5

Polymer Chemistry

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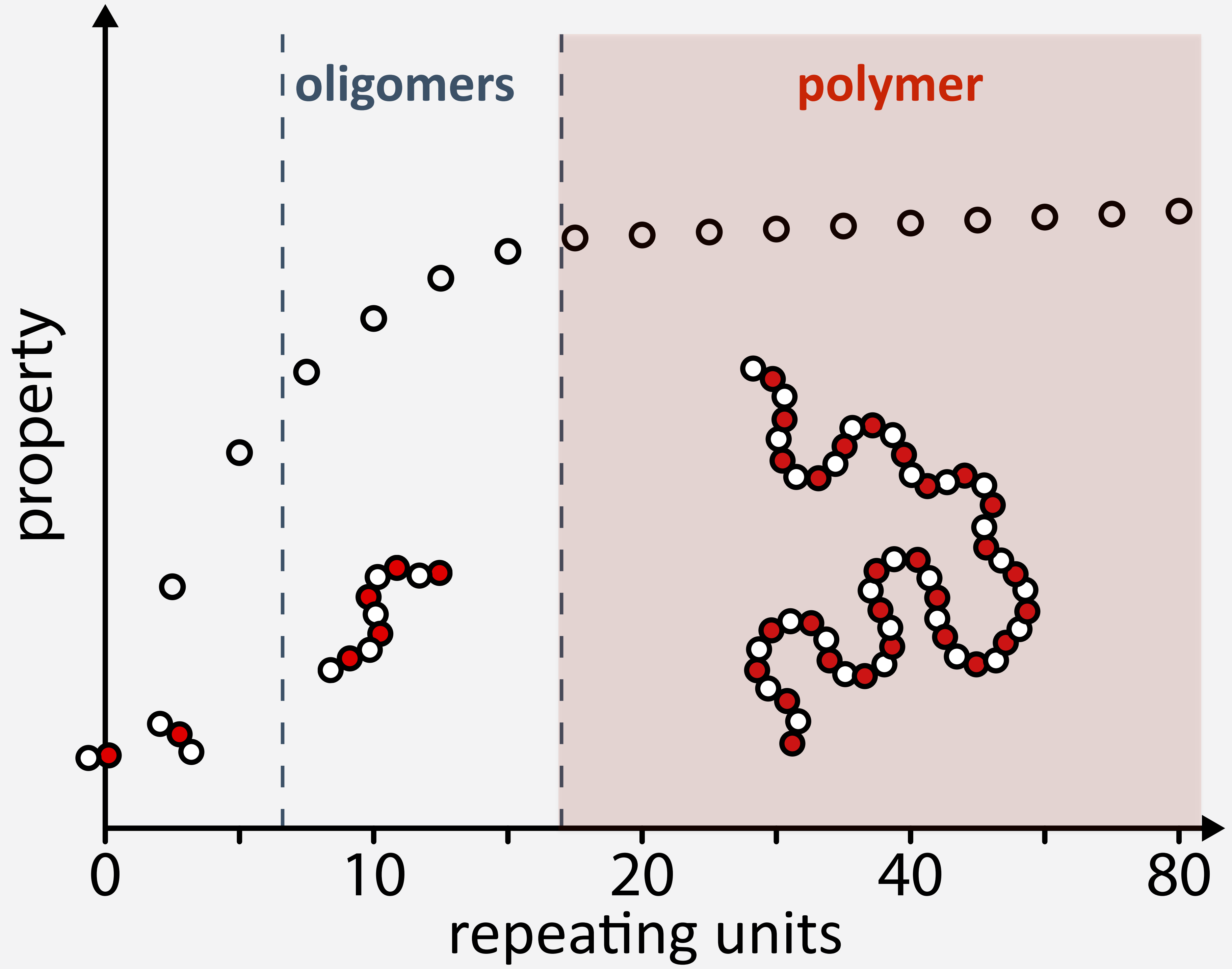
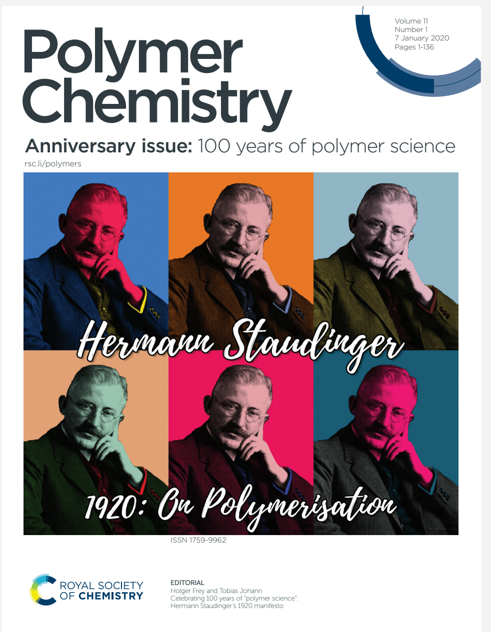
5.1 Introduction to Polymer Chemistry

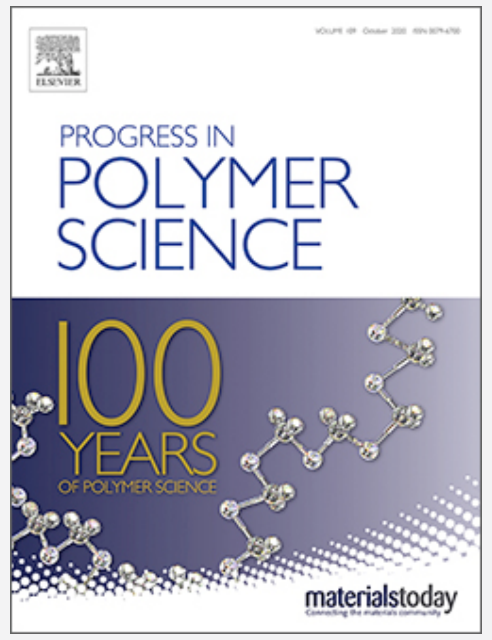
Definition of a Polymer

- definition of a polymer according to Hermann Staudinger:

> *“A polymer is a large molecule constituted from (identical) smaller structural ‘repeat 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**

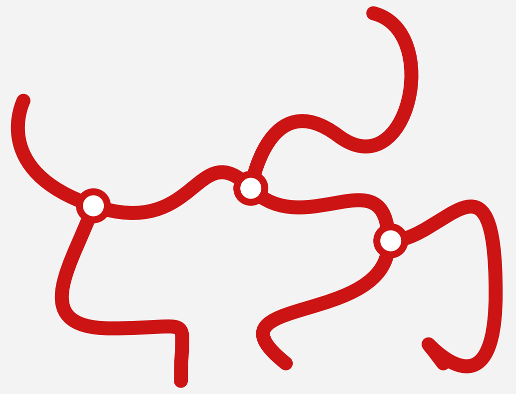
Staudinger, *Helv. Chim. Acta* **1922**, *5*, 785; *Ber. Chem. Ges.* **1920**, *53*, 1073.

Polymer Types and Chain Architectures

- **homopolymers: just one type of repeating units, but different chain architectures possible**


linear


star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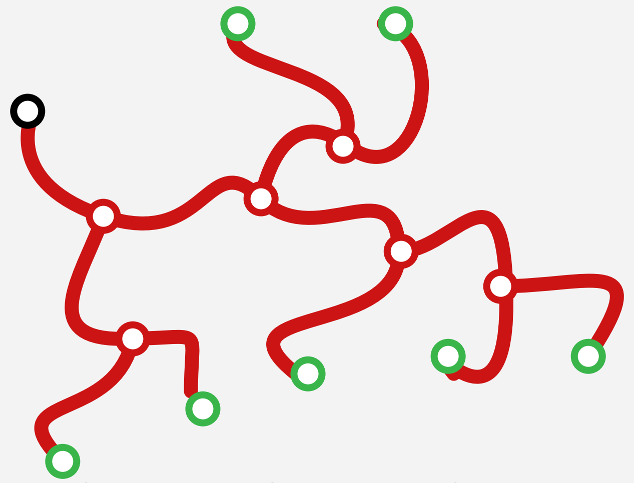
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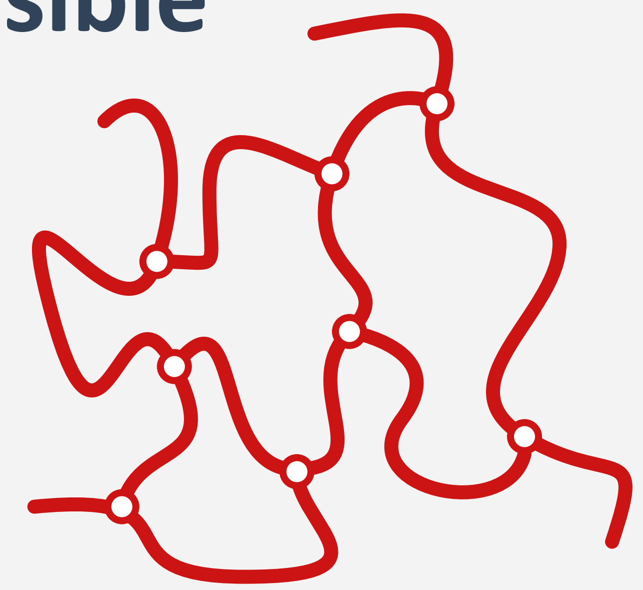
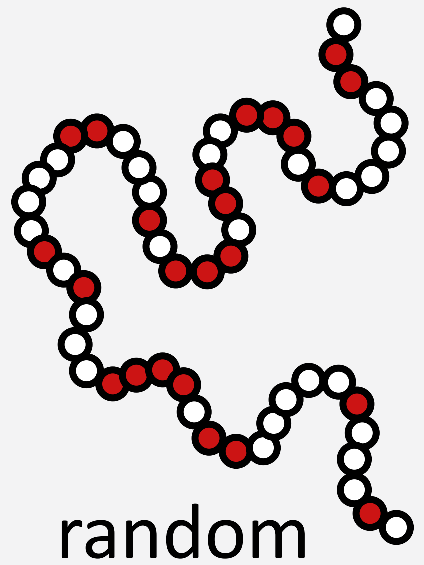

