Introduction to Macromolecular Chemistry

aka polymer chemistry

Mondays, 8.15-9.45 am, NC 02/99

Dr. Christian Merten, Ruhr-Uni Bochum, 2019

A timeline of polymer chemistry

Cotton (Mexico)

Shellac (East indies)
produced by the bug *Kerria lacca*

~ 5000 BC | ~ 3000 BC | ~ 2000 BC | 0 | ~ 1500

Silk (China)
from the cocoons of the larvae of the mulberry silkworm *Bombyx mori*

Gum arabic
harvested in Arabia, Sudan, and West Asia since antiquity

A timeline of polymer chemistry

1806 (J. Gough)
Experimental studies on elasticity of natural gum

1859 (J. P. Joule)
Thermodynamic principles of elasticity

1884/1919 (E. Fischer)
Structure elucidation of sugars and proteins

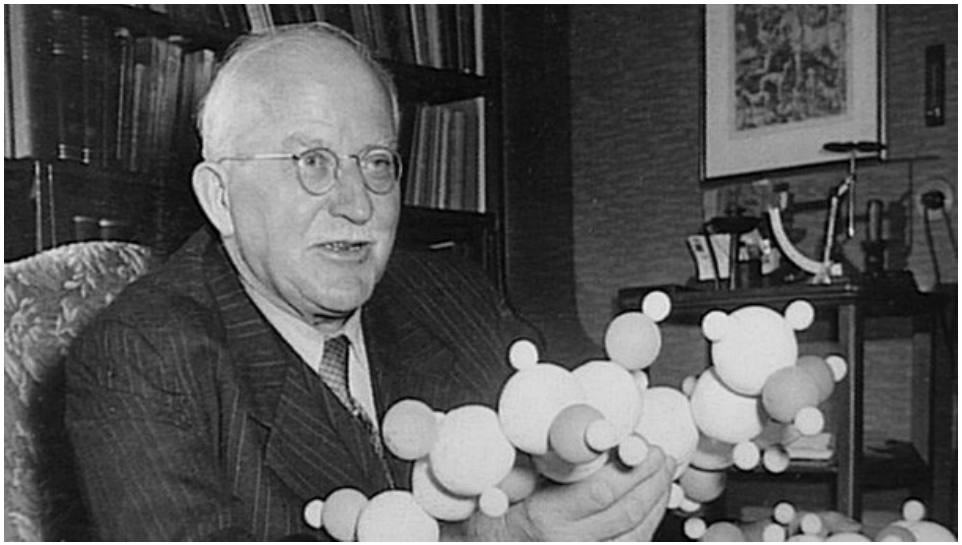
1920s (H. Staudinger)
The idea of a macromolecule

1929 (W. Carother)
Preparation and characterization of polycondensates

1939/45
Debye: light scattering of polymer solutions
Flory: viscosity of polymer solutions

1950
Ethylene polymerization (K. Ziegler)
Polypropylene / tacticity (G. Natta)

Father of polymer chemistry

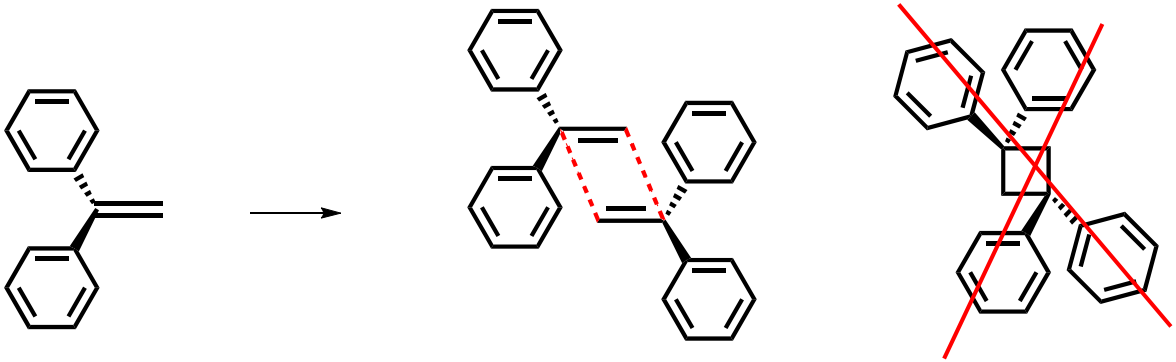


Hermann Staudinger (1881-1965)
Professor of Chemistry, University Freiburg, Germany
Nobel Prize in Chemistry 1953

Birth of polymer chemistry:

Chem. Ber. **53** (1920) 1073-1085

State of the art in 1920:



most obvious explanation

not observable

Some remarkable and important statements of H. Staudinger

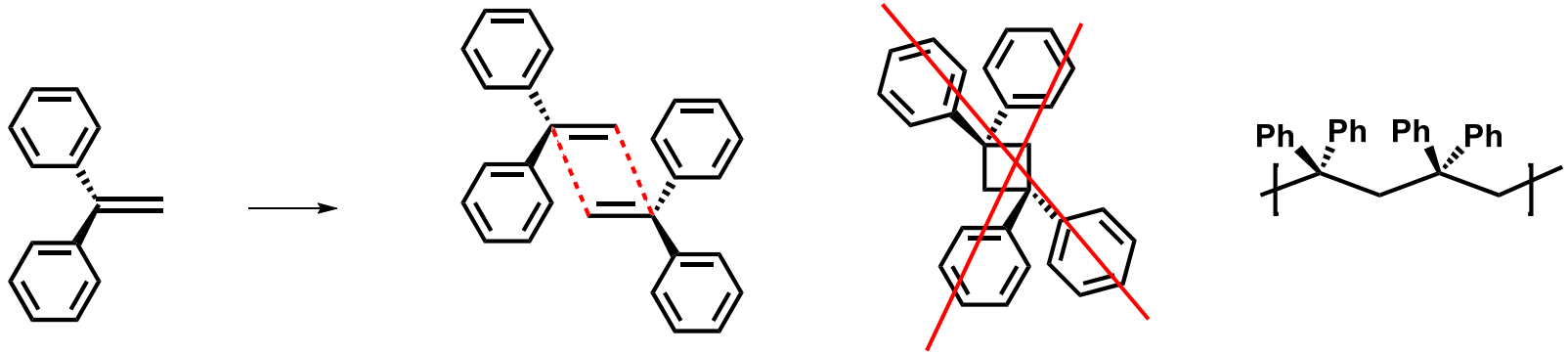
Chem. Ber. **53** (1920) 1073-1085

Solche Annahmen sind heute in der organischen Chemie sehr verlockend, nachdem eine große Anzahl gut charakterisierter Verbindungen, z. B. die Chinhydrone, nach den Untersuchungen von Pfeiffer[4]) als Molekülverbindungen, die durch Nebenvalenzen zusammengehalten werden, aufgefaßt werden. Und doch glaube ich, daß nach dem vorliegenden Beobachtungsmaterial solche Annahmen zur Erklärung des Entstehens der Polymerisationsprodukte nicht gemacht zu werden brauchen; vielmehr können die verschiedenartigsten Polymerisationsprodukte, wie ich im Folgenden zeigen möchte, durch normale Valenzformeln eine genügende Erklärung finden; und gerade in der organischen Chemie wird man so lange wie möglich sich bemühen, die Eigenschaften der Verbindungen durch Formeln mit Normalvalenzen wiederzugeben.

Such assumptions do not need to be made, as all polymerization products can be explained using regular valence bonding…

… and in organic chemistry, we will try to represent properties of compounds using regular valence bonds as long as possible.

State of the art in 1920:



most obvious explanation | **not observable** | **Staudinger's idea**

Some remarkable and important statements of H. Staudinger

Chem. Ber. **53** (1920) 1073-1085

Hochmolekulare Polymerisationsprodukte.

Sehr häufig bilden sich bei Polymerisationsprozessen hochmolekulare Produkte, über deren Konstitution man bisher keinen Aufschluß hat. Diese Produkte sind amorphe, kolloidale Körper. Sie

Often, products of high molecular weight are formed. Nothing is known about their constitution. They are amorphous and colloidal.

Bei allen diesen Kolloiden kann man natürlich kein Molekulargewicht angeben, und es hat auch keinen Sinn, mit solchen Substanzen Molekulargewichtsbestimmungen vorzunehmen. Man wird

Molecular weights cannot be determined, and it also does not make sense to do so.

Will man sich eine Vorsteltung über die Bildung und die Konstitution solcher hochmolekularer Stoffe machen, so kann man annehmen, daß primär eine Vereinigung von ungesättigten Molekülen eingetreten ist, ähnlich wie bei der Bildung von Vier- und Sechsringen, daß aber aus irgend einem, event. sterischen, Grunde der Vier- oder Sechsringschluß nicht stattfand, und nun zahlreiche, event. hunderte von Molekülen sich zusammenlagern, so lange bis sich ein Gleichgewichtszustand zwischen den einzelnen großen Molekülen, der von der Temperatur, Konzentration und dem Lösungsmittel abhängen mag, eingestellt hat.

