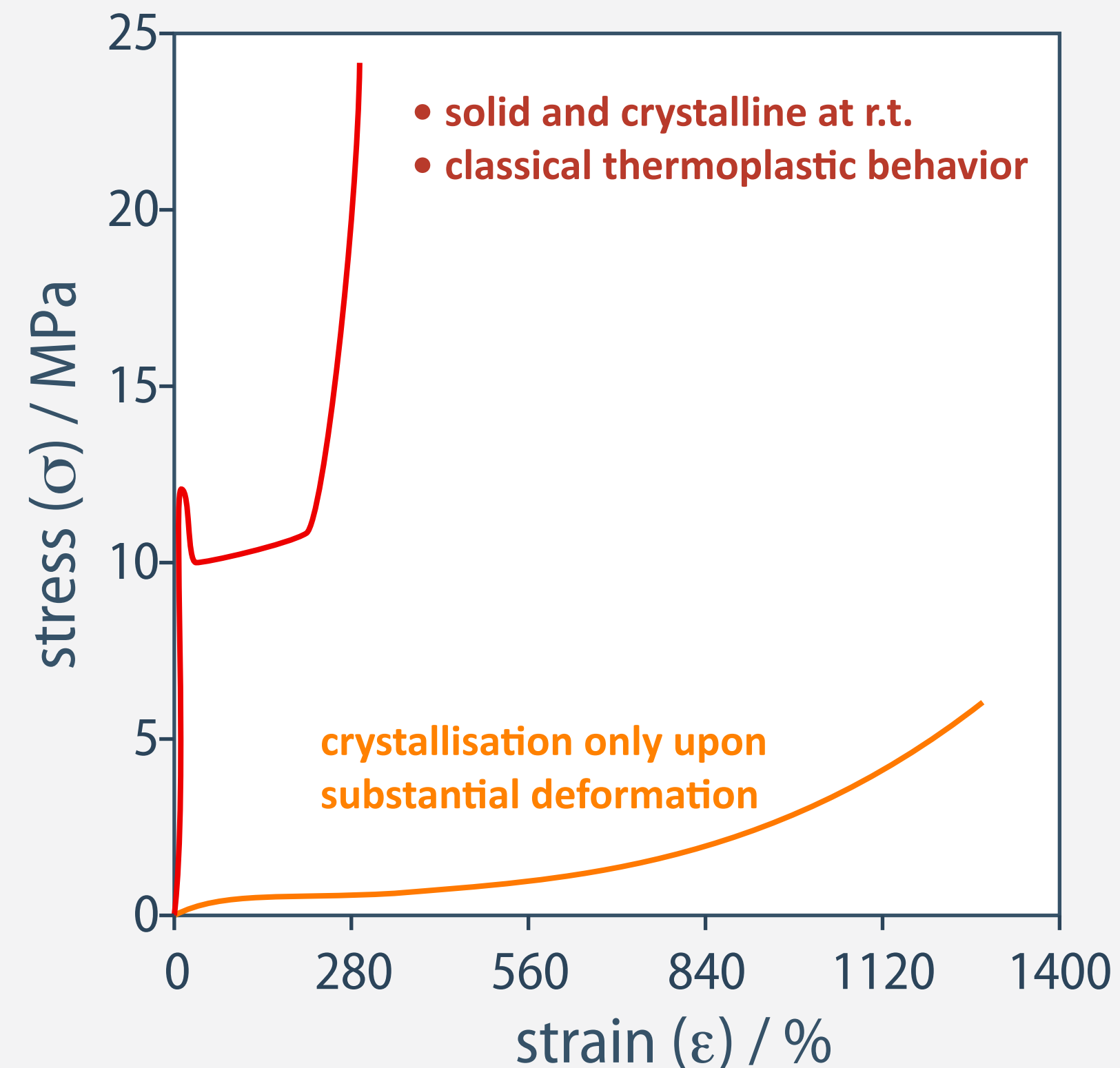
elastomers



isoprene



trans-1,4-polyisoprene

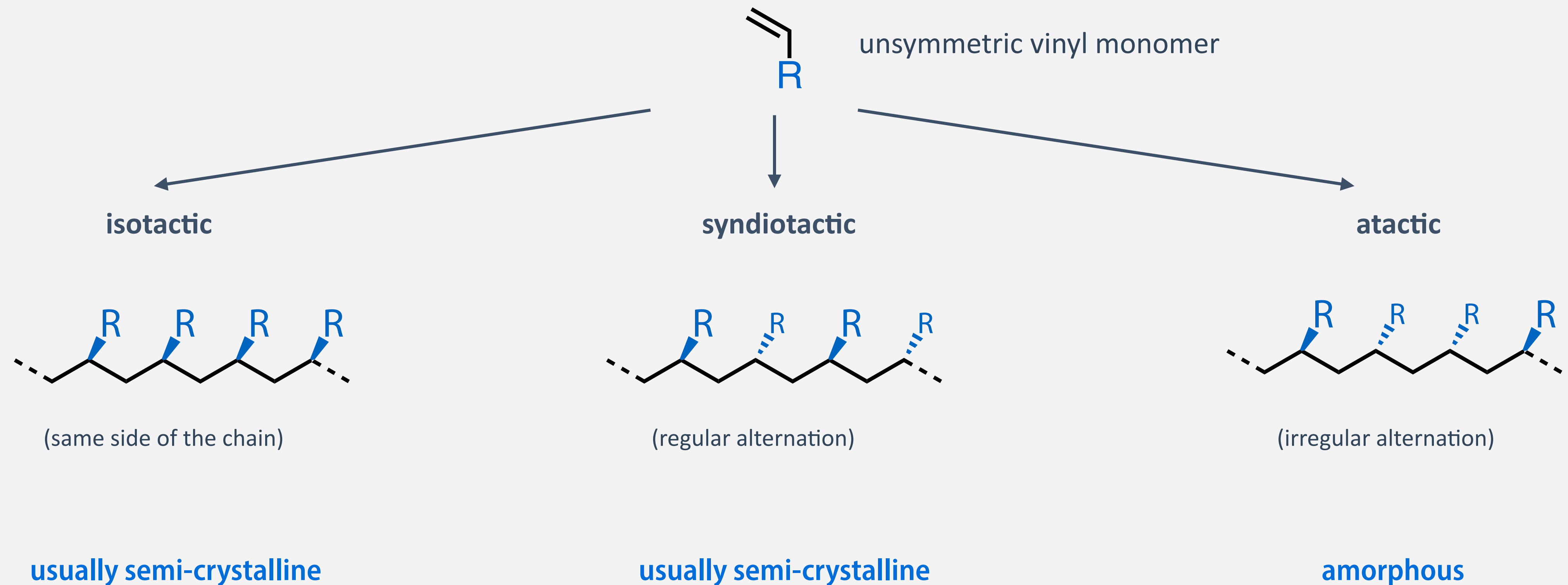


semi-crystalline

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

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



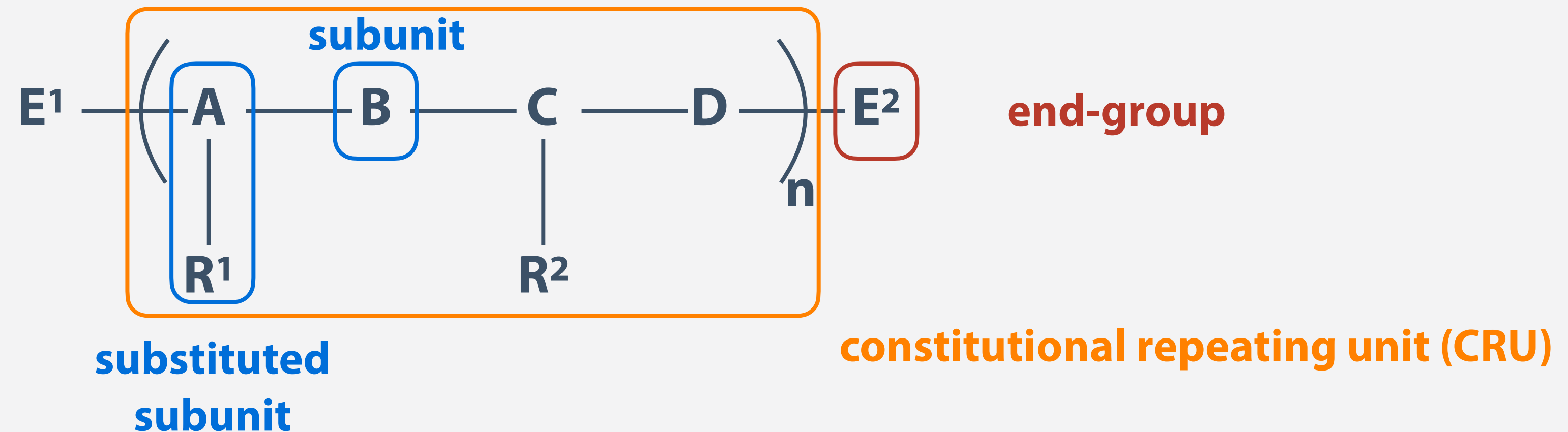
- tacticity has huge impact on the physical properties of polymer materials (see crystallization, **Chapter 4.3**)

