Introduction to Macromolecular Chemistry

aka polymer chemistry

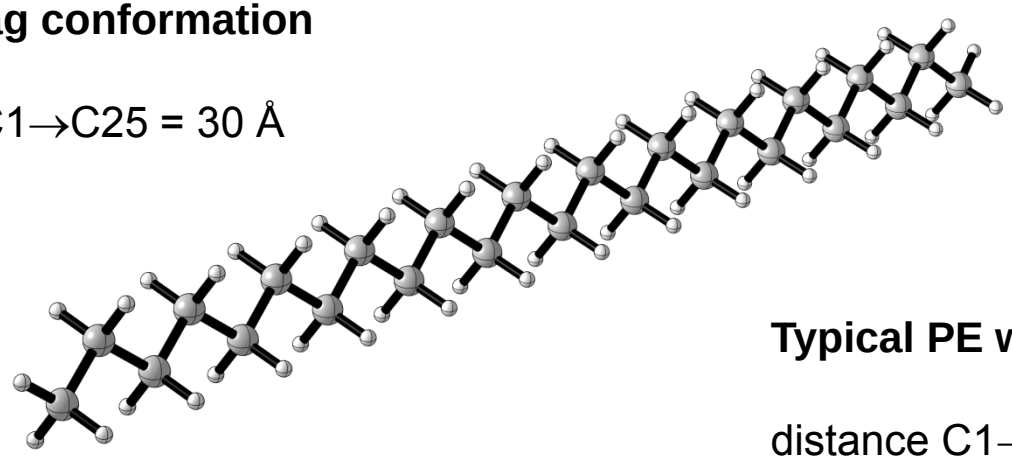
Mondays, 8.15-9.45 am, NC 02/99

Dr. Christian Merten, Ruhr-Uni Bochum, 2019

Solid state structures of polymers

C_{25}, zic zag conformation

distance C1→C25 = 30 Å



UNLIKELY OVER THE FULL LENGTH OF A POLYMER!

Typical PE with n=5000:

distance C1→C10000 = 1200 Å = 1.2 µm!

Does this mean, polymers don‘t crystallize? No.

- More ordered structure, more likely to form crystallites
- But: unlikely that molecules are fully crystalline
- But: unlikely that molecules are in only one crystallite

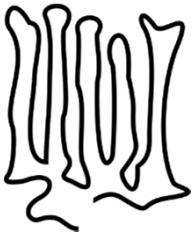
- Crystallization often kinetically hindered
- Slow tempering or slow evaporation of solvent leads to most ideal state

Solid state structures of polymers

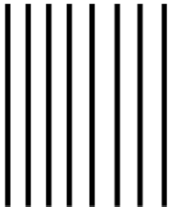
Three general solid state structures can be distinguished:

Amorphous: unordered, polymer chains entangled, hard and brittle

- amorphous structures formed preferentially during fast cooling of molten polymer



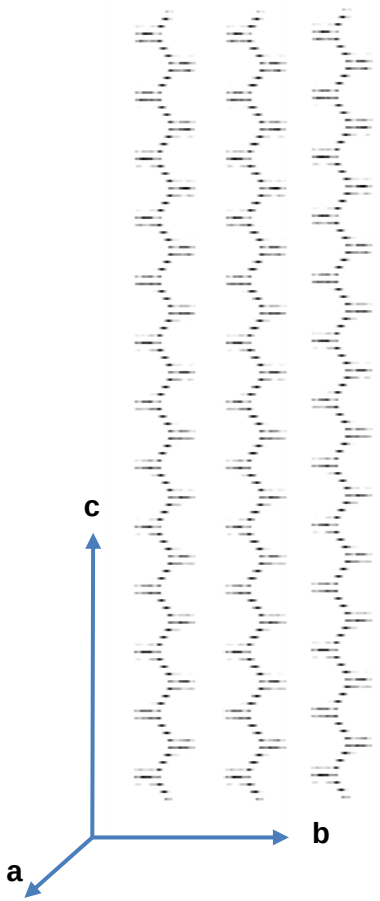
Semi-crystalline: both ordered and unordered domains



Crystalline: highly ordered structures

- formation of crystalline sturctures benefits from slow cooling of molten polymer

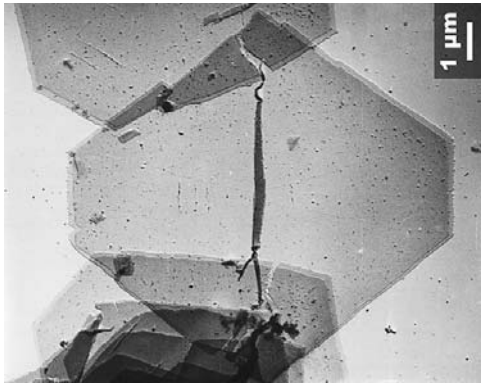
Solid state structures of polymers

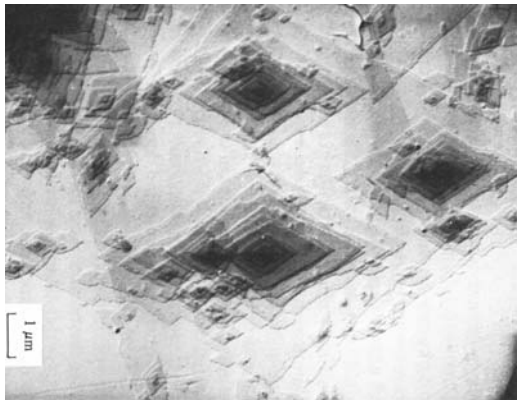


Lamellar growth

Crystallography of polymer crystals:
c-axis usually taken along molecular chain

X-ray diffraction confirms: c-axis perpendicular to surface





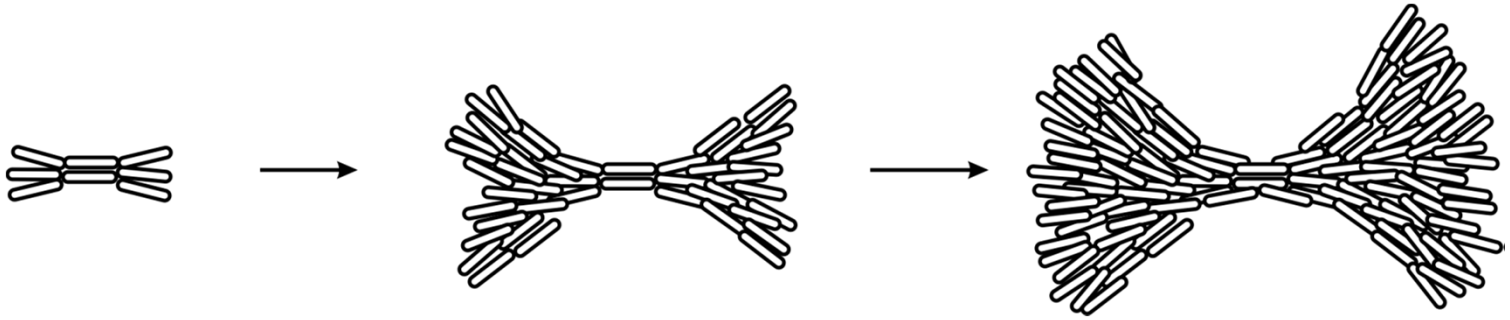
Uniaxial crystal, i.e. refractive indices $n_c \neq n_b \approx n_a$

Examples for single crystal studies
Polyethylene –(CH2)–: *Macromol. Rapid. Comm.* **10** (1982) 733-738
Polyoxymethylene –(OCH2)–: *Polym. Phys.* **20** (1982) 2003-2016

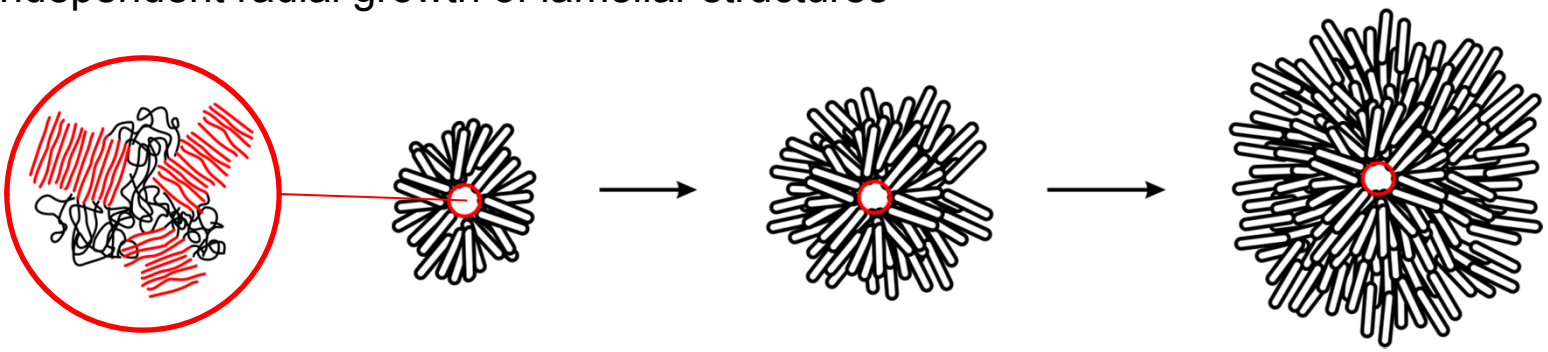
Solid state structures of polymers

How does a polymer crystallize from the melt?:

a) growth starts with lamellar crystal, followed by low angle branching



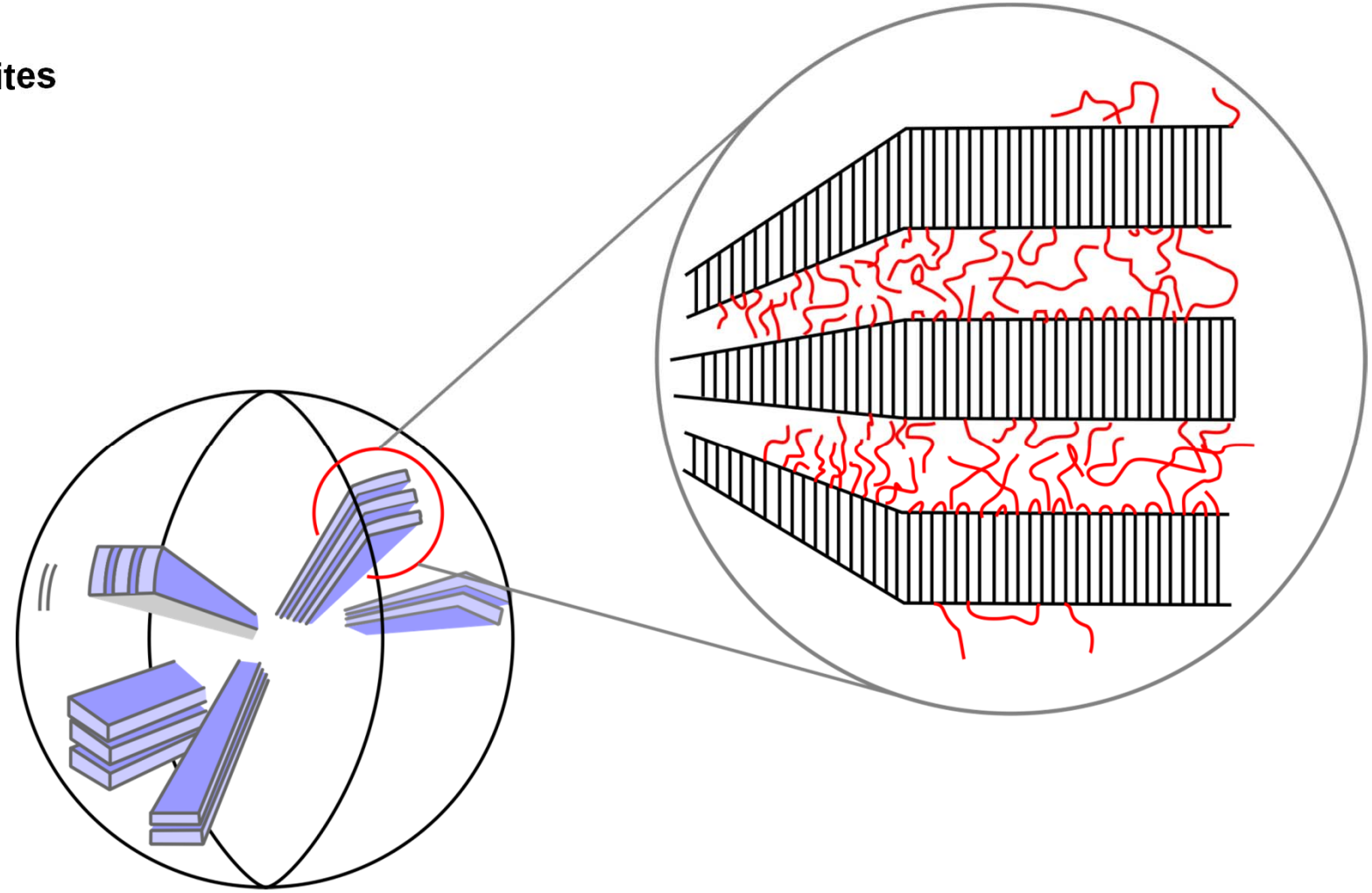
b) Independent radial growth of lamellar structures



Solid state structures of polymers

If this happens in the bulk phase, three-dimensional crystallization occurs:

Spherulites

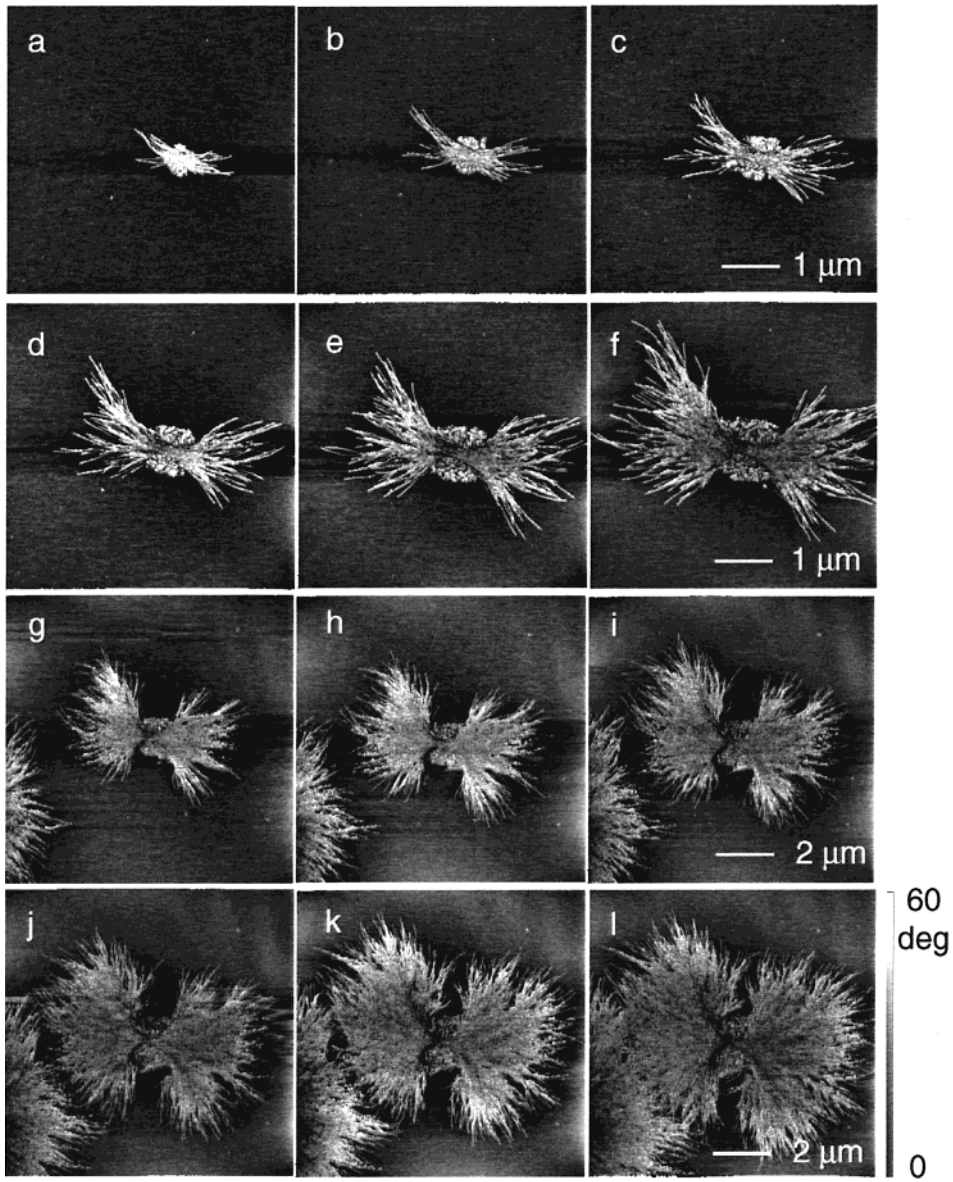


Solid state structures of polymers

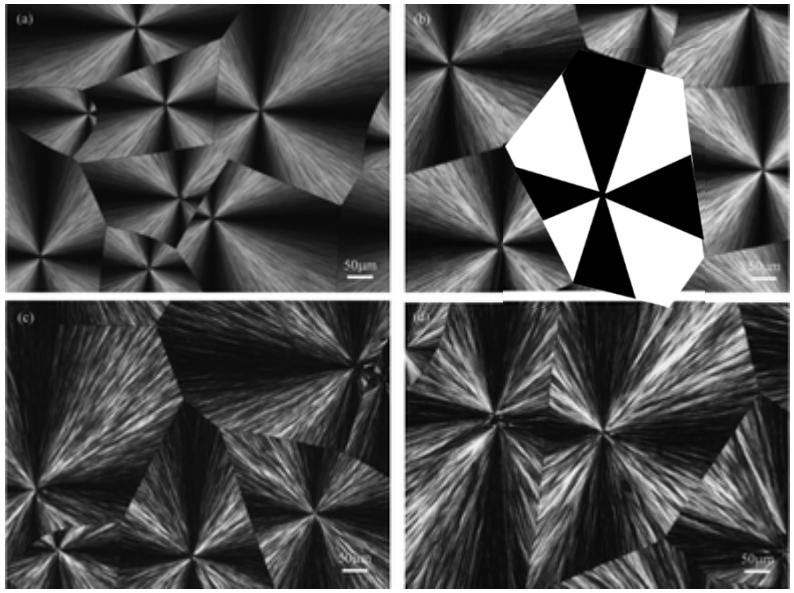
Direct Observation of Growth of Lamellae and Spherulites of a Semicrystalline Polymer by AFM

Lin Li et al.

