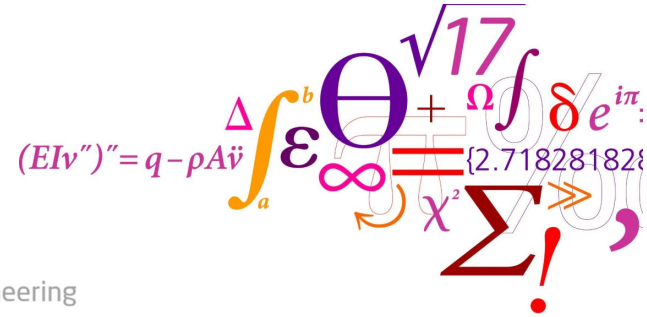
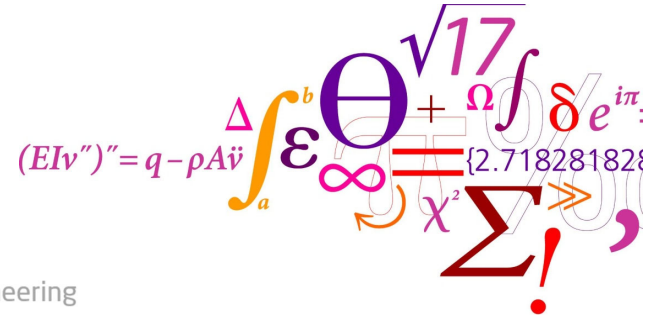
Ceramics and polymers

41680 Introduction to advanced materials

DTU Construct
Department of Civil and Mechanical Engineering



Structures of ceramics



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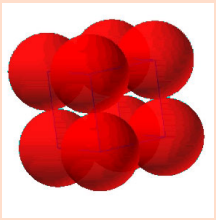
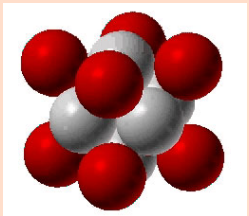
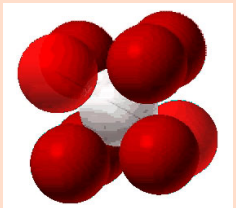
Interstitial sites in cubic lattices

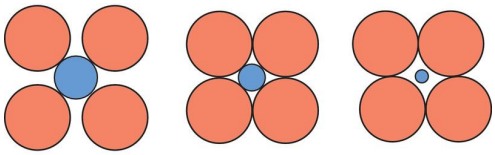
	Simple cubic (sc)	Face-centered cubic (fcc)		Body-centered cubic (bcc)
Crystal lattice				
Atomic packing factor	52%	74%		68%
Interstitial site	Hexahedral	Octah.	Tetrah	Octahedral
Sites per atom	1	1	2	3
Size r / R	0.732	0.414	0.230	0.150

Ionic crystals $A^{n+}X^{n-}$

- Smaller cations A^{n+} (missing electrons), ion radius R_A
- Larger anions X^{n-} (extra electrons), ion radius R_X

- How many larger anions fit around a smaller cation?
- Depending on ratio R_A/R_X (or R_X/R_A in case of $R_A > R_X$)

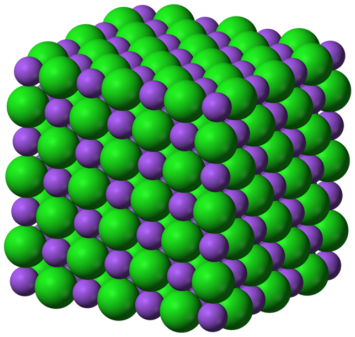
- Planar configurations



  - Slightly to small cations are unstable
  - Slightly to large cations push anions from each other

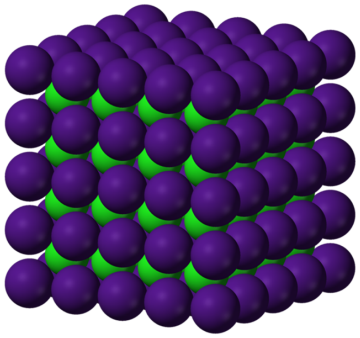
Structure of ceramics $A^{n+}X^{n-}$

- Sodium chloride



- Cl^- on fcc sublattice
- Na^+ in octahedral sites (forming an fcc sublattice)
- r_O/R_X=0.414
- Coordination number 6:6

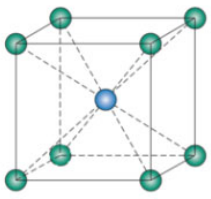
- Cesium chloride

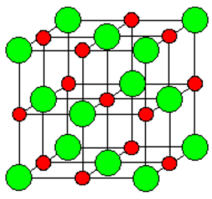


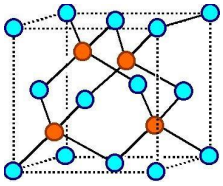
- Cl^- on sc sublattice
- Cs^+ in hexahedral sites (forming an sc sublattice)
- r_H/R_X=0.732
- Coordination number 8:8

Structure of ceramics $A^{n+}X^{n-}$

R_A/R_X range	>0.732	0.414-0.732	<0.414
Structure type	CsCl	NaCl	ZnS
	Cesium chloride	Sodium chloride	Zinc blende
R_A/R_X comp.	0.92	0.56	0.40



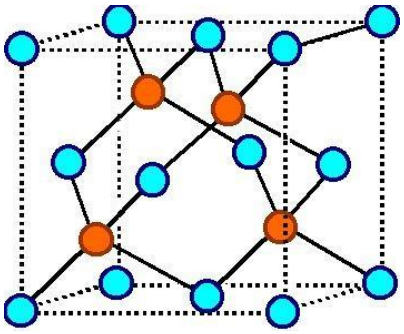




Ion	Ionradius
Cs^+	0.167 nm
Cl^-	0.181 nm
Na^+	0.102 nm
S^{2-}	0.184 nm
Zn^{2+}	0.074 nm