Nomenclature of Single-Strand Polymers

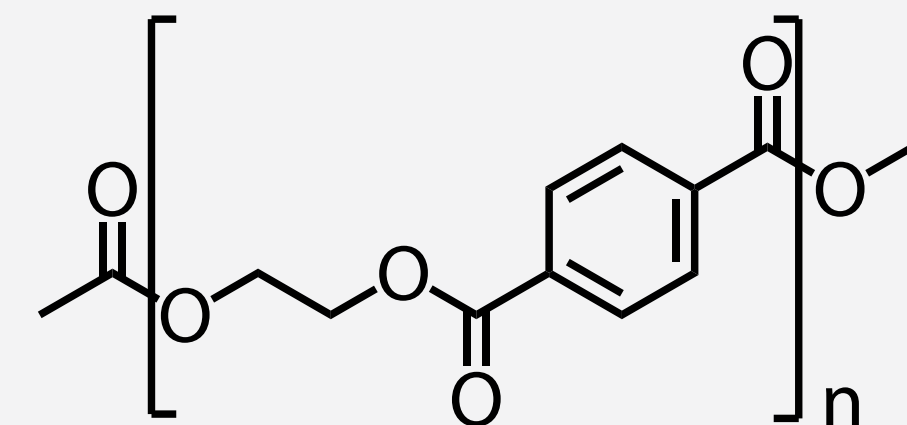
- **attachement of the prefix “poly” to the name of the monomer**

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.

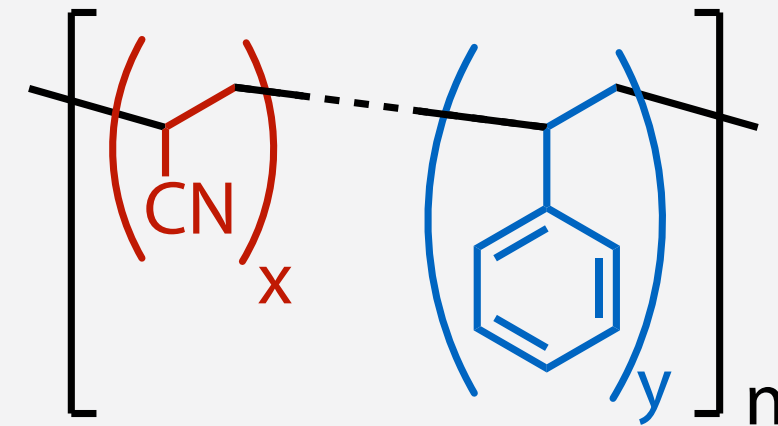
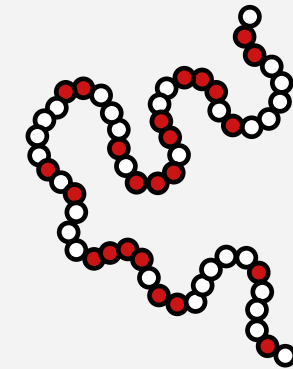


example: α -acetyl- ω -methoxy-poly(oxyethyleneoxyterephthaloyl)



Nomenclature of Copolymers

- random copolymer

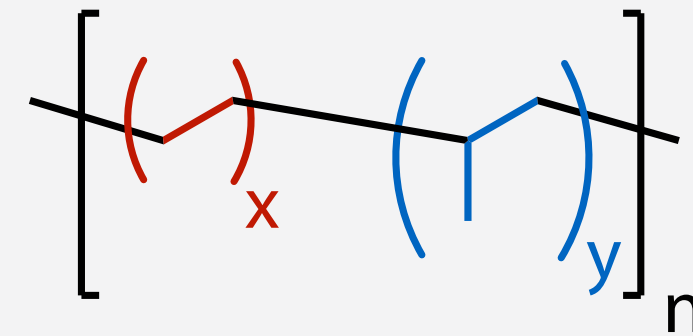
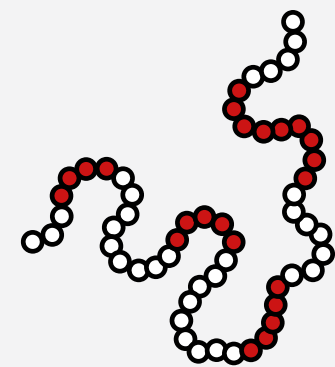


poly(**acrylonitrile-co-styrene**)



SAN

- multiblock copolymer

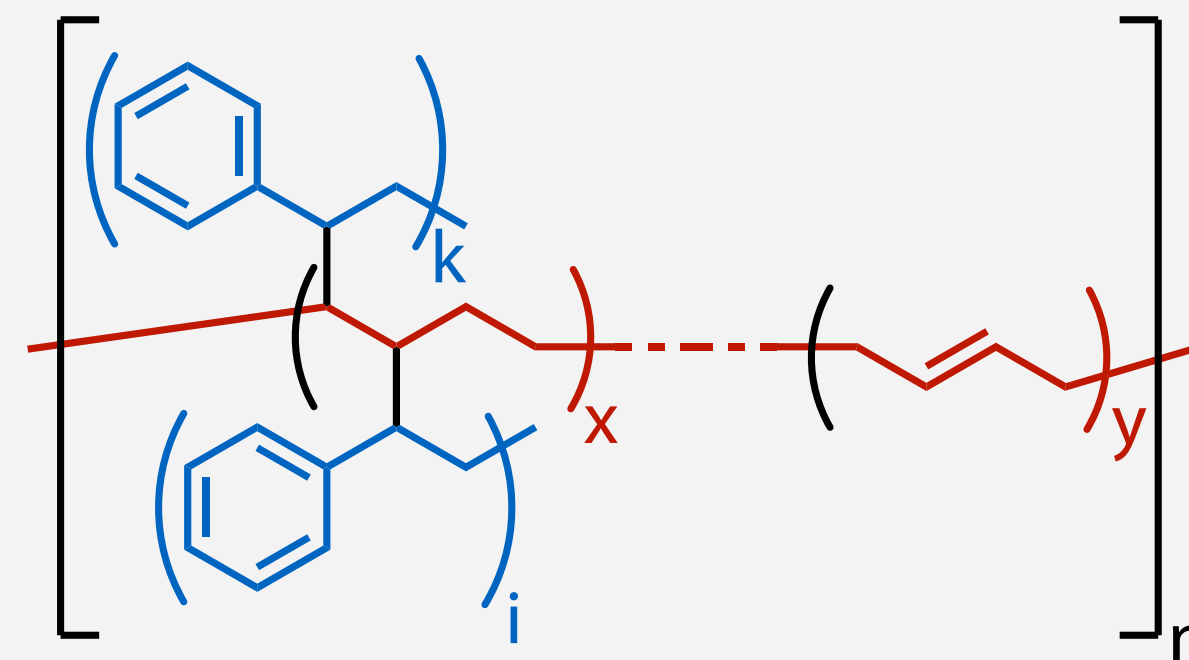
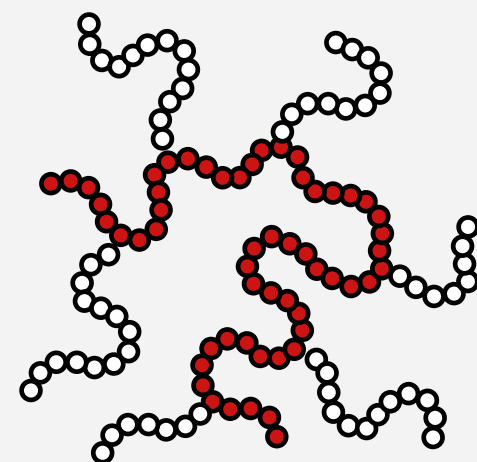


poly(**polyethylene-b-polypropylene**)