network

- **copolymers from different types of repeat units (and chain architectures)**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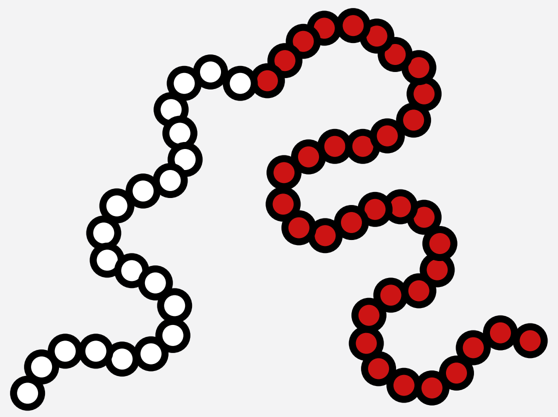
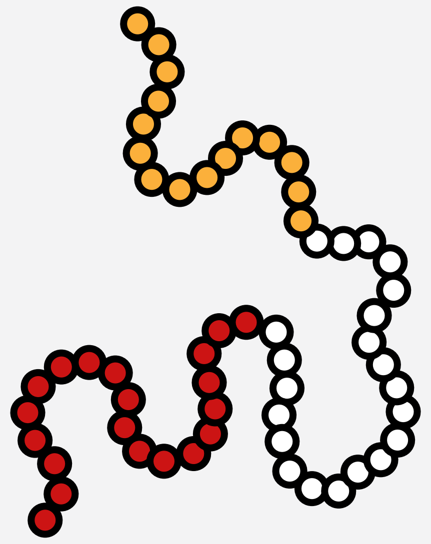

AB diblock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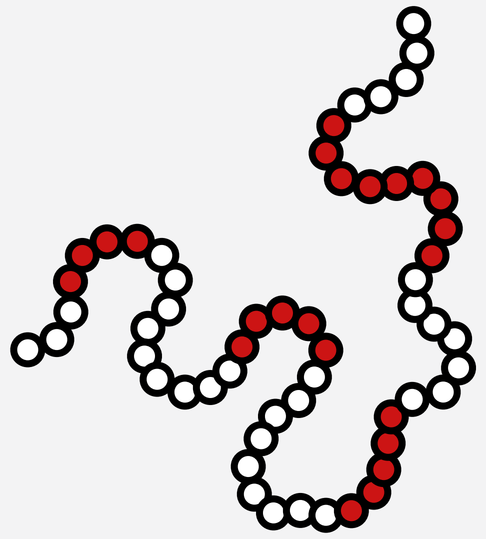
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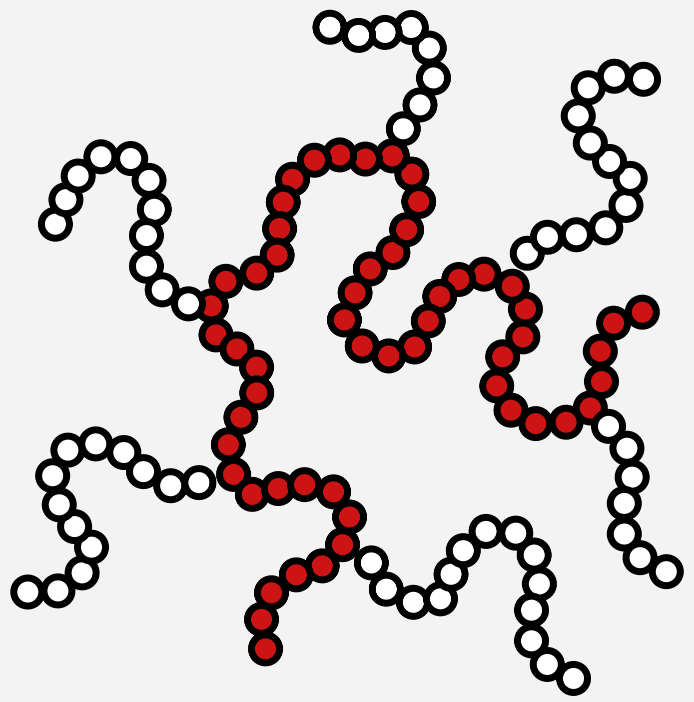
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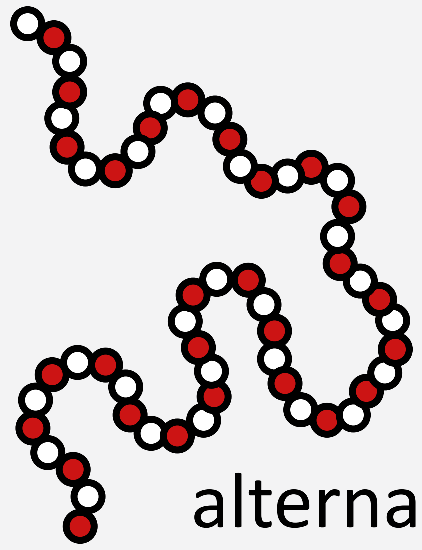
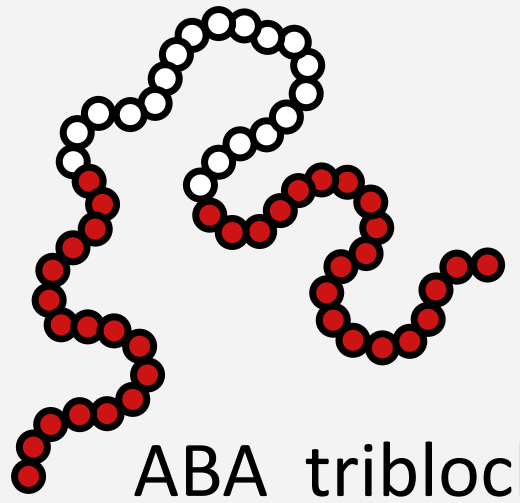

alternating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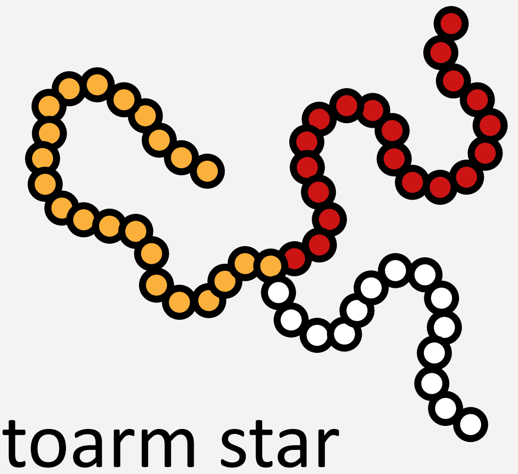
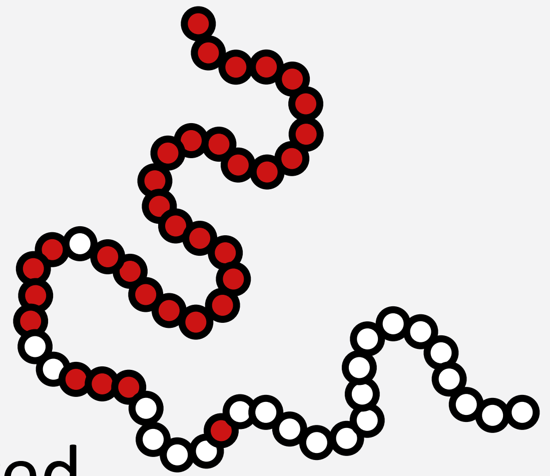