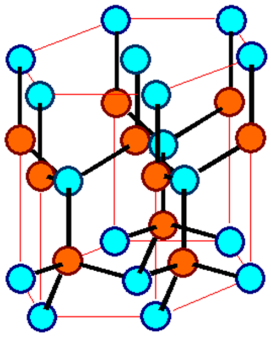
Structure of ceramics (ZnS) Polymorphism

- Zinc blende structure



- S on fcc sublattice
- Zn in tetrahedral sites (forming an fcc sublattice)
- Coordination number 4:4

- Wurtzite structure



- S on hcp sublattice
- Zn in tetrahedral sites (forming an hcp sublattice)
- Coordination number 4:4

Mass density

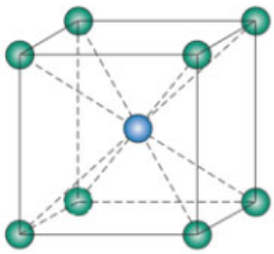
- Two different type of atoms
- Radii R_1, R_2
- Molar masses m_1, m_2
- Number in unit cell N_1, N_2
- Avogadro constant N_A

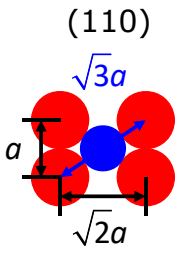
- Mass density (general)

$$\rho = \frac{N_1 m_1 + N_2 m_2}{N_A V_{unitcell}}$$

$$V_{unitcell} = a^3$$

- CsCl structure



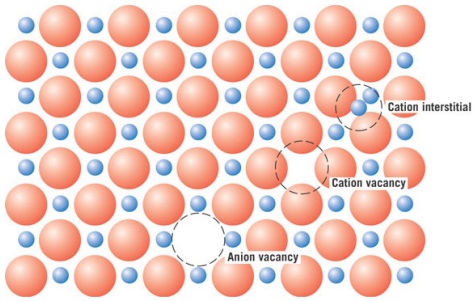


- Relation between lattice constant and radii

$$2R_1 + 2R_2 = \sqrt{3}a$$

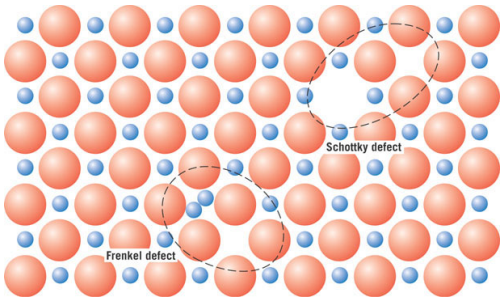
Lattice defects in ionic ceramics

- Point defects



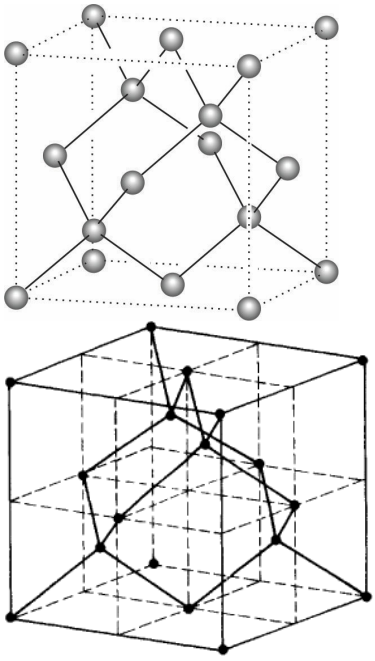
- Electric charge
- Do not exist in equilibrium

- Point defect pairs



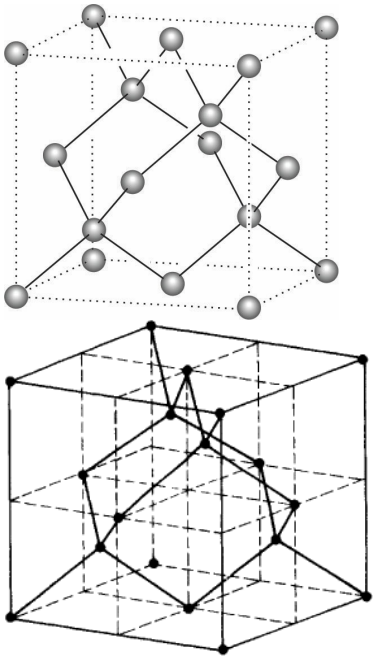
- Electric neutral
- Relevant for
  - optical properties
  - AC conductivity

Diamond structure



- Coordination number
- Number of atoms in unit cell
- Relation between radius and lattice constant (are there spheres touching each other?)
- Atomic packing factor 0.34
- Examples: Diamond, Si, Ge

Diamond structure



- Coordination number 4
- Number of atoms in unit cell 4 + 6/2 + 4/8 = 8
- Relation between radius and lattice constant (are there spheres touching each other?)

