Examination – questions 2022

10 Polymers - basic concepts, properties, crystallinity, chemical composition.

11 Synthetic polymers and their preparation, properties of selected synthetic fibres.

12 Natural polymer fibres, damage detection, chemical nature, regenerated cellulose fibres.

13 Surfactants, properties and applications.

14 Textile finishing, pretreatment, cotton pretreatment processes.

15 Dyeing of textiles - basic concepts and principles, dyes and pigments.

16 Printing of textiles - basic principles, digital printing.

17 Fiber finishing - principles of selected finishes (e.g. hydrophobic, flame retardant).

18 Fibre blending - reasons, complications in finishing, analysis of fibre blends, bicomponent fibres.
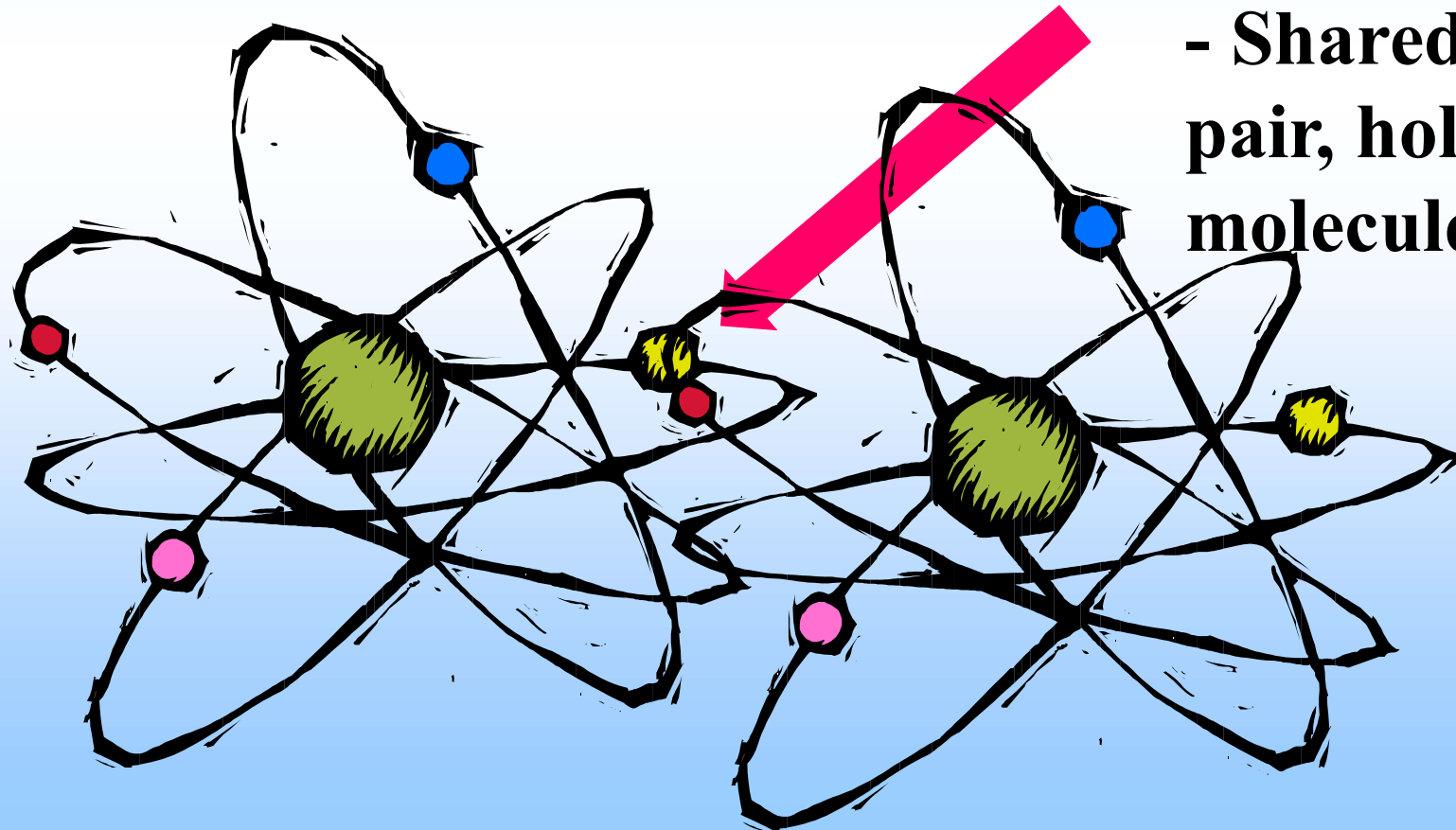
19 Environmental aspects and recycling of textiles - key issues, recycling practices, colour fastness and durability of textiles