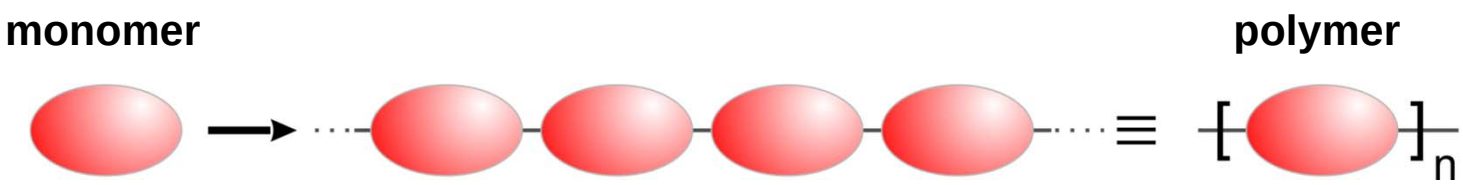
Primarily, unsaturated monomers have united, but for whatever – maybe steric – reason did not form cyclic molecules. Instead, numerous molecules, potentially hundreds, agglomerate to large molecules until an equilibrium state is reached which might even be related to temperature, concentration, and solvent.

What is macromolecular chemistry / polymer chemistry today?

Very interdisciplinary field of science

- **Organic chemistry:** Most technically relevant polymers are based on carbon chains
- **Metalorganic chemistry:** About half of todays polymers are prepared using metalorganic catalysts
- **Physical chemistry:** Description of thermal properties of solid polymers and polymer solutions and (large scale) reaction kinetics
- **Engineering:** Processing of polymers and shaping of materials

What‘s a polymer?



- Large molecule, made of small builing blocks: **monomers**
- **Covalent** linkage
- Typical notation: n M $\rightarrow$ -(-M-)$_n$-

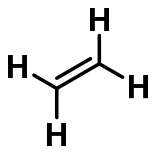
  n < 20: oligomer

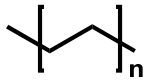
  n > 20: polymer
- High molecular weight molecule
- Often regular polymer consisting of identical monomers, but also copolymers

Nomenclature

The name of the polymer is usually derived from its monomer

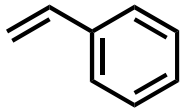
Ethylene

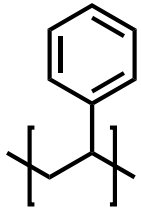




Poly(ethylene)

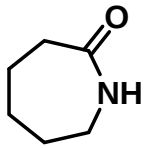
styrene

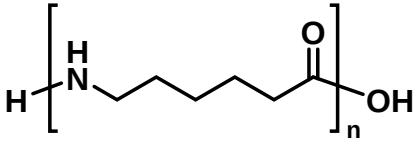




Poly(styrene)

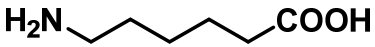
ε-caprolactam

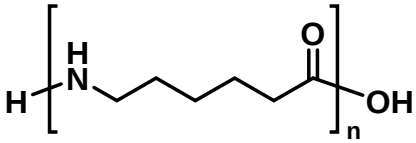




Poly(ε-caprolactam)

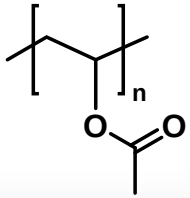
ε-aminocaproic acid

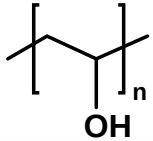




Poly(ε-aminocaproic acid)

poly(vinyl acetate)

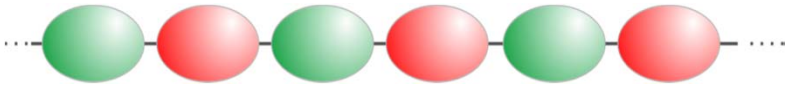




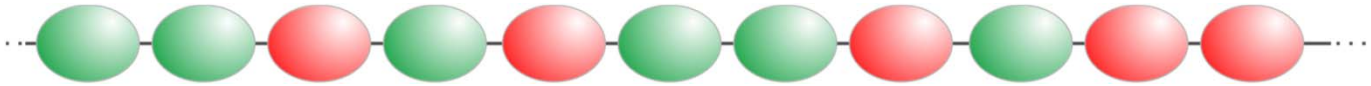
poly(vinyl alcohol)

Copolymers

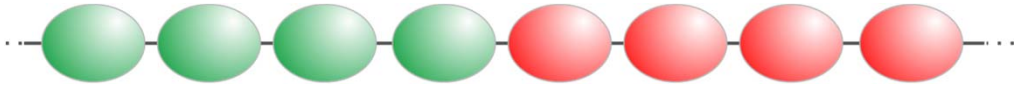
alternating copolymer
poly(A-*alt*-B)



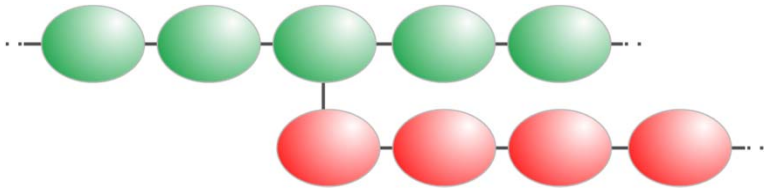
statistical copolymer poly(A-*stat*-B)



block copolymer
poly(A)-*block-poly(*B)



graft copolymer
poly(B)-*graft-poly(*A)



What determines material properties?