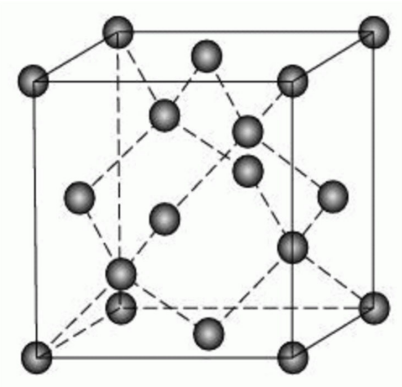
$$2R = a\sqrt{3}/4$$

- Atomic packing factor 0.34

$$\frac{V_{atoms}}{V_{unitcell}} = \frac{8}{a^3}\left(\frac{4\pi}{3}\left(\frac{a\sqrt{3}}{8}\right)^3\right) = \frac{\pi\sqrt{3}}{16}$$

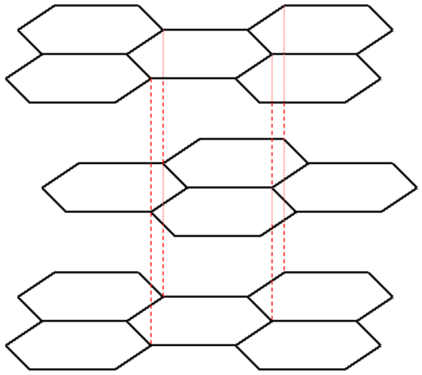
Structure of ceramics (C)

- Diamond structure



- Coordination number 4
- Packing factor 0.34

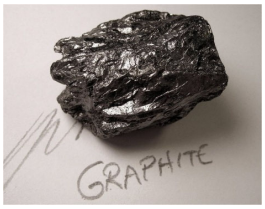
- Graphite structure



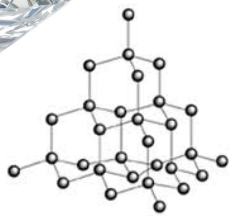
- Coordination number 3
- Covalent bonds within plane
- Van der Waals bond between

Allotropy in carbon

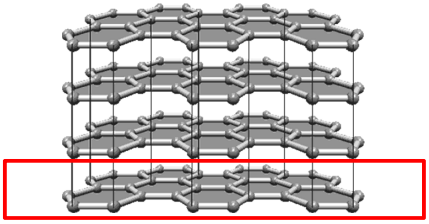
Diamond	Graphite
Highest hardness	Low hardness
Best grinding material	Very good lubricant
Electrical isolator	Good electrical conductor
Best thermal conductor	Good thermal conductor
Transparent	Opaque
•Jewelry •Cutting tools •Grinding tools	•Pencils, batteries, motors •Lubricant •**Steel**



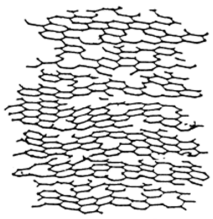
Even more allotropes of carbon



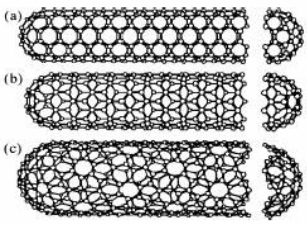
- 6 electrons, electron configuration $1s^2$ $2s^2$ $2p^2$
- 4 valence electrons = 4 covalent bonds
- diamond (hardest material)

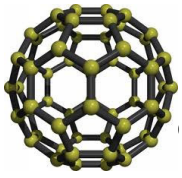


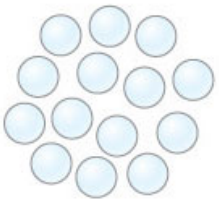
- Graphite (thermodynamically stable)
- Graphite fibers (1958)



- Graphene (1962/2004)
  (strongest and stiffest material)
- Fullerenes (1985)
  ”Buckyballs”
- Carbon-nanotubes (1991)

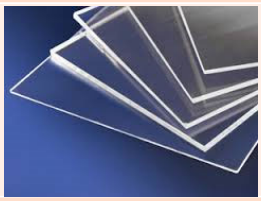
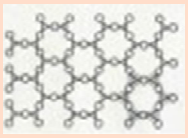
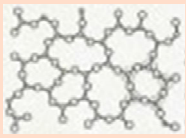


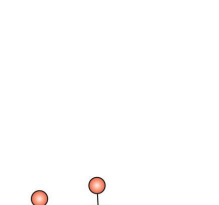




Amorphous solids

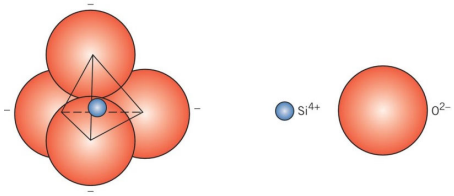
- Solids without crystalline arrangement

	Order	Disorder
Solid	Crystals	Glass
Liquid	Liquid crystals	Melt
SiO_2	Quartz	Quartzglass
	Trigonal	Fused silica
		
		

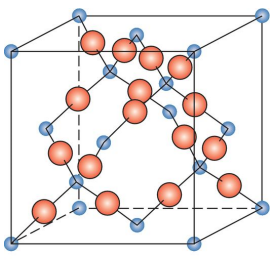


Amorphous solids

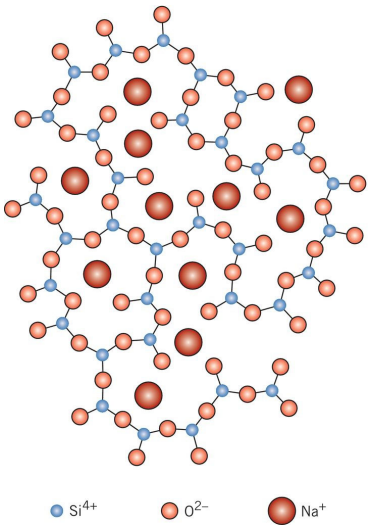
- SiO_4 tetrahedron



- Crystalline phase (Cristobalite)