Macromolecules **2001,** *34,* 316-325



Solid state structures of polymers

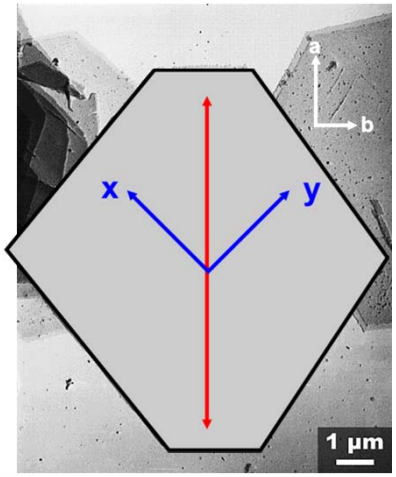


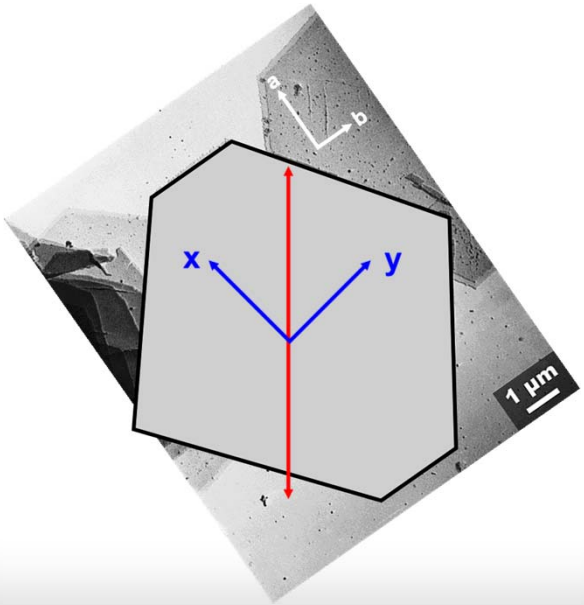
CrystEngComm. 2012, 14, 3586-3595

Polarized optical microscopy (POM) images

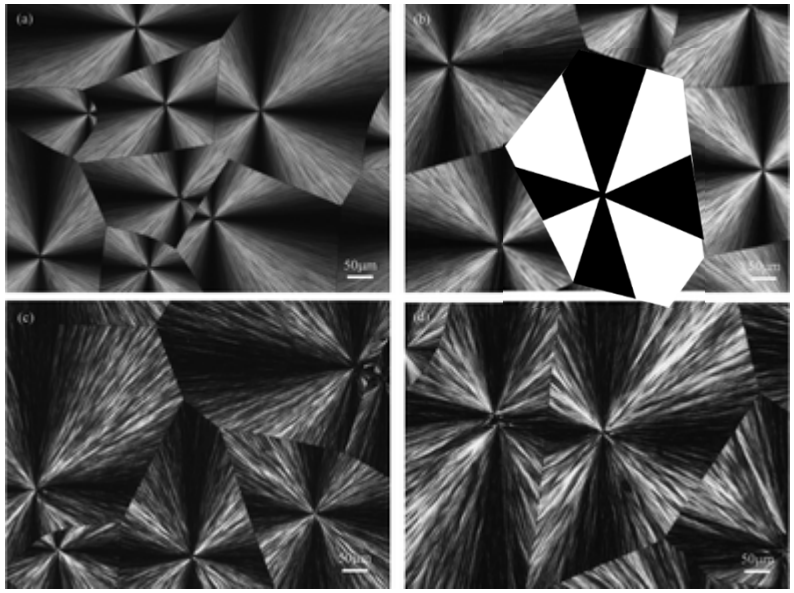
Typical Maltese cross pattern under crossed polarizers arising from birefringance of polymer lamella

How can this pattern be explained?





Solid state structures of polymers



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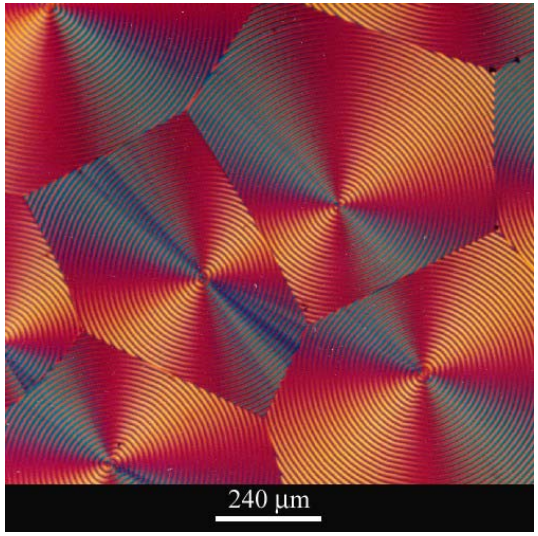
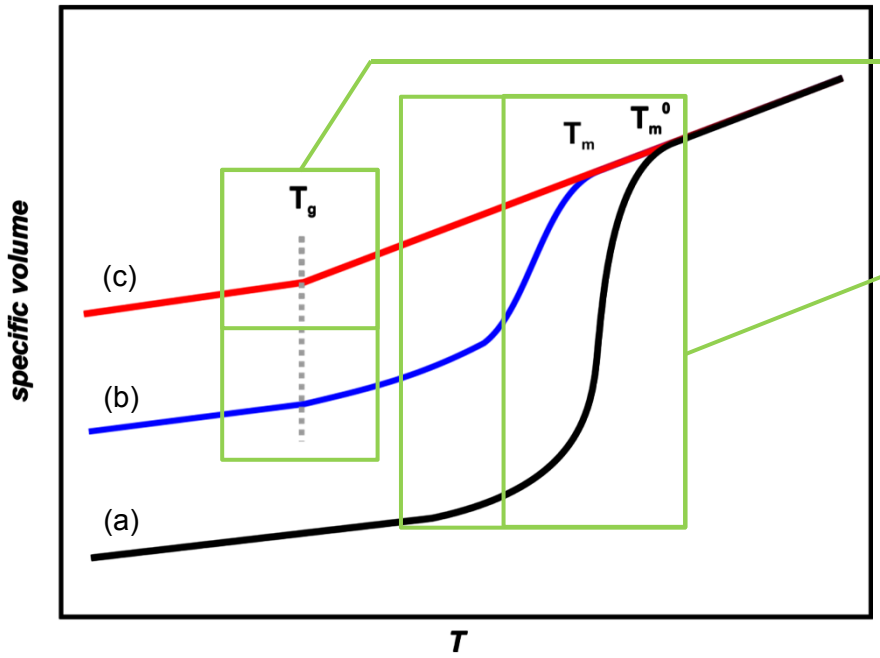


micrograph 601 in the DoITPoMS Micrograph Library
University of Cambridge

Banded spherulites arising from helical twisting of lamellar structures during growth

Solid state structures of polymers

When melting polymers, some charactersitic transition temperatures can be observed:



Note: T_g
Kink in melting curve denotes glass transition

Note: T_m
Broad melting range instead of sharp melting point due to different chain lengths

(a) crystalline polymer
(b) semi-crystalline polymer
(c) amorphous polymer

Differential Scanning Calorimetry (DSC)

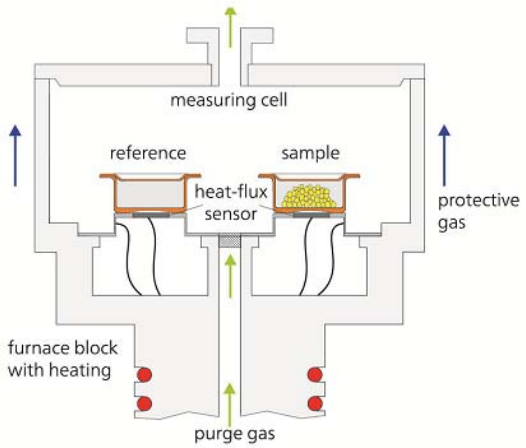
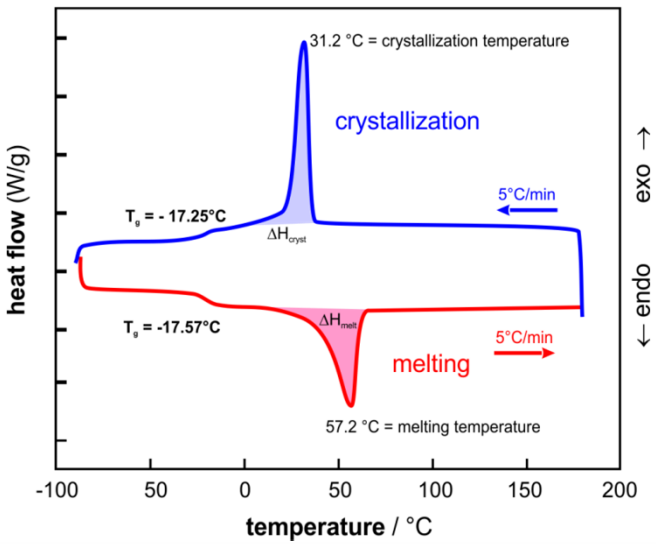


Figure: Netzsch (www.netzsch-thermal-analysis.com)

Working principle of DSC is simple:

- Slow heating to maintain equilibrium (constant rate)
- Measure heat flow necessary to maintain heating rate
- Possible coupling with other techniques such as thermogravimetry, MS, …



Analysis

Heat flow correlates with heat capacity cP

At T_g: jump due to increased/decreased chain flexibility
At T_m: latent heat can be measured (ΔH_m)

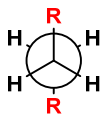
Possibilities:
Melting and crystallization rates, thermal history

Melting temperature

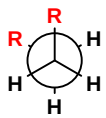
Factors influencing the melting temperature

- **Conditions of crystallization**
  - *Rule of thumb:* Crystallization possible between (T_g + 30°C) and (T_m - 10°C)
  - Temperature determines chain flexibility: if too low, chains not flexible enough to crystallize
  - Due to chain entanglement, crystallization generally slow → cooling rate determines crystallinity

- **Chain flexibility**
  - Crystal (= highly ordered) vs. Entropy
  - Loss in entropy due to crystallization correlated with number of conformations in molten state



vs.