PP-b

- branched copolymer



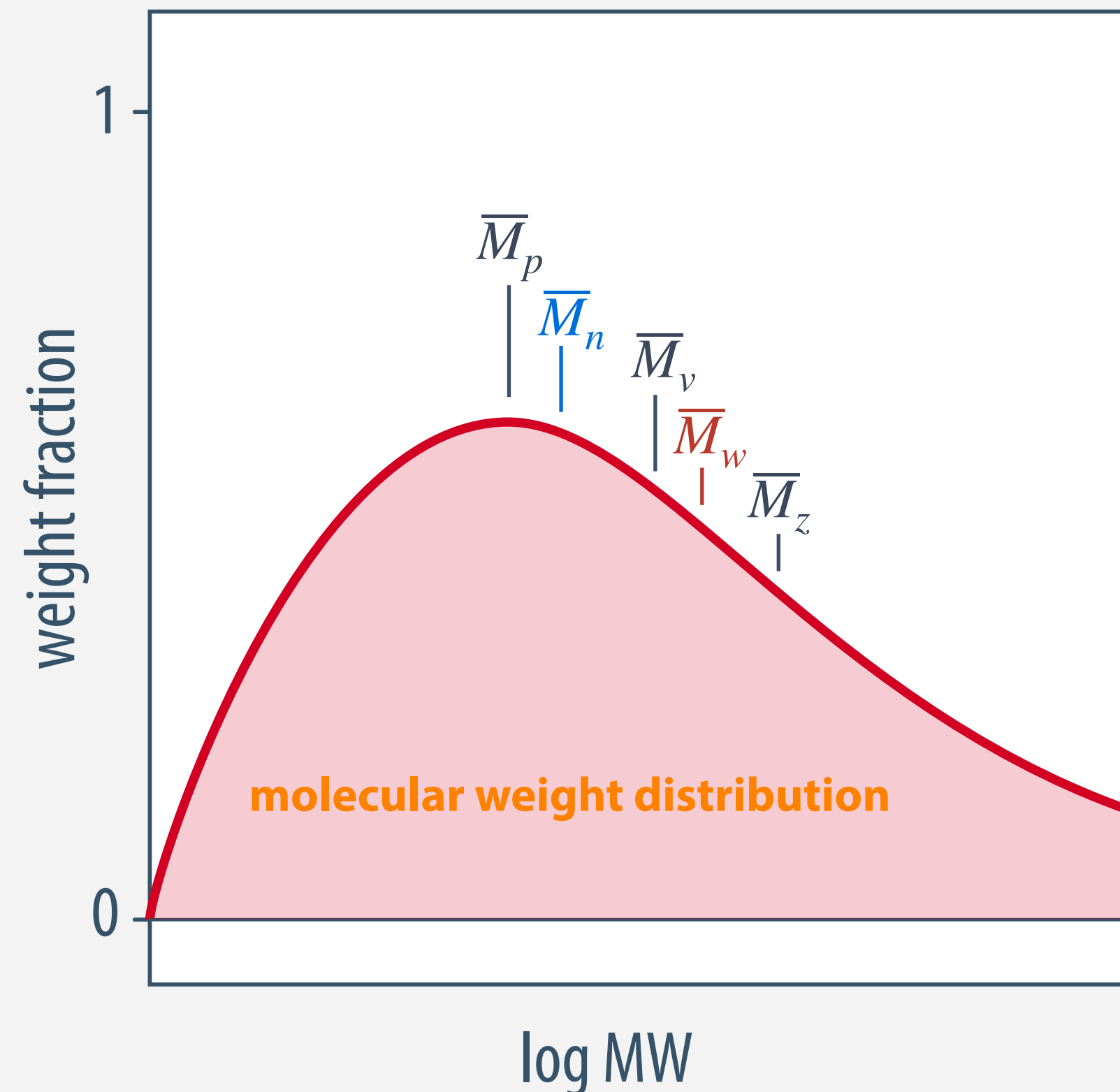
poly(**butadiene-g-polystyrene**)



"high-impact Polystyrene" (HIPS)

Molecular Weight (MW) and Molecular Weight Distribution (MWD)

- polymers do not have defined molar masses but **molecular weight distributions** (MWD)
- different molecular weight averages, width, and shape
- molecular weight averages are moments of the molecular weight distribution



number average molecular weight

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

weight average molecular weight

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

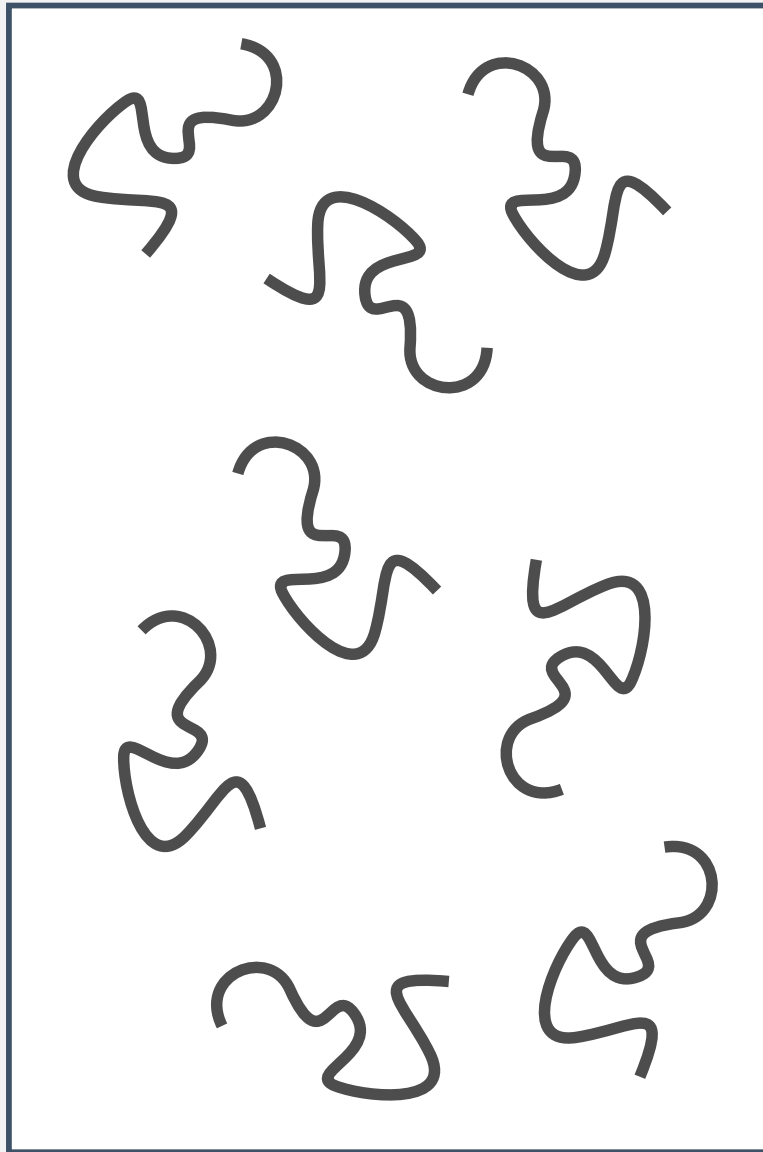
dispersity (formerly, polydispersity index)

$$\bar{D} = \frac{\bar{M}_w}{\bar{M}_n}$$

- moreover, z-average molecular weight, $\bar{M}_z$, and viscosity average molecular weight, $\bar{M}_v$ (**Chapter 2.4**)

Number Average and Weight Average Molecular Weight

Number Average and Weight Average Molecular Weight

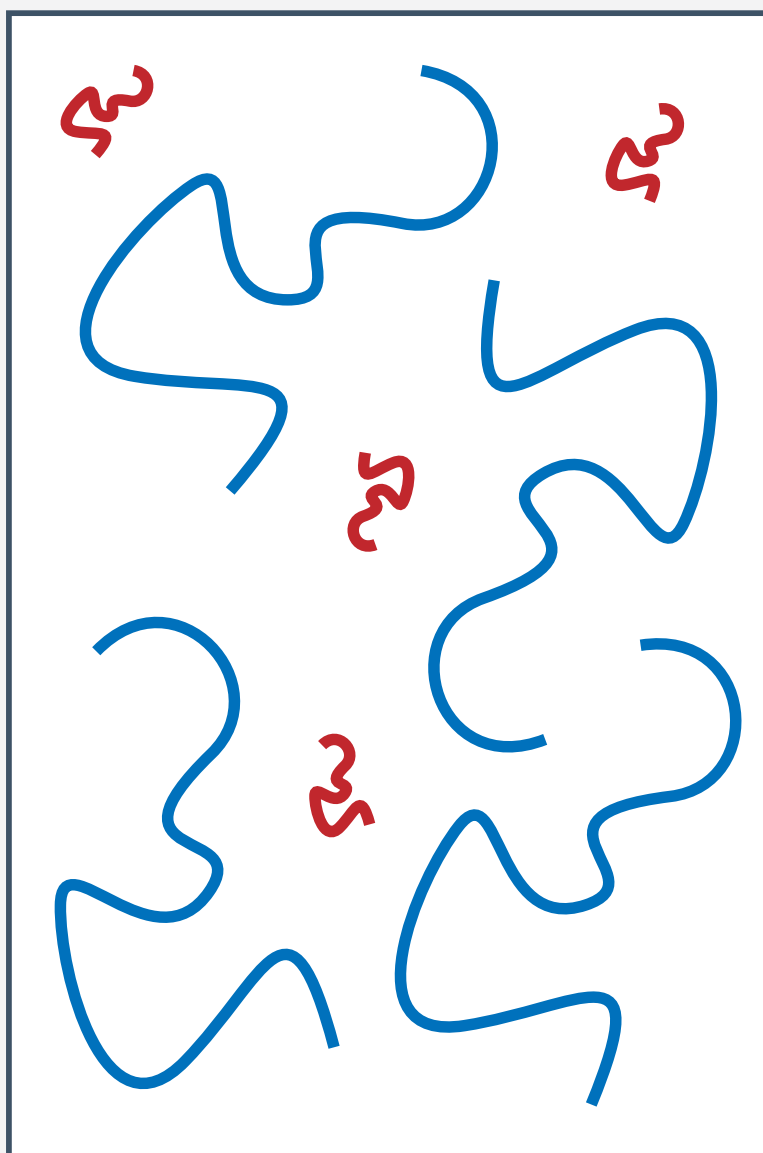


$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{8 \cdot 5000}{8} = 5000$$

$$\mathcal{D} = \frac{\overline{M}_w}{\overline{M}_n} = 1$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{8 \cdot 5000^2}{8 \cdot 5000} = 5000$$