- Glass



- Net builder Na

Defects in ceramics

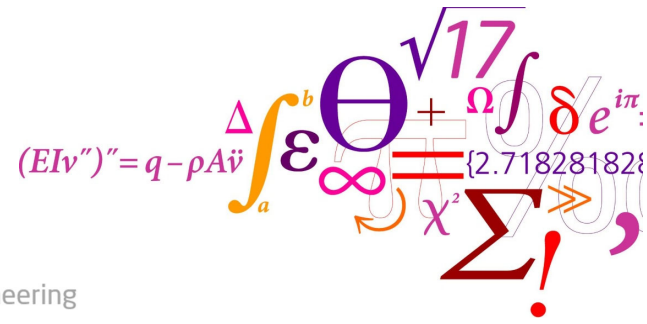
Lattice defects
in crystalline ceramics

- Point defects
- Dislocations
  - Motion may or may not to lead to neighboring ions with same charge
  - Low number of slip systems
- Grain boundaries

General
for all ceramics

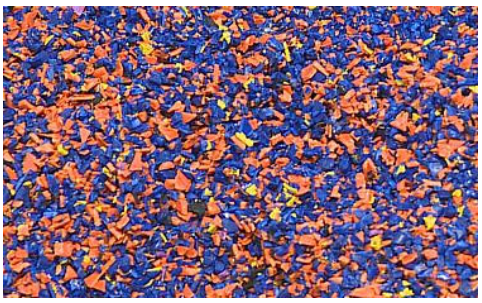
- Pores (from manufacturing)
  - Lower density and related properties (conductivities, strength)
- Microcracks

Structures of polymers



Polymers

- Common term
  - Plastics
  - Rubber
  - Viscos oils



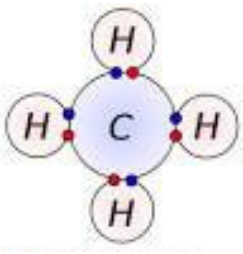
- Meaning of the term

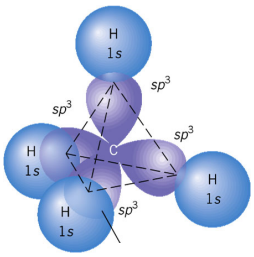
poly -	*mer*
πολύς	μέρος
many	parts

- An individual part is called monomer

Monomer

- Individual molecule before assembled to polymer
- Covalent bonds

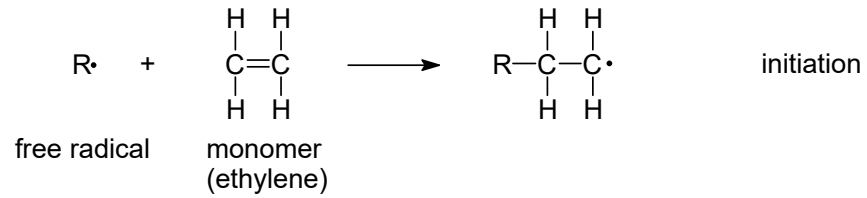


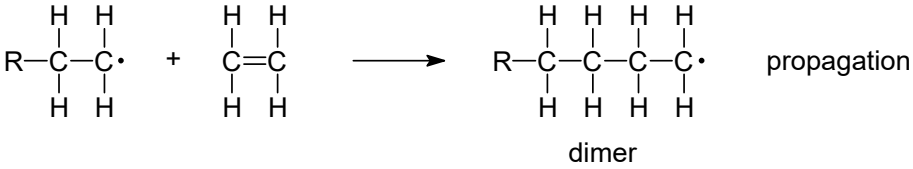


- Polymerization
- Monomers must have possibility to react in chemical reaction with other monomers
  - Extra electron pair from double bond
  - Reaction by releasing a small molecule (e.g. H_2O)

Polymerization

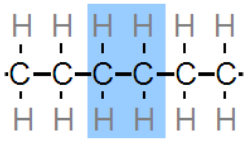
- Chain polymerization



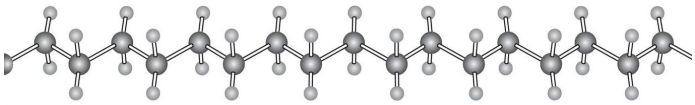


Carbon skeleton (Hydrocarbons)

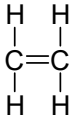
- Polyethylene



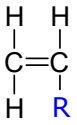
Repeat unit



- Monomer (Ethylene, Ethene)

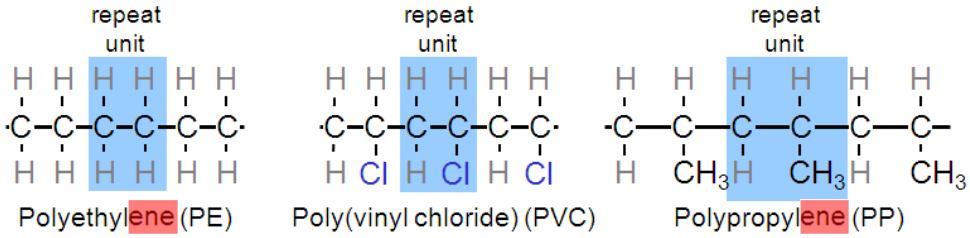


Polymers (more examples)

- Monomer  with side group R

- Polymer

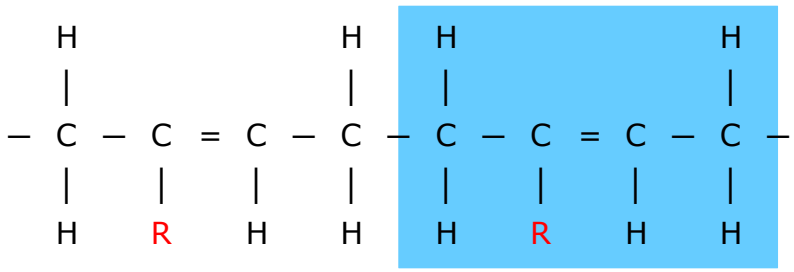
R=Cl R=CH_3



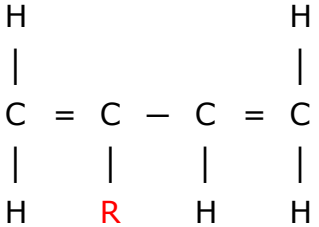
- Aromatic side group $R=C_6H_5$ Polystyrene

