New Ideas. New Materials.

UNIVERSITÄT DES SAARLANDES

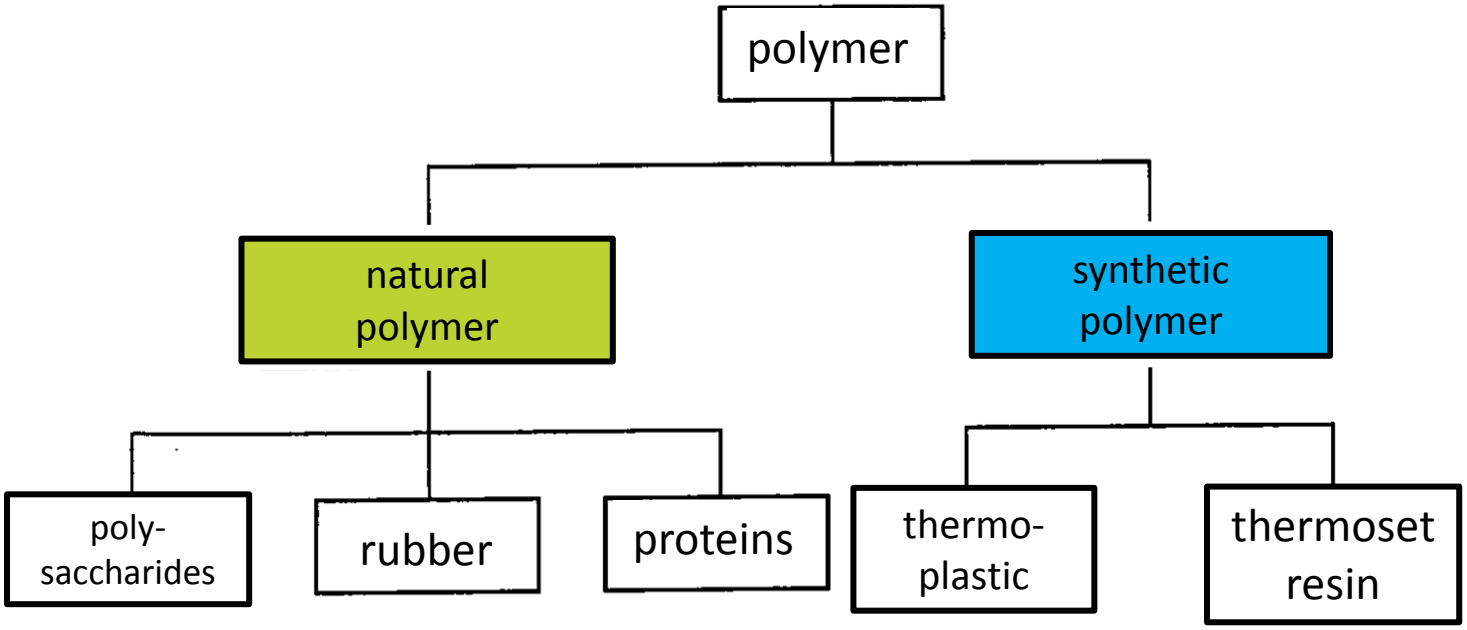
INM

TECHNOLOGIE POLYMERE & KOMPOSITE

MC07, UdS WS 2019/2020

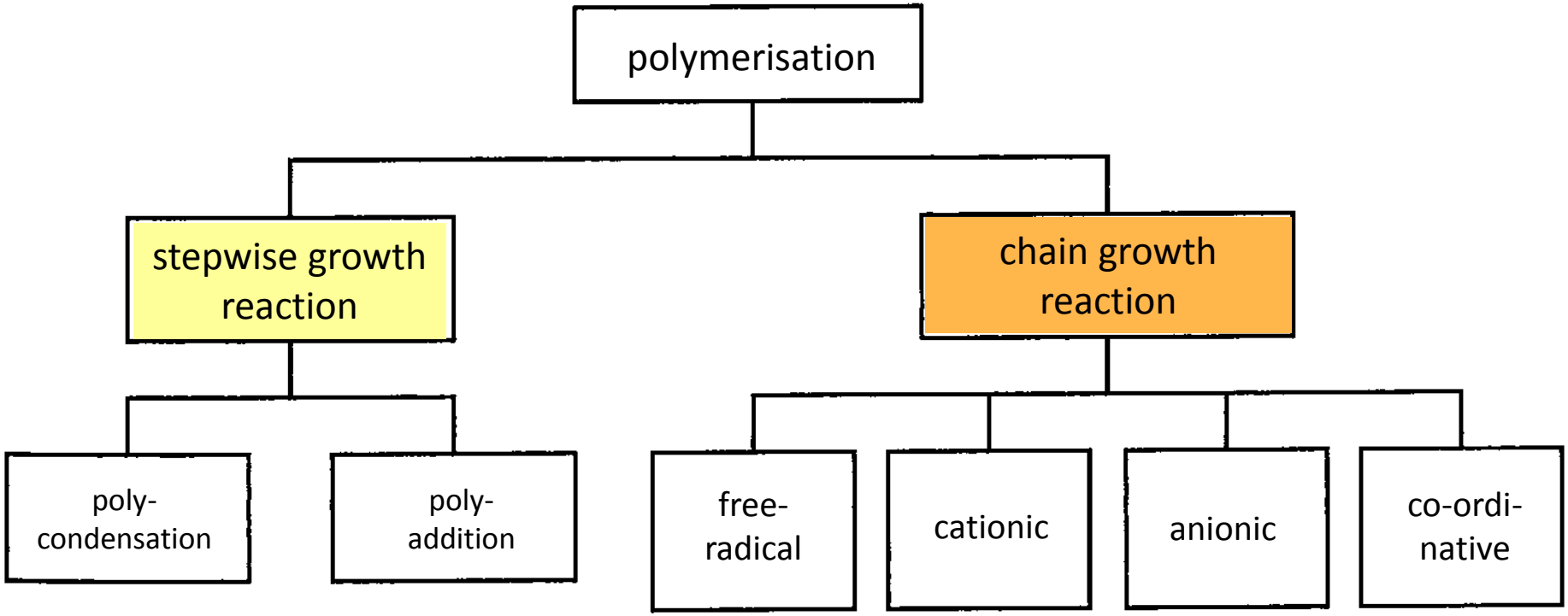
Chapter 1: Thermoplastic Polymers

Classification of polymers: General view



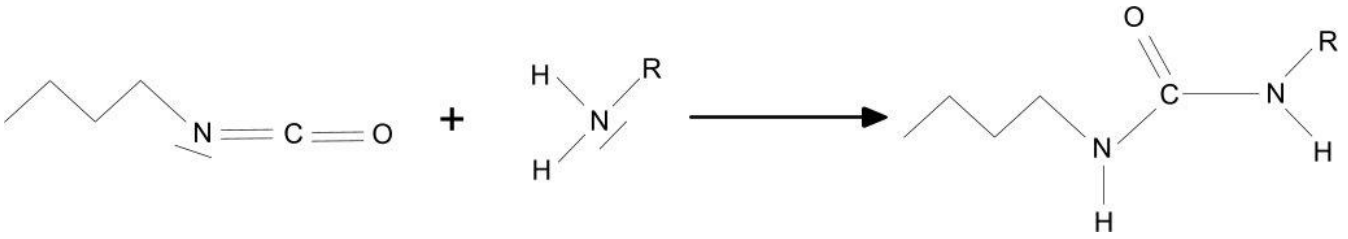
B. Tieke

Formation of polymers: Different reaction pathways



B. Tieke

Mechanism of stepwise growth polymerisation reaction



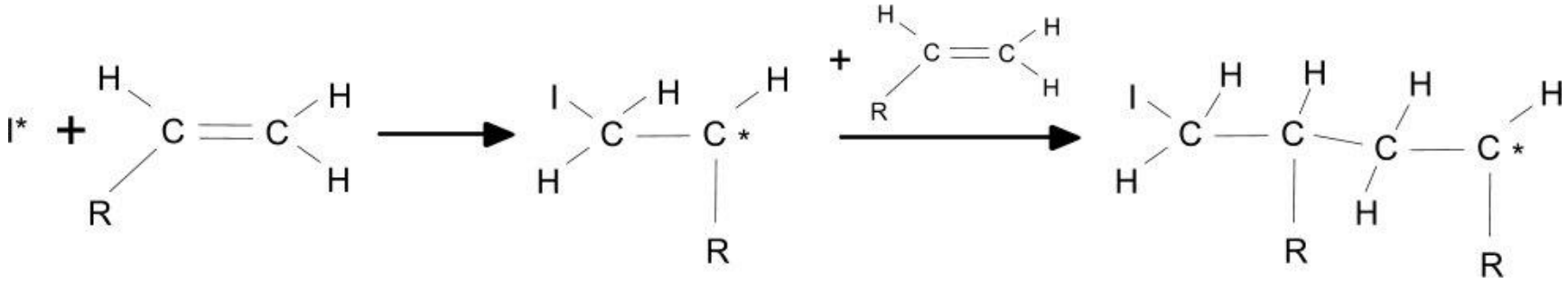
A + B ⟶ A-B

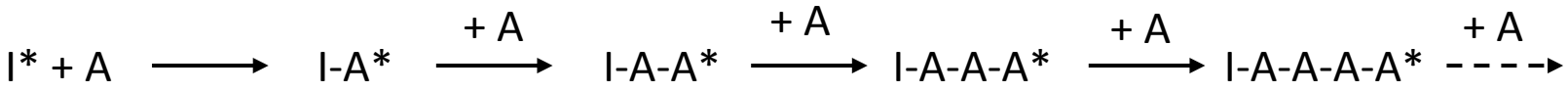
A-B + A-B ⟶ A-B-A-B ⟶ A-B-A-B-A-B-A-B …

A-A + B-B ⟶ A-A-B-B ⟶ A-A-B-B-A-A-B-B …

- stepwise increase of Mw: monomers, dimers, tetramers, …
- high molecular weight only at high conversion rates

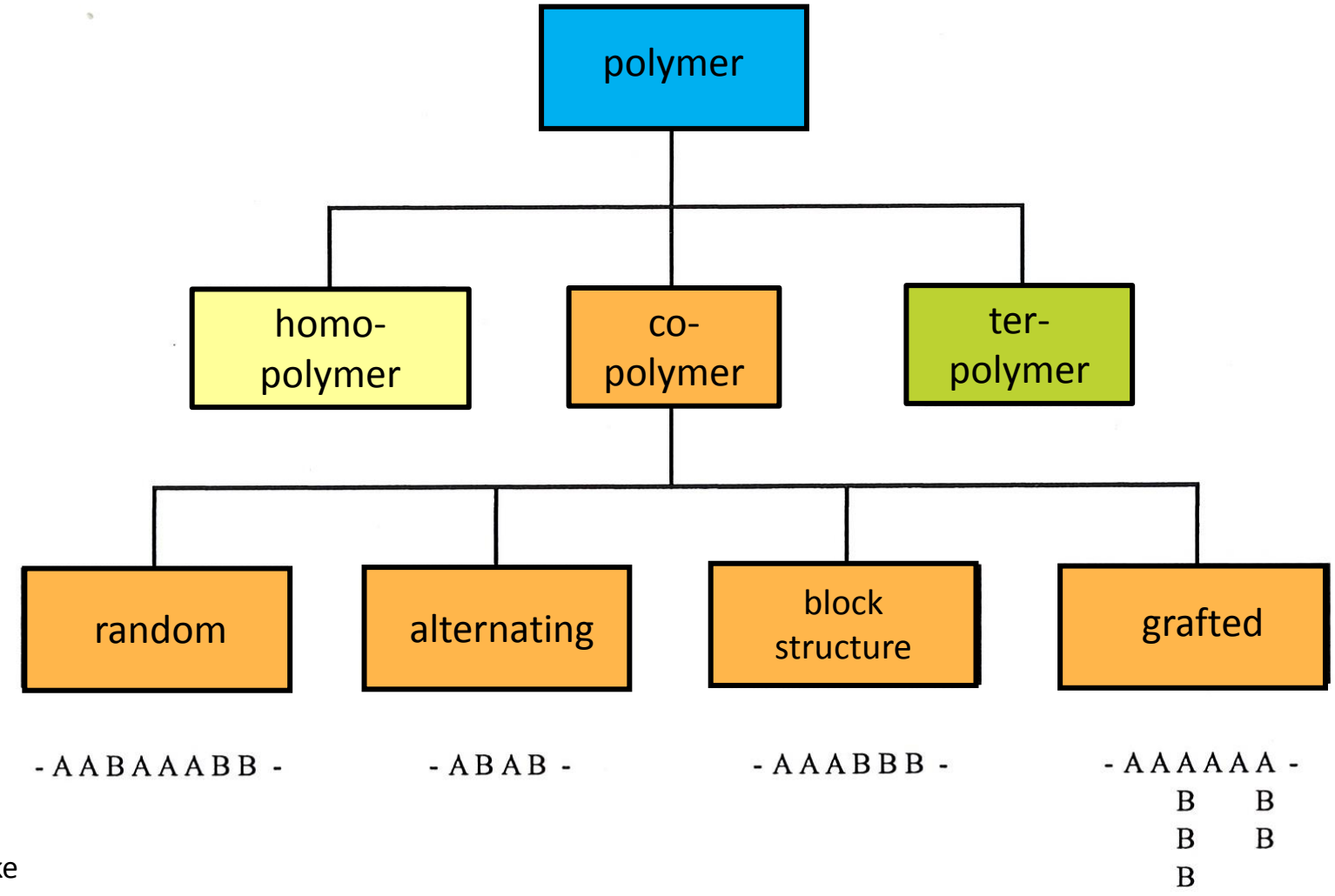
Mechanism of chain growth polymerisation reaction





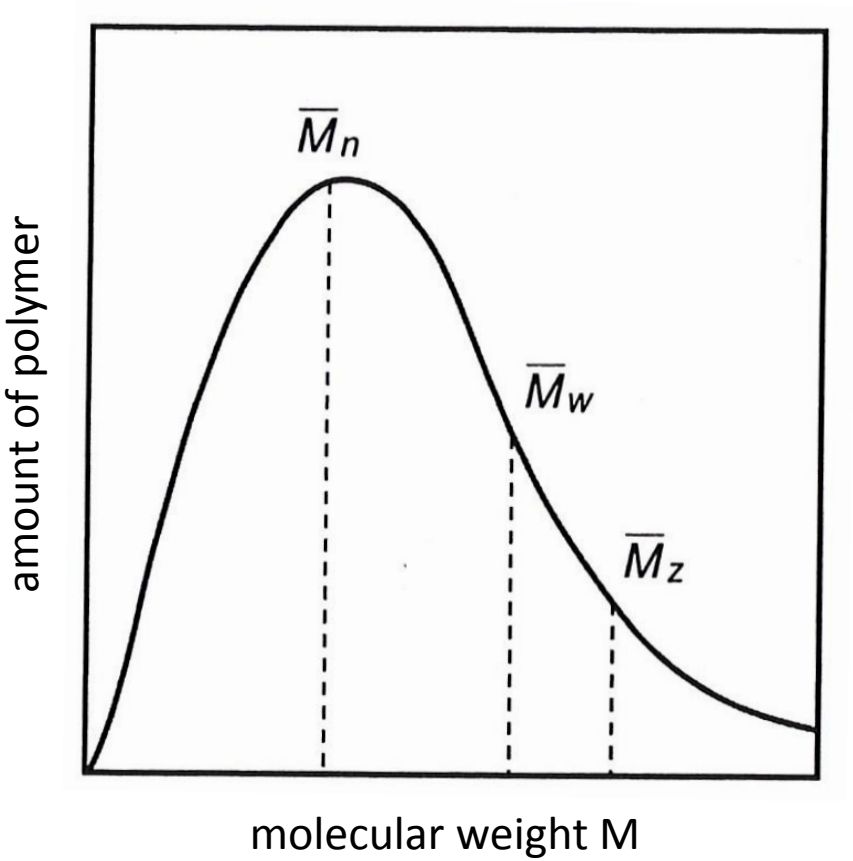
- fast chain growth
- high Mw already at low conversion rates at the beginning
- high Mw polymer and unreacted monomer existing in parallel

Classification of polymers according to number and arrangement of monomer units



B. Tieke

Molecular weight distribution of synthetic polymers: Schulz-Flory distribution



$$polydispersity = \frac{\overline{M}_w}{\overline{M}_n}$$

Average molecular weight

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}.$$

weighted by number

osmometry, GPC, vapor pressure osm.