PE	ΔE = 3 kJ/mol	T_m = 137 °C
PTFE	ΔE = 18 kJ/mol	T_m = 372 °C

  - If ΔE between conformers is small, polymer tends to form random coil

    → high conformational entropy, low melting point

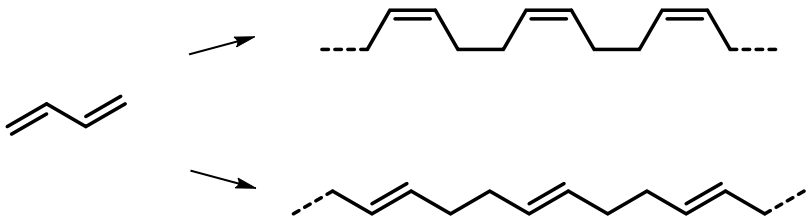
Melting temperature

Factors influencing the melting temperature

- **Chain symmetry**

  Unsymmetric units or kinks in chain prevent/disturb packing in solid state → decreased melting point

  Example:

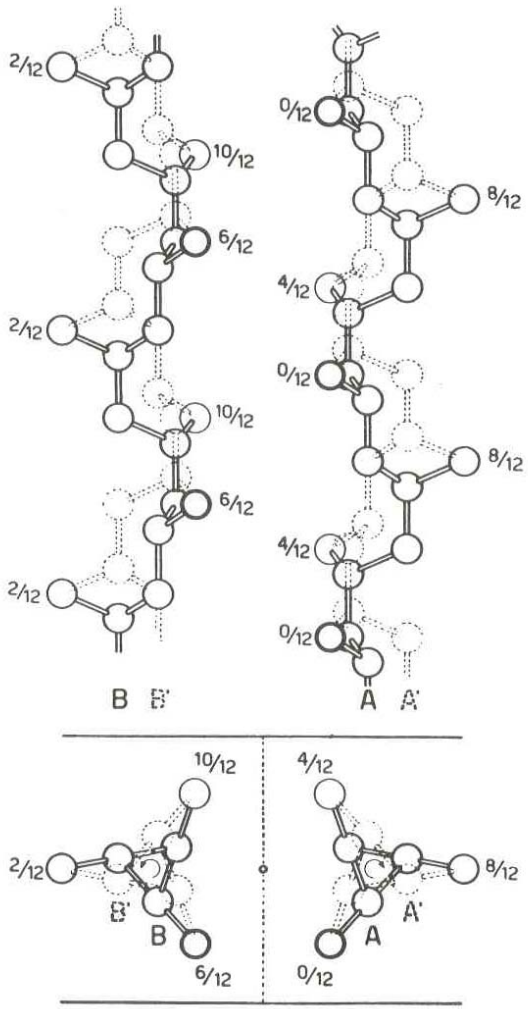


cis-1,4-polybutadiene
amorphous, sticky

trans-1,4-polybutadiene
semi-crystalline, high melting point

  Chain elements leading to kinks in polymer chain:

Melting temperature



it-PP

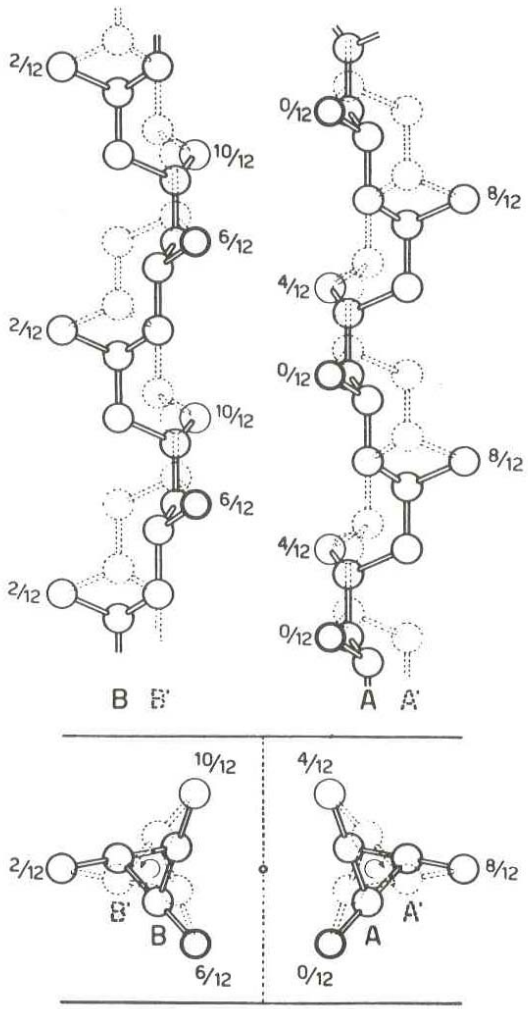
from Takamoto, Structure of Crystalline Polymers, Wiley, 1979

Factors influencing the melting temperature

- **Tacticity**
  - Isotactic polymers usually form helical superstructures to compensate interactions of the side chains
  - Helices packed regularly in crystallites
  - Syndiotacticity forces backbone out of most favorable helical structure towards zig zac
  - Atactic polymers cannot form superstructure

Example:	it-PS	T_m = 240 °C
	st-PS	T_m = 270 °C
	at-PS	amorphous (T_g ~ 90 °C)

Melting temperature



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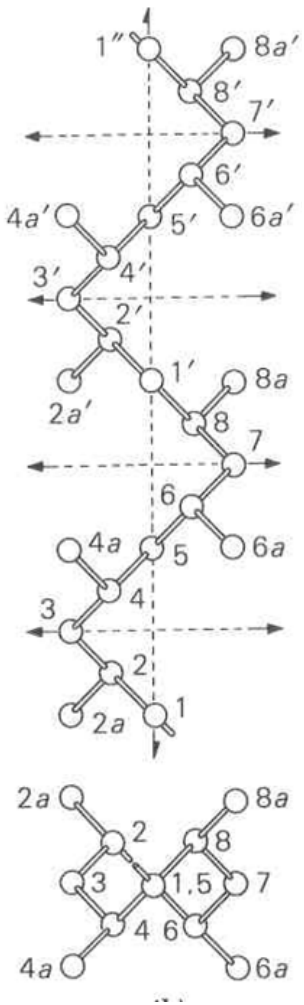
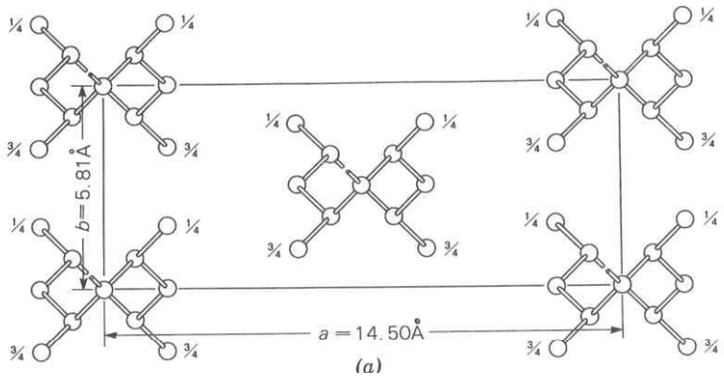


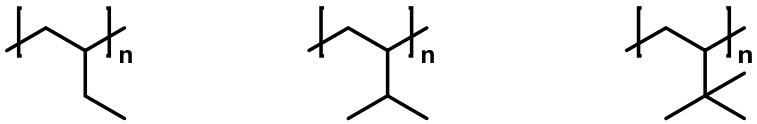


st-PP

Melting temperature

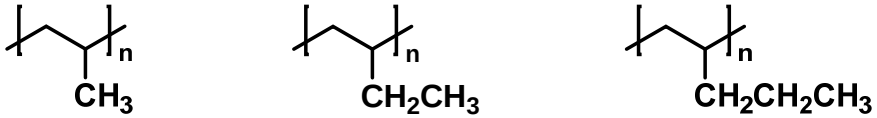
Factors influencing the melting temperature

- **Branching**
  - Bulky side groups: Lower crystallization entropy, higher melting point



T_m = 126 °C T_m = 145 °C T_m = 326 °C

  - Long side chains, however, disturb packing; if long enough, crystallization effects of side chain become important as well



T_m = 170 °C T_m = 145 °C T_m = 80 °C

  - Branching of main chain (cf. LDPE)

Melting temperature

Factors influencing the melting temperature

- **Molecular weight**
  - Short chains:

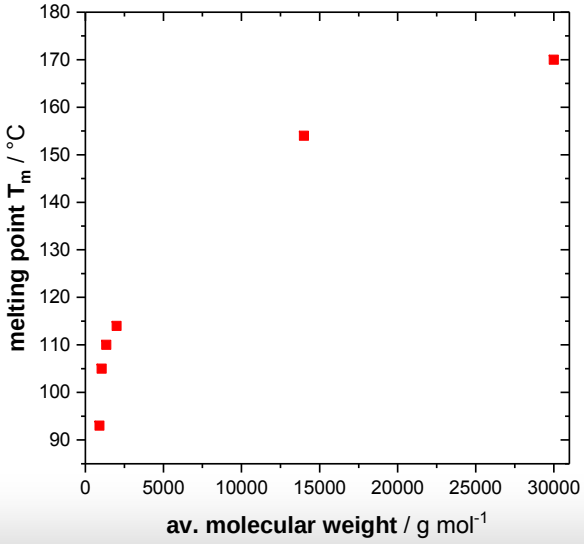
    Chain ends are more flexible than units along the chain

    → Disturbing crystal packing, lower T_m : *Thermodynamic effect*

  - Very long chains:

    Crystallization is slow; especially at high cooling rates, the crystallinity might be lowered: *Kinetic effect*

  - *Example:* it-PP



Glass transition temperature

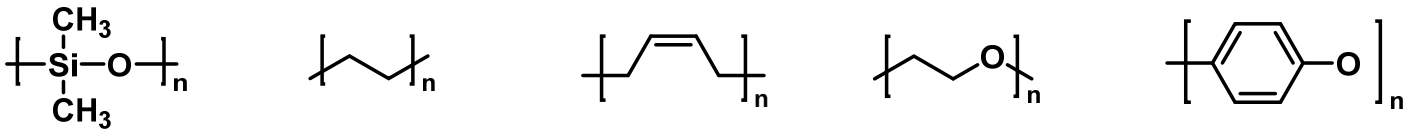
Reminder:

- Glass transition is a second order phase transition
- Below T_g, chain is frozen; above T_g, chain becomes flexible and can undergo conformational changes

Most important factors influencing T_g:

- Chain flexibility
- Tacticity
- Branching and crosslinking
- Molecular weight

Example for chain flexibility:



T_g / °C =	-123	-93	-85	-67	+85

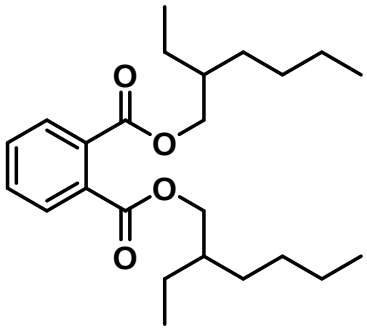
Glass transition temperature

Most important factors influencing T_g:

- Chain flexibility
- Tacticity
- Branching and crosslinking
- Molecular weight

- **Plasticizer!!**

  Non-volatile, low molecular weight compounds → increase chain flexibility, lower T_g