Polymers (another example)

- Polybutadiene R = H repeating unit



- Monomer

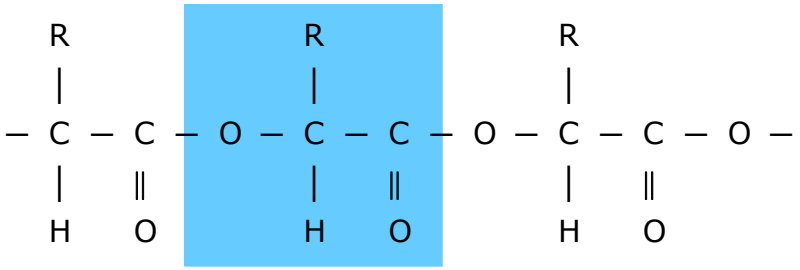


R = H butadiene

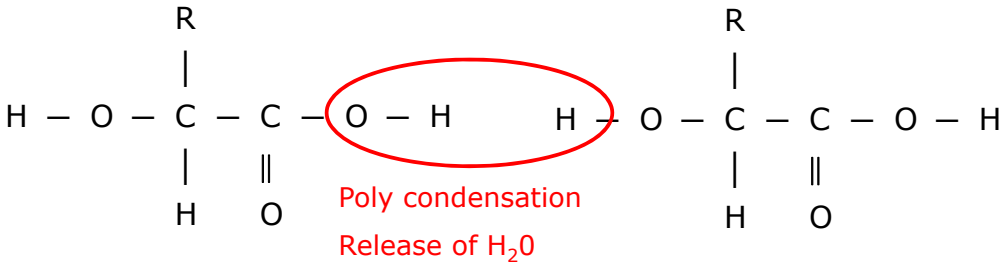
R = CH_3 isoprene

Polymers (PLA biodegradable)

- Polylactic acid repeating unit



- Monomer

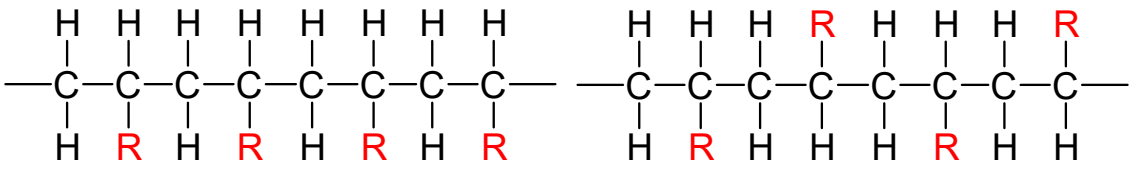


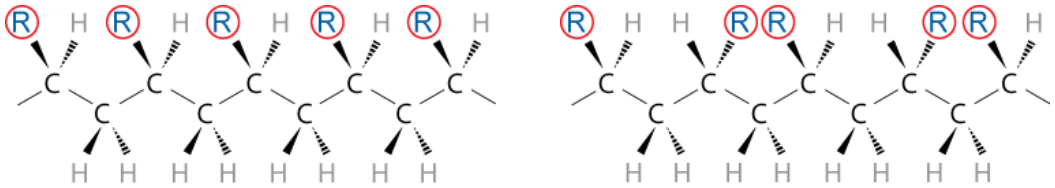
Example R=CH_3
Polypropylene

Stereoisomerism
- Arrangement of side groups

- Isotactic
- R groups on same side

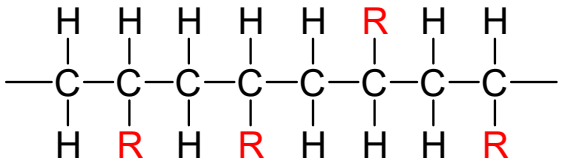
- Syndiotactic
- R groups on alternate sides

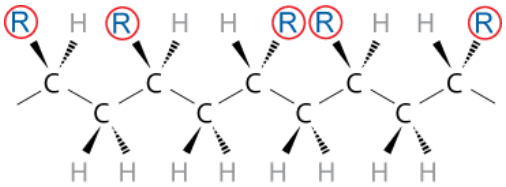




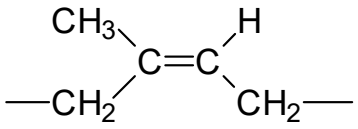
Stereoisomerism
- Arrangement of side groups

- Atactic
- R groups at random positions

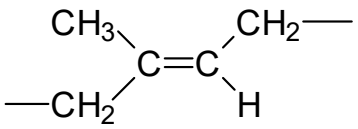




- Geometrical isomerism
- Cis-isoprene (natural rubber)

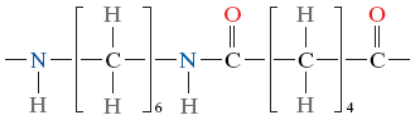


- Trans-isoprene

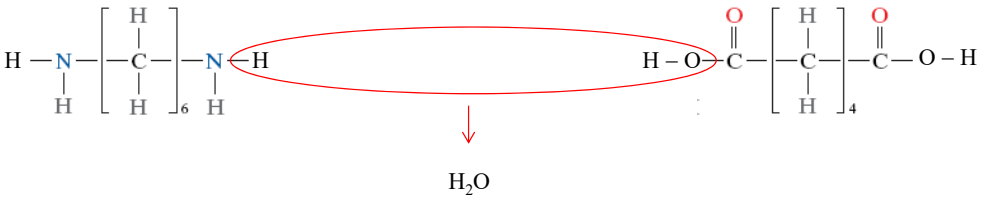


Co-polymers

- Two different monomers
- Nylon 6,6



- Hexane-1,6-diamine — Hexane-1,6-dicarboxylic acid



- Hexa-methylene-diamine — Adipic acid
- Condensation reaction!