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}.$$

weighted by mass

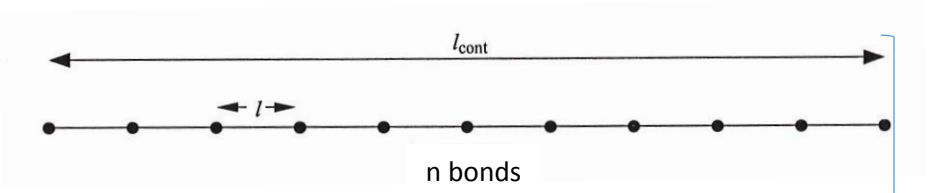
light scattering, viscosimetry

z-average

$$\overline{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2} = \frac{\sum w_i M_i^2}{\sum w_i M_i}.$$

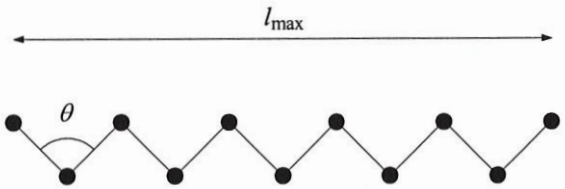
sedimentation by centrifugation

Polymer molecules are random coils

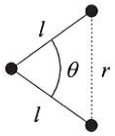


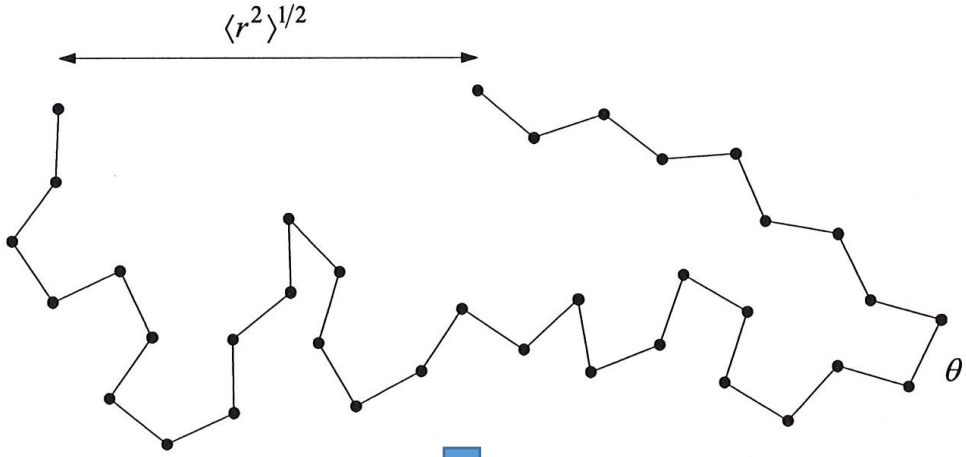
n bonds

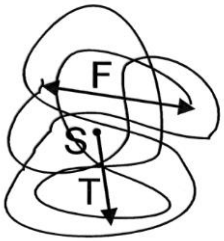
$l_{max} = nl \cdot \sin(\theta/2).$



+





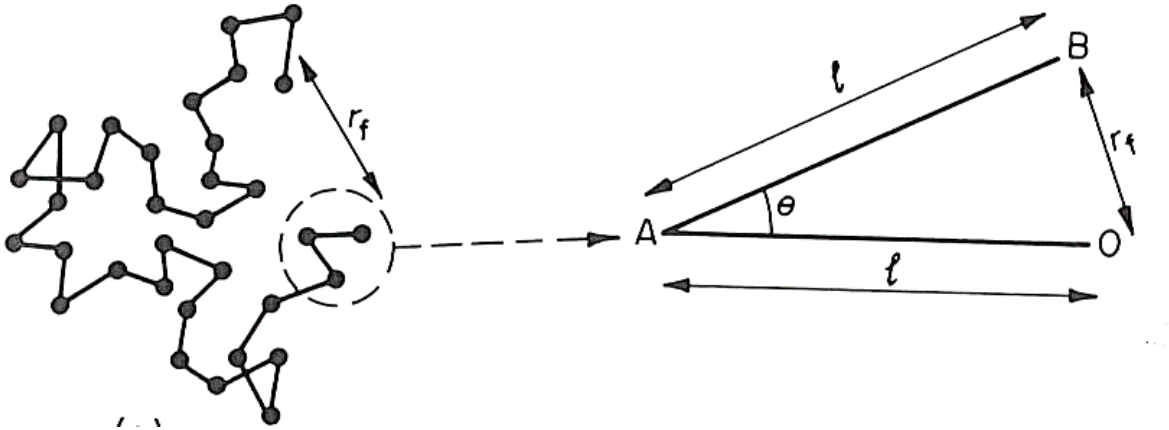


random coil

B. Tieke

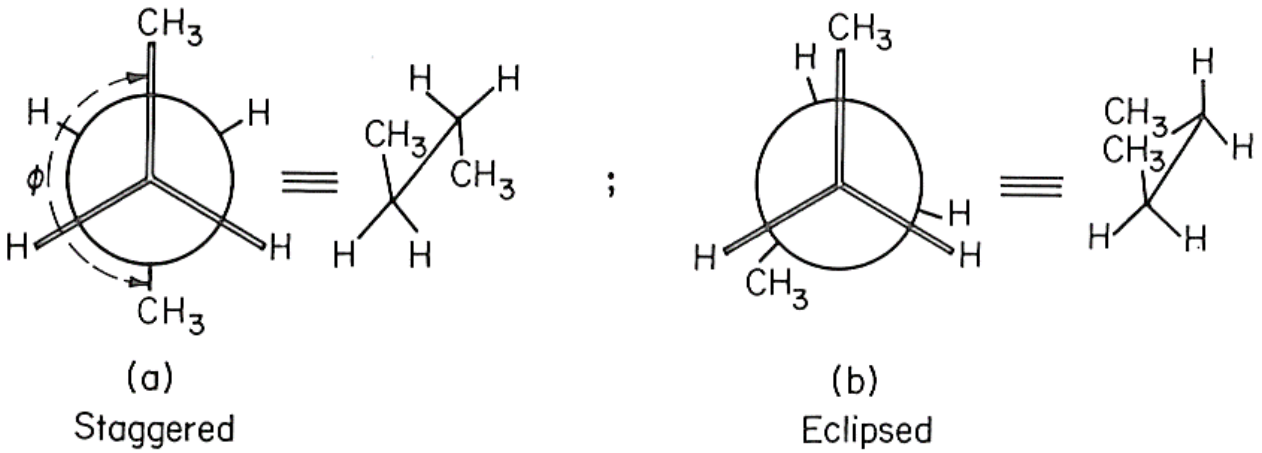
Random walk

random walk chain of 32 steps



Elias

Conformations I

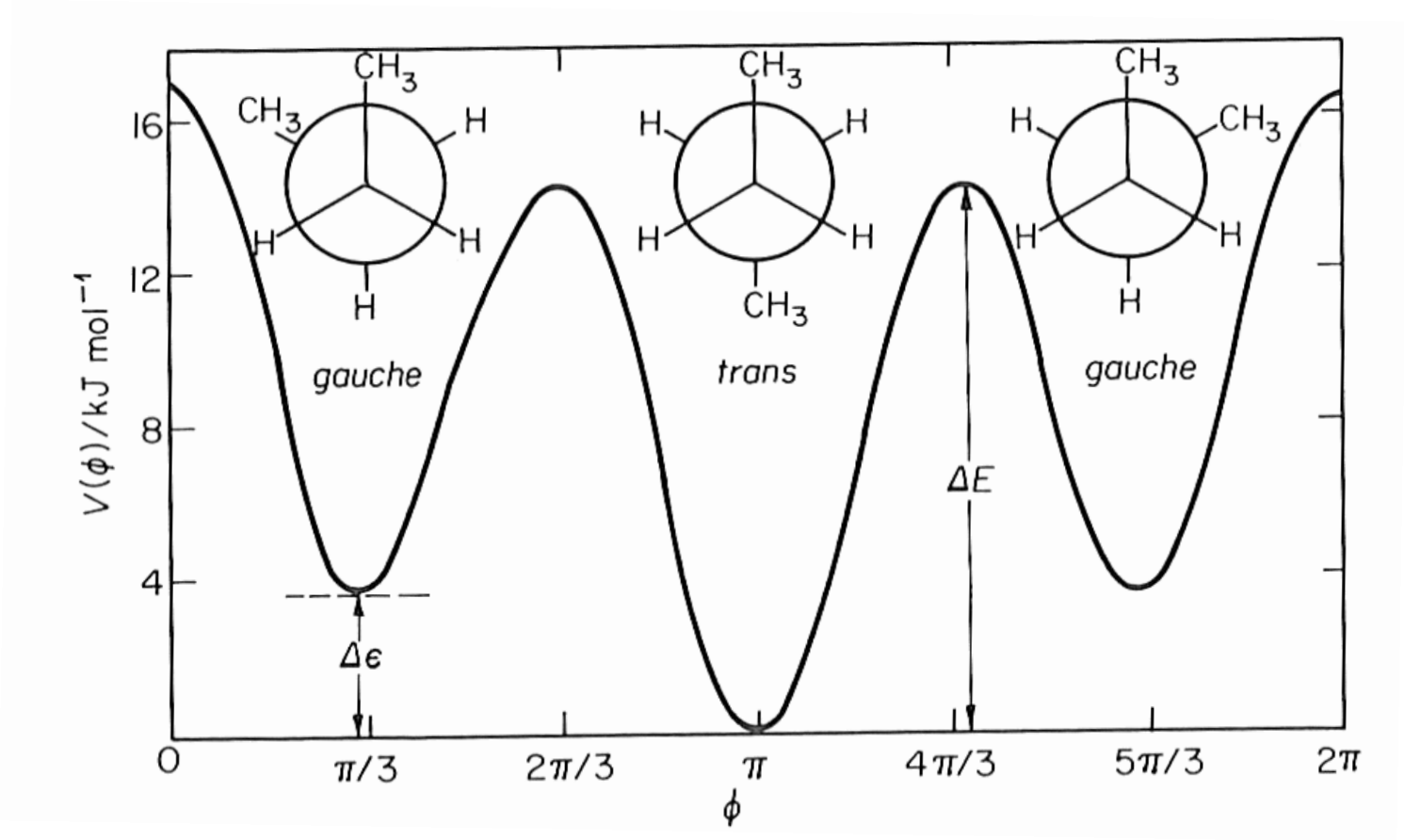


(a)
Staggered

(b)
Eclipsed

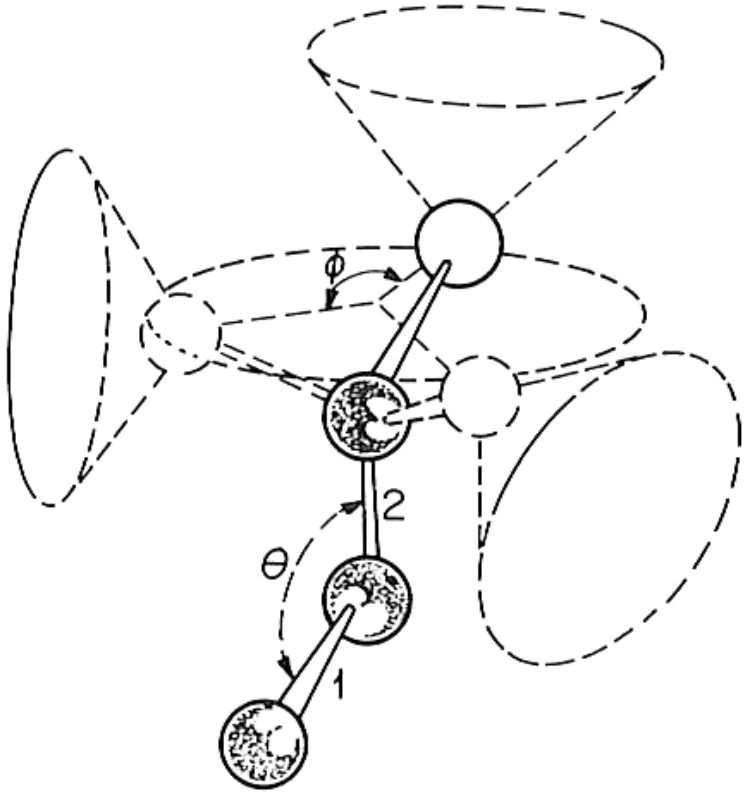
Conformations II

- potential energy V(ϕ) as a function of dihedral angle ϕ



Chain mobility

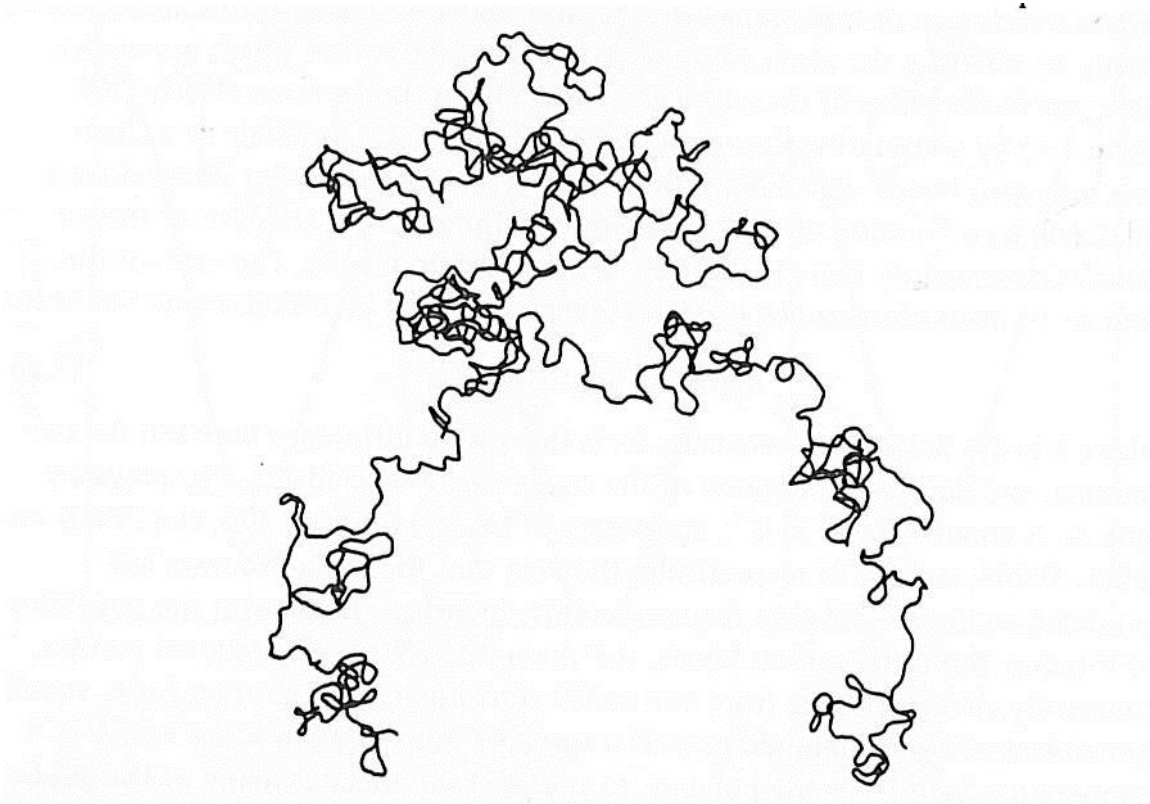
- cones of revolution available to the 3. and 4. bonds of a simple carbon chain
- fixed bond angle θ



Elias

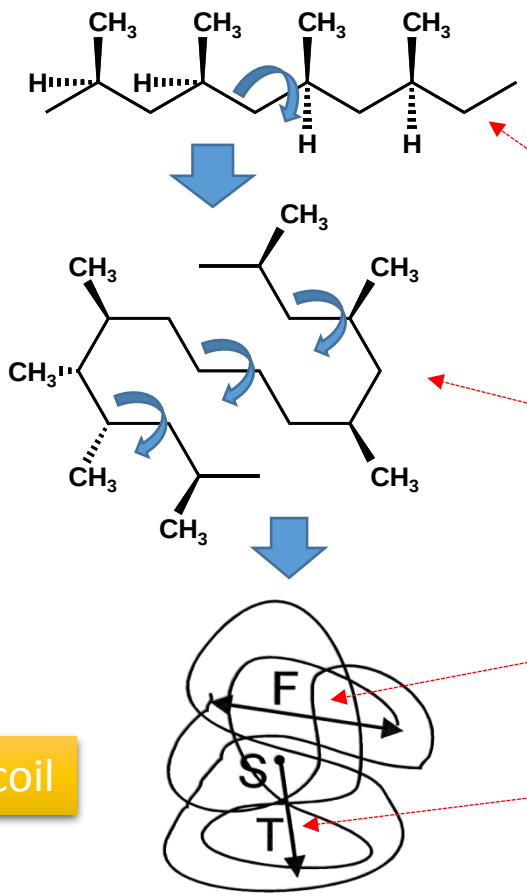
Random coils

- random arrangement of PE containing 1000 freely rotating C-C bonds
- successive bond: random choice of 6 equally spaced angular positions