**molecularly uniform
(monodisperse)**



$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{4 \cdot 9000 + 4 \cdot 1000}{4 + 4} = 5000$$

$$\mathcal{D} = \frac{\overline{M}_w}{\overline{M}_n} = 1.64$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{4 \cdot 9000^2 + 4 \cdot 1000^2}{4 \cdot 9000 + 4 \cdot 1000} = 8200$$

disperse

Important Consequences of High Molar Mass

1. Physicochemical Properties

- absence of a precise relation between T_m and M (Chapter 4.3)
- absence of a gaseous phase (Chapter 4.1)
- dominant chain entropy impacting both thermodynamics and mechanics (Chapter 5.1)

2. Processing

- high viscosity (in solution and in the molten state) (Chapter 5.2)
- energy storage capacity in the molten state (viscoelasticity) (Chapter 5.2)
- capability of film and fiber formation from the molten state (viscoelasticity) (Chapter 6)

3. Viscoelastic and Mechanical Properties

- spectrum of relaxation times (Chapter 5.2)
- vitrification (Chapter 4.2)
- elongation at break and high strength (Chapter 5.3)

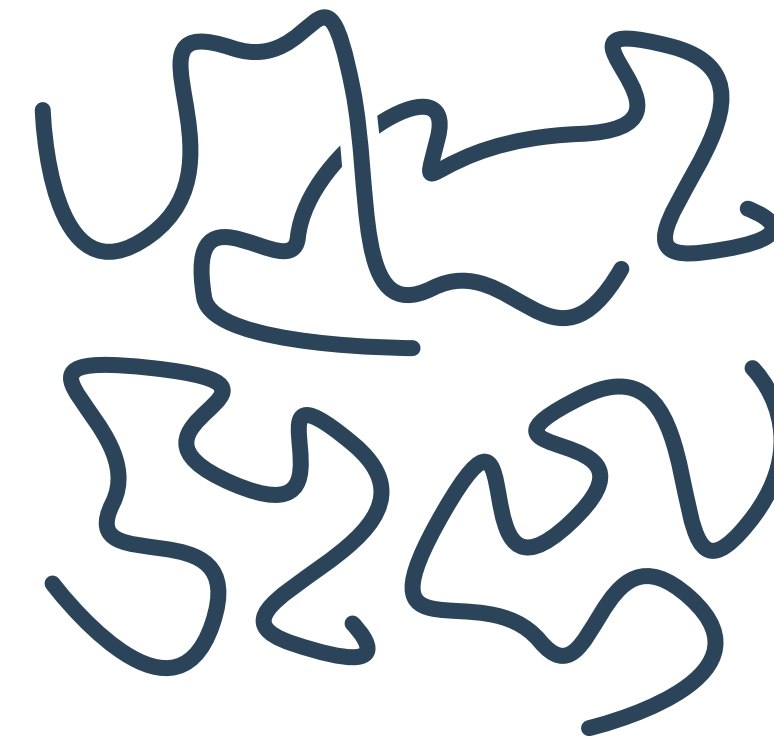
Thermal Transitions of Polymers

- abrupt transformation from glassy (hard) to soft state
- onset of chain motion

(Chapter 4.3)

glass
transition

T_g



polymer melt (Chapter 5.2)

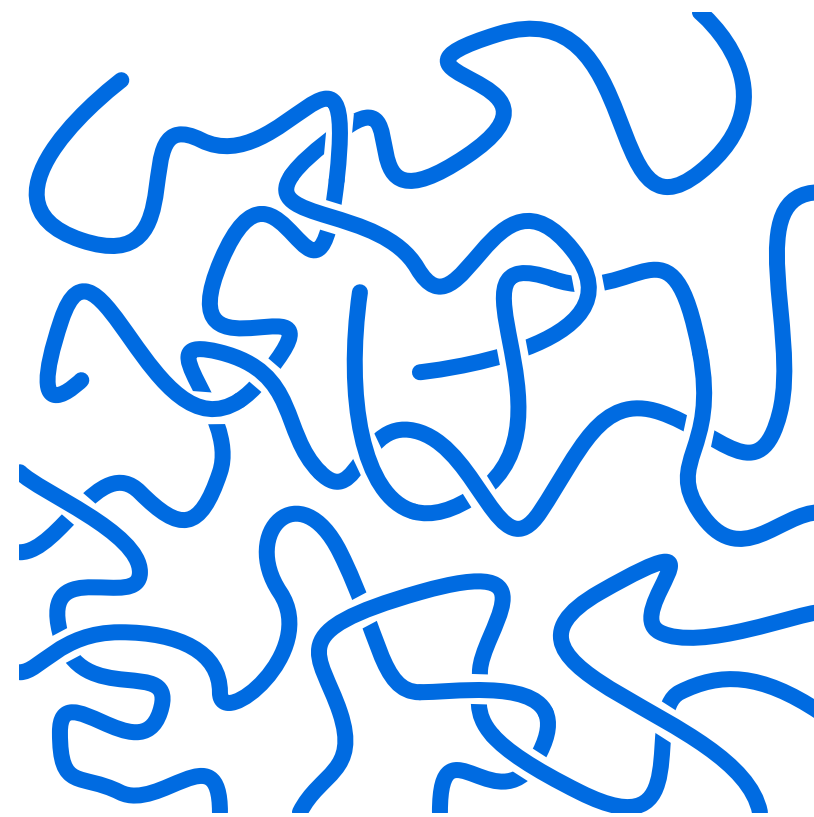
melting
transition

- formation of ordered crystalline domains

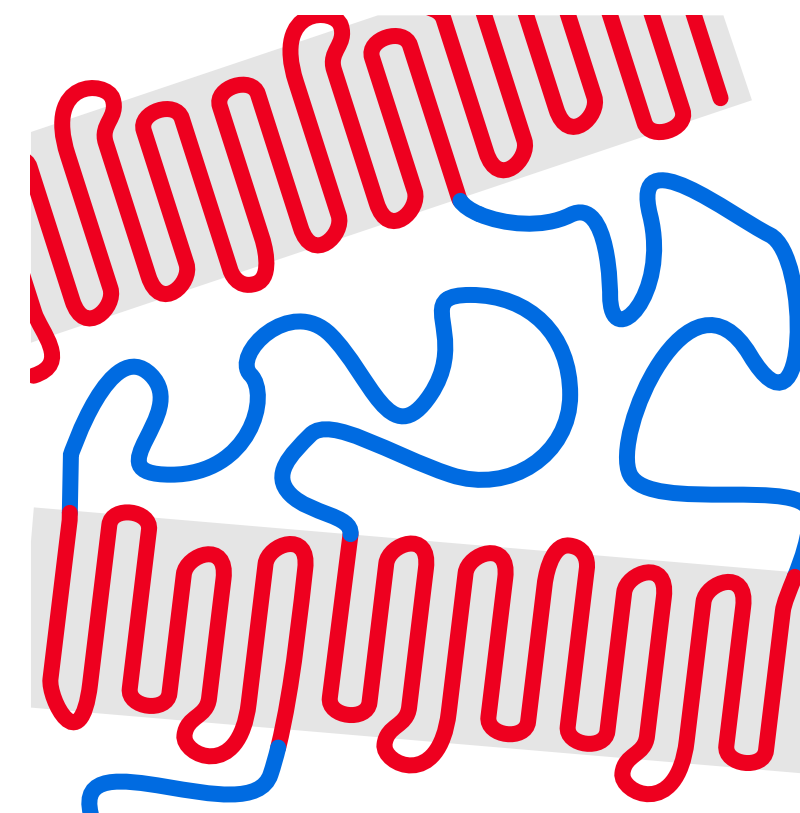
(Chapter 4.4)