miktoarm star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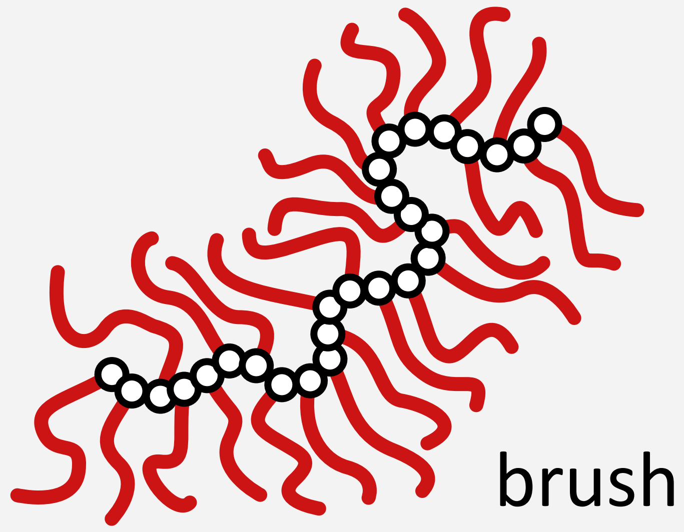
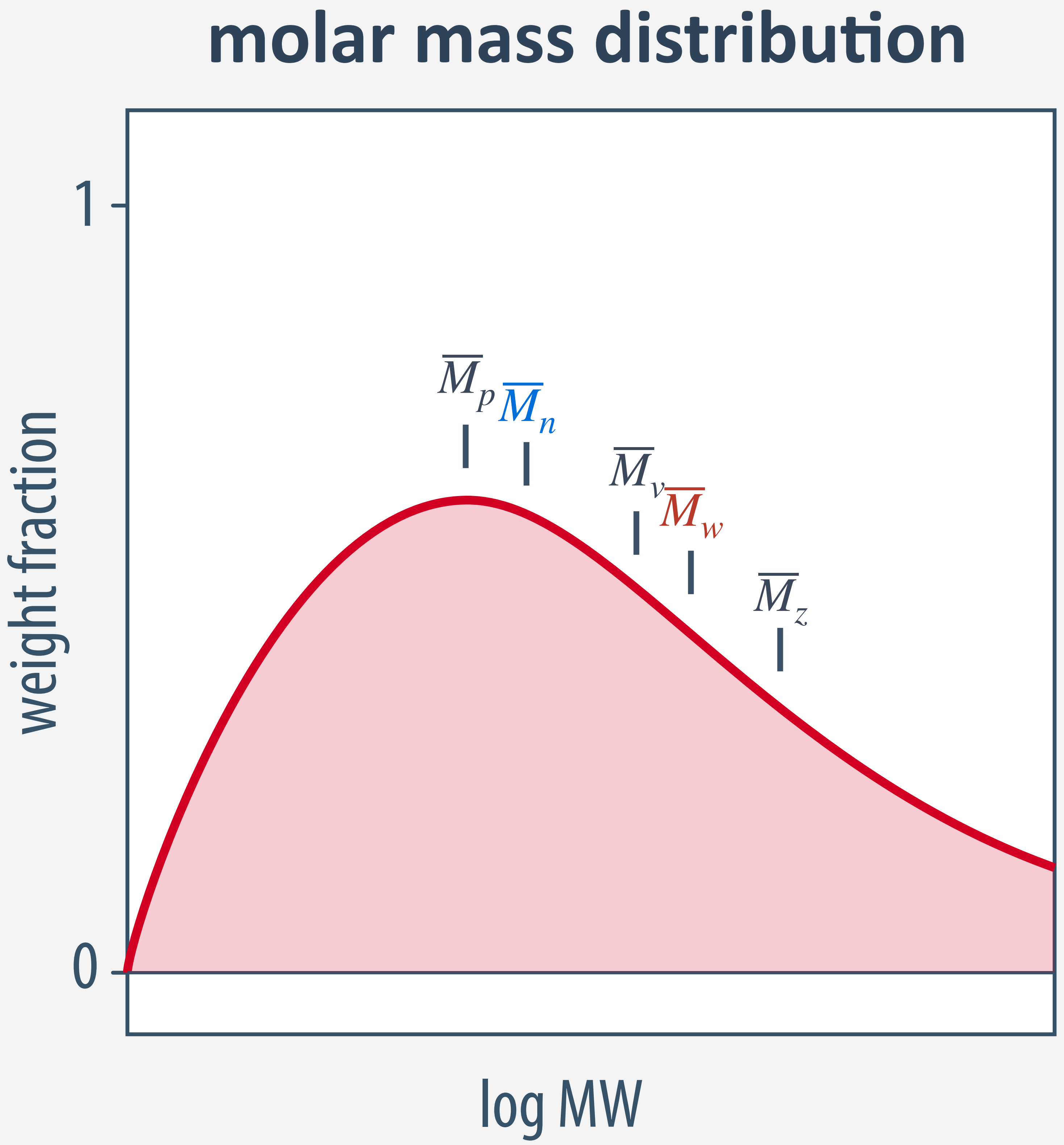

brush

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)

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

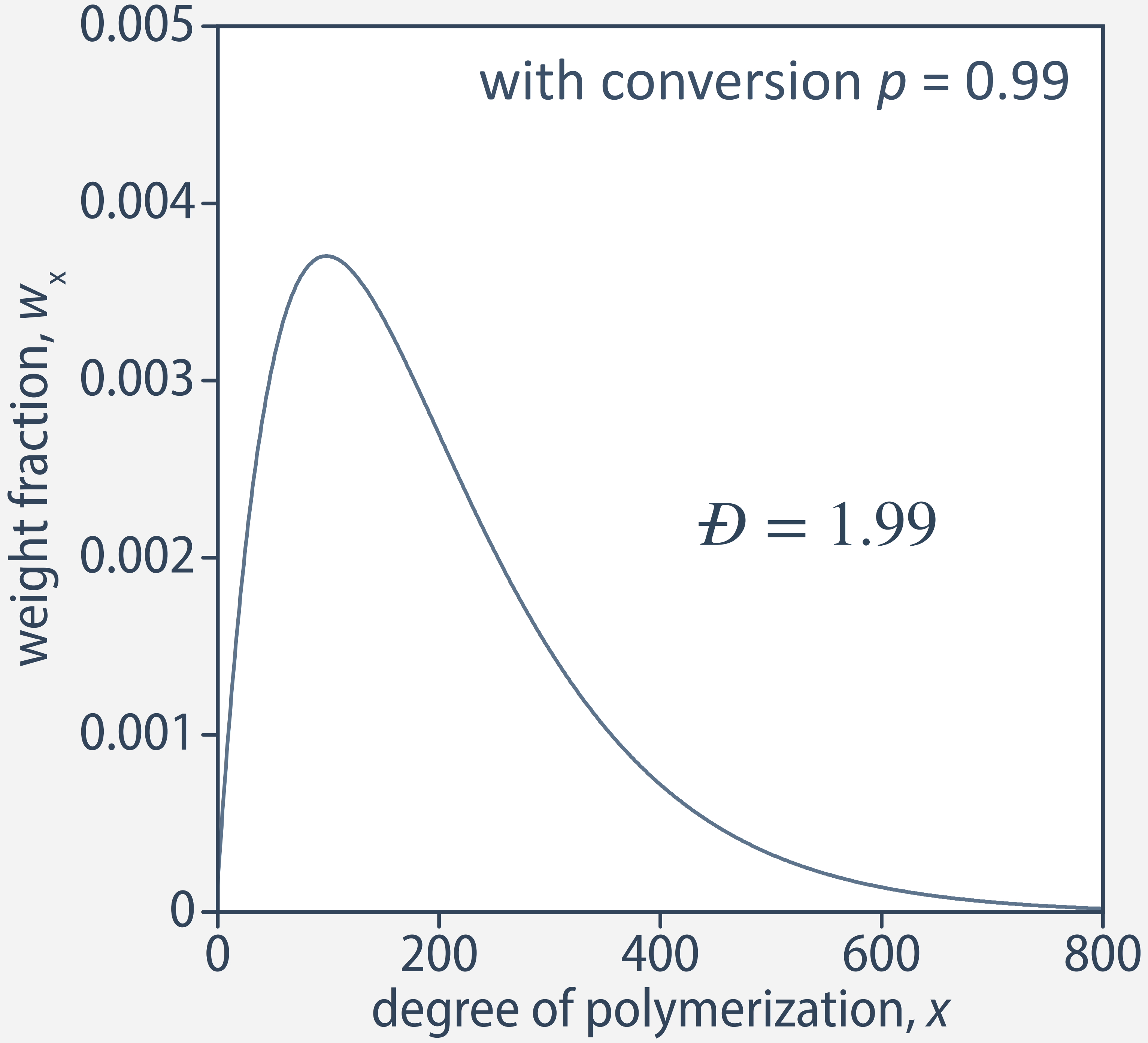
- **polymers do not have defined molar masses but molar mass distributions**
- **different molar mass averages based on “moments” (μ') of the molar mass distribution**