Molar mass (Molar weight)

The more monomers in a chain, …

- the longer the chain
- the higher the molar mass
- the higher the melting temperature

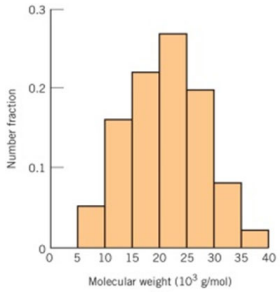
- Molar mass of chain molecule

$$M = nm$$

- Molar mass or repeating unit m
- Number of repeating units n

Distribution of molar masses

- Not all chains have same length



- Average molar mass (number weighted)

$$\overline{M}_n = \sum x_i M_i$$

- Fraction x_i of all chains having molar mass M_i

Degree of polymerization

- **IUPAC** Definition: number of **monomers** in a chain

$$N = M/m$$

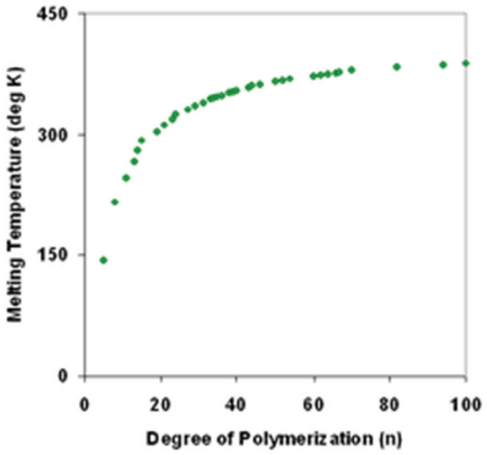
- Molar mass of chain M
- Molar mass of monomer m
- In case of co-polymers:
  - average molar mass of monomers $\overline{m}$
  - Degree of polymerization is **not** number of repeat units *(as in Callister Rethwish)*, but number of monomers!!
- Chain length distribution
  - Degree of polymerization

$$\overline{N} = \overline{M}_n/m \quad \text{or} \quad \overline{N} = \overline{M}_n/\overline{m}$$

  - Number weighted average molar mass $\overline{M}_n$

Structure property relation

- Molar mass and melting temperature



- Melting temperature T_m

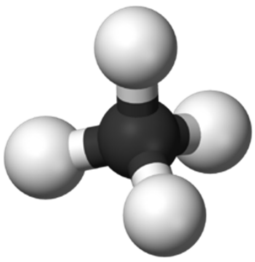
$T_m\uparrow$

- High molar mass
- Low chain flexibility
  - Large side groups
  - Double bonds or aromatic rings in chain
  - Strong secondary bonds

$T_m\downarrow$

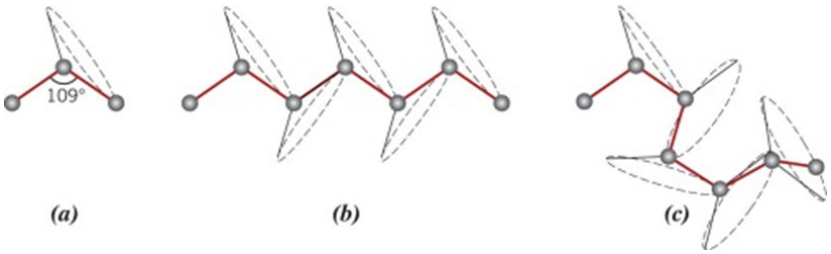
- Side branches
- randomly ordered side groups (atactic)

Bonds



- Carbon has four bonds, e.g. methane
- Bond angle θ_{CC} = 109°

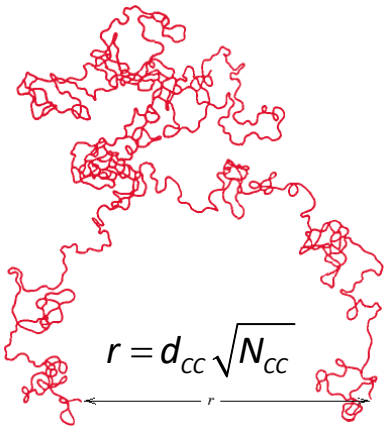
- Carbon skeleton: free rotation around single bonds



- Straightened chain length $L = N_{cc} d_{cc} \sin(\theta_{cc}/2)$
  - Bond length d_{CC} = 0.154 nm
  - Number of single carbon carbon bonds along chain N_{CC}

Flexible chains with different shape (conformation)

- Average start to end distance
- Average: spherical shape



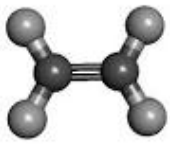
- Bond length d_{CC} = 0.154 nm
- Number of single carbon carbon bonds along chain N_{CC}

Considerations on shape

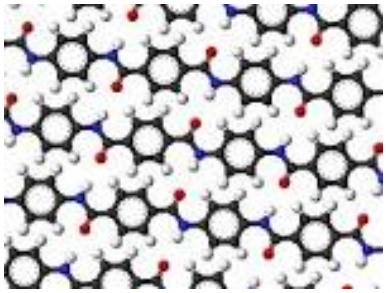
- Which conformation has the longest start to end distance?
- How many conformations have this longest start to end distance?
- How many conformations have a start to end length equal to the average?
- What does that mean thermodynamically?