T_g, T_m

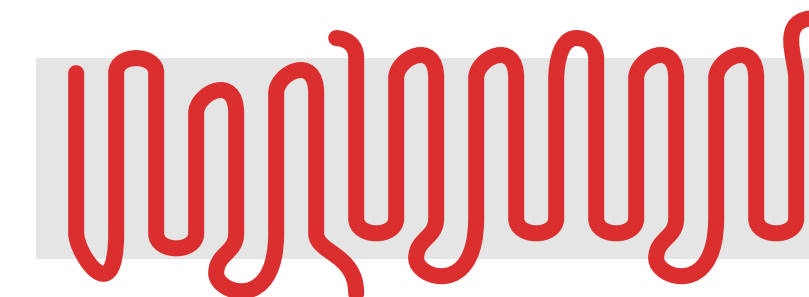
T_m



amorphous, glassy



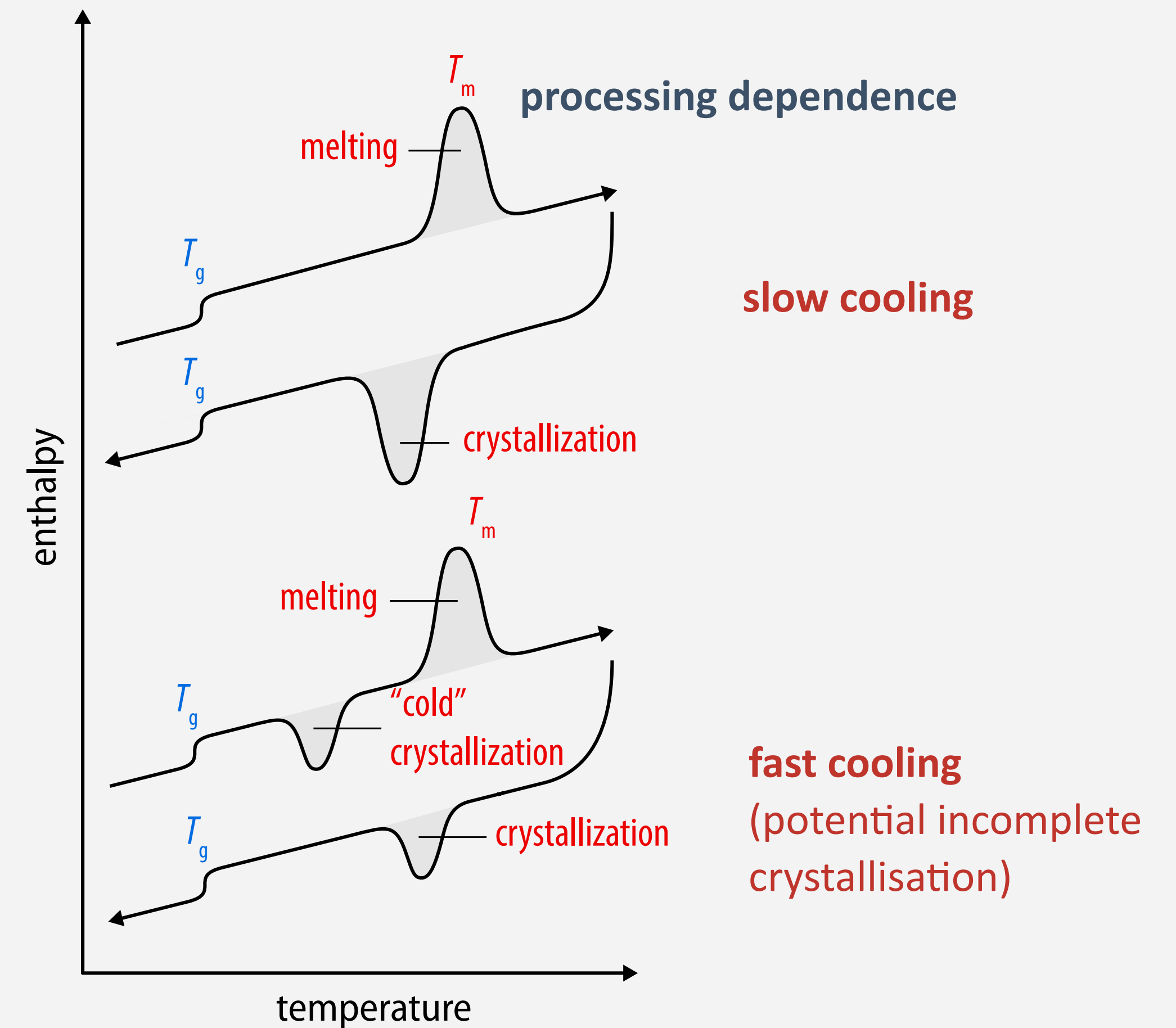
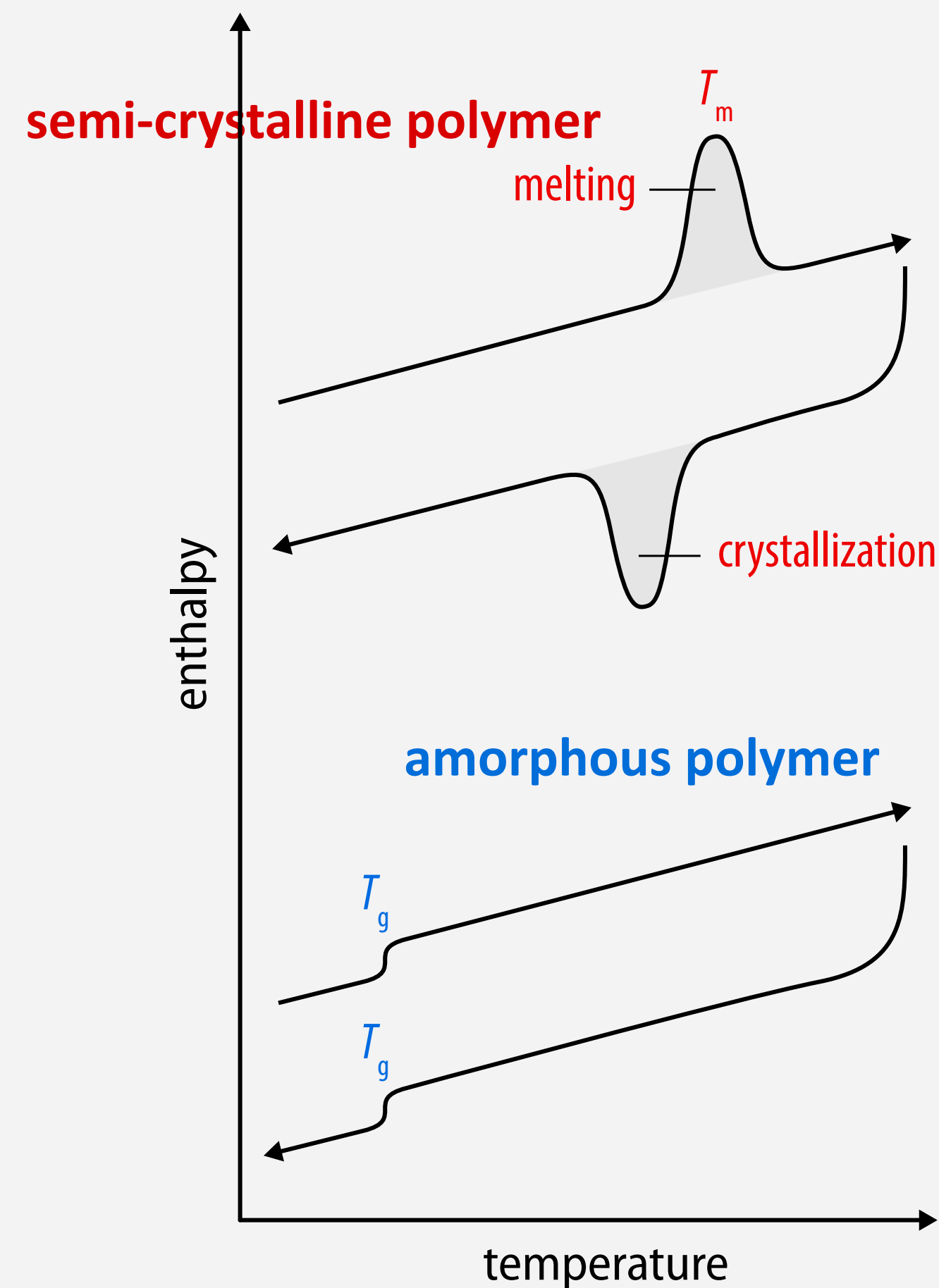
semi-crystalline