Treloar (1958), Physics of Rubber Elasticity

Relations between dimensions of polymer molecules

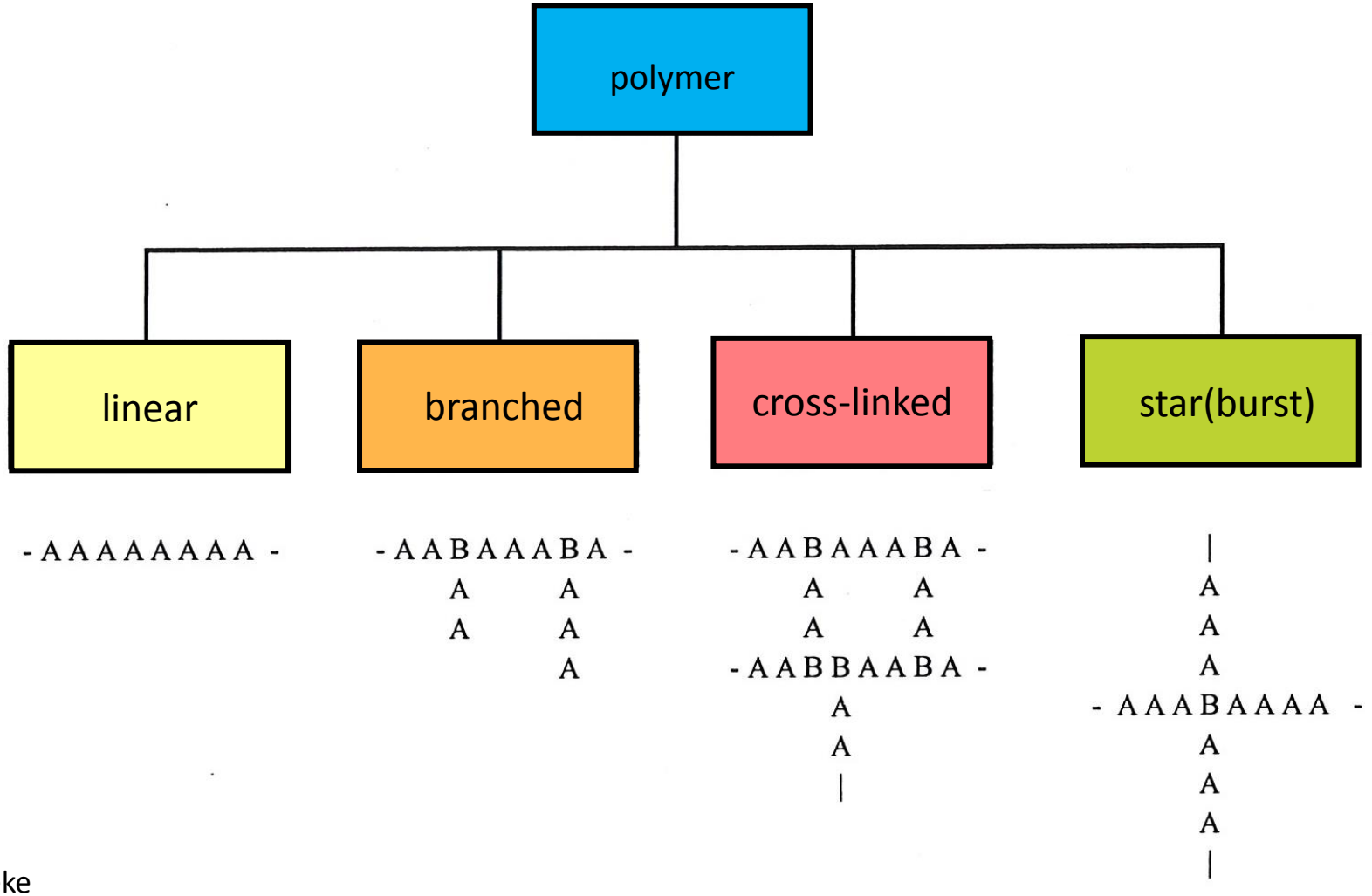


random coil

- **Dimensions of polymer molecules**
- e.g. linear PP: $M_n = 3*10^5$ g/mol

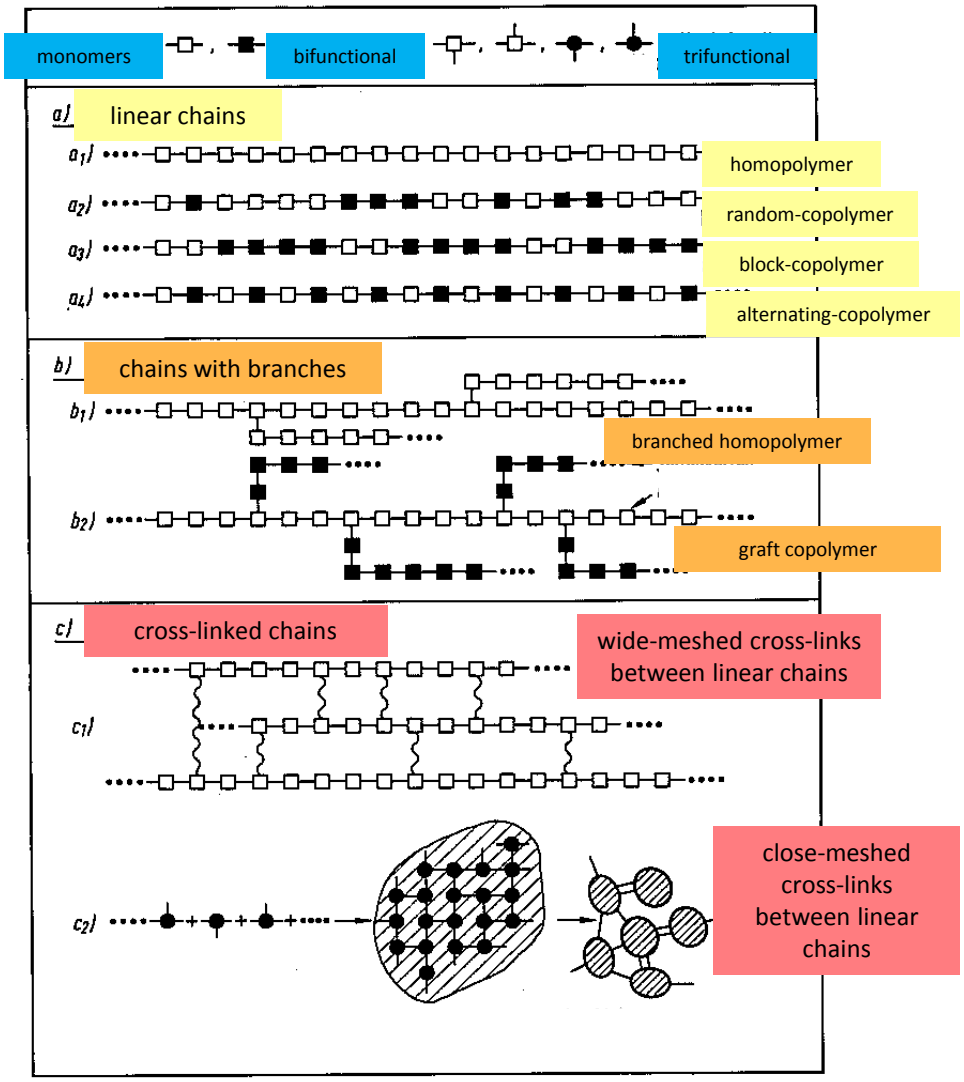
  ≅ 10.000 monomer units
- stretched chain ≅ 2.5 µm
- folded chain
- thread end to end distance (F) ≅ 30 nm
- Radius of gyration (T) ≅ 12 nm

Classification of polymers according to structure



B. Tieke

Classification of polymers



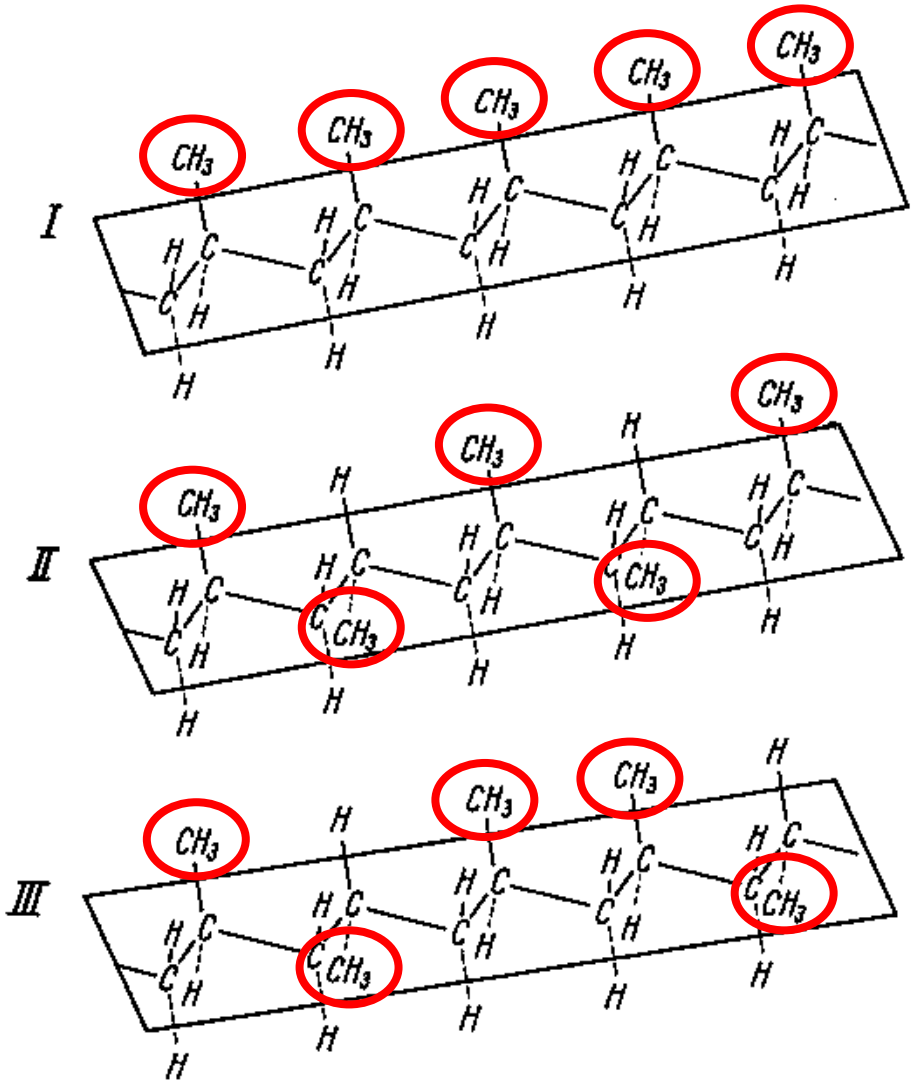
thermoplastics

thermoplastics

elastomers

thermoset resins

Stereochemistry in e.g. polypropylene

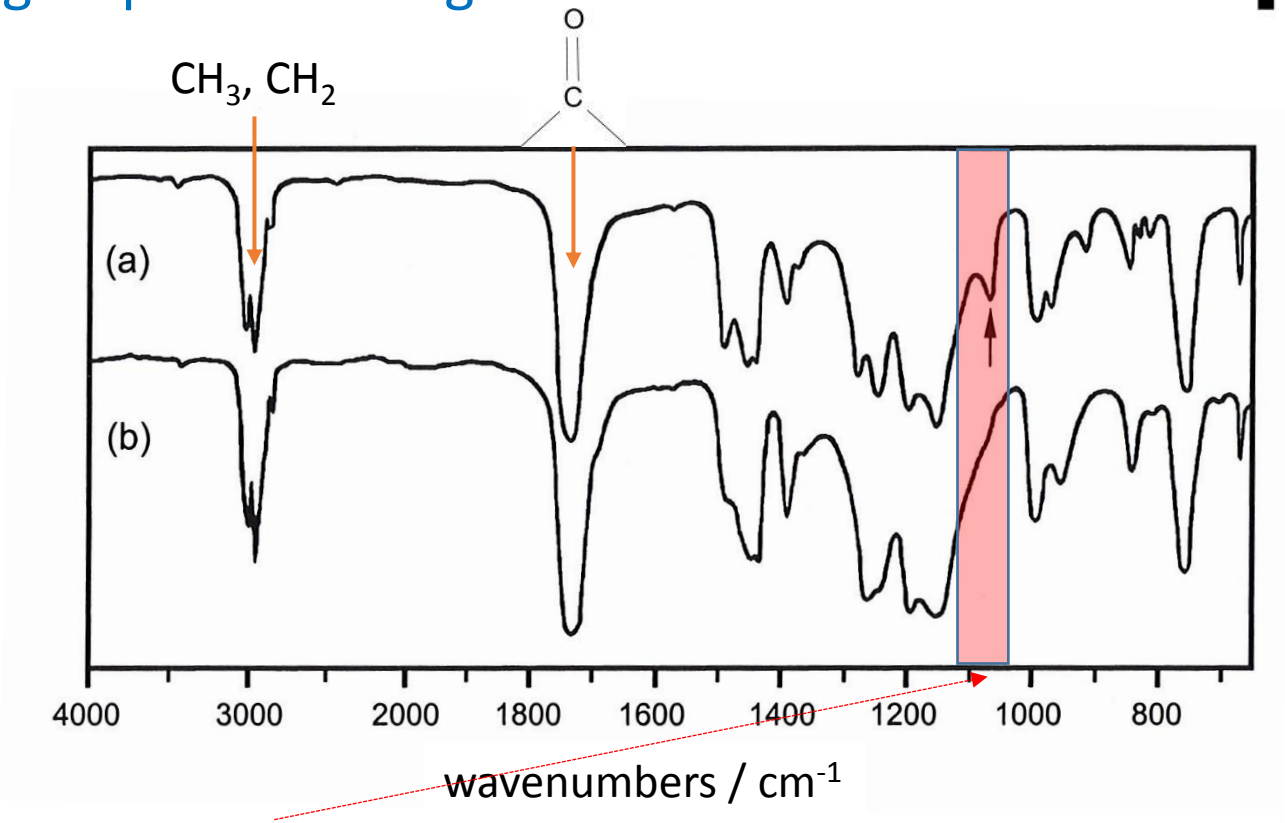


isotactic

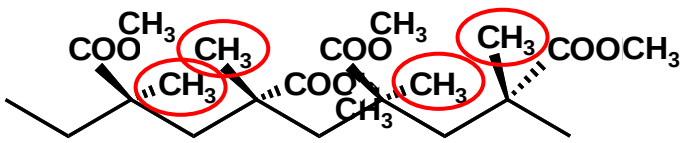
syndiotactic

atactic

Characterisation of polymer matrices: Determination of functional groups and arrangement of side chains

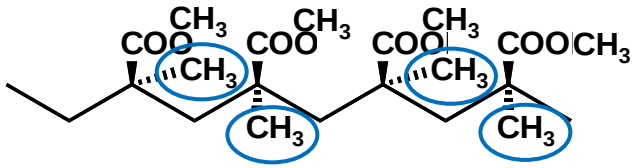


a: syndiotactic PMMA

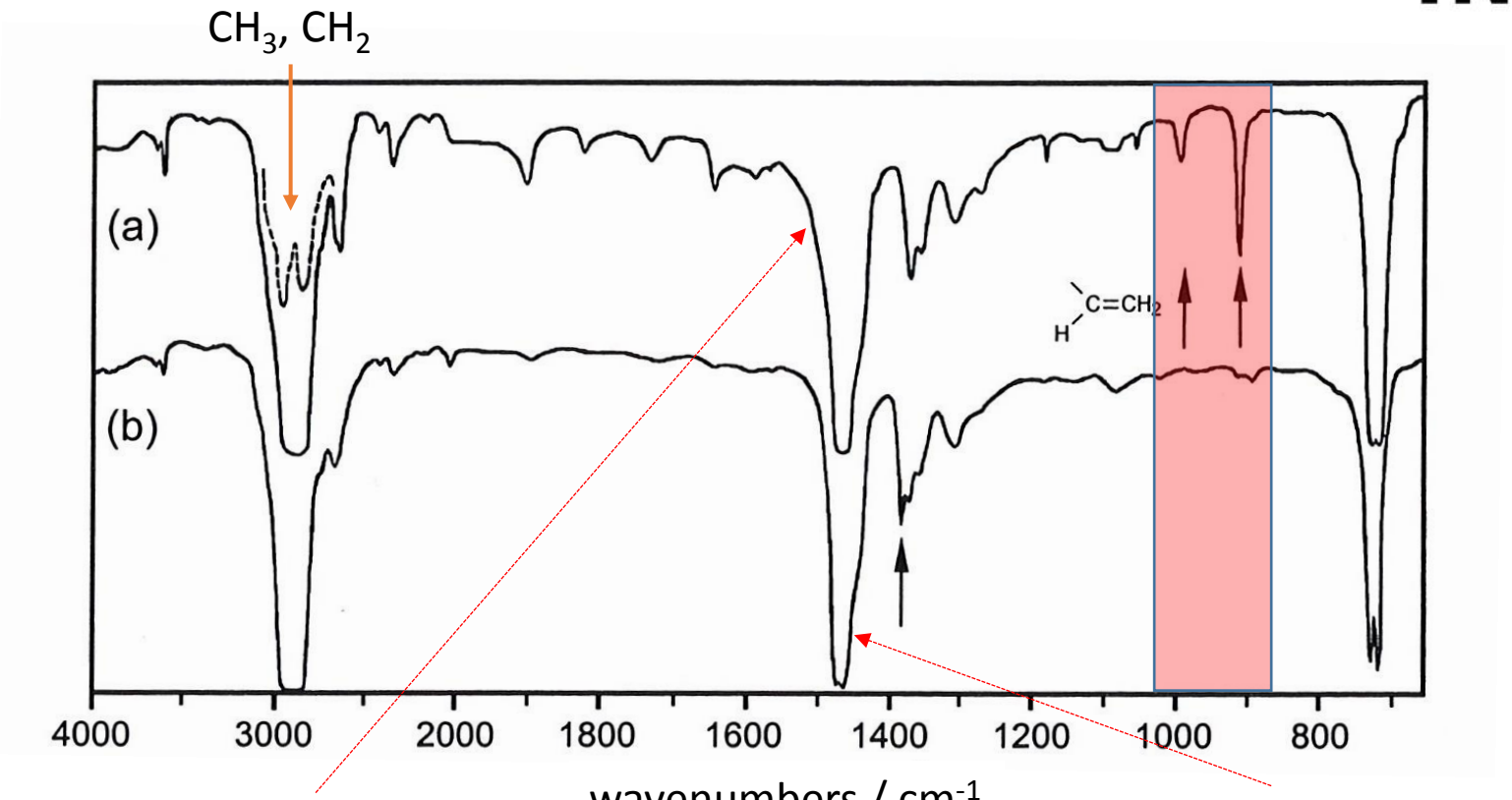


H.G. Elias

b: isotactic PMMA

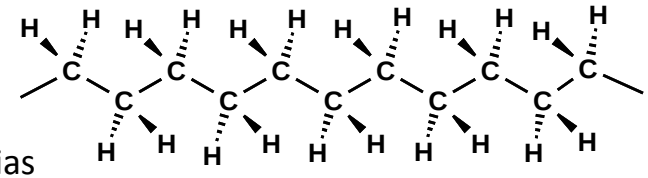


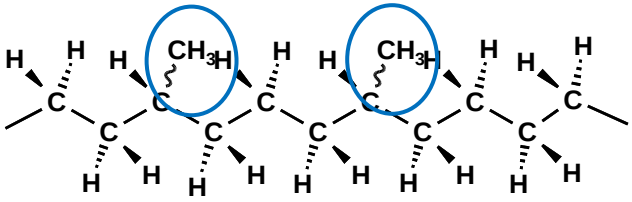
IR-spectroscopy on linear and branched polyethylene