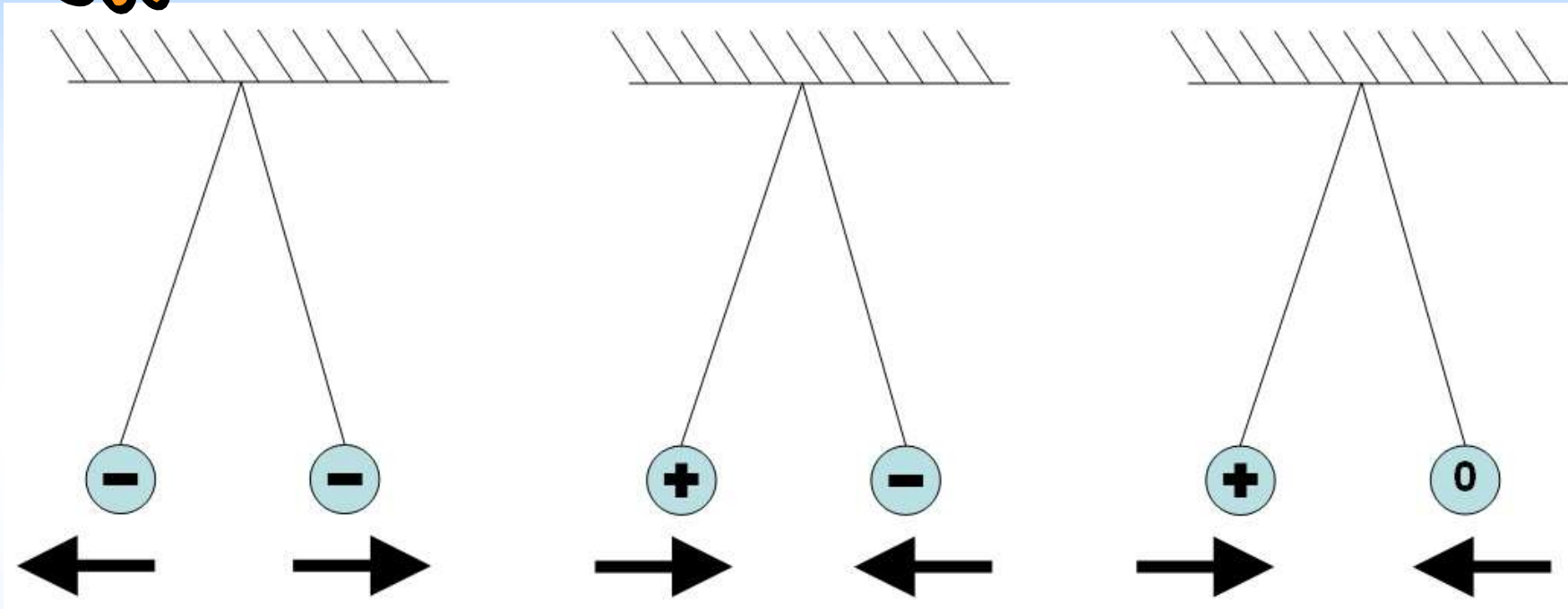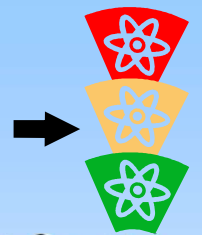# Chemical bond, formation of molecules
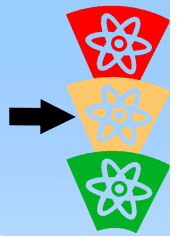
MOLECULE (a structure formed from atoms by joining their electron shells by sharing an electron pair)

Chemical bonding - Shared electron pair, holds the molecule together
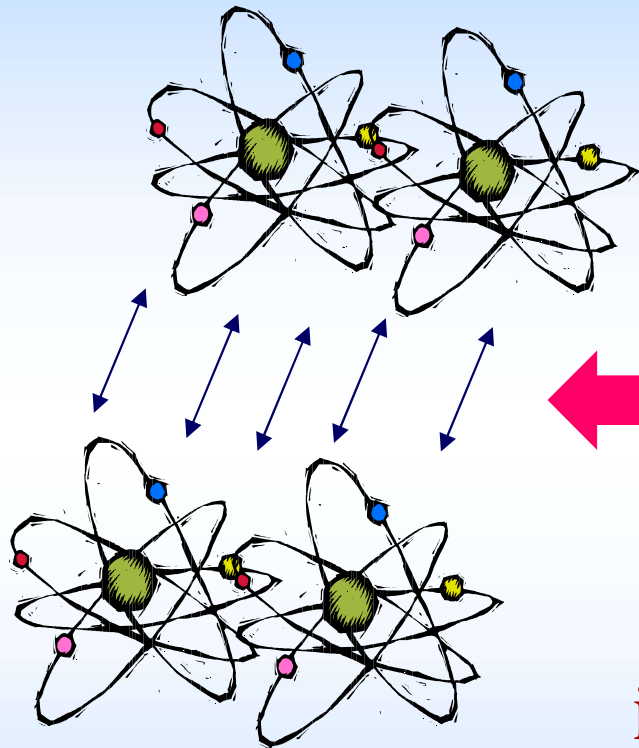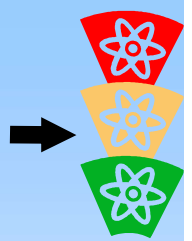
Interaction of electric charges