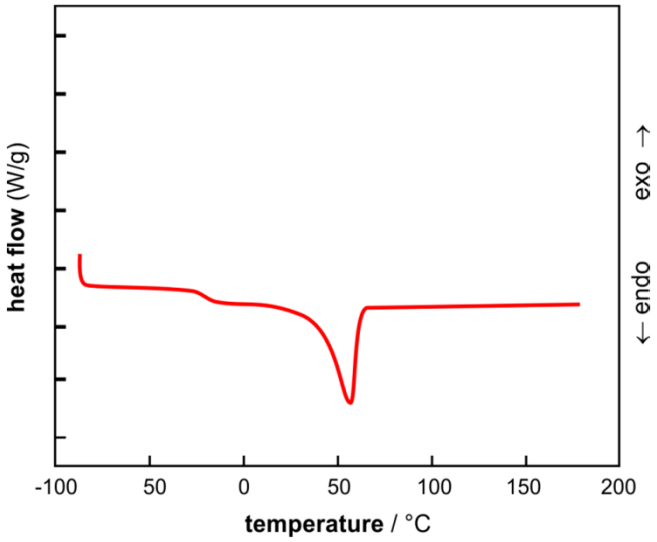
PVC	T_g = 81 °C
PVC + 30-40 % DEHP	T_g < 0 °C

Estimation of effect: $$\frac{1}{T_g} = \frac{w_{pol}}{T_{g,pol}} + \frac{w_{pl}}{T_{g,pl}}$$

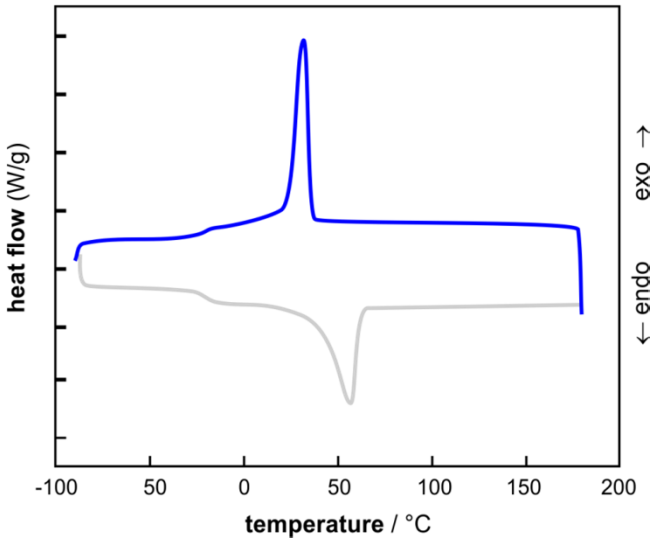
w_{pol} = mass fraction polymer
w_{pl} = mass fraction plasticizer
$T_{g,pol}$ = glass temp of pure polymer
$T_{g,pl}$ = freezing point of plasticizer

Exercise: DSC diagrams

How does a DSC melting curve change when the polymer is less crystalline?

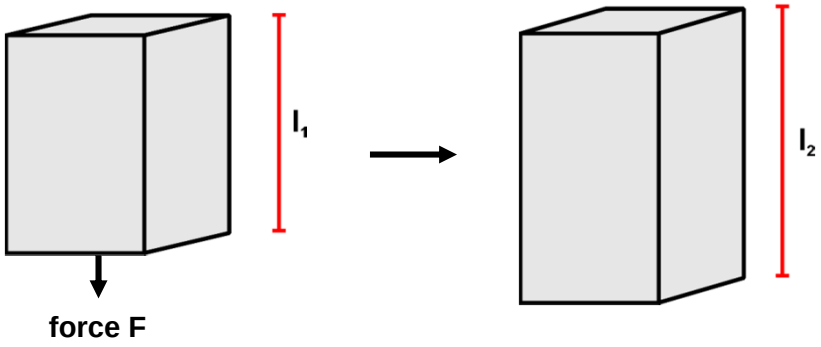


How does a DSC crystallisation peak change when the polymer is cooled down fast?



Mechanical properties: A few terms explained

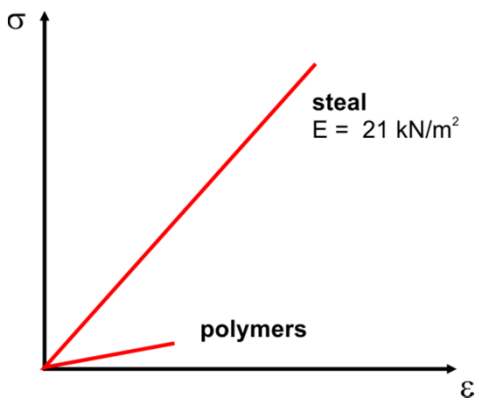
Tensile load (fully elastic):



A force applied perpendicular to surface results in change in length:

$$\frac{l_2 - l_1}{l_1} = \frac{\Delta l}{l_1} = \varepsilon$$ ε: elongation

$$\frac{F}{A} = \sigma$$ σ: tensile strength



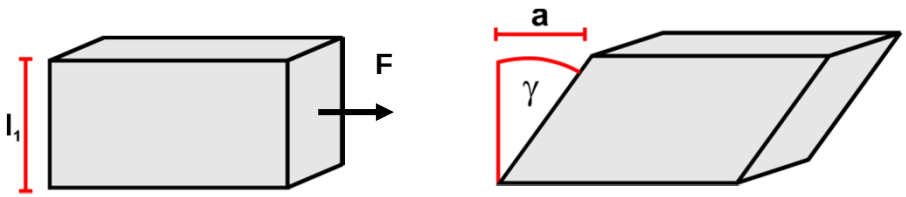
If deformation is fully reversible: Hooke's law

$$\boxed{E \cdot \varepsilon = \sigma}$$ E: Young's modulus / N m^2

… hence, only valid for small forces

Mechanical properties: A few terms explained

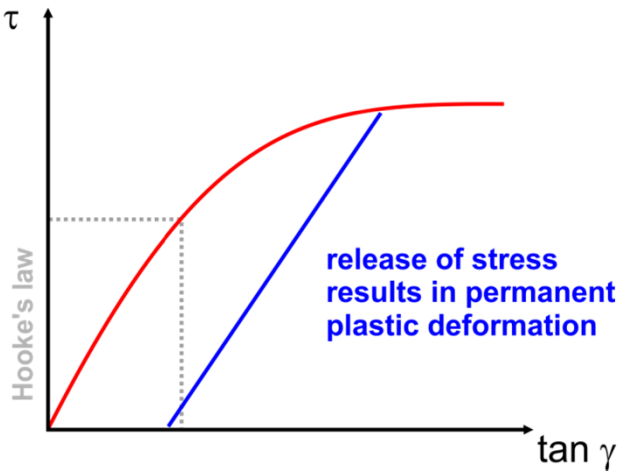
Shear stress:



A force applied parallel to surface results in change in shearing:

$$\tan\gamma = \frac{a}{l_1}$$ γ: shear angle

$$\frac{F}{A} = \tau$$ τ: shear stress



If deformation is fully reversible (ideal elasticity):

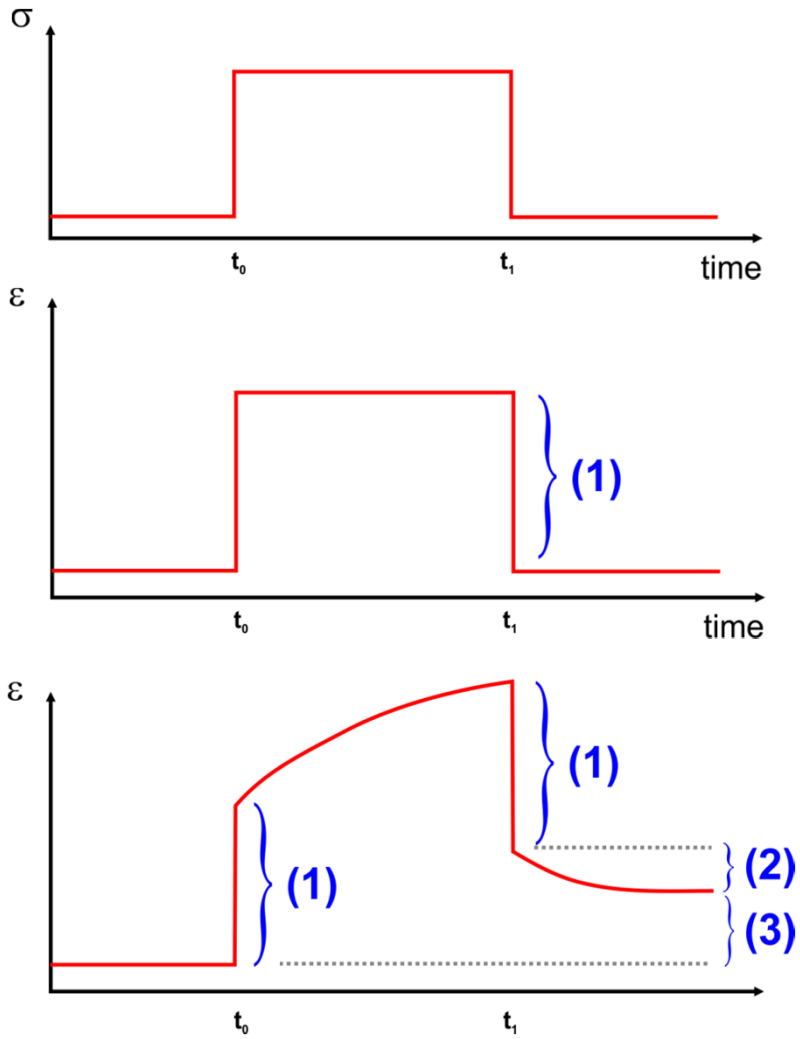
$$\tan\gamma \cdot G = \tau$$ G: shear modulus / N m^2

Elastic deformation: fully reversible

Plastic deformation: permanently deformed

Mechanical properties: Viscoelasticity

Time dependence of deformation:



Assume we apply a tensile strength σ for a certain time t_1 to a material slightly above T_g

A fully elastic material will completely relax into its initial shape after the force is removed

(1) Ideal elastic behaviour

For long time stress, or if going beyond the elastic regime, one observes:

(2) viscoelastic deformation (time dependent)

(3) plastic deformation

Mechanical properties: Viscoelasticity

What happens?:

(1) Elastic behaviour – short time stress

If force is released, polymer chain can go back to initial position ➢ material behaves like spring

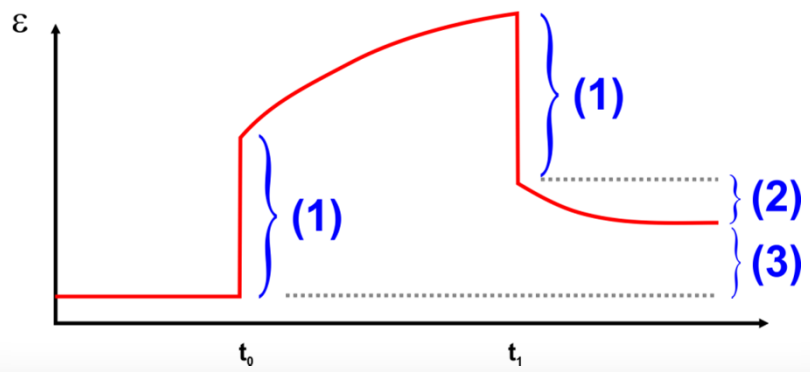
(2) Viscoelastic behaviour / creeping – long time stress

As consequence of reorientation of chains, they cannot return to initial position ➢ **materials flows!**

Increase in temperature enhances viscoelasticity

(3) Plastic deformation

Although stress is removed, polymer chain remain reoriented



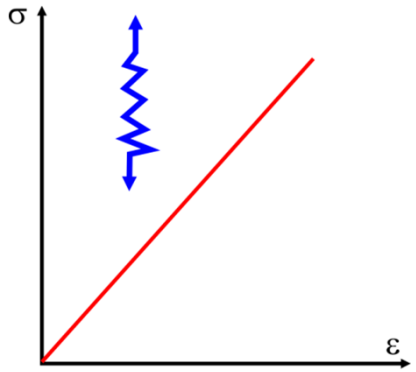
Mechanical properties: Viscoelasticity

Under mechanical stress, a polymer can behave like an elastic solid or a highly viscous liquid!

… depending on the temperature and the intensity and duration of the stress.

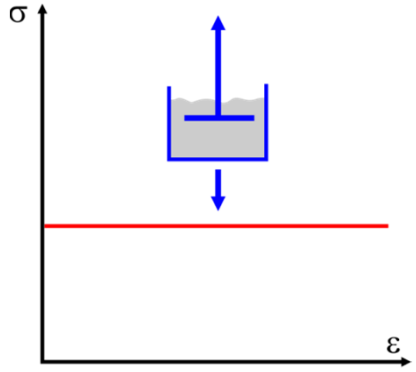
Mechanical description of each state

elastic behaviour (energy storage):
spring model



Hooke: $E \cdot \varepsilon = \sigma$

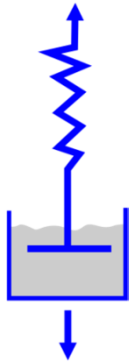
viscous liquid (energy disscipation):
dampener model



Newton: $\sigma = \eta \frac{d\varepsilon}{dt}$

Mechanical properties: Viscoelasticity

Mechanical description: Maxwell-Ansatz



Viscoelastic system described as serial combination of spring and dampener

Total elongation $\varepsilon = \varepsilon_{elast} + \varepsilon_{visc}$

Combining Hooke and Newton: $\frac{d\varepsilon_{elast}}{dt} = \frac{1}{E} \cdot \frac{d\sigma}{dt}$ and $\frac{d\varepsilon_{visc}}{dt} = \frac{\sigma}{\eta}$

leads to $\frac{d\varepsilon}{dt} = \frac{1}{E} \cdot \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$

$$E \cdot \varepsilon = \sigma$$

$$\sigma = \eta \frac{d\varepsilon}{dt}$$

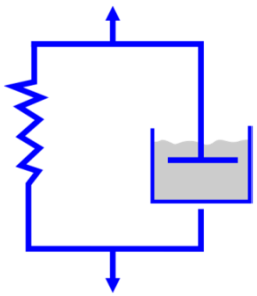
and for constant elongation, i.e. for $d\varepsilon/dt = 0$, we get

$$\sigma = \sigma_0 \cdot \exp(-\frac{E}{\eta} t)$$

- Description for stress relief of quickly elongated sample:
  Force needed for elongation (resp. to keep material elogated) decreases exponentially over time!

Mechanical properties: Viscoelasticity

Mechanical description: Voigt-Kelvin model



Viscoelastic system described as parallel combination of spring and dampener

Total stress $\sigma = \sigma_{elast} + \sigma_{visc} = E\varepsilon + \eta \frac{d\varepsilon}{dt}$

Applying a force/stress, it follows (after integration) that

$$\varepsilon = \frac{\sigma_0}{E}\left(1 - \exp\left(-\frac{E}{\eta}t\right)\right)$$

$$E \cdot \varepsilon = \sigma$$

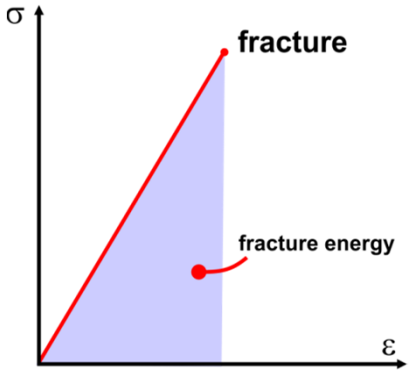
$$\sigma = \eta \frac{d\varepsilon}{dt}$$

- Description for time-dependence of elongation at constant force:
  At first, dampener delays elognation, which then increases and finally slows down due to restoring force of spring

Note: Both Maxwell and Voigt-Kelvin do not allow complete description. More complex models are needed!

Mechanical properties: Mechanisms of failure

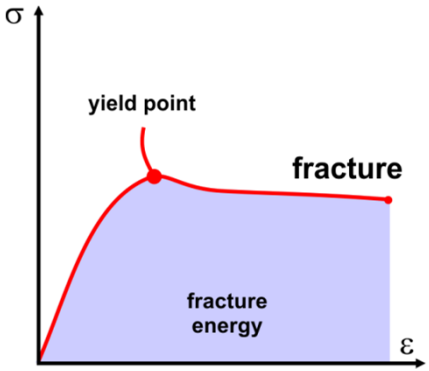
Very broad materials properties adjustable, so mechanisms of polymer fracturing are manifold!



(A) Brittle fracture

High Young modulus: small elogation -> high tension

Typical for brittle, hard materials, *i.e.* for polymers below T_g.



(B) Tough fracture

Less stiff materials

Begins to flow at yield point, after that, stress-strain curve little defined

Comparable to shewing gum.

Fracture behaviour is also temperature dependent!

Mechanical properties: Controlling mechanical properties

General aspects

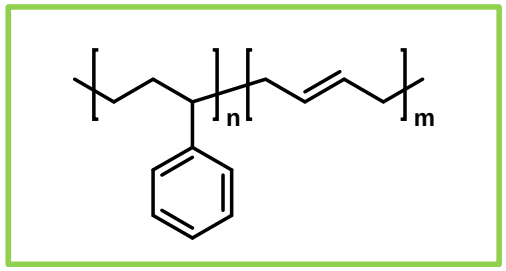
All polymers have approx. the same main chain stability (all are made of C-C, C-O, C-N, …).

Hence, most mechanical properties are controlled by intermolecular interactions:

- PE / PP: van-der-Waals interactions
- Polar groups like nitrile (-CN): dipole-dipole interactions → increase stiffness
- For thermoplastic polymers: Increase in molecular weight / removal of low molecular weight impurities

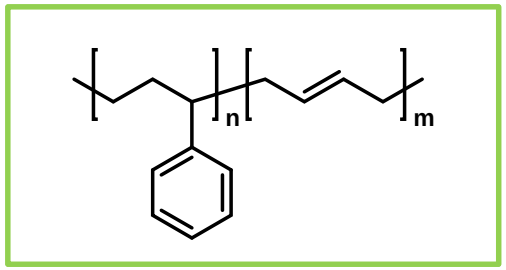
… which is all valid for homopolymers.

But how about block copolymers such as SBS?



Mechanical properties: Controlling mechanical properties

But how about block copolymers such as SBS?



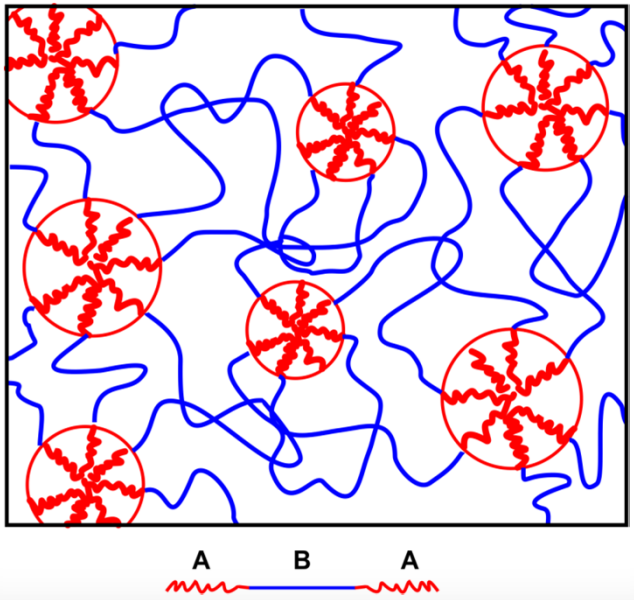
- Chemically different polymers are usually not mixable in molten state (just like water and hexane)
- Same is true for block co-polymers → solid state segregation/demixing

- Due to chemical linkage between polymers, no macroscopic segregation for block copolymers:

  ➢➢ heterogenic phase on nanoscale!