a: linear polyethylene

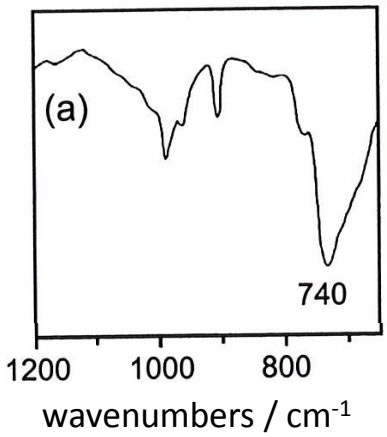
b: branched polyethylene

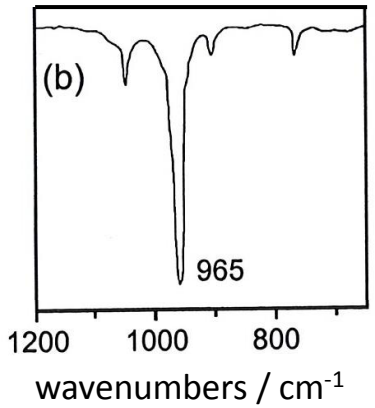


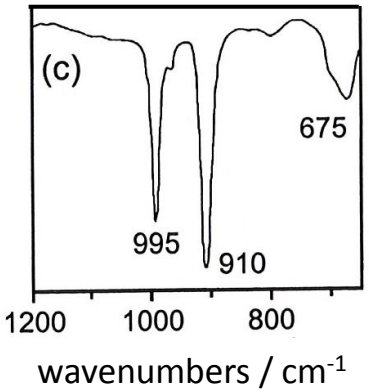


H.G. Elias

IR-spectroscopy: Detection of stereochemistry







cis –poly(1,4-butadiene)

trans –poly(1,4-butadiene)

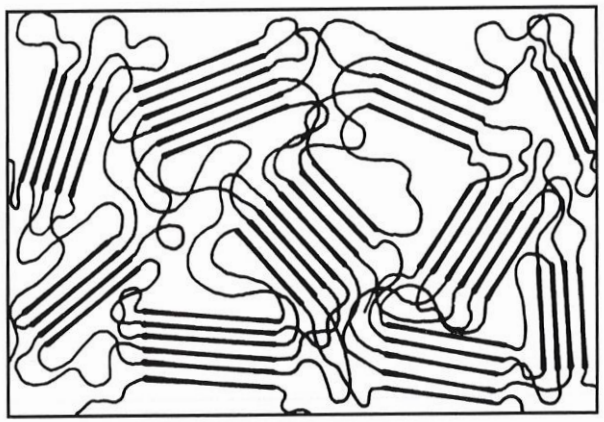
poly(1,2-butadiene)

- different C-H bending vibrations of polybutadiens with different stereochemistry
- Infrared spectroscopy (IR) can be a powerful tool for structural investigation

H.G. Elias

Crystallinity in polymers

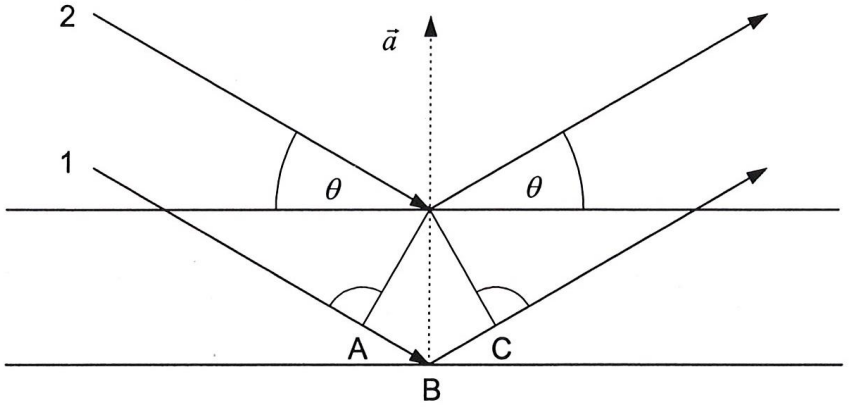
old micellar model = not true



X-ray diffraction

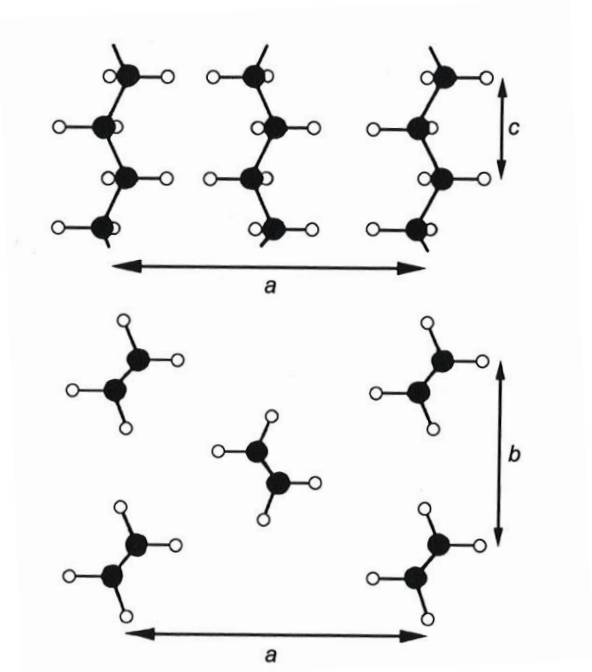
$$\Gamma = 2d\sin\theta\,.$$

d: lattice constant
θ: Bragg's angle



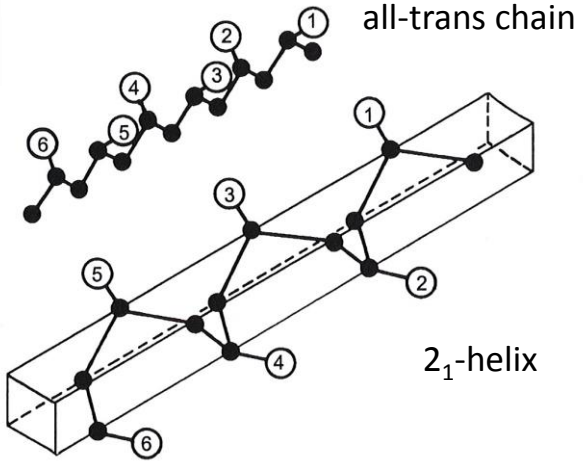
B. Tieke

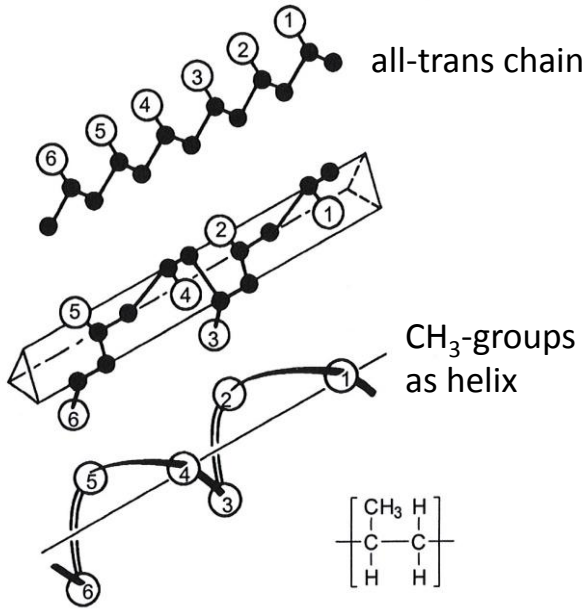
Some typical crystalline polymers



crystalline polyethylene
a = 0.741 nm
b = 0.494 nm
c = 0.255 nm

syndiotactic polypropylene

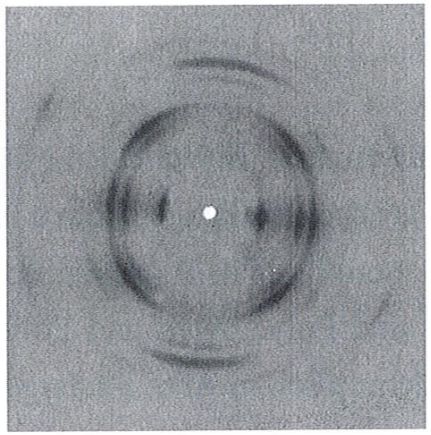




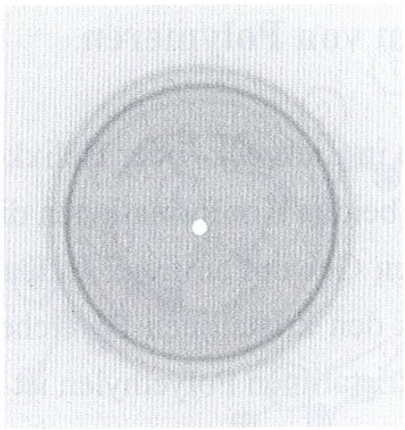
isotactic polypropylene

B. Tieke

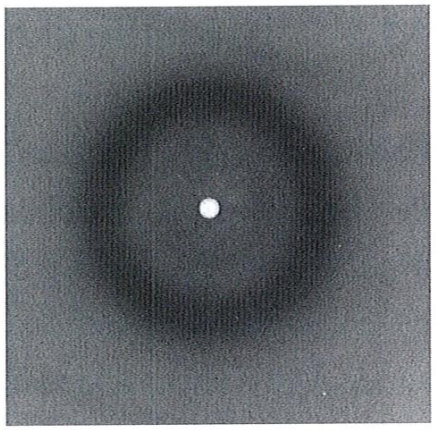
Typical diffraction patterns and crystalline structures



oriented isotactic
poly(butene-1)

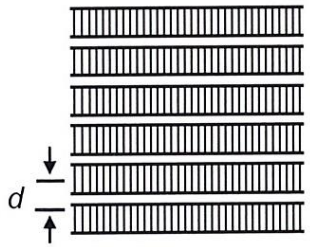


partially crystalline
polyethylene

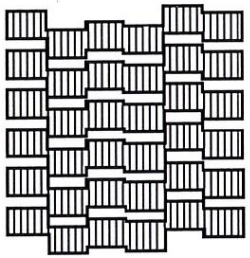


amorphous atactic
poly(octene-1)

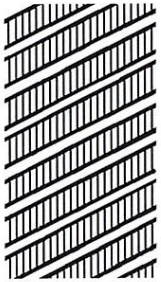
G. Trafara



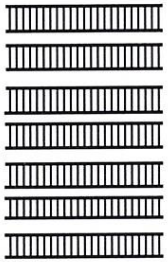
ideal lamellar
lattice



fibrillar lamellar
lattice



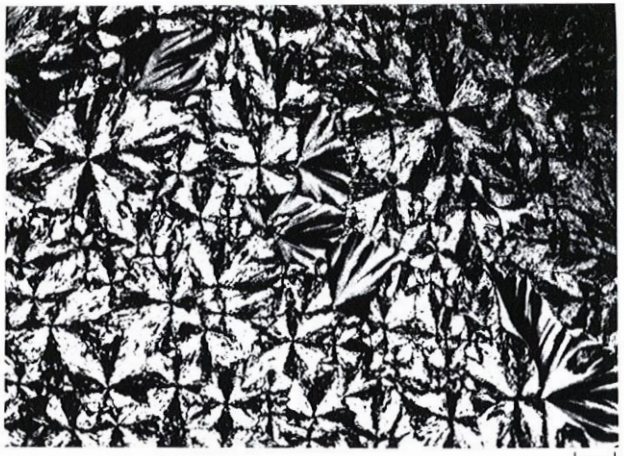
oriented
lamellae



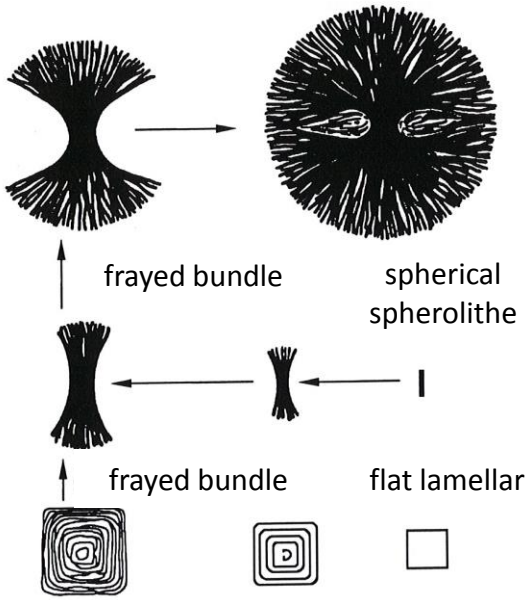
paracrystalline
lamellar lattice

B. Tieke

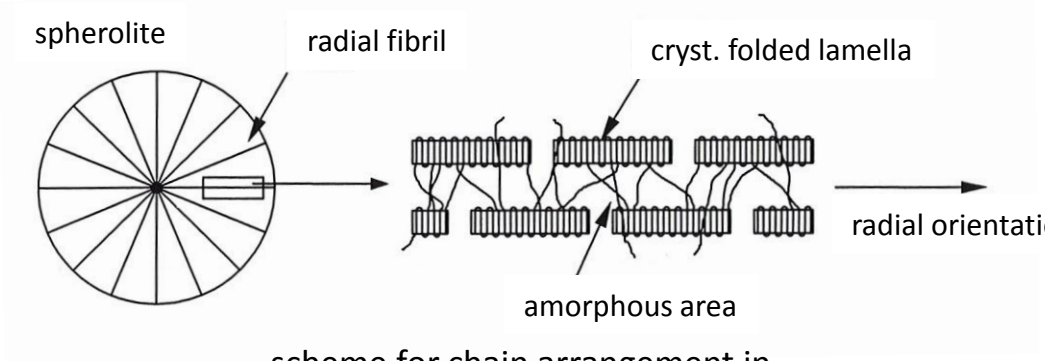
Crystallisation of polymers from molten state



spherolithes from polyethylenesebacate between crossed polarisers

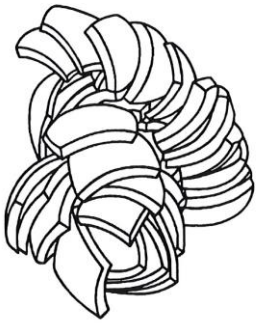


different stage of spherolithe growth



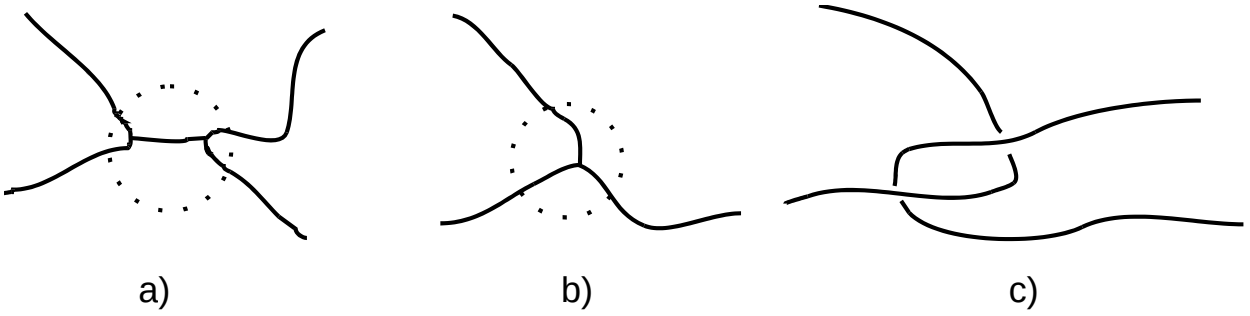
B. Tieke

scheme for chain arrangement in spherolithes



buckled crystalline lamellae in a HDPE spherolithe

Structural models of polymers



a) 4-fold cross-linking point (covalent bonding)