Key concept: See reader on *Molar Masses*

Common Distributions in Polymer Materials

Schulz-Flory distribution

$$w_x = x(1-p)^2 p^{x-1}$$



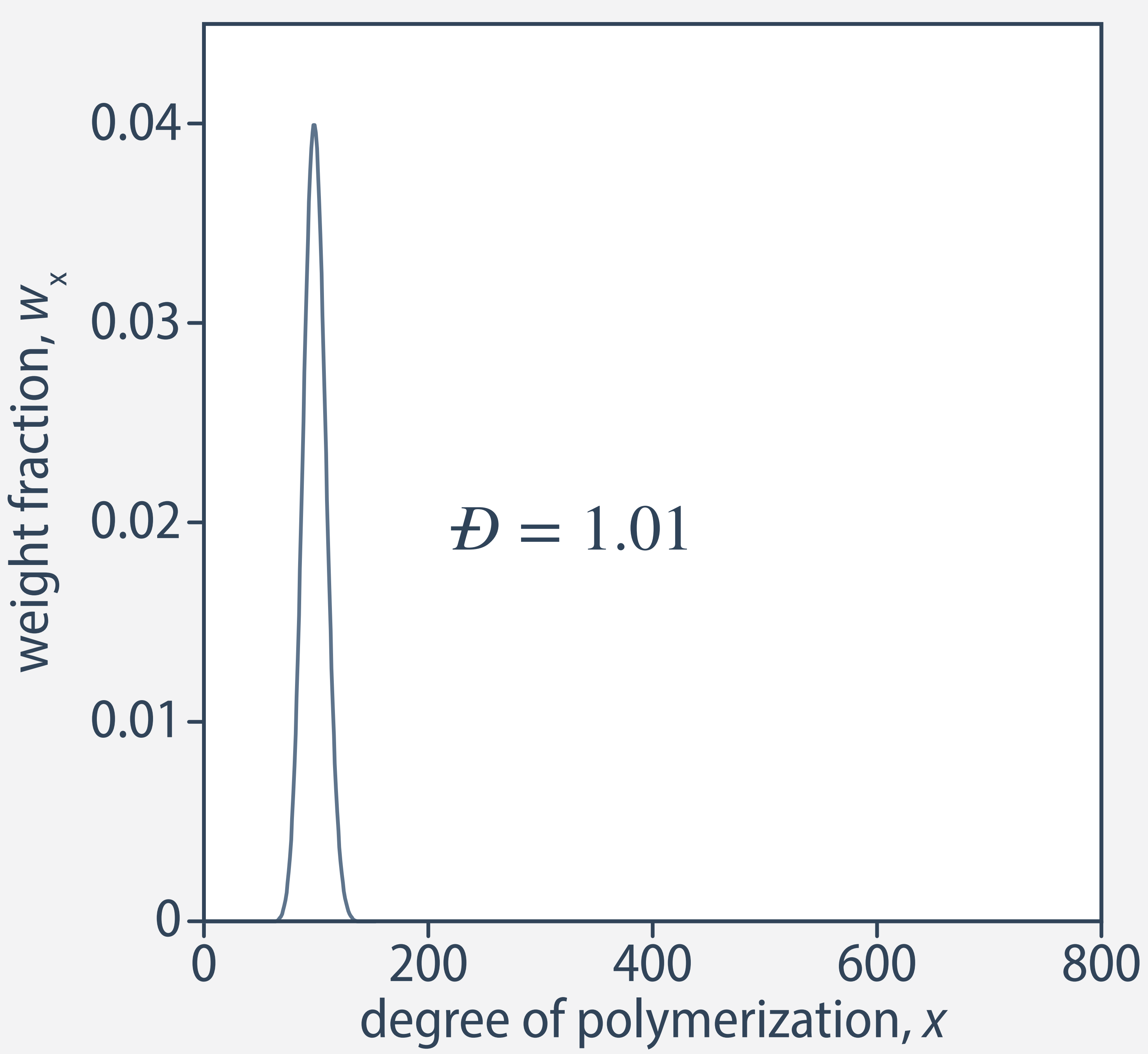
with conversion p = 0.99

Đ = 1.99

- **step-growth polymerization**
- **free radical polymerization**

Poisson distribution

$$w_x = \frac{e^{-\mu}\mu^x}{x!}$$

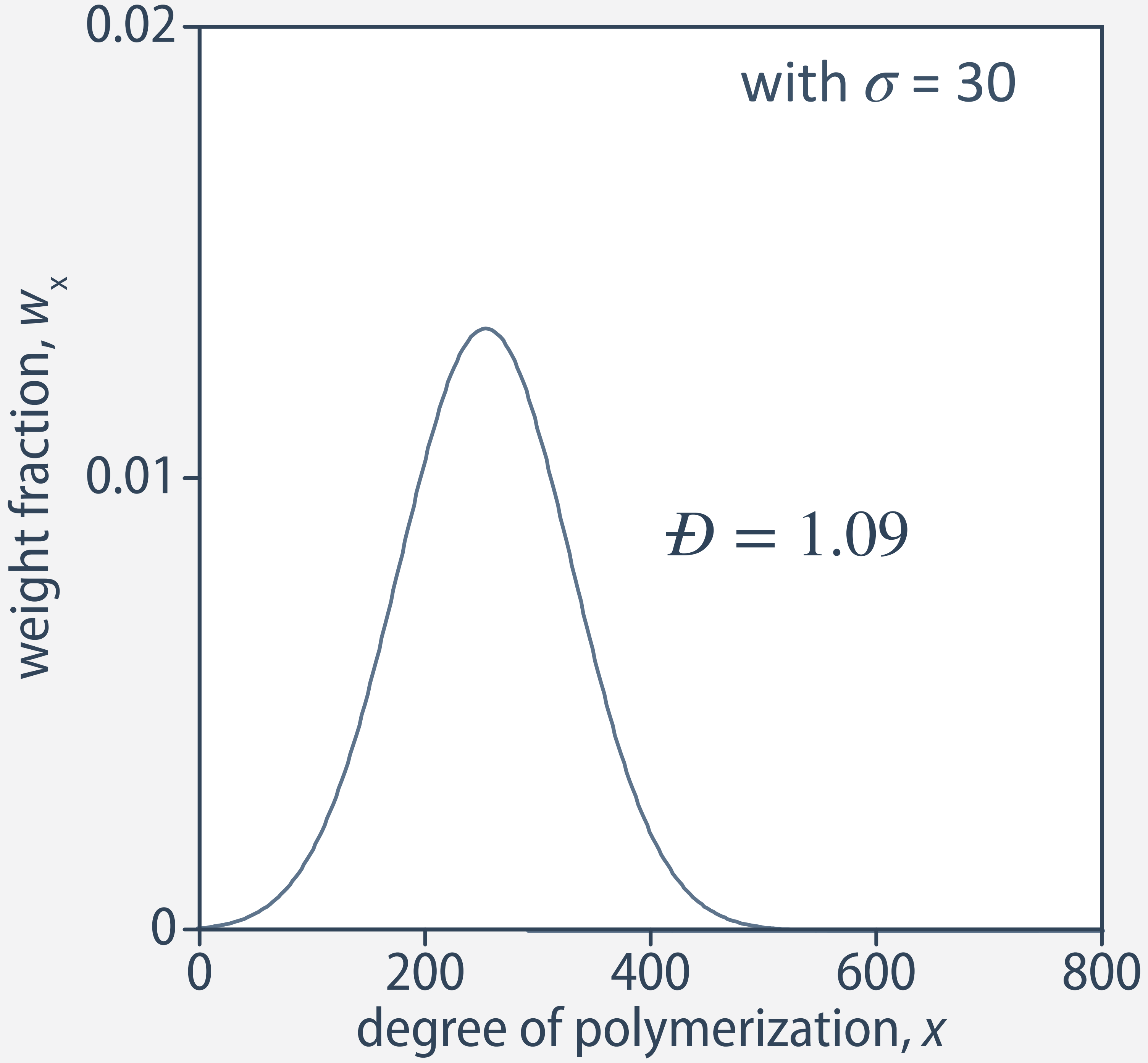


Đ = 1.01

- **living polymerization**
- **controlled polymerization**

Gaussian distribution

$$w_x = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$



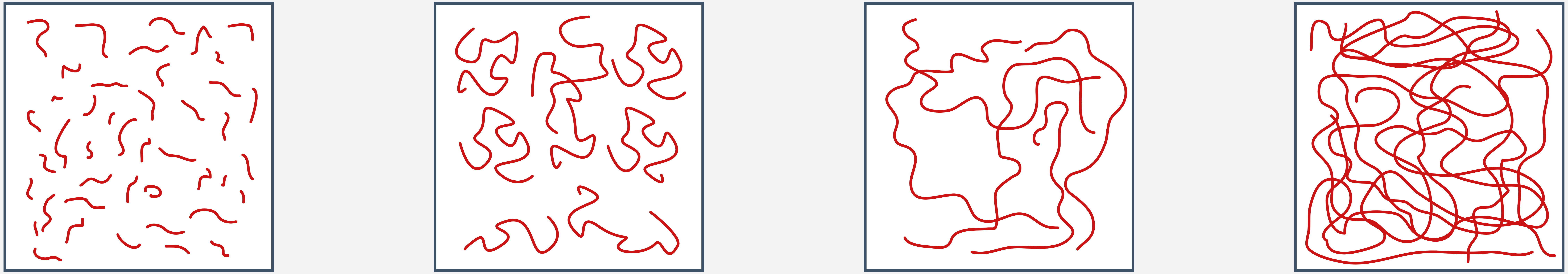
with σ = 30

Đ = 1.09

- **Ziegler-Natta polymerization**

μ = 100 in each case

Influence of Chain Length on Physical Properties



liquid oil wax solid

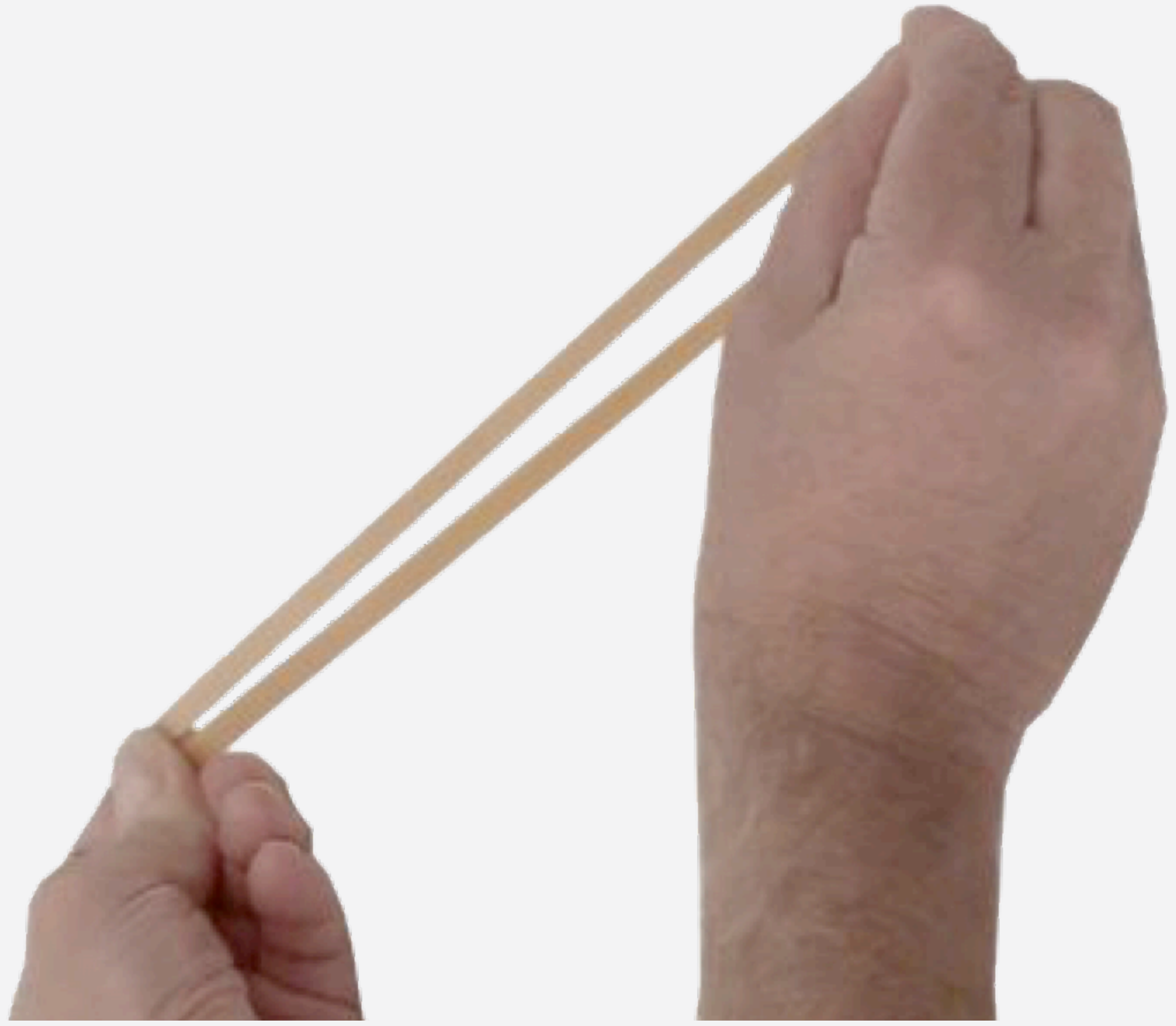
number of C atoms	aggregation state (25 °C)	example	use case