monocrystalline

Thermal Transitions of Polymers

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



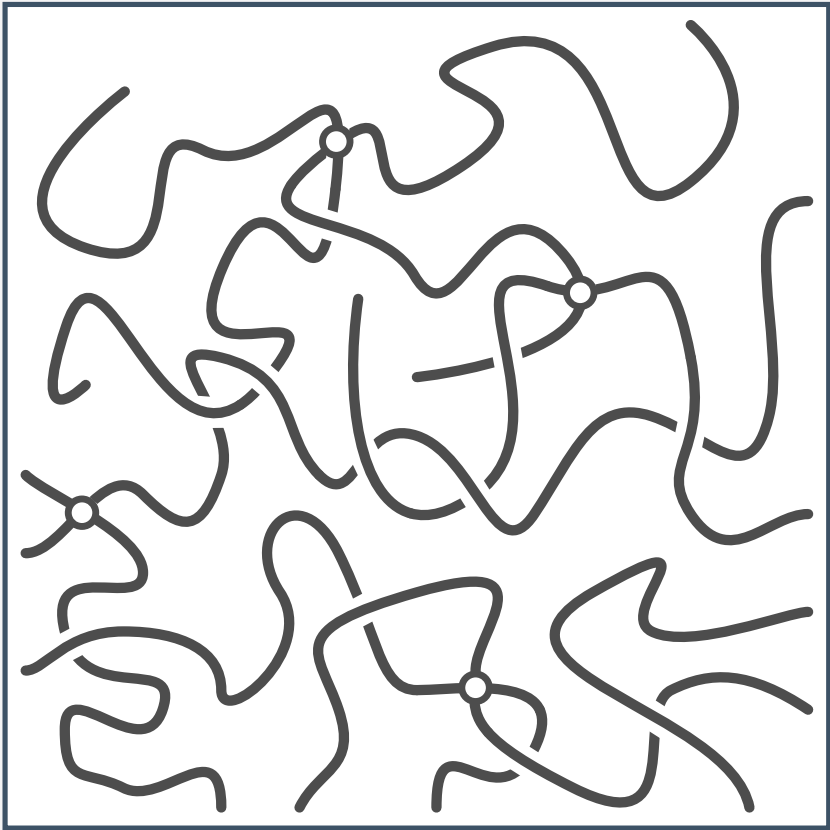
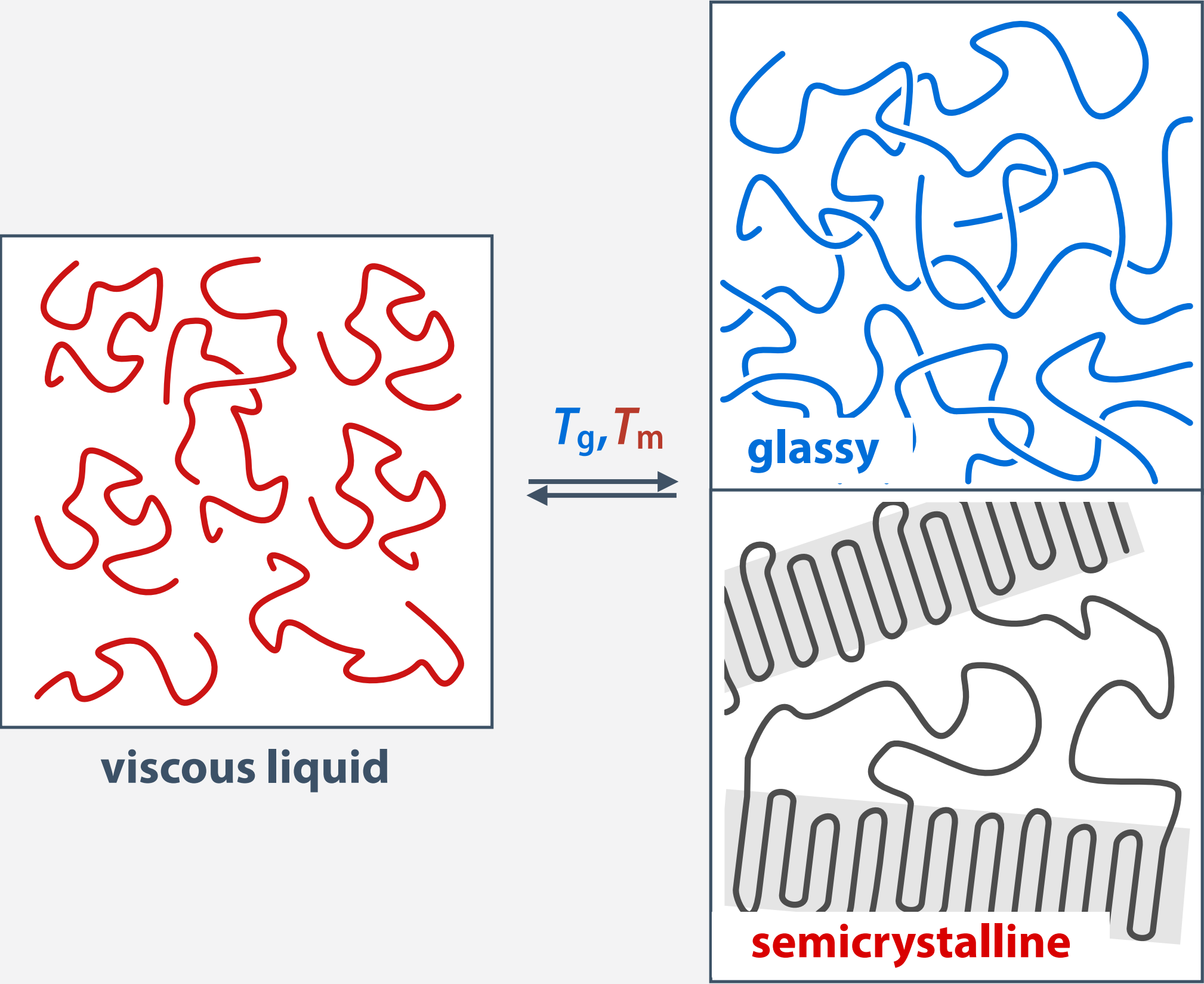
- both T_m and T_g are important parameters that characterise a given polymer

Classification of Polymer Materials According to Structure

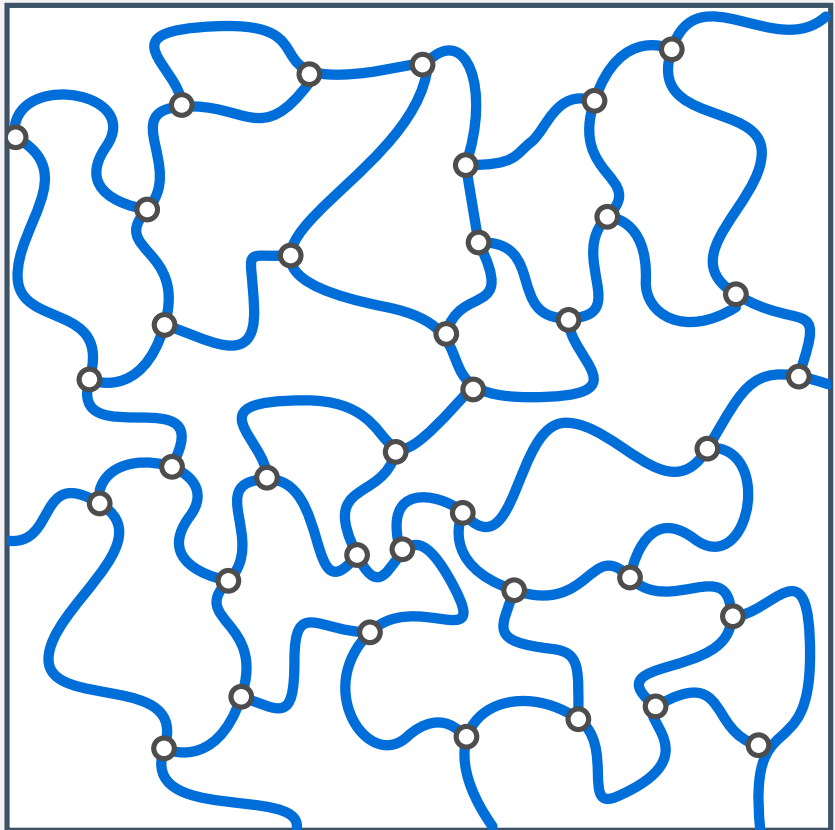
Thermoplastics

Elastomers

Thermosets



slightly cross-linked
soft ($T_g < \text{r.t.}$)



usually glassy, hard
and brittle solids

liquid and processable at high T
(Chapter 5.2)