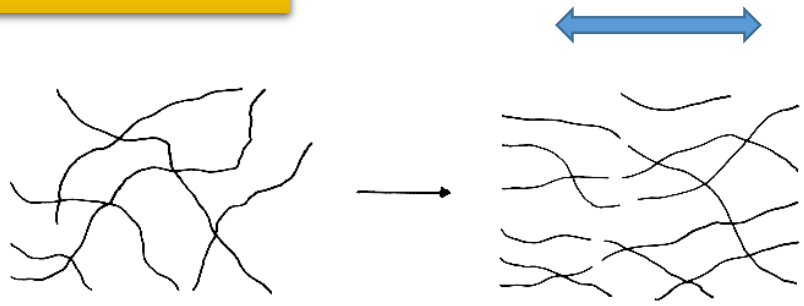
b) 3-fold cross-linking point (covalent bonding)

c) entanglement (non cross-linking polymer)

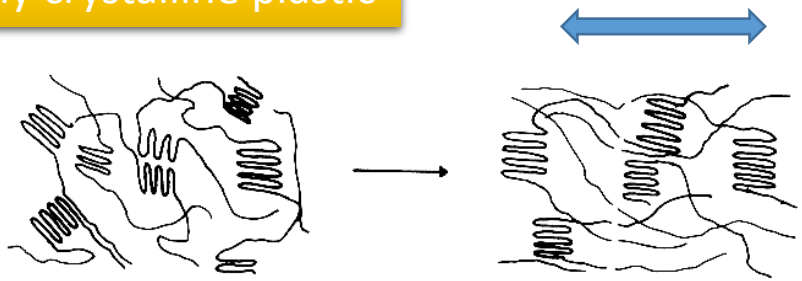
H.G. Elias

Deformations on the molecular level during tensile load

amorphous plastic

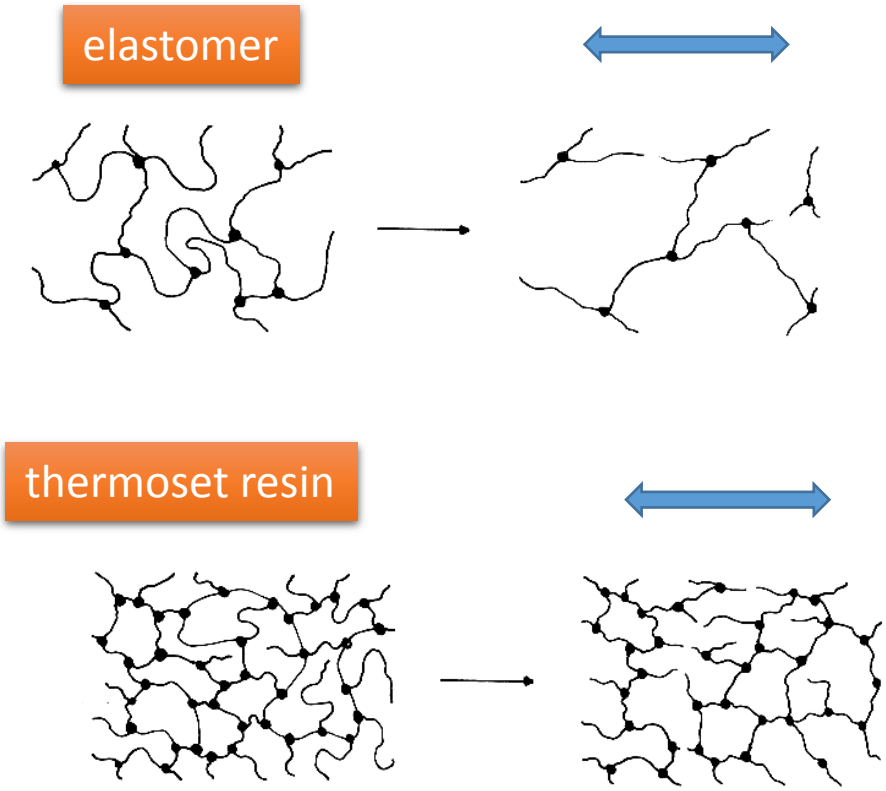


partially crystalline plastic



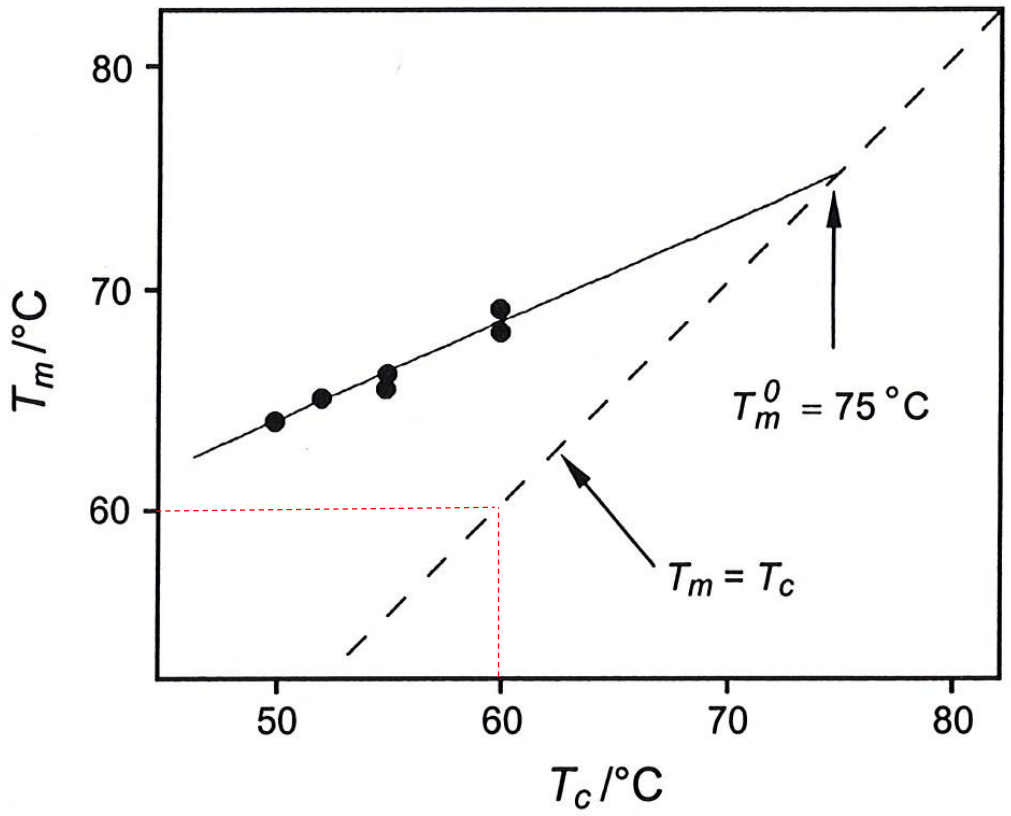
H.G. Elias

Deformations on the molecular level during tensile load

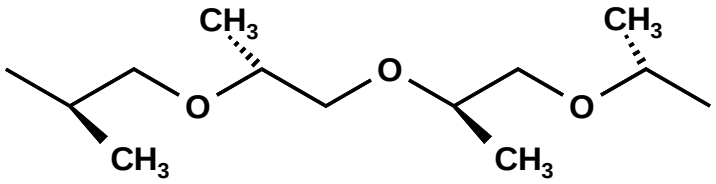


H.G. Elias

Melting temperature T_m vs crystallisation temperature T_c



example:
poly-propylene-oxide

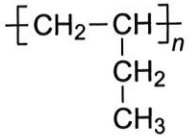
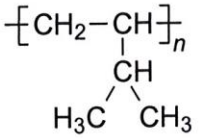
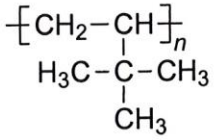
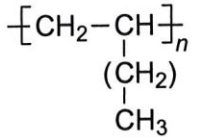


identification of melting temperature at equilibrium state (= infinitely extended crystal) T_m^0

B. Tieke

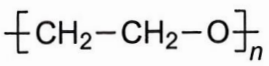
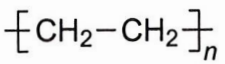
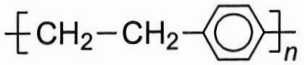
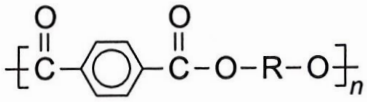
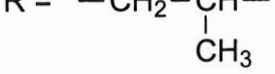
Factors influencing melting point of polymers

steric effects: bulky side groups

Polymer	T_m [K]
	399
	418
	> 593
aber:	
	< 390

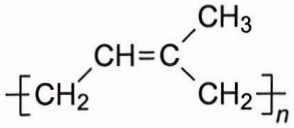
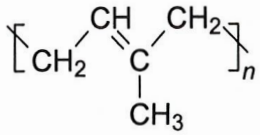
Factors influencing melting point of polymers

chain stiffness

Polymer	T_m [K]
	340
	410
	670
	
R = $-CH_2-CH_2-$	538
R = $-CH_2-CH_2-CH_2-$	493
R = 	not crystalline

Factors influencing melting point of polymers

steric effects: geometric isomers

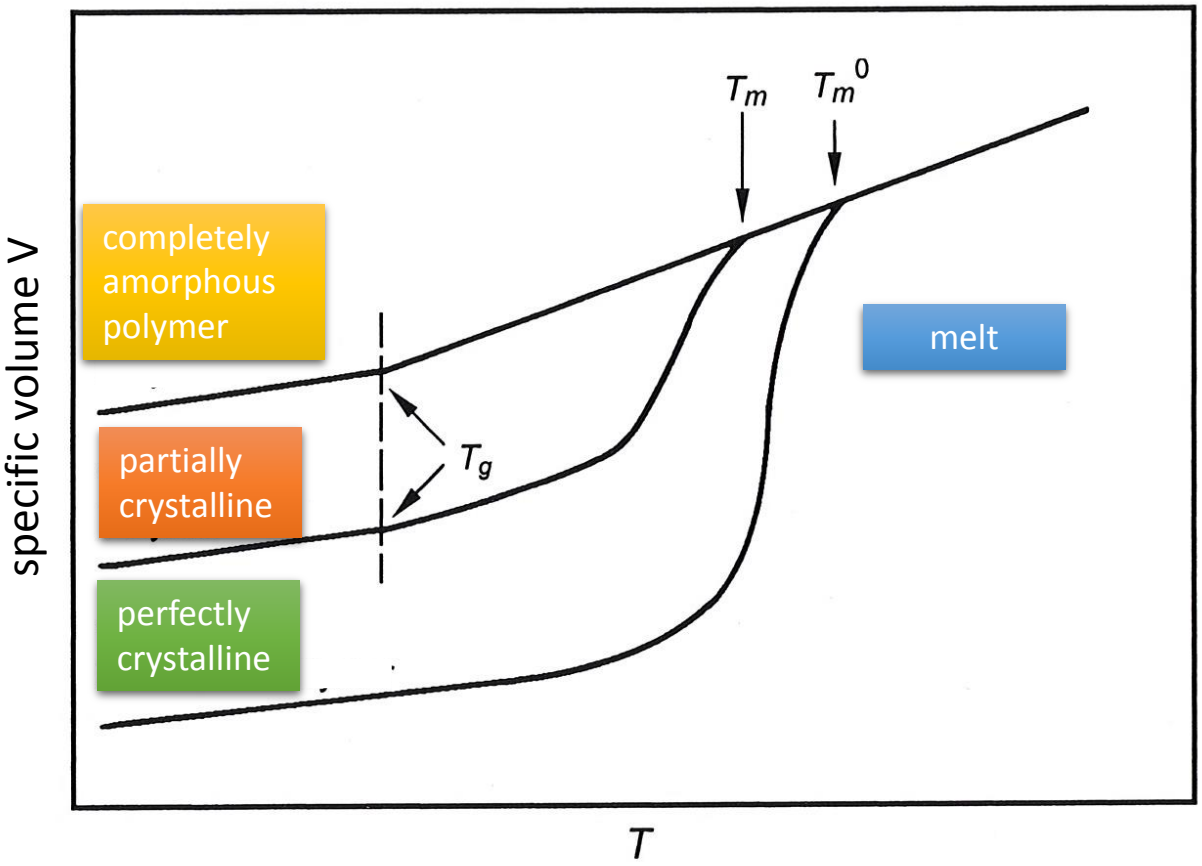
Polymer		T_m [K]
cis-Polyisopren		262
trans-Polyisopren		421