1–4	gas	propane	gaseous fuel
5–15	low-viscosity liquid	gasoline	liquid fuel
16–25	high-viscosity liquid	motor oil	oils and greases
20–50	soft solid	paraffin wax	candles and coatings
> 1000	tough plastic material	polyethylene	bottles and toys

- **increasing cohesive energy and entanglement finally give rise to “typical” polymer properties**

Unique Mechanical Properties

- polymers show unique mechanical properties not shown by other materials classes

rubber elasticity



large elastic deformation
specific to elastomers

viscoelasticity

viscoelastic in the melt state
important for processing

plasticity

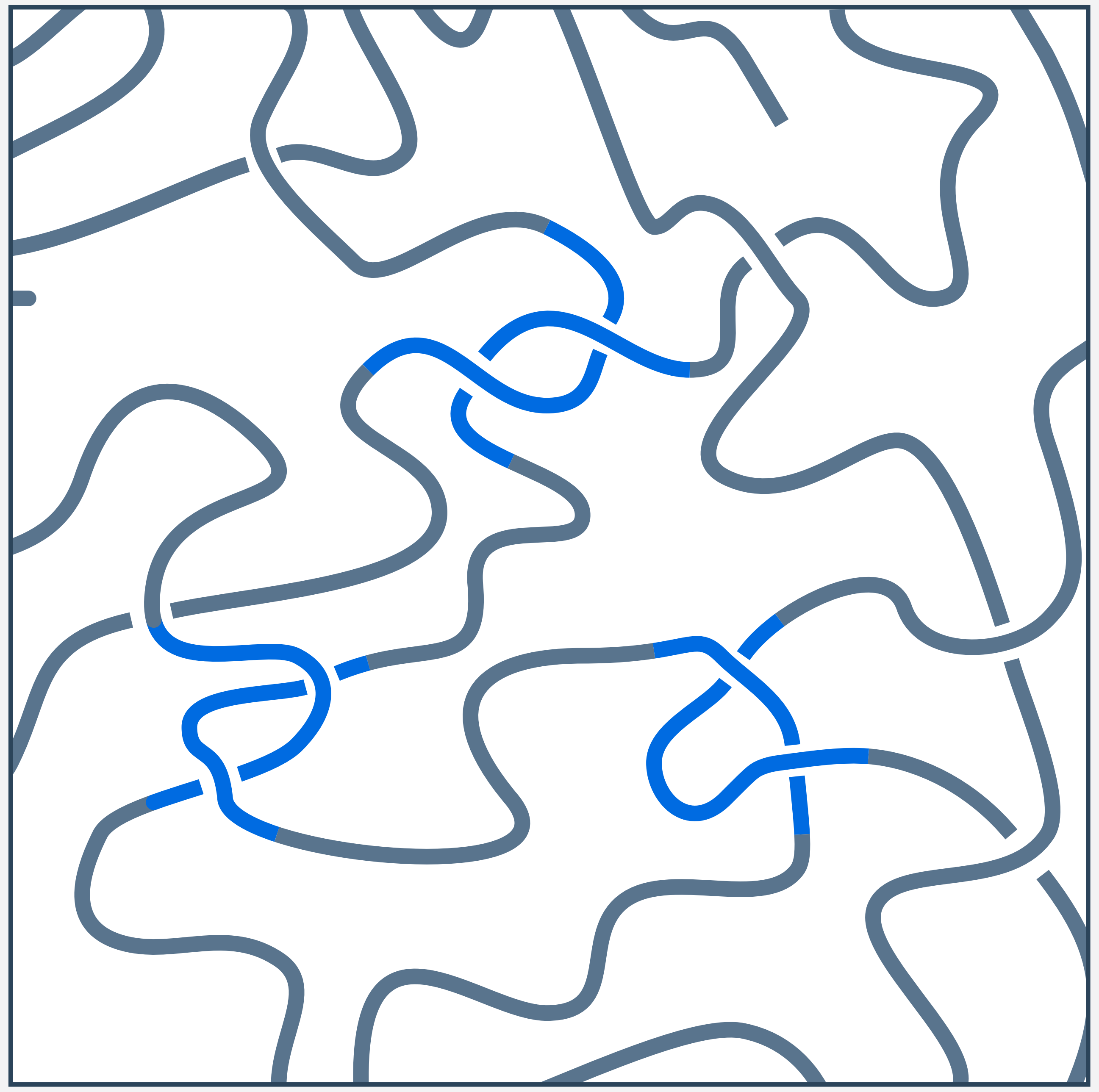
ductile behavior, plastic deformation
important for processing

- **strength, toughness, impact resistance, ductility, melt elasticity increase with molar mass**