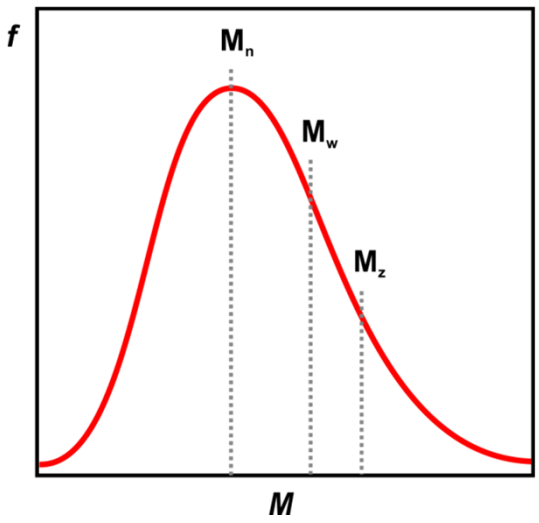
Most important parameters which determine polymer properties:

- type of monomer
- chemistry of monomer linkage, e.g. ether vs. amide bond
- degree of polymerization
- chain architecture, e.g. linear vs. branched
- monomer sequence in copolymers
- specific interactions between polymer chains
- …

Additional (non-chemical) parameters:

- additives
- thermal history
- processing
- …

Molar mass distribution



Polymers usually don‘t have an exact mass

- Mass distribution…
- …many ways to define the average mass of a polymer

(a) Number average molar mass, M_n

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

with x_i being the molar fraction of molecules of length *i*

Equally emphasizes smaller and larger molecules

- Important for colligative and mechanical properties

(b) Mass average molar mass, M_w

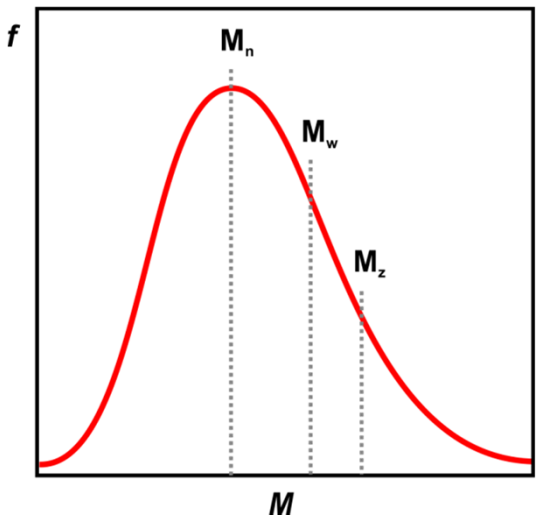
$$\bar{M}_w = \sum w_i M_i \;\Rightarrow\; \bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

with w_i being the weight fraction of molecules of length *i*

emphasizes larger molecules

- Bulk properties often depend on M_w

Molar mass distribution



Polymers usually don‘t have an exact mass

- Mass distribution…
- …many ways to define the average mass of a polymer

(a) Number average molar mass, M_n

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

(b) Mass average molar mass, M_w

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

(c) Z average molar mass, M_z

$$\bar{M}_n = \frac{\sum M_i^3 n_i}{\sum M_i^2 n_i}$$

No intuitive meaning; Z for centrifuge (Zentrifuge in german, as it is determined from sedimentation rates)

$$\bar{M}_n < \bar{M}_w < \bar{M}_z$$

Mass (=population) distribution of the Ruhr area

Bochum	362000
Bottrop	116000
Castrop	75400
Dortmund	572000
Duisburg	486600
Ennepetal-Kreis	331000
Essen	567000
Hagen	186000
Hamm	181000
Herne	154000
Mülheim	167000
Oberhausen	212000
Recklinghausen	115000
Unna	66000
Wesel	60700
Witten	103000

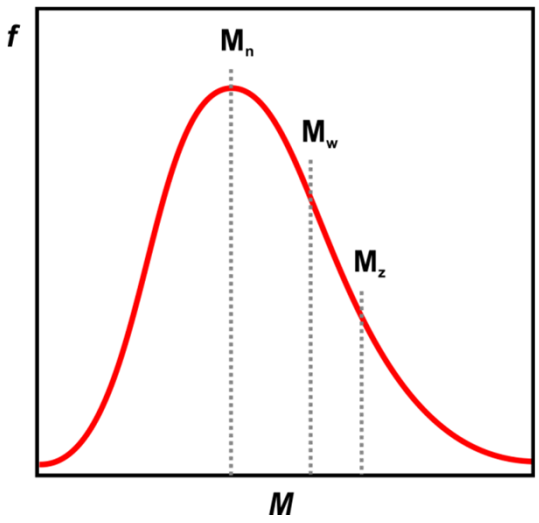
$$\bar{M}_n = 234669$$

$$\bar{M}_w = \frac{1 \times (Bochum)^2 + 1 \times (Bottrop)^2 + \cdots}{3754700}$$

$$\bar{M}_w = 357146$$

You are the average Ruhrgebietler!