Factors influencing melting point of polymers

polar groups

Polymer	T_m [K]
$-[CH_2-CH_2]_n-$	410
$-[CH_2-CH(CN)]_n-$	590

Determination of T_g and T_m: specific volume in dependence on temperature



T_g: glass transition temp. amorphous part

T_m: melting point partially crystalline polymer

T_m^0: melting point perfectly crystalline polymer

B. Tieke

Differential thermal analysis (DTA): Determination of T_g and T_m

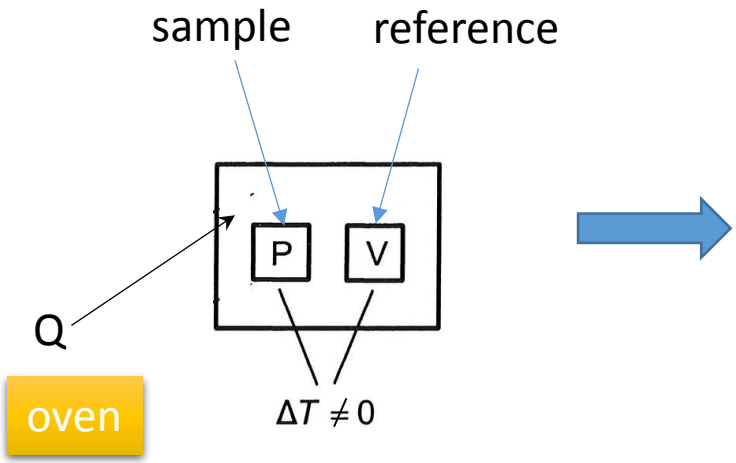
DTA – signal under constant heating

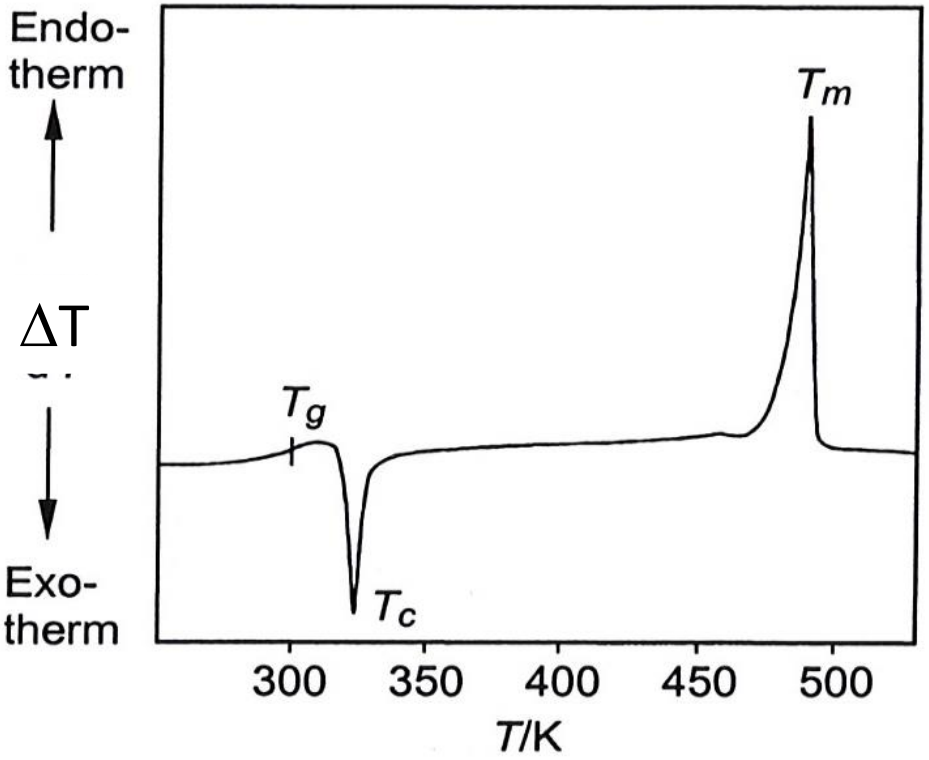
T_m: melting point

T_c: re-crystallisation temperature

T_g: glass transition temperature

DTA





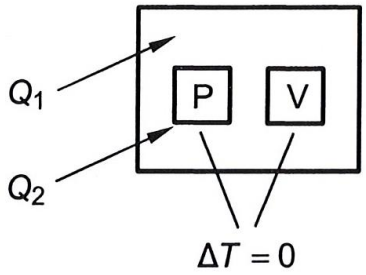
B. Tieke

Differential scanning calorimetry (DSC): Determination of T_g and T_m

DSC – signal under constant heating

oven

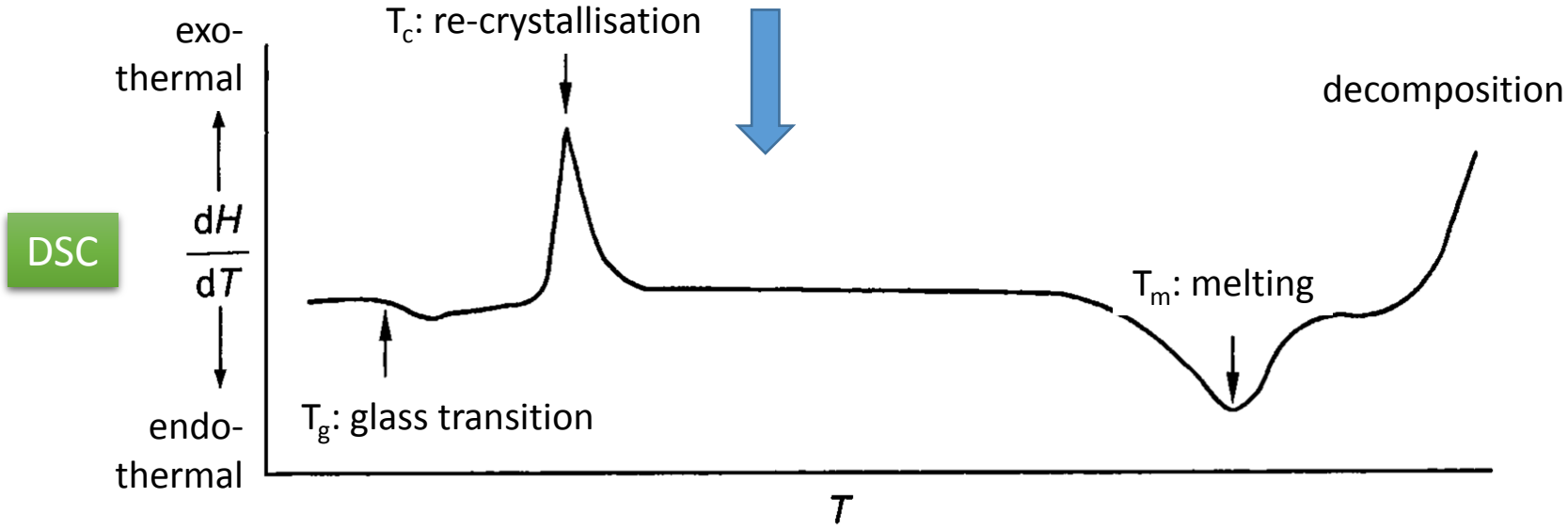
separate heating of sample



T_m: melting point

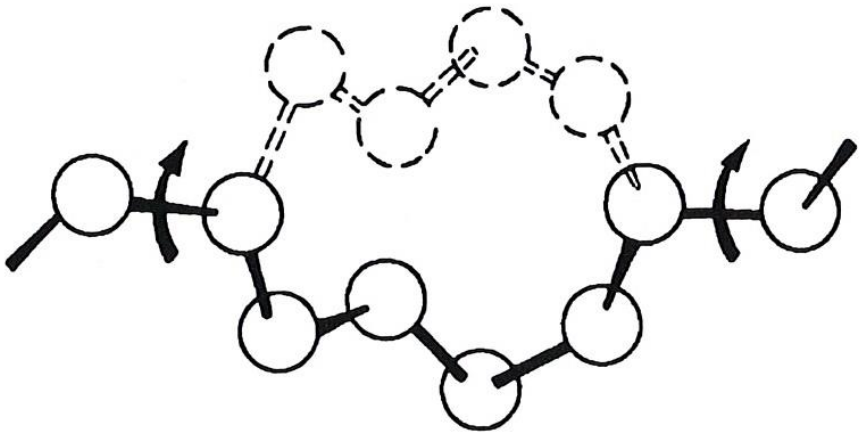
T_c: re-crystallisation temperature

T_g: glass transition temperature



B. Tieke

Molecular dynamics of polymers: Crankshaft motion at T_g



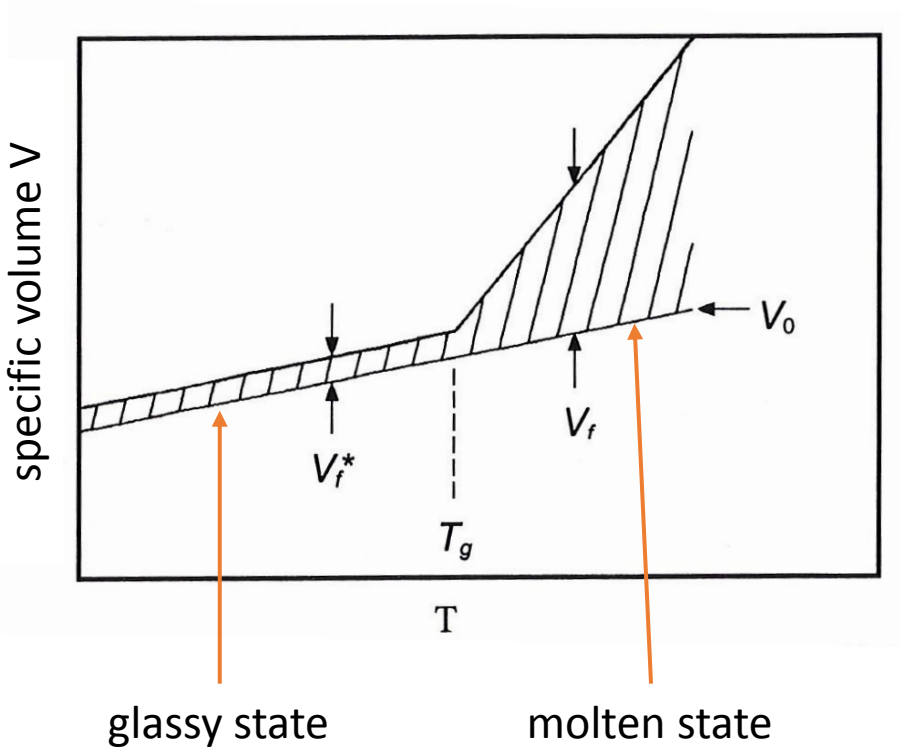
T_g = 2nd order transition

$$c_p = \left(\frac{\delta H}{\delta T}\right)_p, \quad \alpha = \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p$$

c_p: specific heat capacity
α: coefficient of thermal expansion

B. Tieke

T_g and the concept of free volume



- V_f: free volume
- V_0: volume of the polymer chains
- V_f^*: frozen free volume
- T_g: glass transition temperature
- f: volume fraction
- α_f: coefficient of thermal expansion for free volume

$$V_f = V_f^* + (T - T_g)\left[\frac{\delta V}{\delta T}\right]$$

$$f = f_g + (T - T_g)\alpha_f$$

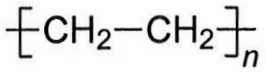
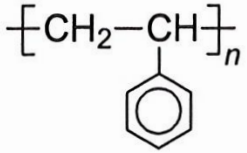
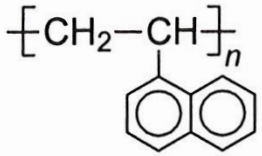
$$f = V_f / V$$

$$f_g = V_f^* / V$$

B. Tieke

Factors influencing glass transition temperature

voluminous substituents

Polymer	T_g [K]
	188
	373
	408

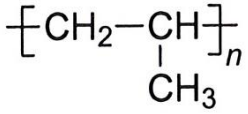
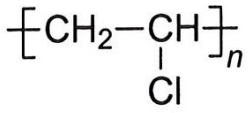
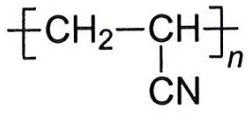
Factors influencing glass transition temperature

flexible substituents

Polymer	T_g [K]
$-[CH_2-CH]_n-$ (CH$_3$)	253
$-[CH_2-CH]_n-$ ($CH_2)_3-CH_3$	223
$-[CH_2-CH]_n-$ $COOCH_3$	279
$-[CH_2-CH]_n-$ $COO-(CH_2)_3-CH_3$	218

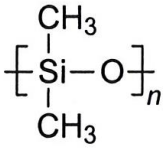
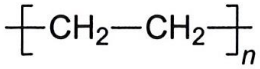
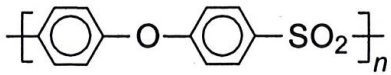
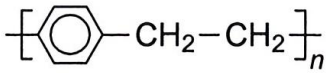
Factors influencing glass transition temperature

polar substituents

Polymer	T_g [K]
	253
	354
	378

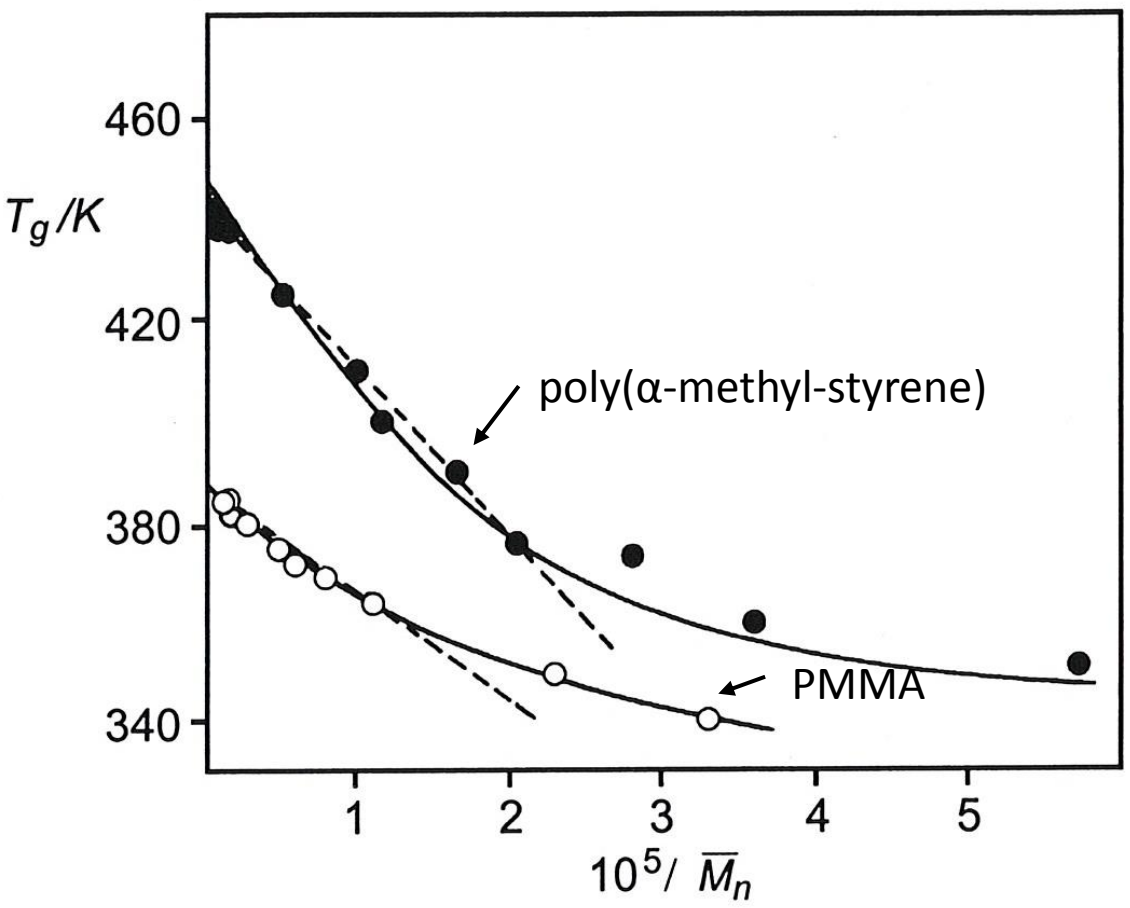
Factors influencing glass transition temperature

chain mobility

Polymer	T_g [K]
	150
	188
	523
	553

+ additional network points: Tg ↑
+ additional branches: Tg ↓

Glass transition temperature T_g in dependence on molecular weight M_n

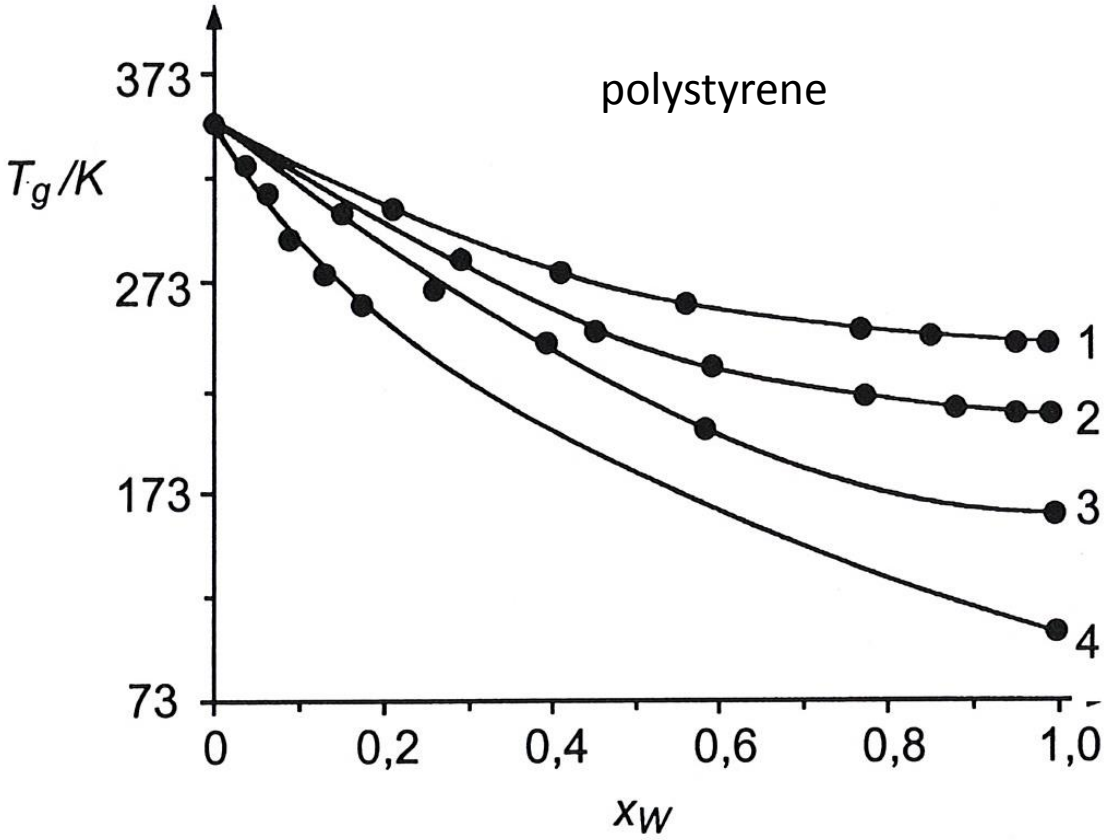


$$T_g = T_g^{\infty} - \frac{K}{M}$$

- K: const.
- M: molecular weight
- T_g^{∞}: glass transition temperature at infinite molecular weight

B. Tieke

Influence of plasticisers



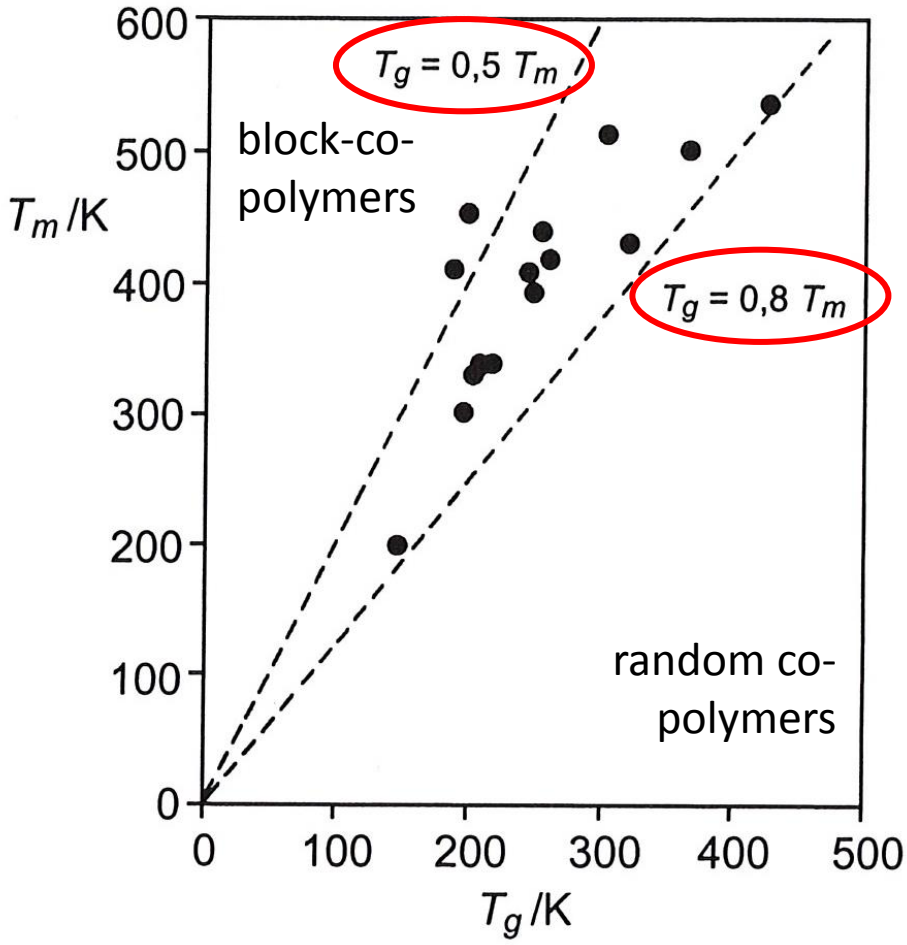
1: naphthylsalicylate
2: tricresylphosphate
3: methylsalicylate
4: methylacetate