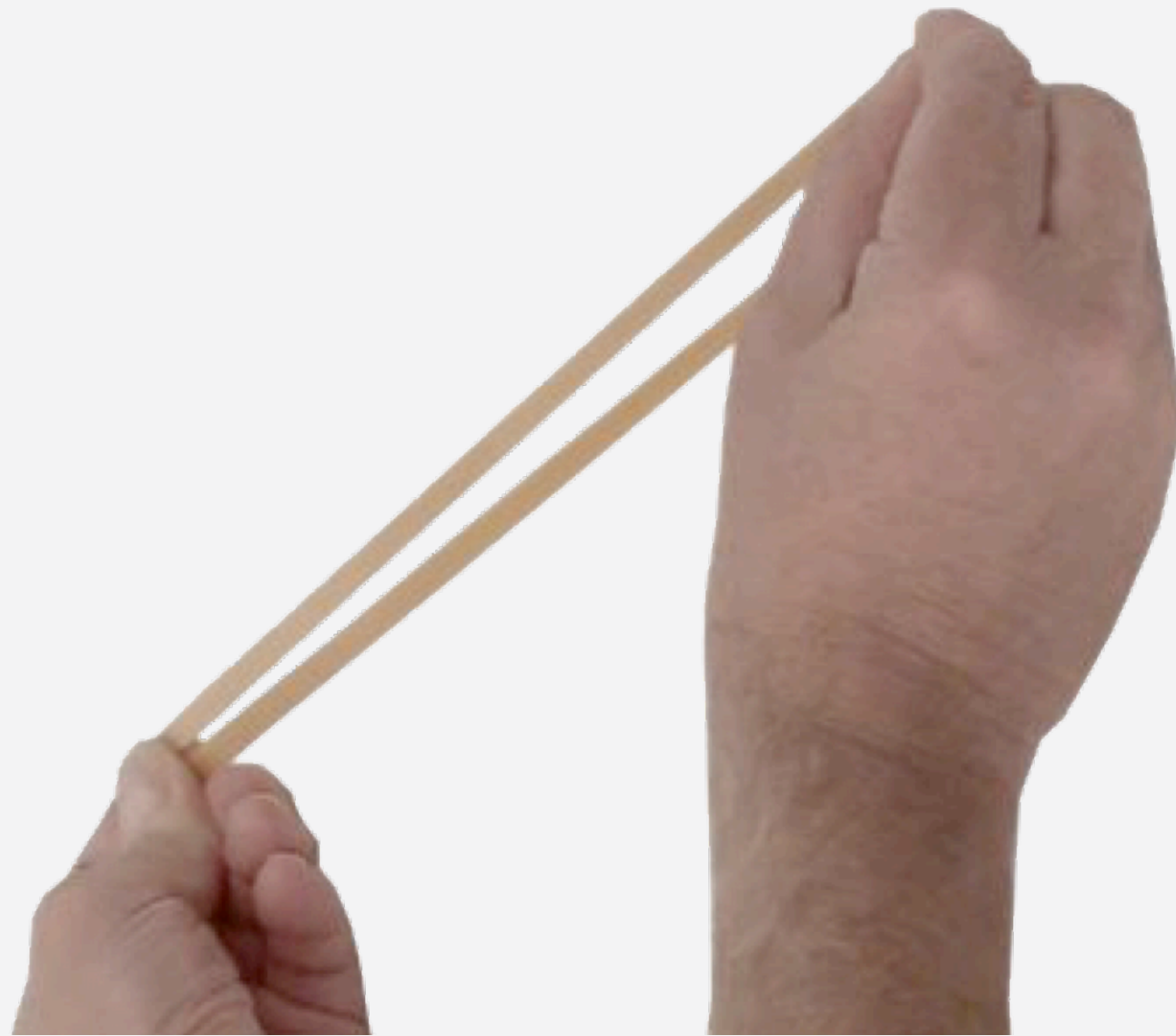
stretchable
(Chapter 5.1)

rigid, intractable
(Travaux Pratique)

Unique Mechanical Properties

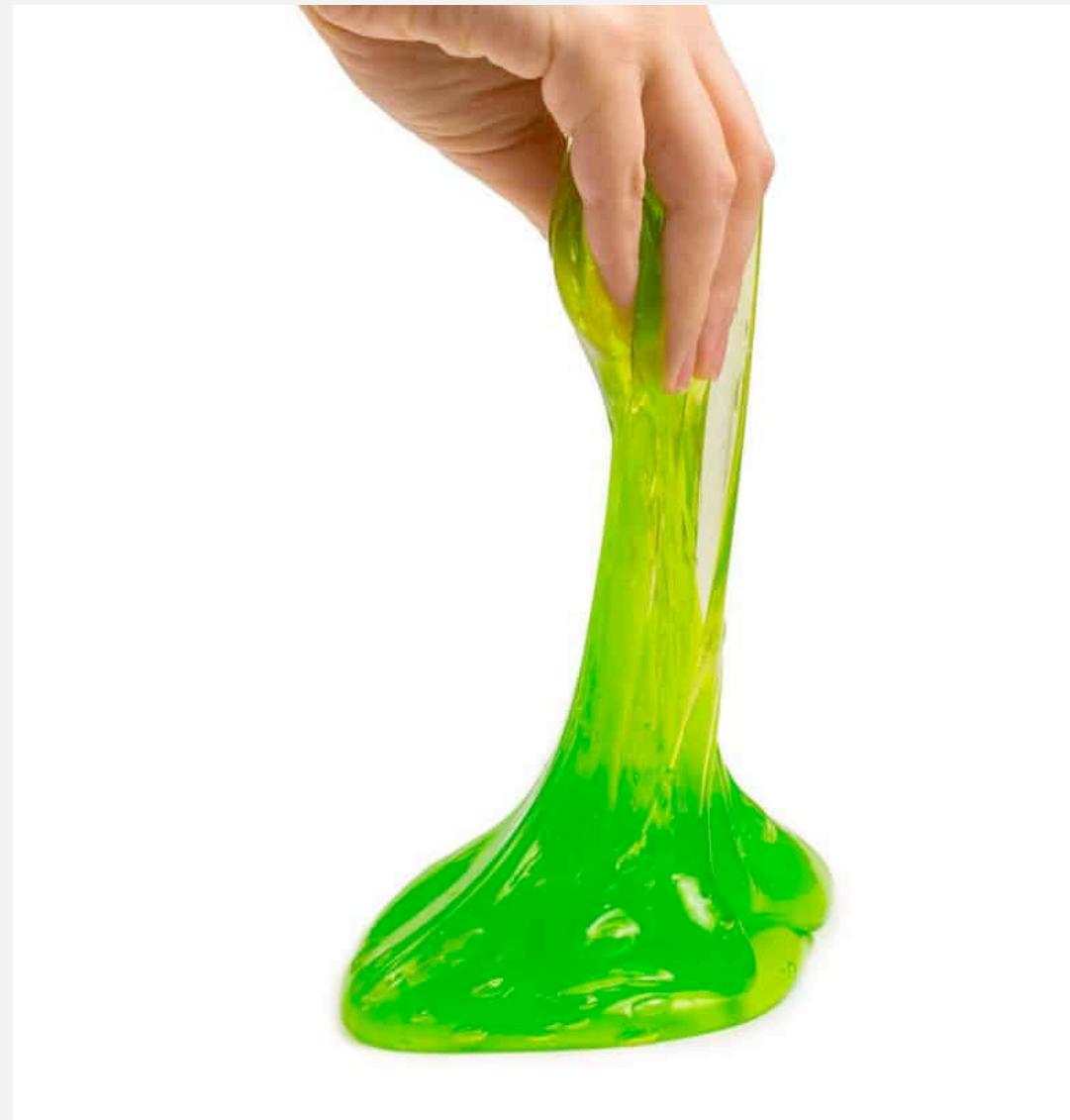
- polymers show unique mechanical properties not shown by other materials classes (see **Chapter 5**)