Exercise: Calculate average molecular weights



Number average molar mass, M_n

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

Mass average molar mass, M_w

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

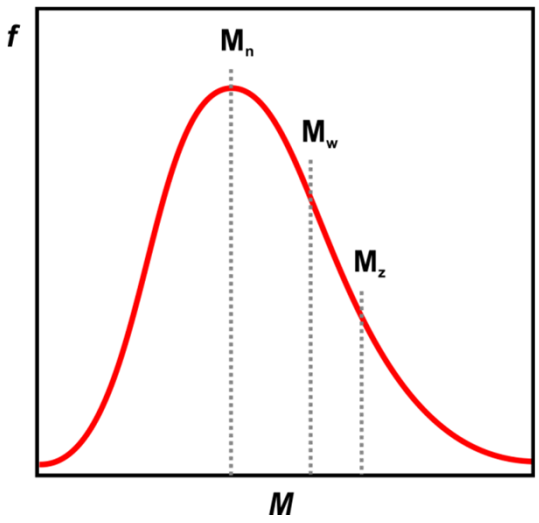
A polymer consists of

- 1 molecule of molar weight 100000
- 5 molecules of molar weight 200000
- 3 molecules of molar weight 500000
- 1 molecules of molar weight 1000000

$$\bar{M}_n = 3.6 \times 10^5 \text{ g/mol}$$

$$\bar{M}_w = 5.45 \times 10^5 \text{ g/mol}$$

Molar mass distribution: Two other important numbers



Number average molar mass, M_n

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

Mass average molar mass, M_w

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

polydispersity index

$$\boldsymbol{PDI = \frac{\bar{M}_w}{\bar{M}_n}}$$

usually ~2, but for monodisperse PDI = 1

average degree of polymerization

$$\boldsymbol{\bar{P}_n = \frac{\overline{M_n}}{M_0}}$$

Effect of molecular weight on materials properties

Example: poly(ethylene) C_nH_{2n+2}

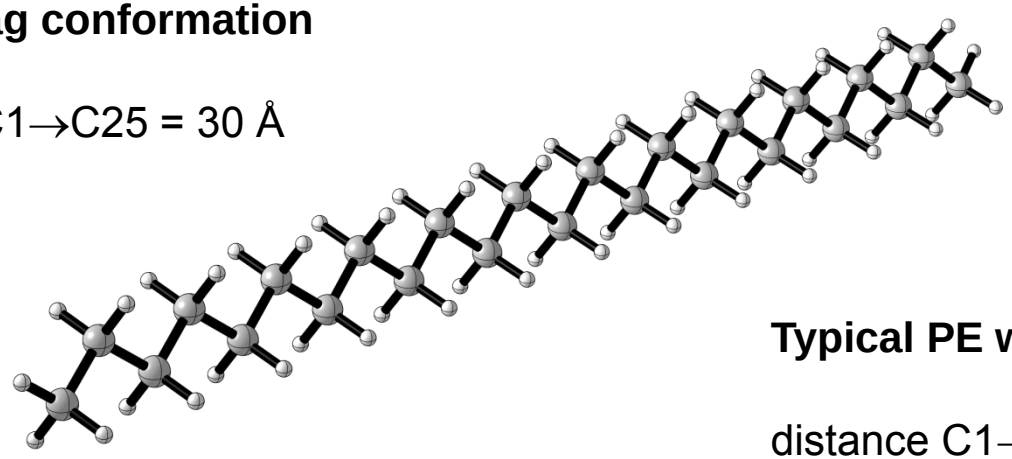
- Low molecular weight PE: < 1000 monomer units
  - greasy parafin

- Ultrahigh molecular weight PE (UHMWPE): 100000-250000 monomer units
  - almost insoluble
  - extermely tough material
  - in molten state, high viscosity ➢ difficult to process
  - Usage: strong synthetic fibres, mechanically highly stressed materials
  - Trivia: commercialized in the 1950s by Ruhrchemie AG

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

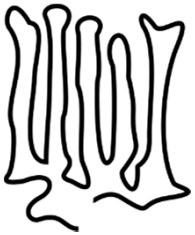
- Crystallization often kinetically hindered
- Slow tempering or slow evaporation of solvent leads to most ideal state

Solid state structures of polymers

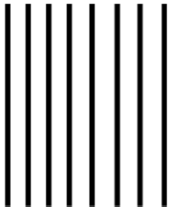
Three general solid state structures can be distinguished:

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



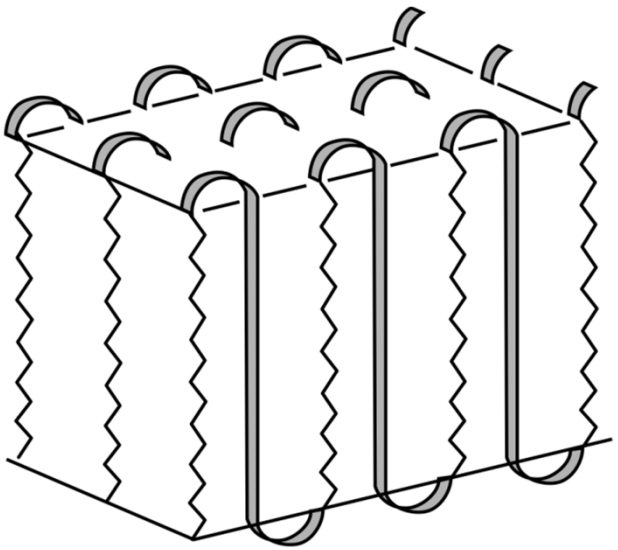
Crystalline: highly ordered structures

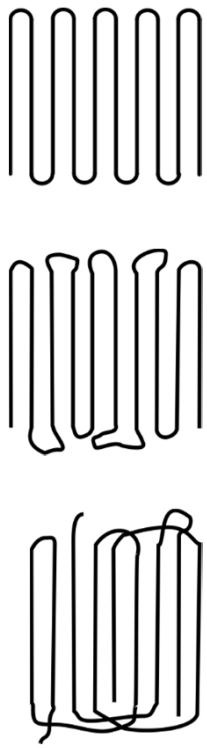
- formation of crystalline sturctures benefits from slow cooling of molten polymer

Solid state structures of polymers

In fact, wherever polymer chains need to fold back into the crystallite,

there are somewhat unordered, amorphous structures:





Backfolding:

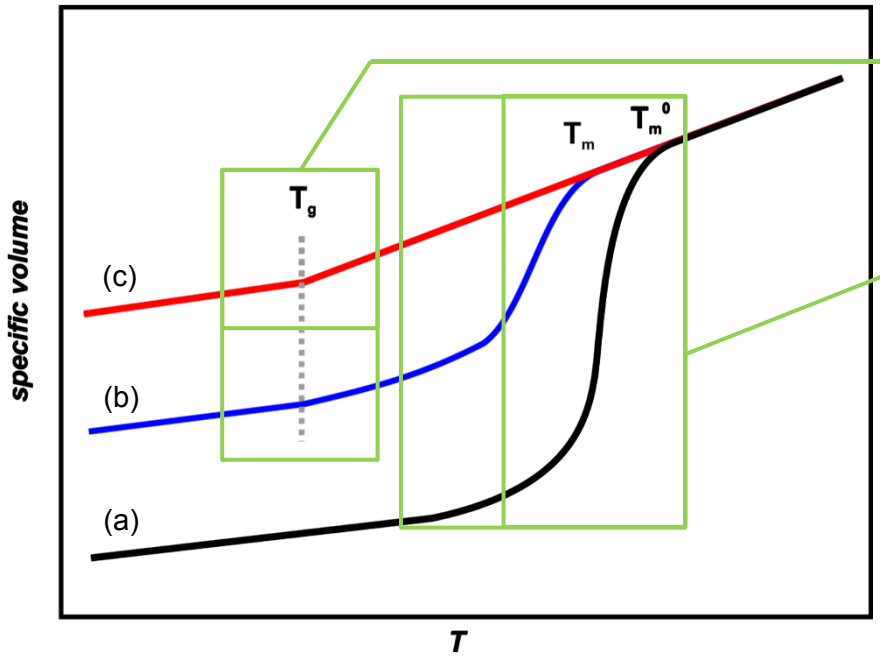
Sharp

Loose

Unordered
(switchboard model)

Solid state structures of polymers

When melting polymers, some characteristic 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

Solid state structures of polymers

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

(a) Melting point at temperature T_m: crystalline phase to isotropic melt

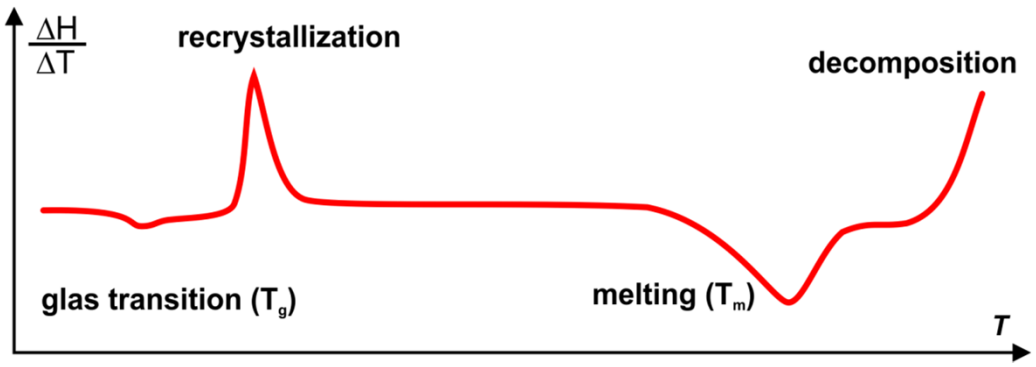
- Not sharp, but rather broad due to differently sized crystallites
- Semi-crystallinity causes decrease in melting point: $T_m < T_M^0$