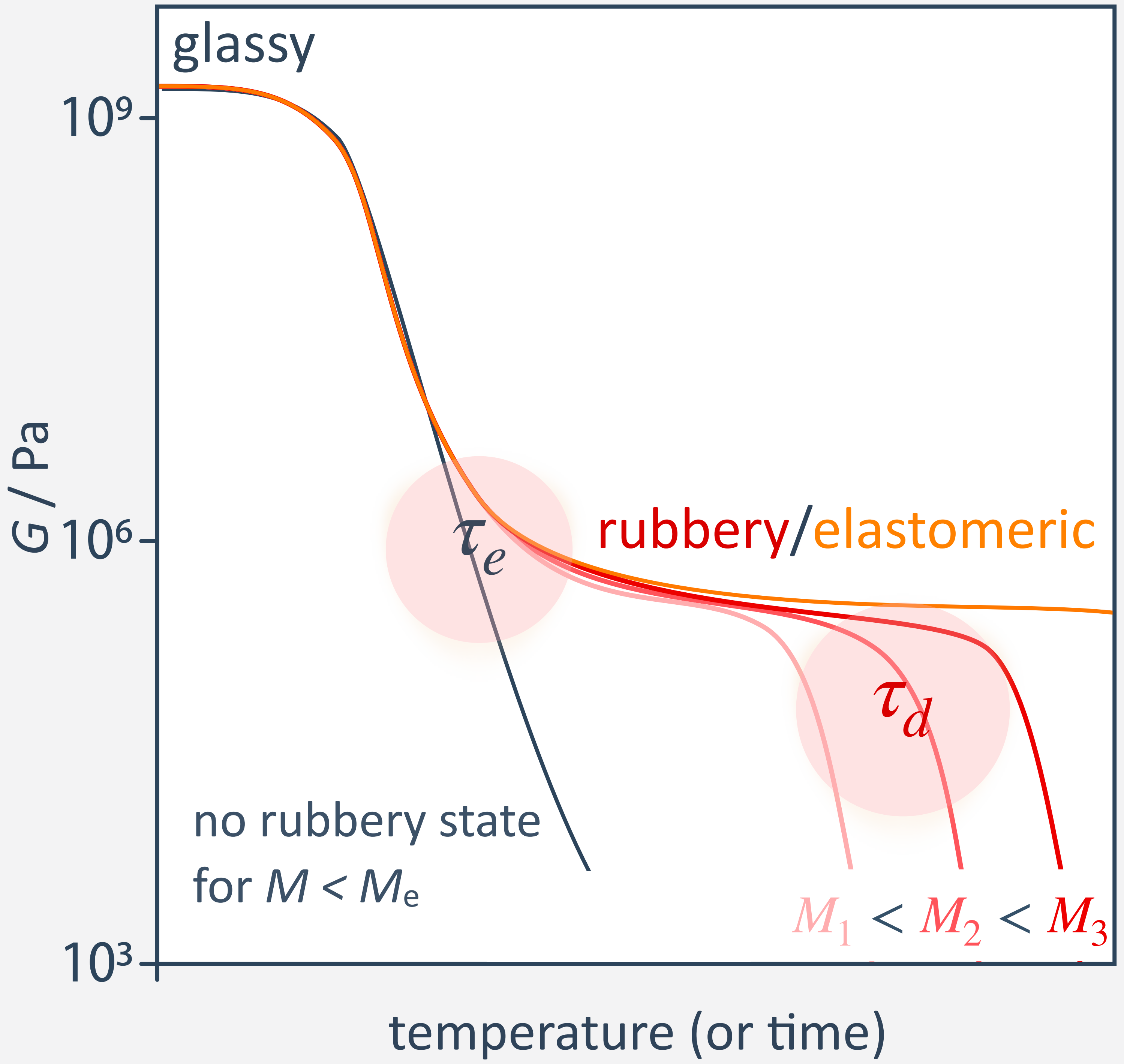
Entanglement and Viscoelasticity

- 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



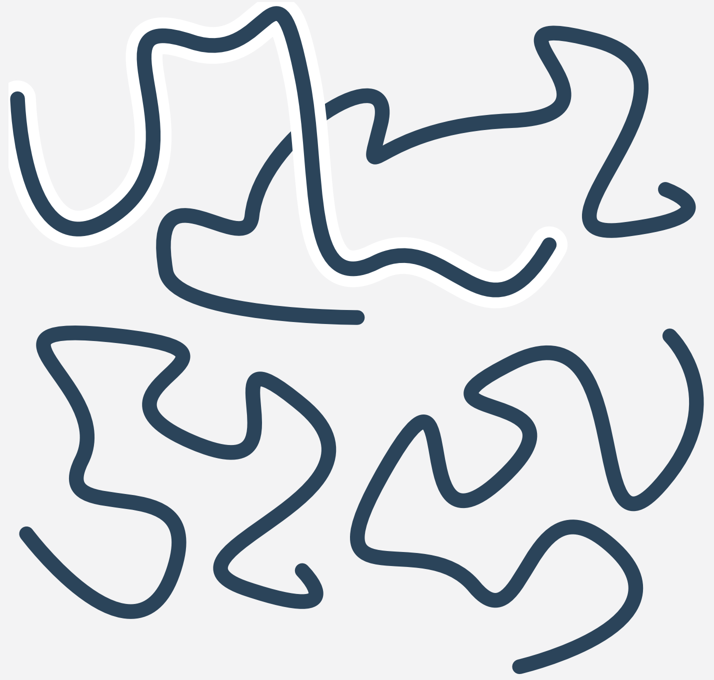
rubbery state above T_g



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)**

Thermal Transitions of Polymers



polymer melt

glass transition

vitrification ↔ softening

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

T_g

T_g, T_m

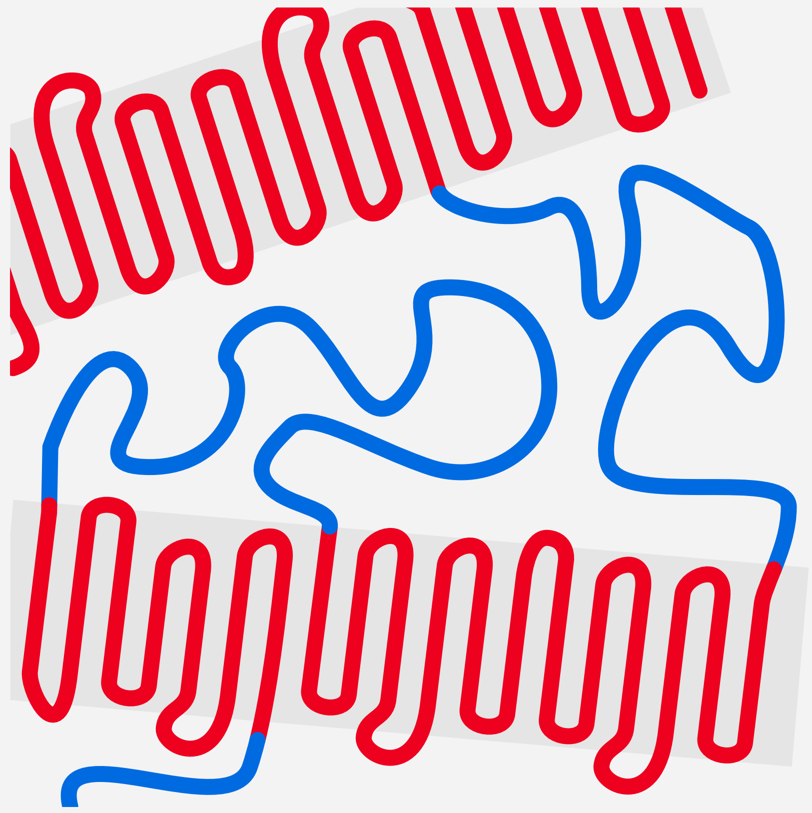
T_m

melting temperature

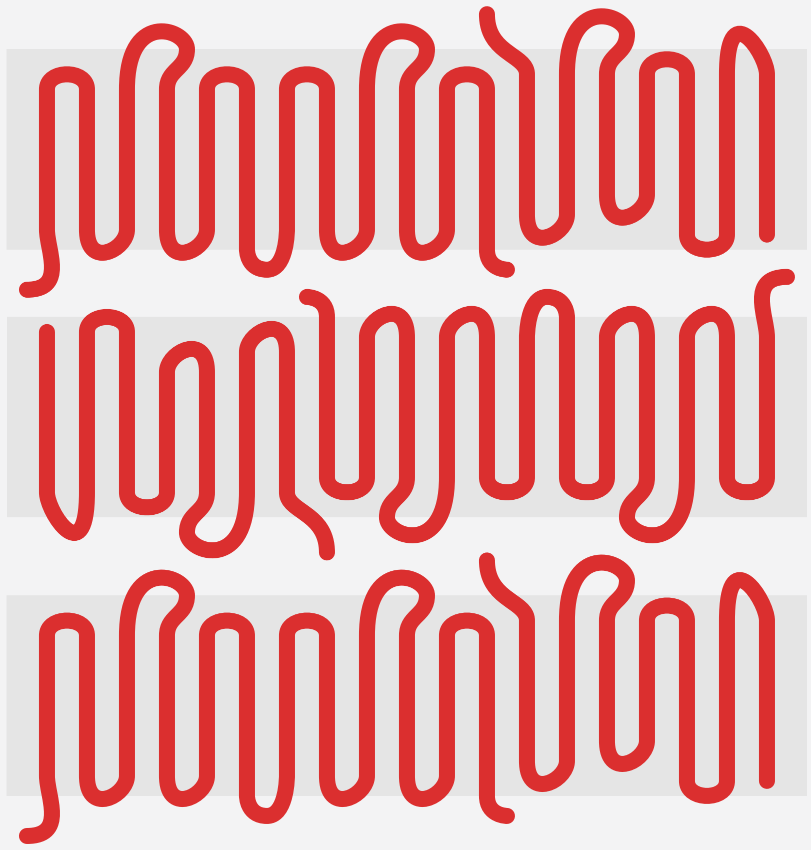
crystallization ↔ melting

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

amorphous, glassy



semi-crystalline

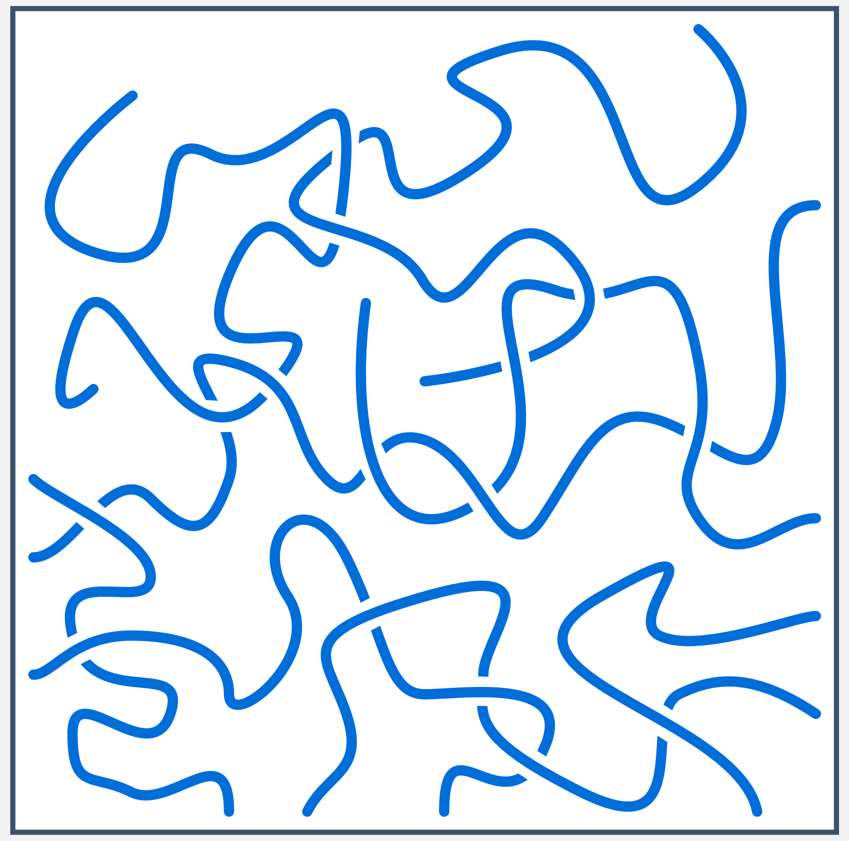


monocrystalline

- **T_m and T_g are important intrinsic materials parameters; crystallization strongly dependent on kinetics**