Stiff monomers and stiff chains

- No rotational degree of freedom for double bonds

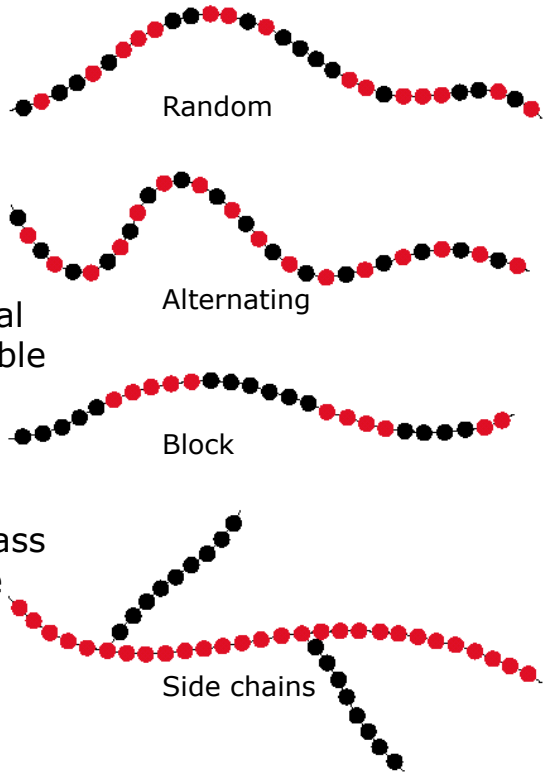


- No rotational degree of freedom for aromatic rings (Kevlar)



Copolymers

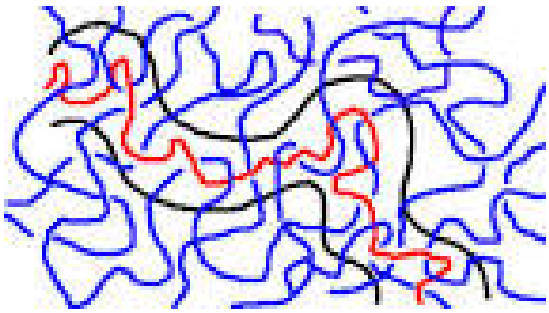
- Two different types of monomers A and B
- Advantage: better spatial distribution of not-miscible polymer types
- Note: Average molar mass of monomers for degree of polymerization



Chains ”knitted” into each other

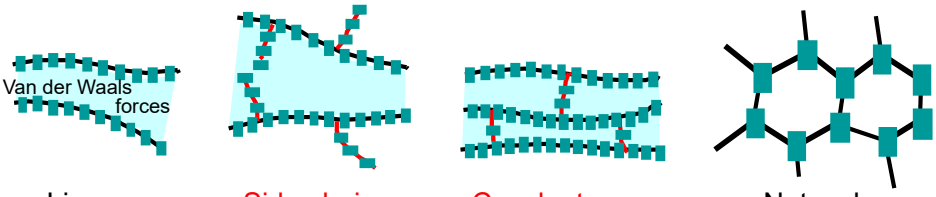
Each individual monomer

- Does not recognize end of its chain
- Can not distinguish between own and alien chains
- Can not pass through other parts of the chain



Interaction between chains

- Along chains: covalent bonds
- Between chains: secondary bonds (or covalent bonds)



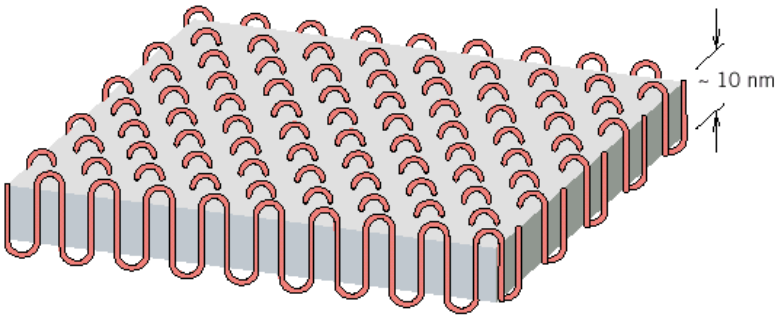
Linear chains	Side chains Branches	Covalent cross bonds	Network
Typical for			
thermoplast	thermoplast (PE-LD)	elastomer	thermoset

Thermoplastic versus Thermoset

	Thermoplastic	Thermoset
Heating	Softening (and melting)	Neither becoming softer, nor melting
Cooling	Harder	Become hard during manufacturing
Typically	Chains with few branches	Network with cross bonds
Bonds	Secondary bonds (van der Waals)	Covalent cross bonds
Manufacturing	High temperature and high pressure	Hardening during cooling or radiation
	Reversible	Irreversible
Degradation	At too high temperatures	At too high temperatures

Crystallinity

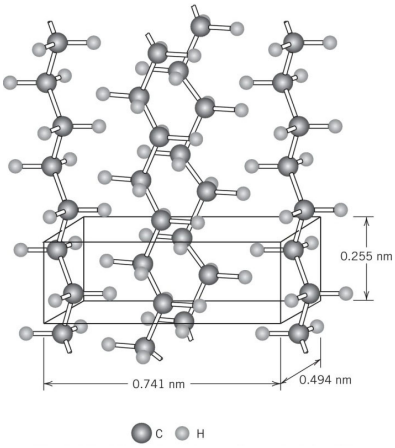
- Crystalline regions
- Thin platelets with folded chains
- Chains are locally straightened