intermolecular

(b) Glass transition at temperature T_g: glassy state to rubber-like state

- Increase in temperature allows for more flexible chain movements in solid state
- Comparison: Cooked spagetti in freezer vs. at room temperature

intramolecular



Differential Scanning Calorimetry (DSC)

Solid state structures of polymers

Is the glass transition really relevant for anything?

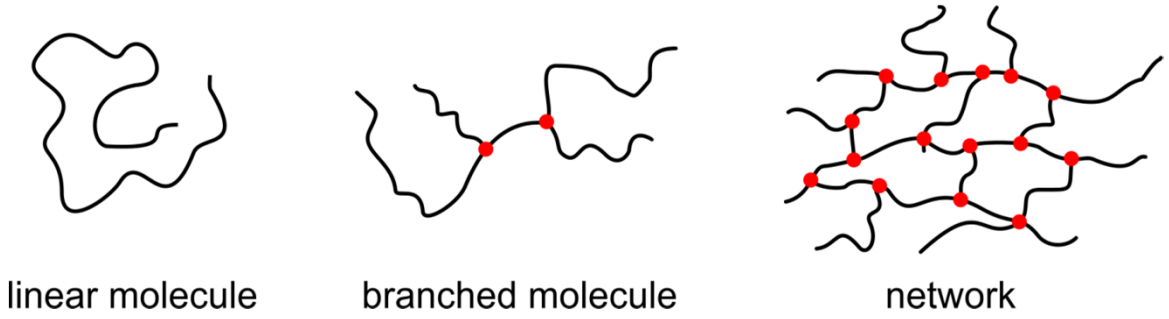
T_g: glassy state to rubber-like state

If you want to have a ***hard and stiff material***,
which may even withstand some mechanical force: Use a polymer with **high T_g**!

If you want to have an ***elastic material***, which can
be stretched and deformed up to a certain degree: Use a polymer with **low T_g**!

Note: Crystallization occurs in the range $T_g < T \leq T_m$, but below T_g secondary crystallization might occur on time scales of days to years! ➢ Materials life time

Network structures affect mechanical strength



Example: poly(ethylene) C_nH_{2n}

- High density PE (HDPE): 7 branches / 1000 C-atoms
- Linear low density PE (LLDPE): 15 C4/C8-branches / 1000 C-atoms
- Low density PE (LDPE): 30 C_4-branches / 1000 C-atoms

property	LDPE	LLDPE	HDPE
T_g [°C]	-125		-80
softening temp. [°C]	110	120-130	> 130
density [g/cm³]	0.915-0.935	0.915-0.935	0.94-0.97
tensile strength [MPa]	24	37	43
crystallinity	35-55 %	55-65%	70-80%

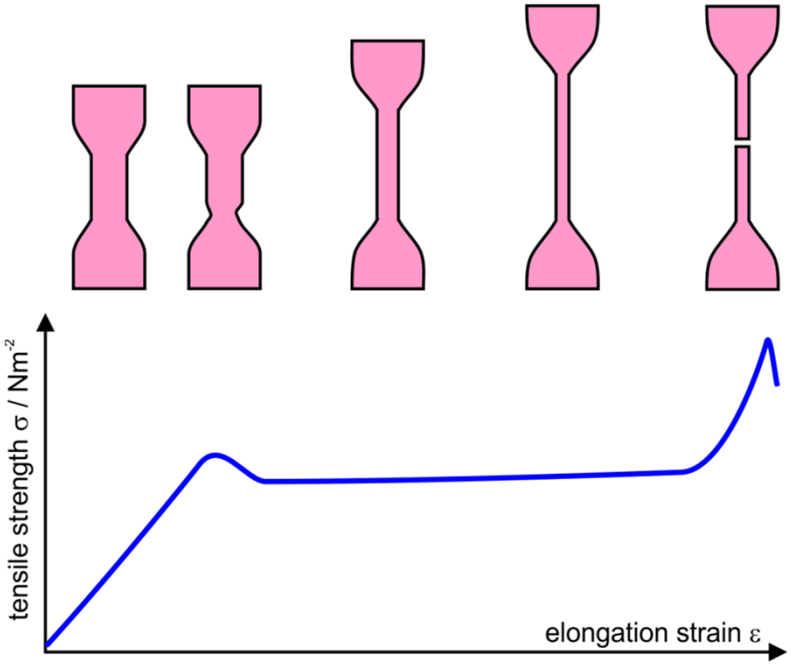
Probing mechanical properties

What happens, if a stretching force is applied to a polymer?