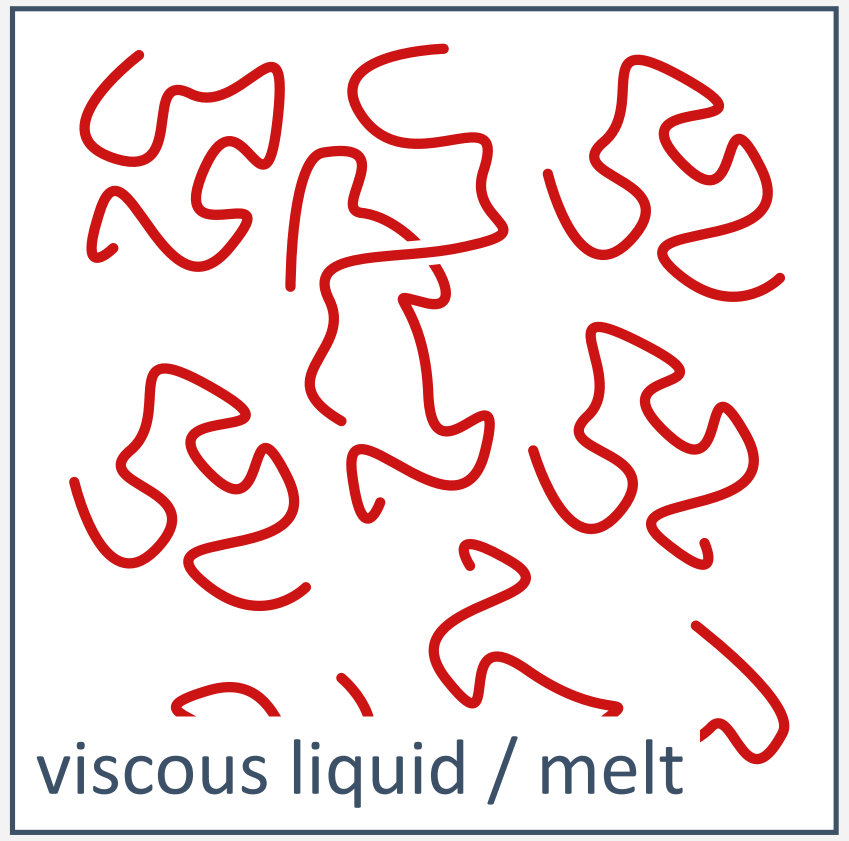
Classification of Polymers According to Structure