- Two glass transition and melting points!

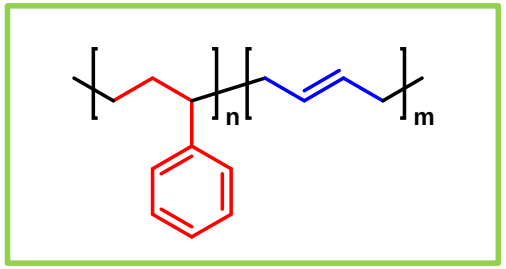
  … with the lower T_g and higher T_m are important



Mechanical properties: Controlling mechanical properties

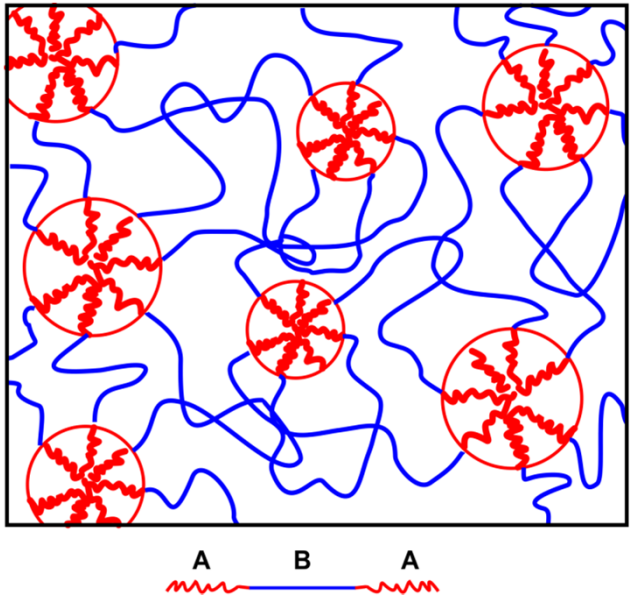
Segregation at the nanoscale

➢➢ heterogenic phase on nanoscale!



For poly(styrene)-block-poly(butadiene), i.e. SBS:

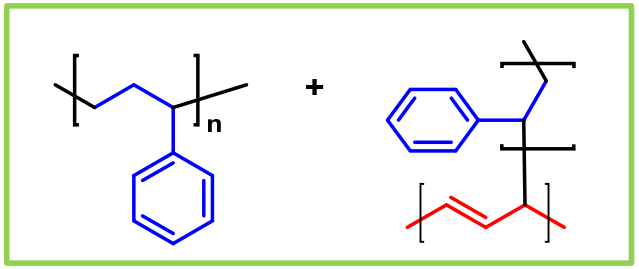
continous phase:	soft elastic polymer
aggregated, spherical phase:	stiff polymer
Below T_M of PS-phase:	crosslinked elastomer
Above T_m of PS-phase:	plastically deformable



Mechanical properties: Controlling mechanical properties

Segregation at the nanoscale

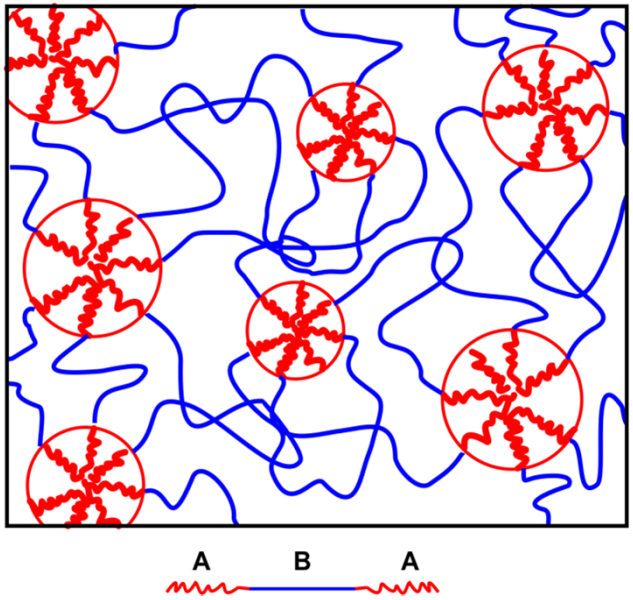
➢➢ heterogenic phase on nanoscale!



For mixture of PS and PS-graft-polybutadiene:

continous phase: stiff polymer (PS)

aggregated, spherical phase: elastic polymer

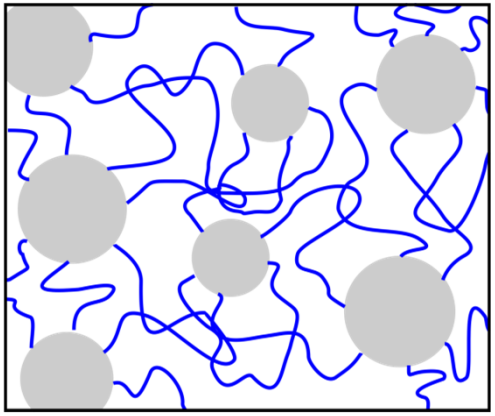


Soft phase can dissipate impact energy!

➢➢ **Increased impact resistance**

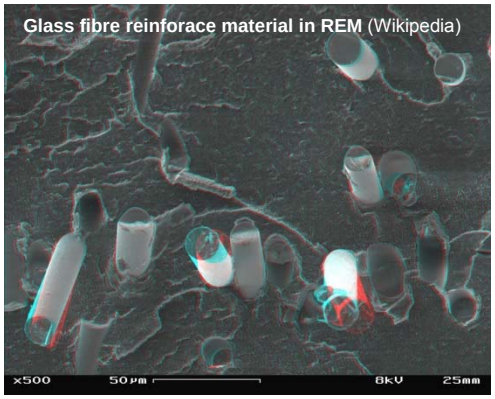
Mechanical properties: Fillers

Mixing polymers with solid fillers



(A) Soot (carbon black) and graphite:

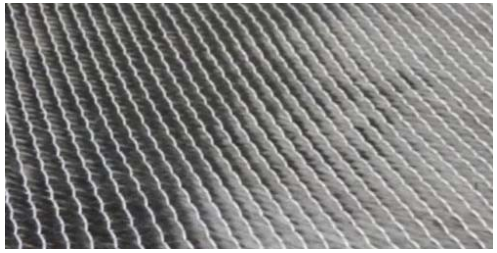
- Filler for technical rubbers (car wheels, transportation belts)
- Electrical conductivity
- Pigments



Glass fibre reinforace material in REM (Wikipedia)

(B) Glass fibres

- Short fibre fragments: good plasticity
- Woven fabric fibres (meshs): lightweight construction

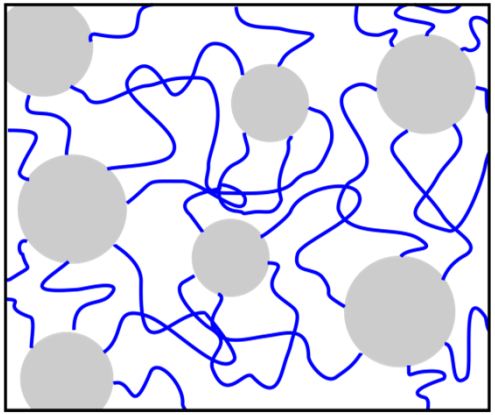


(c) Carbon fibres

- Typically embedded in epoxid resin for lightweight construction (*e.g.* tail unit of Airbus A380!)

Mechanical properties: Fillers

Mixing polymers with solid fillers



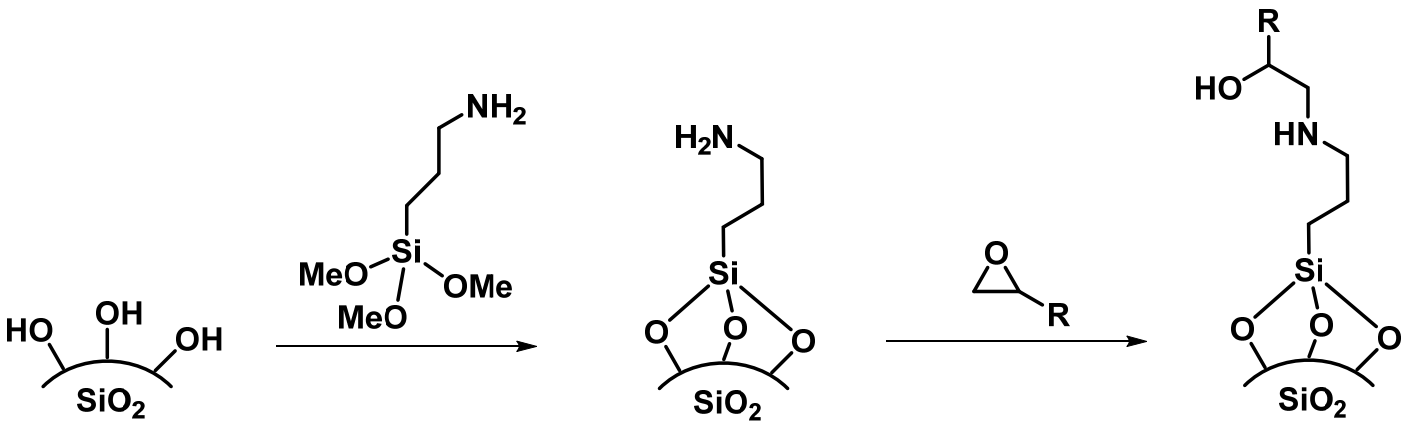
(D) Silica particles

- Can be embedded with and without covalent linkage to polymer

- Covalent linkage:

  (1) Crosslinking with matrix polymer

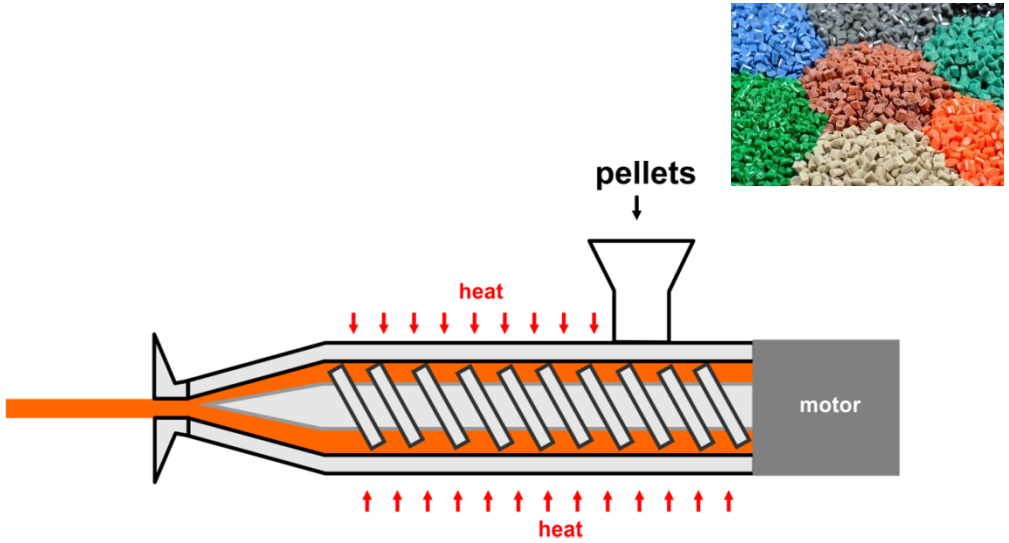
  (2) Initiator for polymerization reaction



Polymer processing: Primary shaping

Extrusion

Polymer pellets are heated/molten and pressed into the desired shape, e.g. rods, plates, foils…



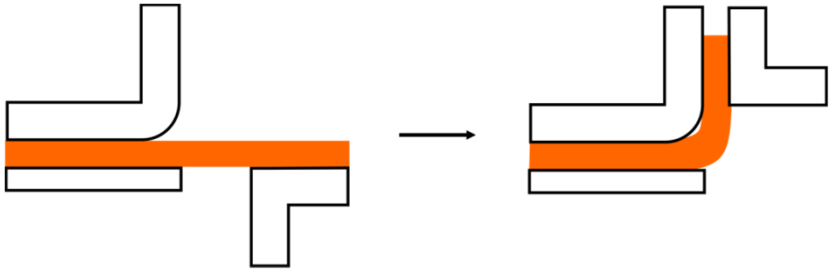
Injection molding

Polymer pellets are heated/molten and pressed into the desired final and complex shape

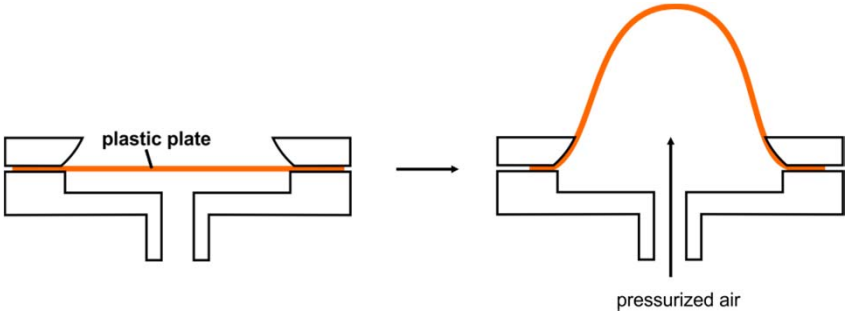
Polymer processing: Reshaping

Reshaping of polymer plates

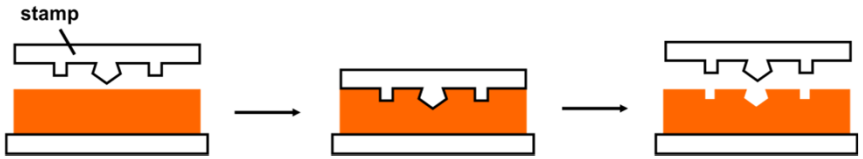
(A) Bending



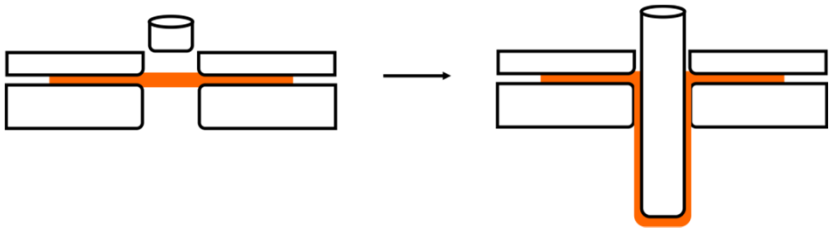
(B) Tensile forming



(C) Pressure forming

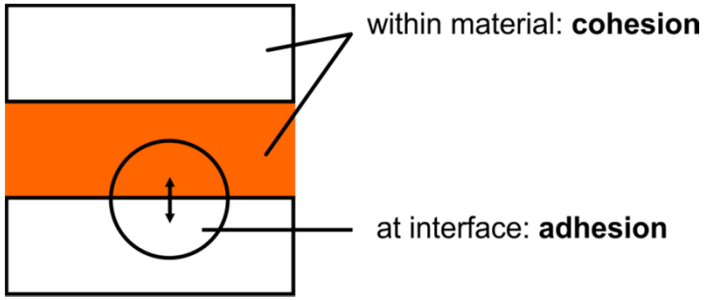


(D) Combined tensile-pressure-forming



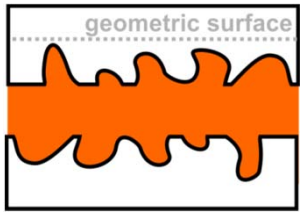
Joining processes: Adhesive bonding

Principle: Polymer brought between two construction parts, provides adhesion and features good cohesion



What determines adhesion?

- **Mechanical adhesion**: penetration of adhesive into microstructure of construction part which leads to mechanical interlocking

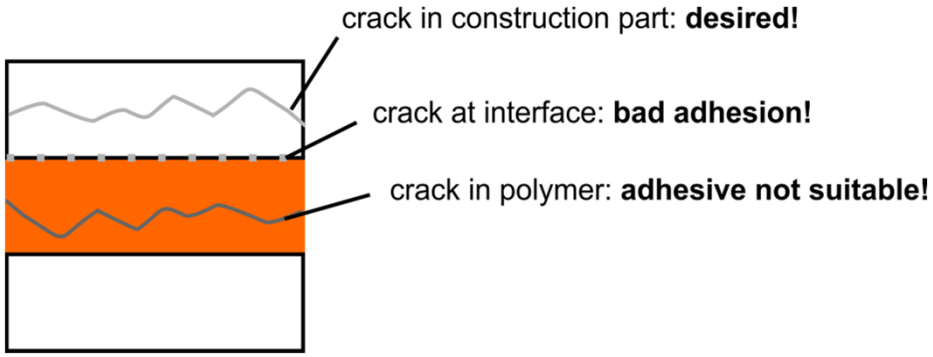


- **Specific surface adhesion:** intermolecular interactions such as dipole-dipole, H-bonding etc. between adhesive and construction part.

Joining processes: Adhesive bonding

What makes a good adhesive?

Ideally, construction part breaks before adhesion layer or adhesive



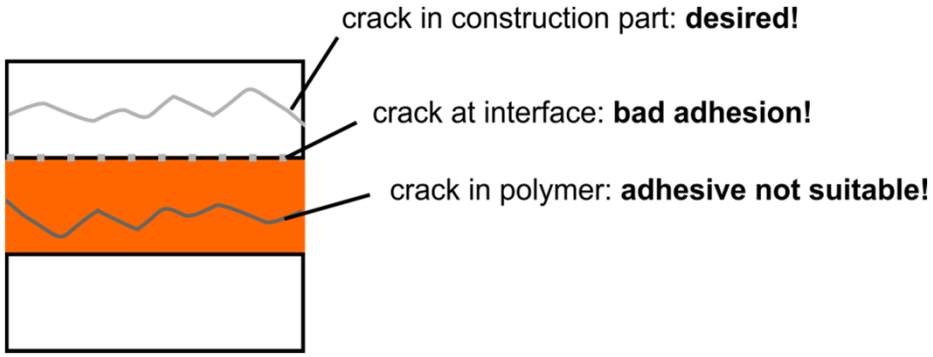
cohesive fracture / mixed fracture / adhesive fracture

cohesive fracture / adhesive fracture

Joining processes: Adhesive bonding

What makes a good adhesive?

Ideally, construction part breaks before adhesion layer or adhesive



What determines adhesion on molecular level?

High wetability of surface with adhesive is important!

- Strongly polar surfaces (metal, glass, ceramics) have good wetability
  - ➢➢ ideal for adhesive bonding
- PE/PTFE are very apolar, hence they show low wetability
  - ➢➢ surface pre-treatment (plasma or chemical) required
- Chemically reactive surfaces: Improved adhesion due to reaction of adhesive with surface

Surface roughening generally improves mechanical adhesion.

Joining processes: Adhesive bonding

How to harden the polymer between construction parts?

(A) Chemically

Prepolymers or monomers react during curing process and form polymer network

Initiation by:

- Oxygen
- Water/humidity (e.g. cyanoacrylates)
- Hardener/catalysts
- Heat,
- UV irradtion

(B) Physically

Adhesive polymer dissolved in solvent (suspension/emulsion)

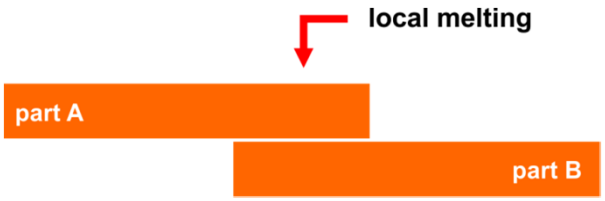
Hot-melt adhesive

(C) Special case for joining polymers: Using organic solvent as adhesive

(dissolving the polymers on the surface allows diffusion of chains)!

Joining processes: Plastic welding

Principle: Local melting of construction parts



Concept:

Due to melting, polymer chains can diffuse and form a homogeneous phase.

Requirements:

- Polymer components must be **meltable**!
- Polymer components must be **mixable**!

➢➢ Works only for thermoplasts