X_w: mole fraction plasticiser

➡ larger range between T_g and T_m achievable

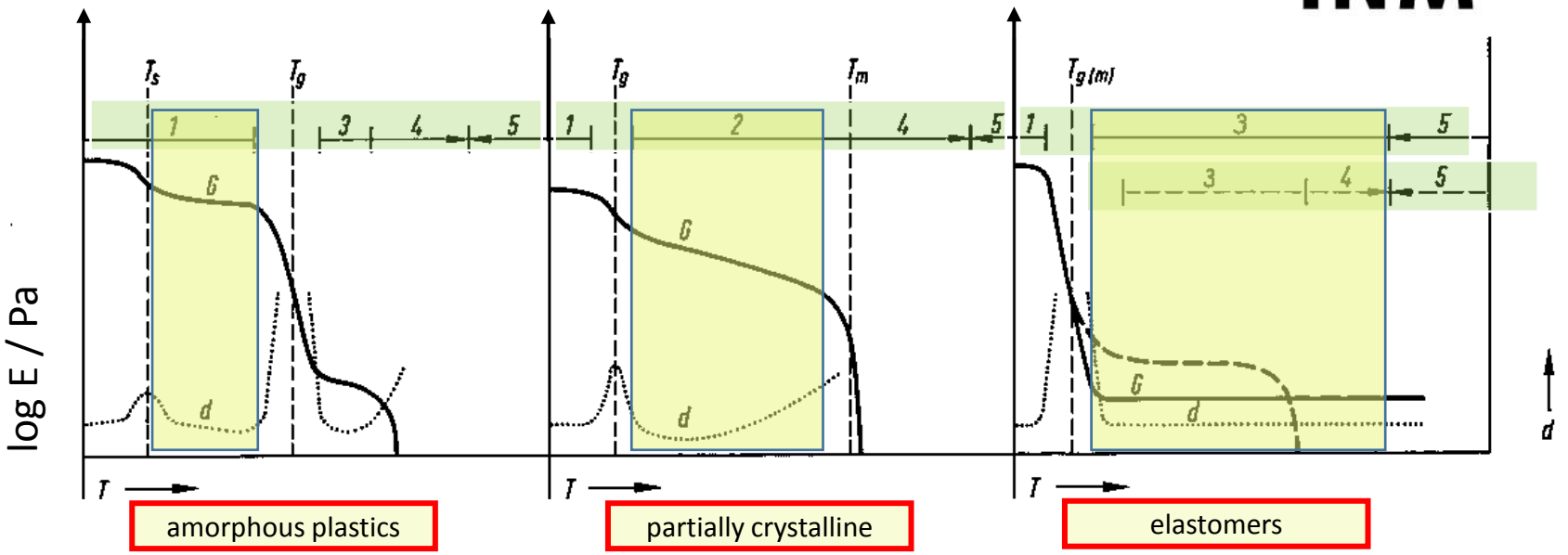
B. Tieke

Melting temperature T_m vs glass transition temperature T_g of different standard polymers



B. Tieke

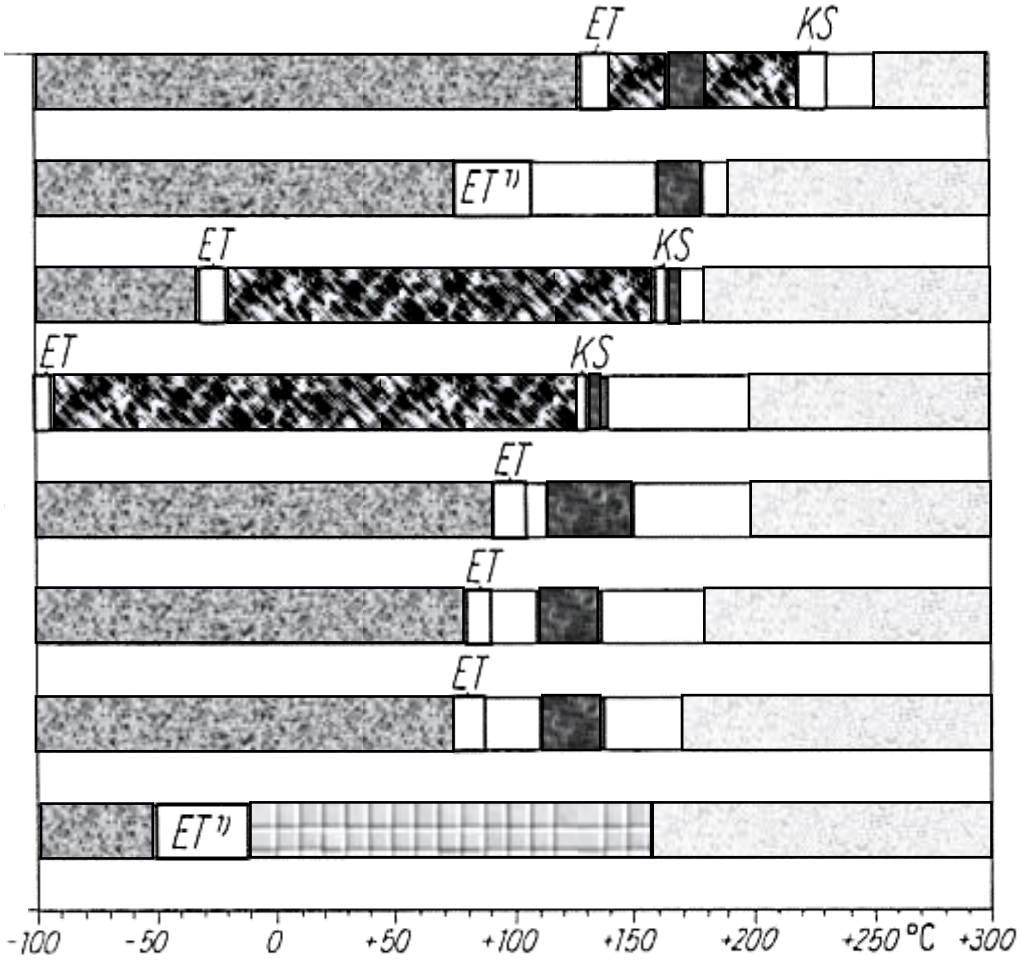
Temperature of use?



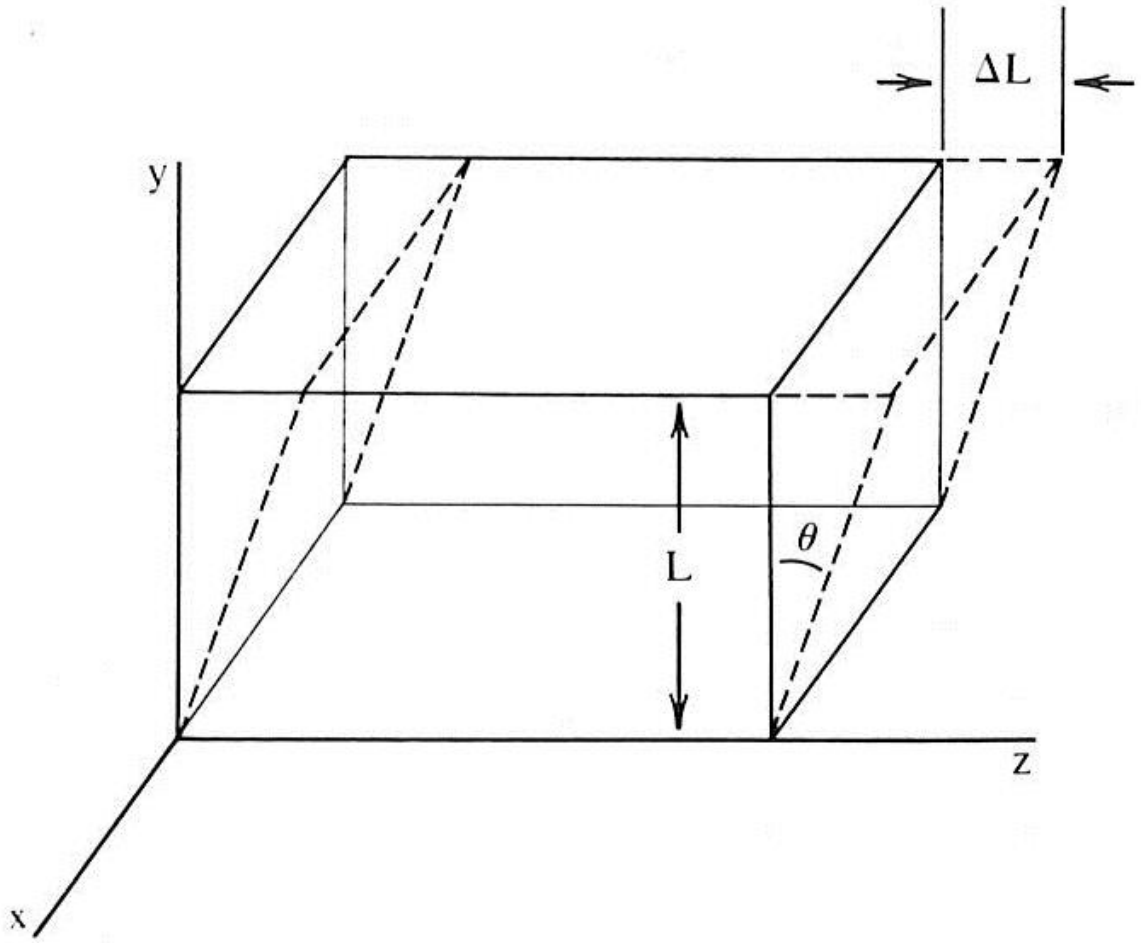
	amorphous plastics	partially crystalline	elastomers
Tg	60–260 °C	< 0 °C	< 0 °C
Tm	–	53–330 °C	
temperature of use	below Tg	between Tg and Tm	above Tg / Tm
plastics are	hard	medium hard	soft
elastic modulus	> 3000 MPa	> 2000–200 MPa	< 100–25 MPa
maximum strength	> 80–30 MPa	70–15 MPa	< 20 MPa
extension	< 2–4%, PVC > 10% bei Bruch	bis 20% Streckdehnung, 600% Bruchdehnung; vollverstreckte Fasern 1–3%, $\sigma_{zB} < 10^3$ MPa	entropieelastisch 100–1000%

1: glassy 2: partially crystalline 3: elastomeric
4: pseudoplastic / viscous flow 5: thermal decomposition

Temperature of use?

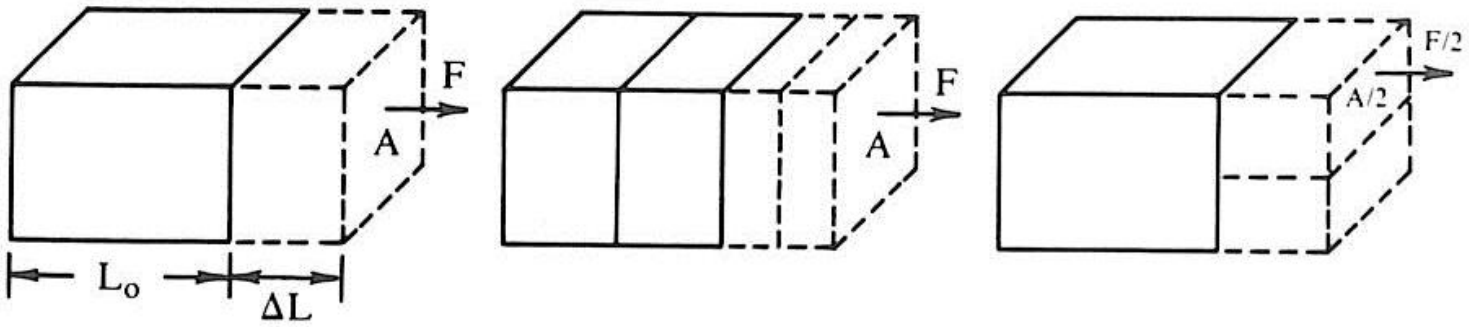


Definition of variables for shear deformation



Tensile: Relative length change

$F/A \propto \Delta L/L$



$$\text{poisson ratio } \mu = \frac{\Delta d/d}{\Delta L/L}$$

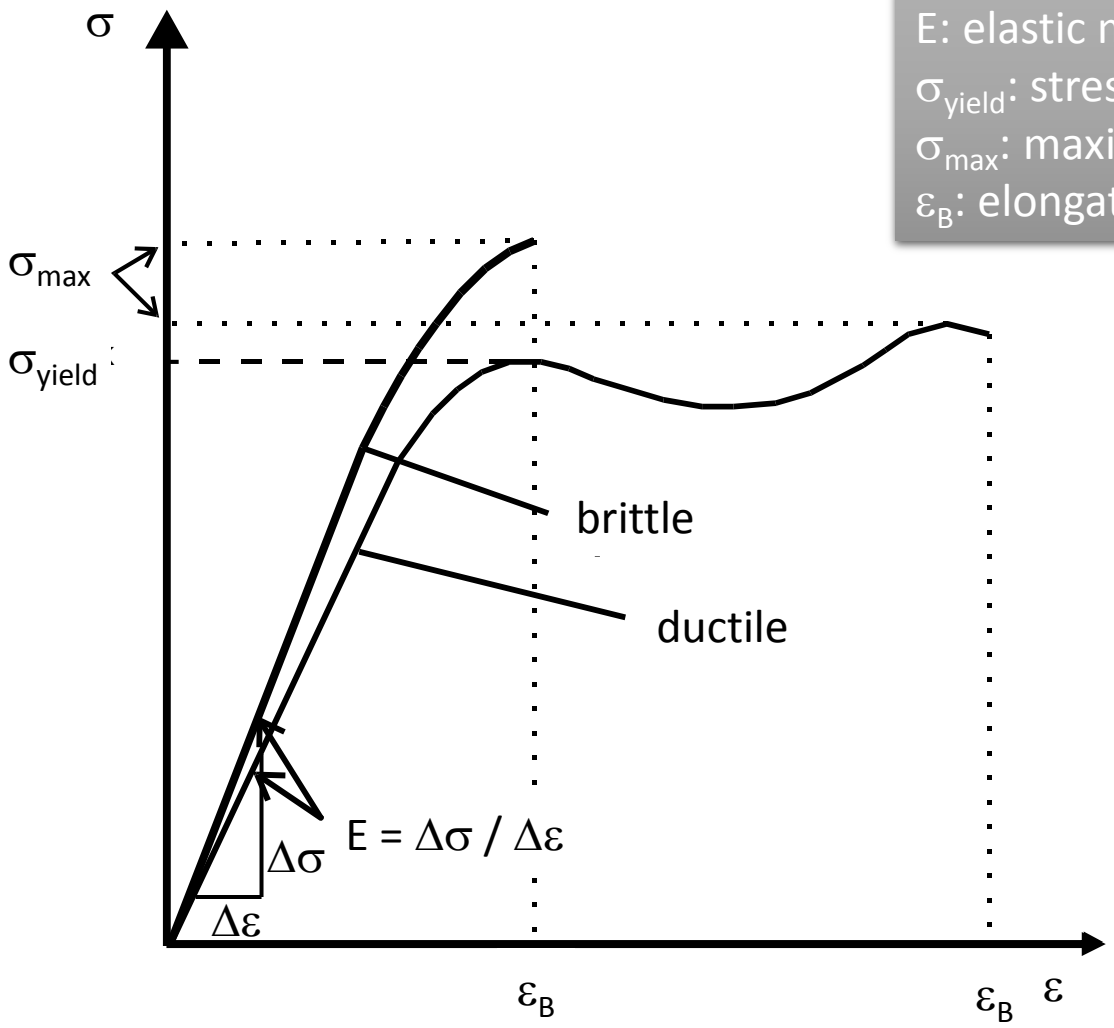
$\Delta d/d$: relative thickness change

$\Delta L/L$: relative length change

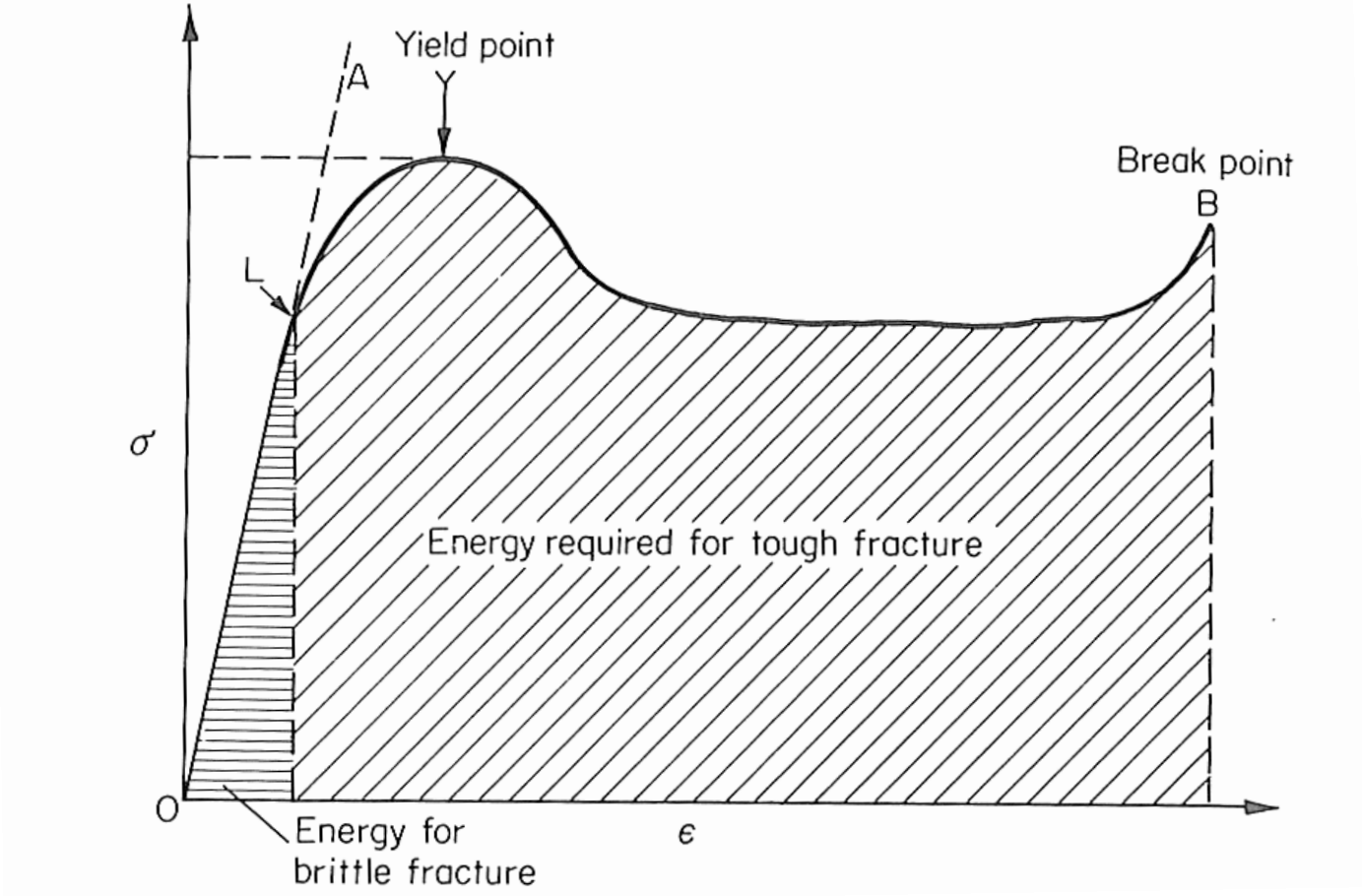
for polymers below T_g
$\mu \cong 0.35$
near T_g $\mu \rightarrow 0.3$