➢ It elongates. By how much is defined by Young‘s modulus E.

Young‘s modulus E

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



(1) Linear elongation for small σ following Hooke‘s law.

(2)→(4) Maximum is reached from which on the cross section of sample decreases while nominal strength is constant. Polymer chains forced to orient in sample.

(5) Once maximum orientation is reached, strength begins to increase until rupture.

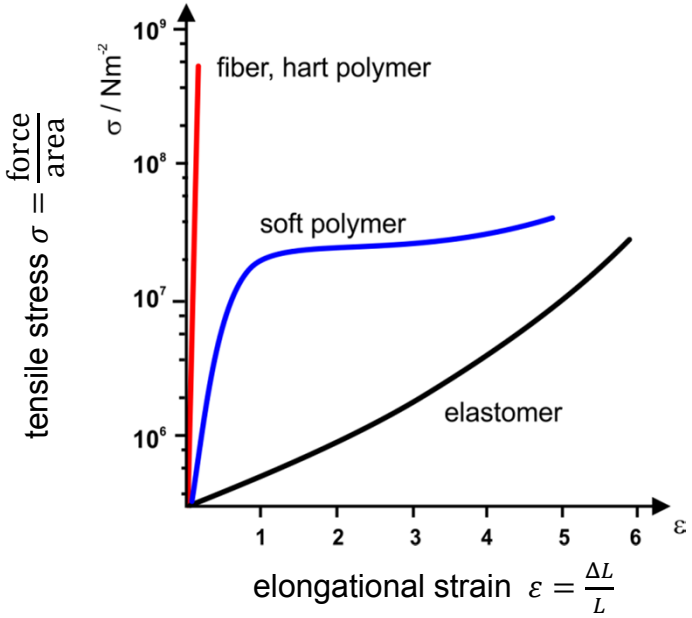
Probing mechanical properties

What happens, if a stretching force is applied to a polymer?

➢ It elongates. By how much is defined by Young's modulus E.

Young's modulus E

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



We differentiate between

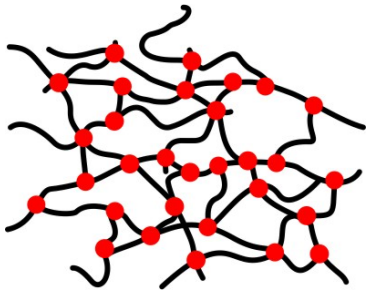
$E \downarrow$

- Stiff („energy-elastic") polymers
- Deformable („visco-elastic") polymers
- Fully elastic („entropy-elastic") polymers

Classification based on processing

Duromers (duroplasts)

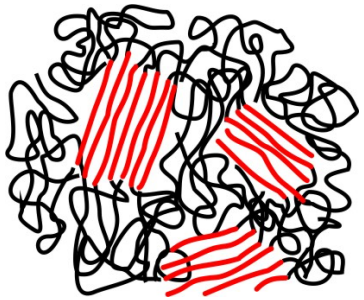
- close-meshed
- Insoluble, not meltable
- often brittle, low ductility



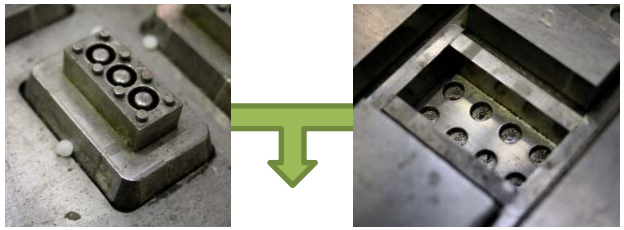
- Brought in shape by filling the monomers into a form and subsequent thermal or photochemical hardening

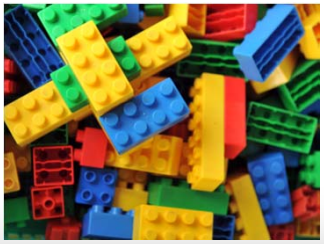
Thermoplasts

- not branched, may contain crystalline domains
- meltable and soluble, can flow under mechanical stress (permanent deformation)



- Brought in shape for instance by injection molding or extrusion





Calender for the semester

~~April 1~~

April 8 Introduction

~~April 15~~

~~April 23~~

April 29 Step growth polymerization

May 6 Chain growth polymerization

May 13 Chain growth polymerization

May 20 Catalytic polymerizations / Copolymers

May 27 Solid structure / Mechanical properties / Processing

May 29 Chiral polymers

June 3 Special lecture „Polymer aging“

by Dr. Elena Gómez Sánchez

Deutsches Bergbaumuseum

Practice exam: June 5, 10 am, NC 02/99

Real exam: June 17, 8.15 am, NC 02/99