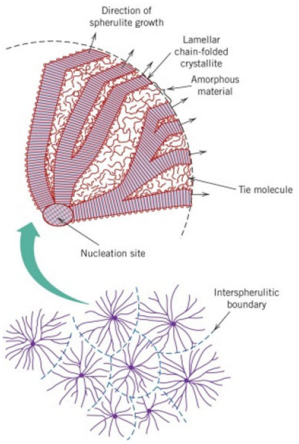


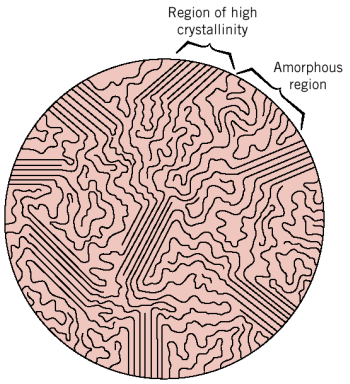
Semi-crystalline polymers

- Both amorphous and crystalline regions
- Crystalline regions act as cross links
- Maximum crystallinity about 80%
- Spherulites

- Properties
  - Higher density
  - Higher melting temperature
  - Mechanically stronger
  - Not translucent







Semi-crystalline polymers (density)

- Crystalline regions ρ_c
- Amorphous regions $\rho_a < \rho_c$ (less dense)
- Semi-crystalline polymers

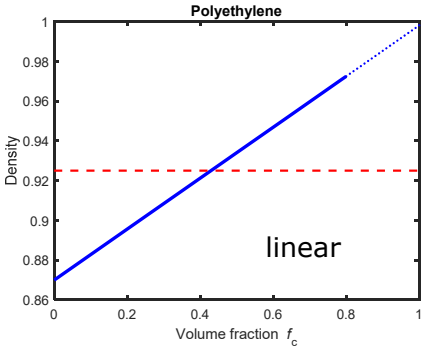
$$\rho_{sc} = f_c \rho_c + (1 - f_c)\rho_a$$

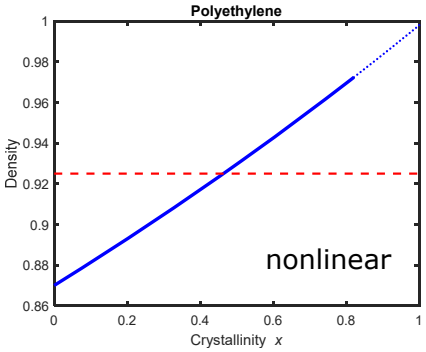
- Volume fraction of crystalline regions

$$f_c = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

- Crystallinity (mass fraction)

$$x = \frac{m_c}{m_{sc}} = \frac{f_c \rho_c}{\rho_{sc}} = \frac{\rho_c}{\rho_{sc}} \frac{\rho_{sc} - \rho_a}{\rho_c - \rho_a}$$





Polyolefine (polyalkene)

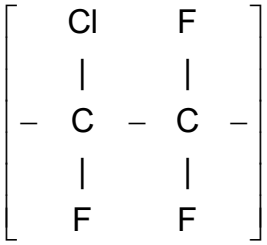
	Poly-ethylene (LD)	Poly-ethylene (HD)	Poly-propylene (isotactic)	Poly-butylene
Mass density g/cm^3	0.910-0.940	0.941-0.954	0.895-0.92	0.910-0.915
Melting temp.	115 °C	137 °C	175 °C	126 °C
Glass transition temperature	-110 °C	-90 °C	-10 °C	-17 °C
Young's modulus MPa	172-282	1080	1140-1550	290-295
Yield strength GPa	8-15	20-30	31-37	12-17
Strain at yield	20%	12%	20%	24%
Tensile strength MPa	8-31	22-31	31-41	36.5
Max. elongation	10-650 %	10-1200 %	100-800 %	300-380 %

branches

linear

Group exercises

- Polychlorotrifluoroethylene



- Molar mass C_2ClF_3

$$m = (2*12 + 35.5 + 3*19)\ \text{g/mol}$$
$$= 116.5\ \text{g/mol}$$

- Degree of polymerization

$$\bar{N} = \bar{M}/m$$
$$= 1000000\ \text{g/mol} / 116.5\ \text{g/mol}$$
$$= 8580$$

- Straightened chain length

$$L = N_{cc} d_{cc} \sin(\theta/2)$$
$$= 2*8580*0.154\ \text{nm}*\sin(109°/2)$$
$$= 2150\ \text{nm}$$

- Start to end distance

$$r = d_{cc}\sqrt{N_{cc}}$$
$$= 0.154\ \text{nm}*\sqrt{2*8580}$$
$$= 20.2\ \text{nm}$$

Group exercises

- Magnesium oxide

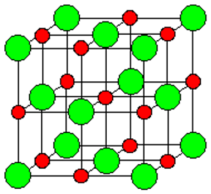
- Ionic fraction

$$f_{Ion} = 1 - \exp\left[-\frac{(X_A - X_B)^2}{4}\right]$$
$$= 1 - e^{-\frac{(X_A - X_B)^2}{4}} = 70\%$$

- Ratio between ion radii

$$\frac{r_{Mg^{2+}}}{r_{O^{2-}}} = 0.51$$

- Sodium chloride structure



- Density

$$\rho = m/V$$
$$= 4 \cdot 40.3\ \text{g/mol} / \left(6.022 \cdot 10^{23}\ \text{mol}^{-1} \cdot \left(424 \cdot 10^{-10}\ cm\right)^3\right)$$
$$= 3.51\ \text{g/cm}^3$$