Behaviour of brittle and ductile thermoplastics in tensile experiment

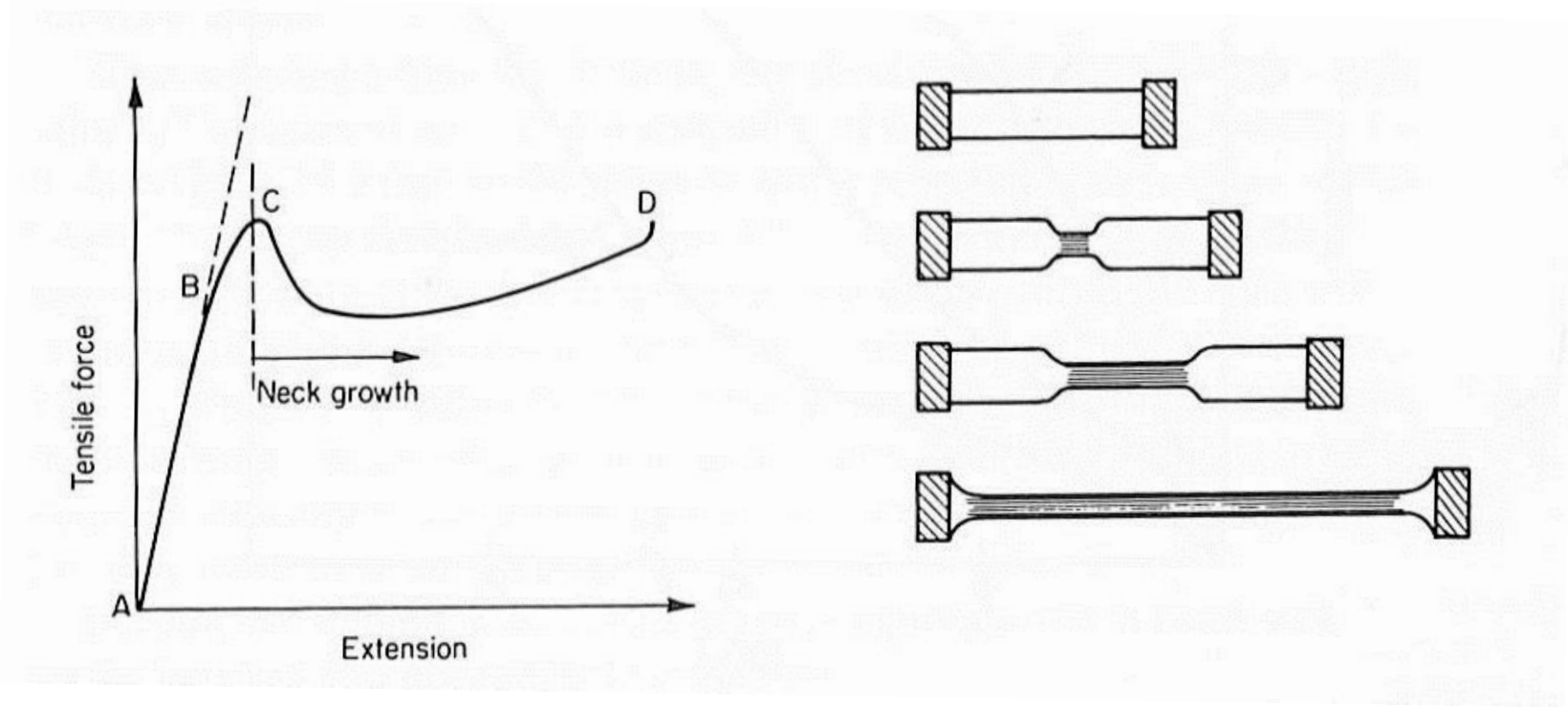
E: elastic modulus (Young‘s modulus)
σ_{yield}: stress at yield point
σ_{max}: maximum stress
ε_B: elongation at break point



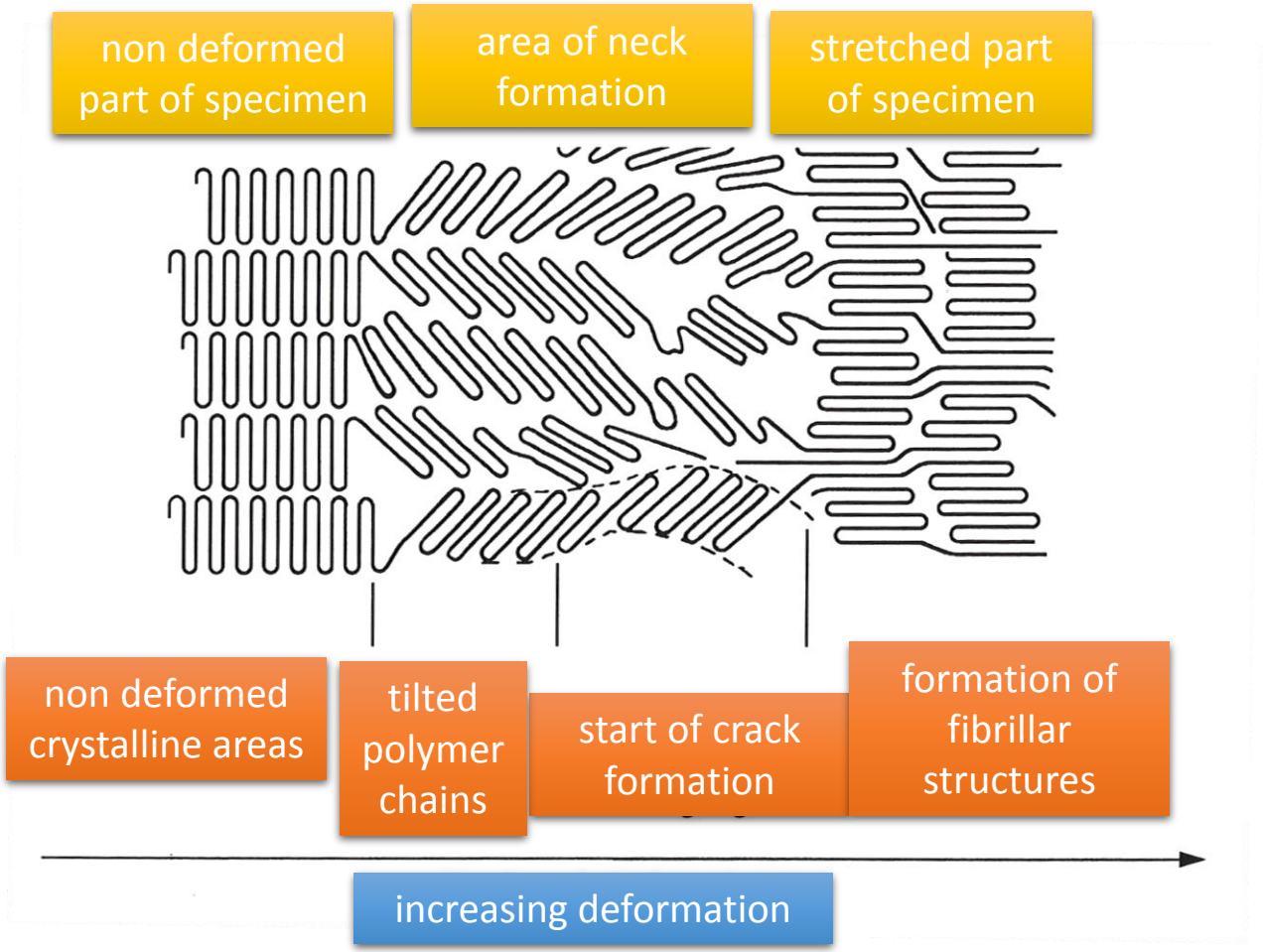
Deformation with low speed: Tensile experiment



Deformation with low speed: Tensile experiment

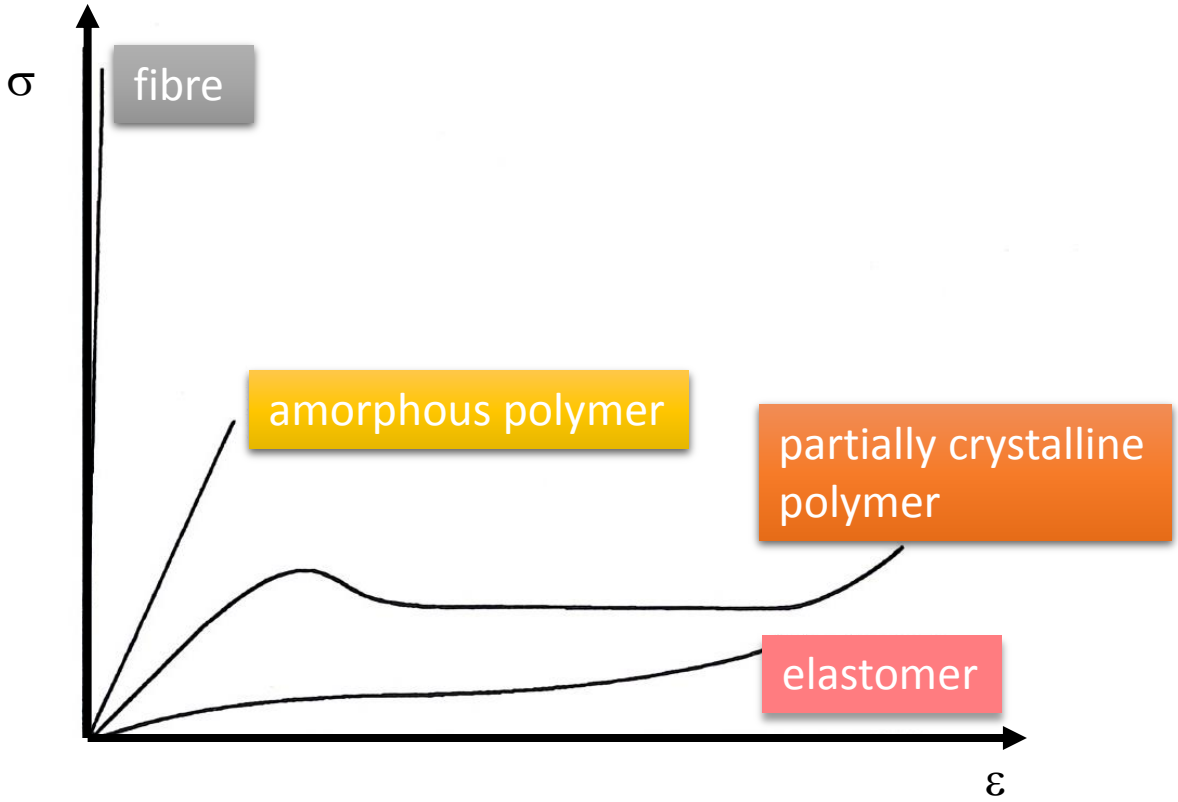


Micromechanical mechanism on the molecular level



B. Tieke

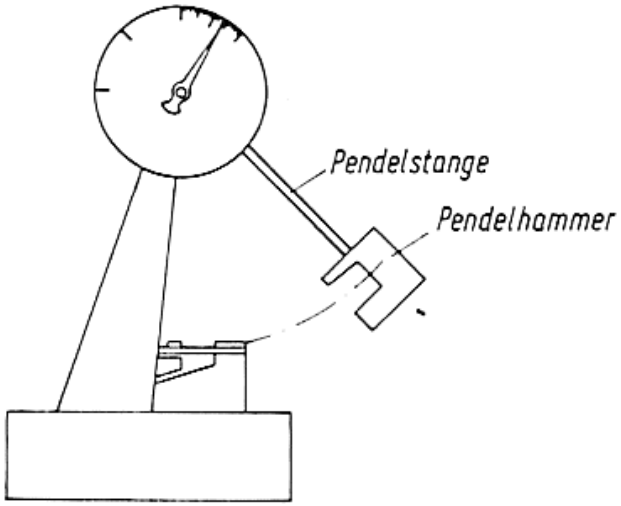
Mechanical properties for different types of samples in e.g. tensile experiment

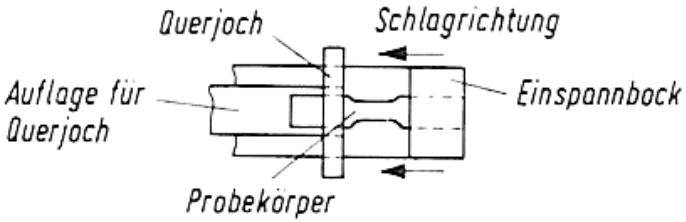


B. Tieke

Deformation with high speed: Impact behaviour

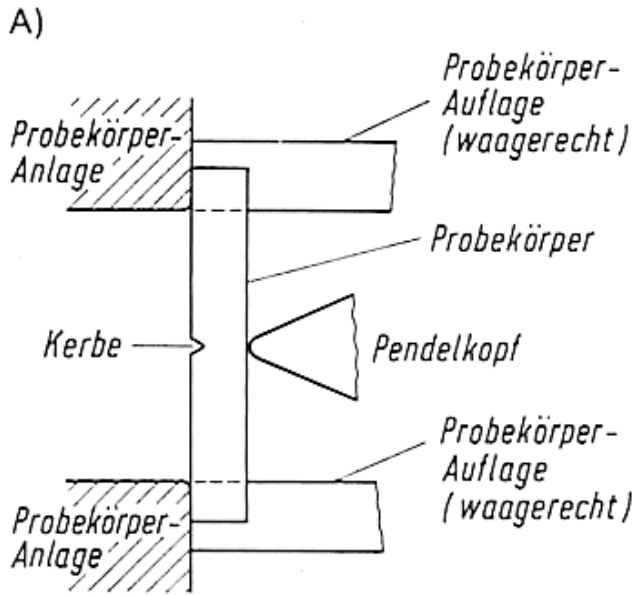
Impact testing



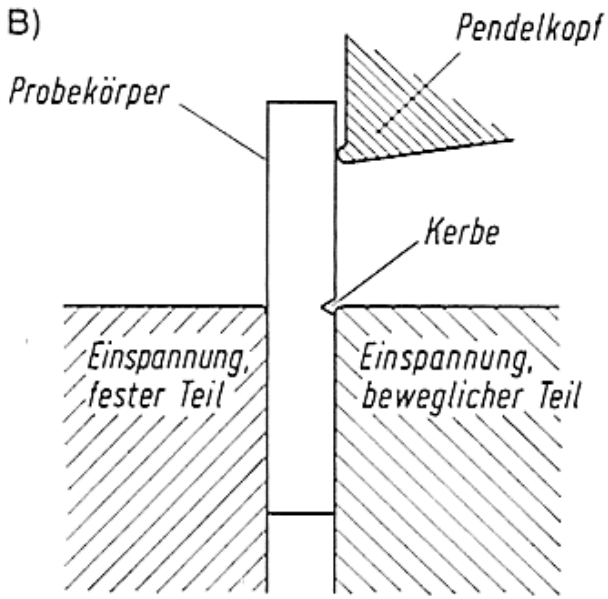


Impact testing: different testing modes

Charpy



Izod



impact strength ≠ strength from low speed experiment

!!! polymers = visco-elastic materials !!!

!!! time plays an important role !!!