rubber elasticity



specific to polymers

viscoelasticity



important for processing

plasticity

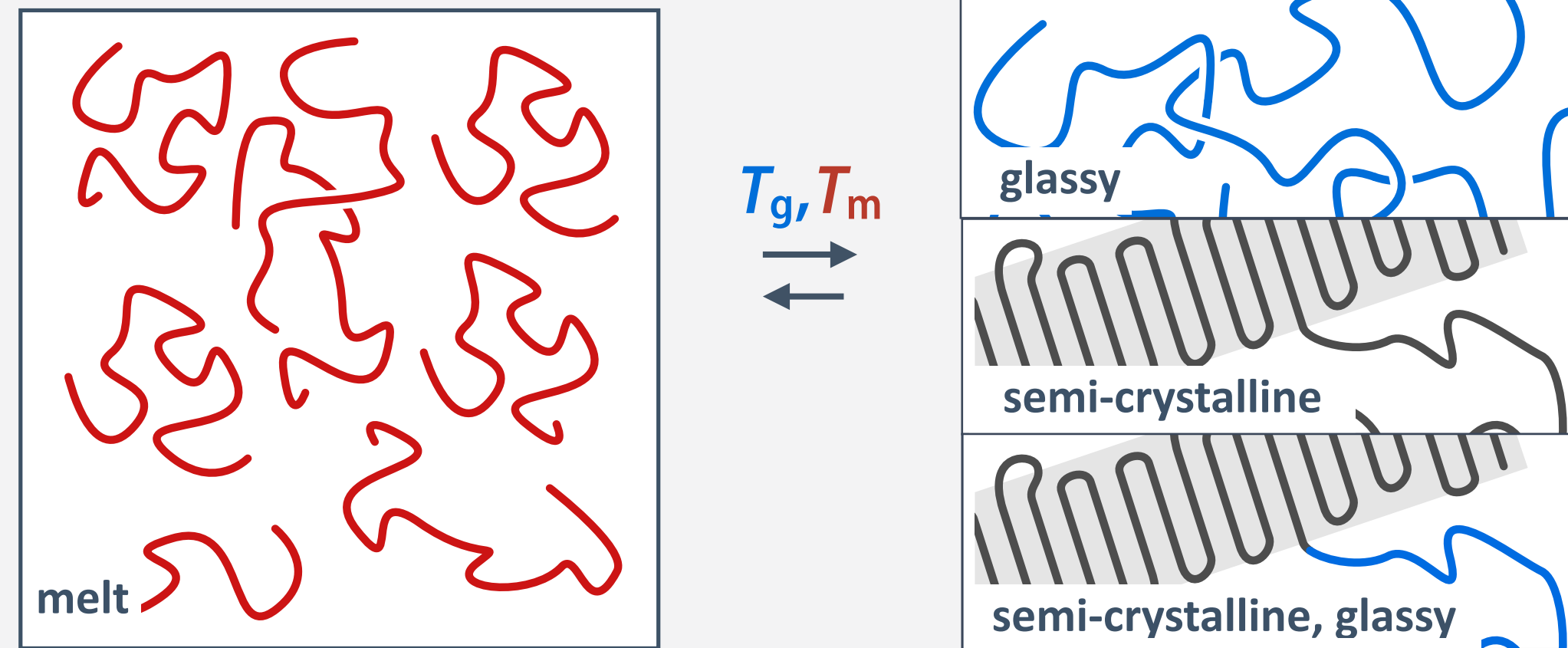


ductile behaviour

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

Synthetic Polymers - Structure & Properties

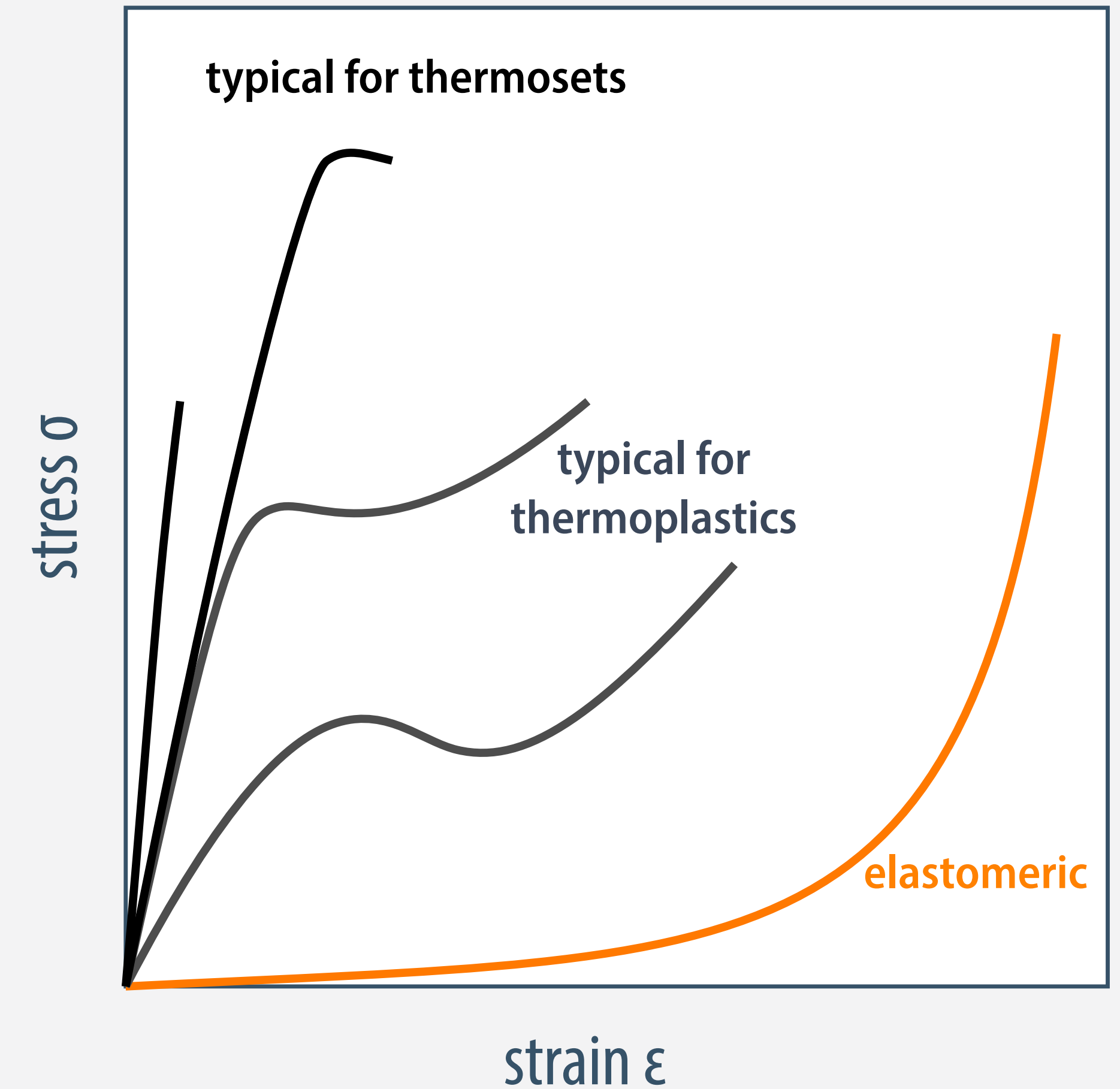
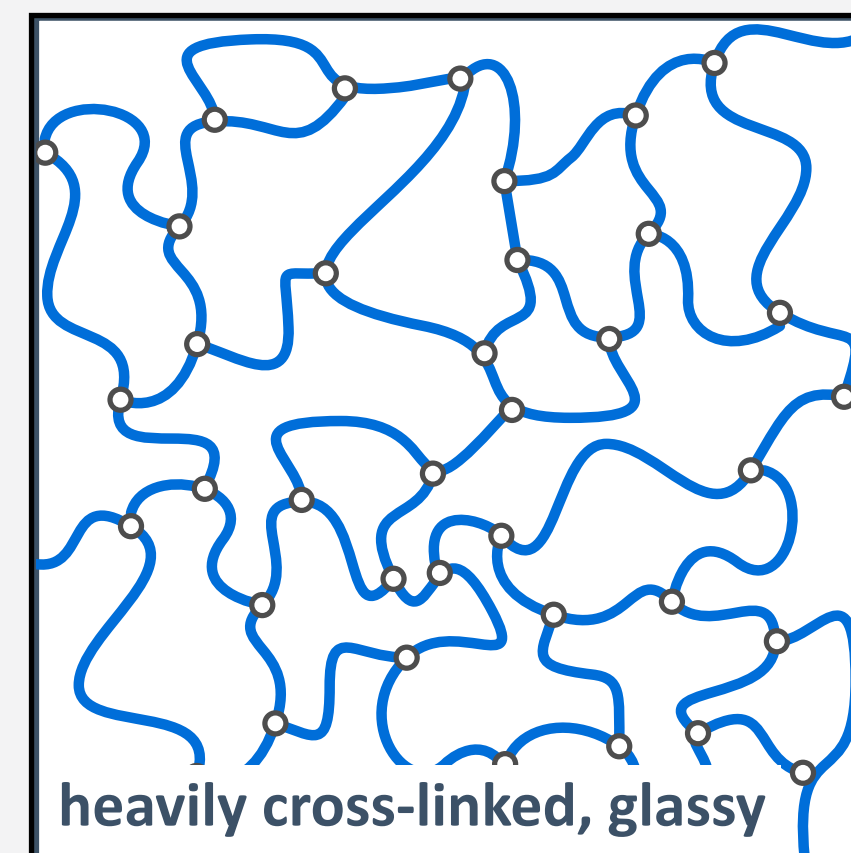
Thermoplastics



Elastomers



Thermosets



Summary

- **polymers, macromolecules:** recognized in the 1920's that they consist of covalently bonded repetitive sequences of subunits derived from monomers
- polymers are characterised by a **molecular weight distribution**, and not by a defined molar mass
- first systematic synthesis in 1938 (Nylon 6,6).
- polymer chemical structures defined by: **composition, configuration (isomers), architectures, copolymers, branching, crosslinking** etc.
- notion of **glass transition temperature** and **melting temperature**
- differentiation of **thermoplastics, elastomers, and thermosets**