Thermoplastics

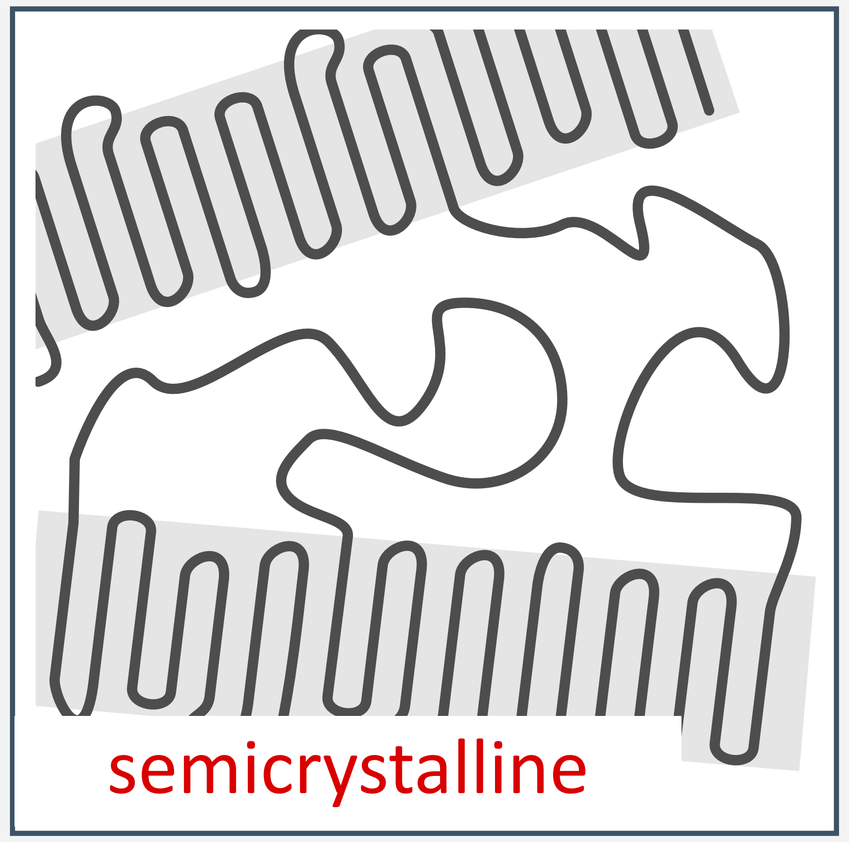


polystyrene
T_g = 100 °C

T_g, T_m
$\rightleftarrows$

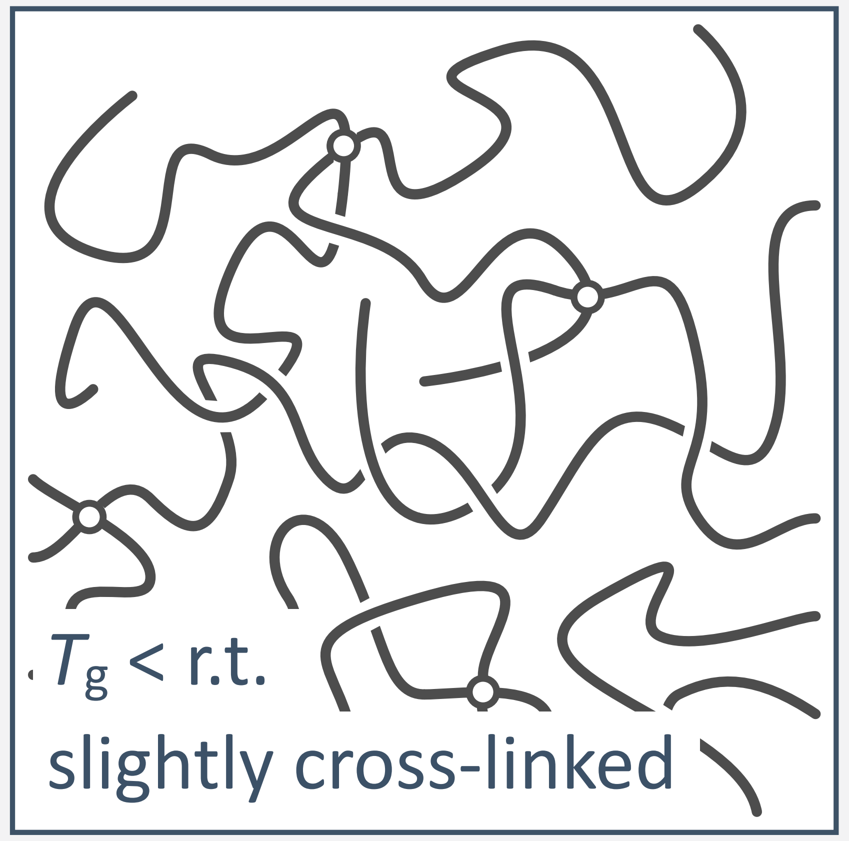


silicones
$T_g = -123$ °C
$T_m = -40$ °C



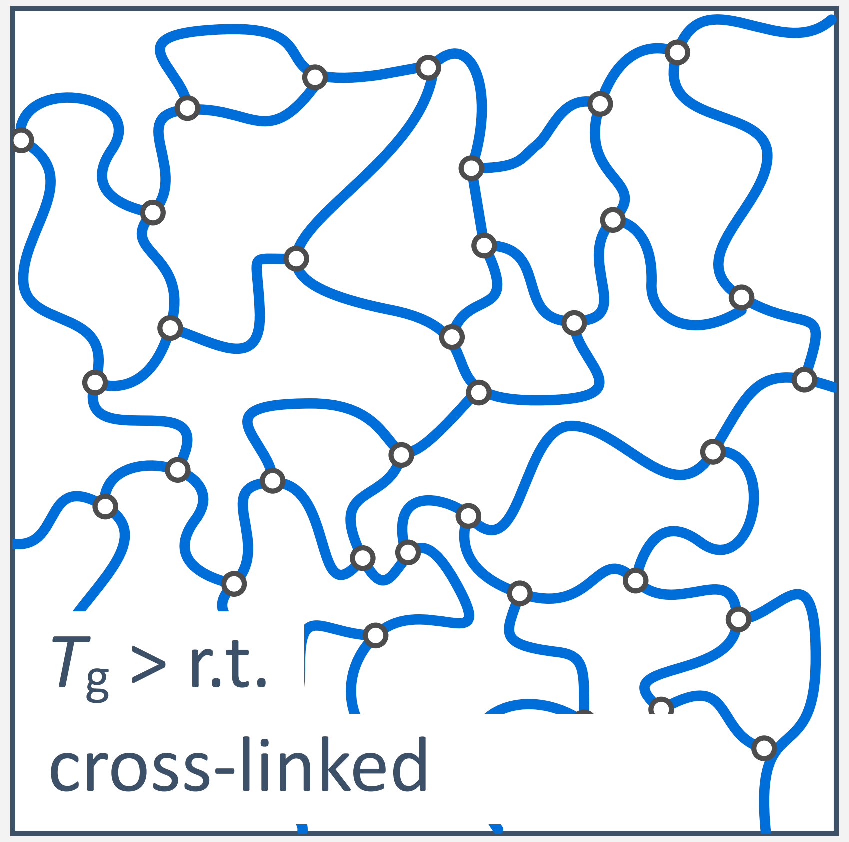
polyethylene
$T_g = -50$ °C
T_m = 140 °C

Elastomers



polyisoprene
$T_g = -73$ °C

Thermosets



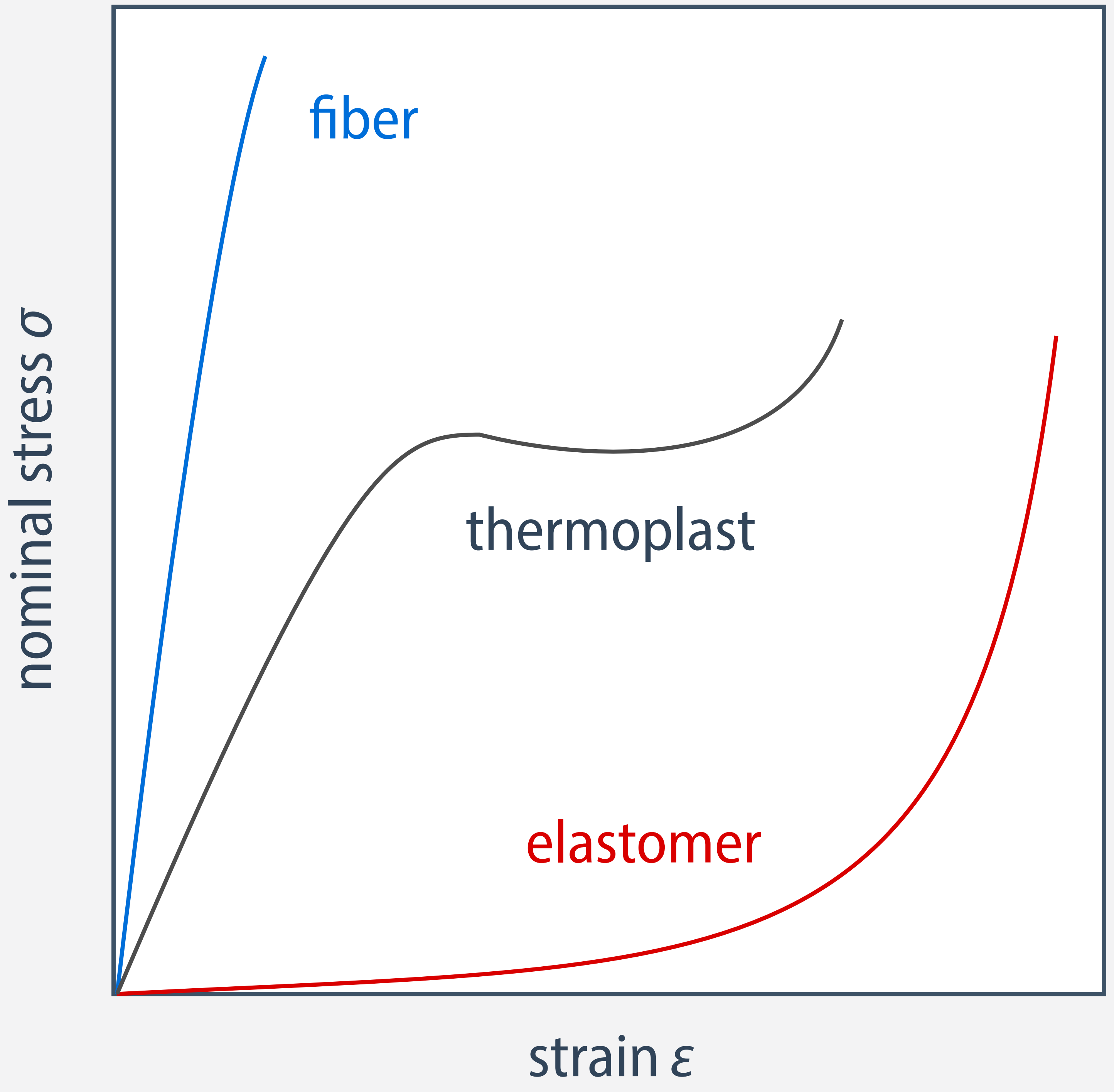
epoxy resin

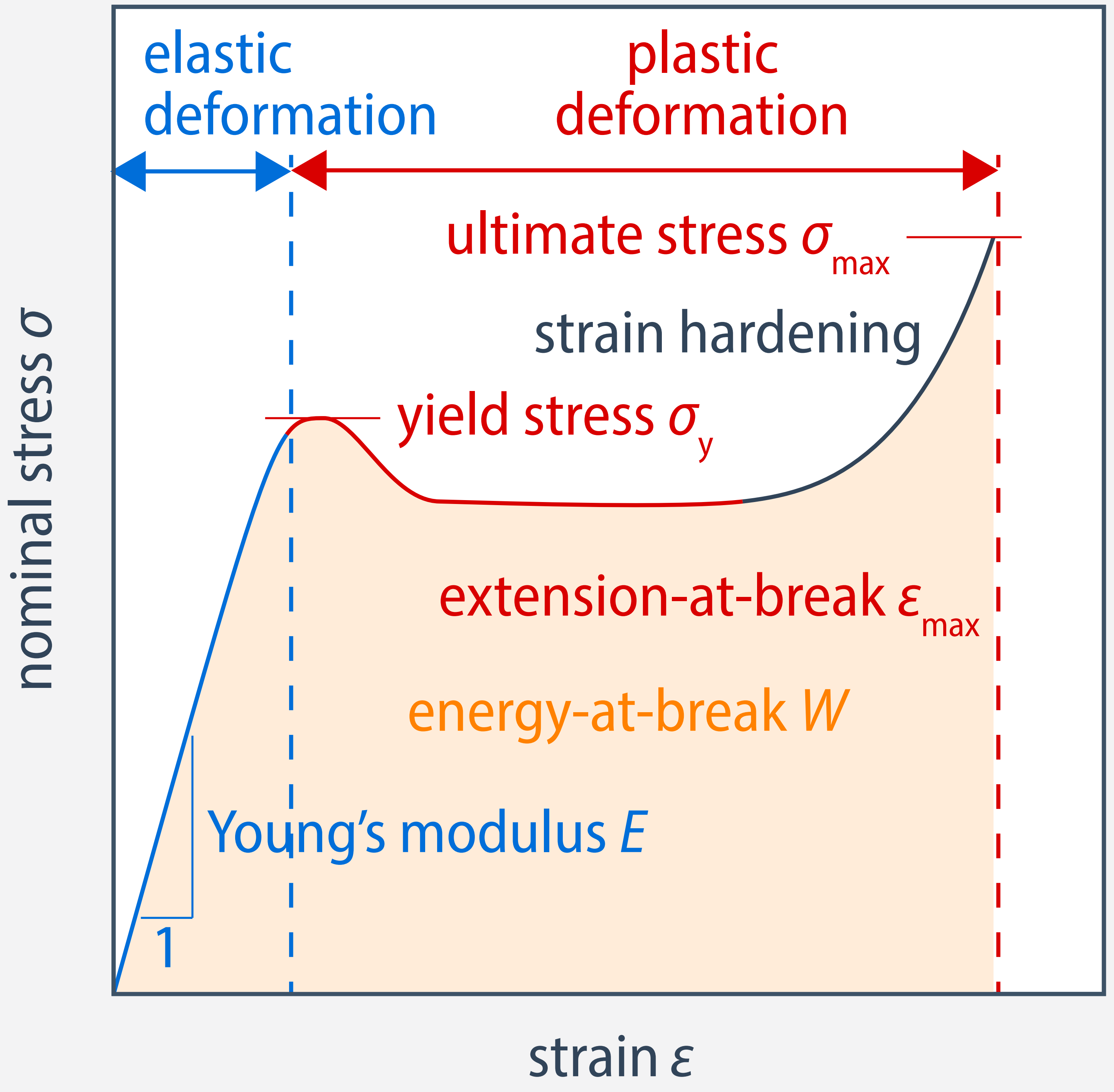
liquid, processable, recyclable at high temperatures

rubber elasticity

rigid, intractable

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**