The electric force acting between two point charges is determined by Coulomb's law, its magnitude depends on the size of the charges, the distance of the bodies and the environment between them. It is calculated by the formula where Q1 and Q2 are the charges of the bodies, r is their distance.

$$F = k \cdot \frac{Q_1 \cdot Q_2}{r^2}$$

Intermolecular interactions

Intermolecular interactions, hold molecules together in condensed systems (liquid, solid), temperature rise cancels them

in gases, molecular interactions are minimal

The stronger the interactions (they have more J/mol - we have to supply more heat to heat and evaporate), the more "resistant" the mass is, it has higher melting and boiling points
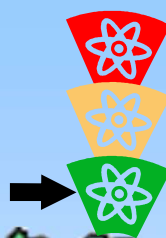
Macromolecular substances
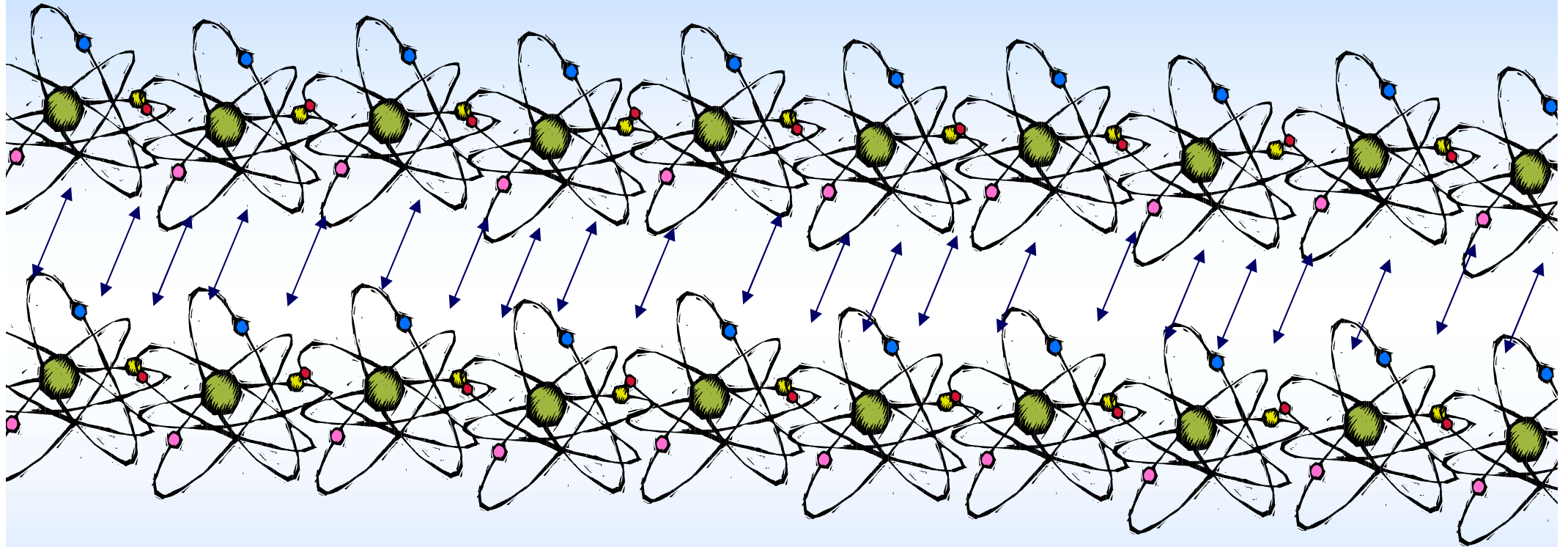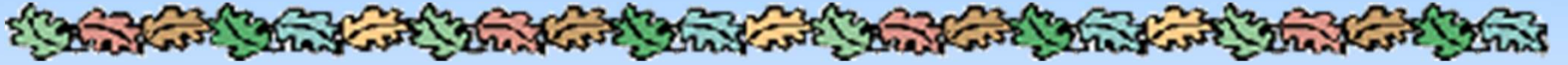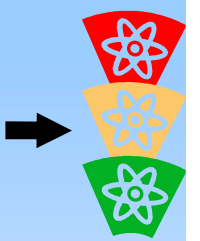
"huge, gigantic molecules" - polymers, macromolecular substances, macromolecules

Even at high temperature there will be some intermolecular interactions - not like a gas, the molecule is destroyed by the temperature rise

History (according to what man can produce and use)
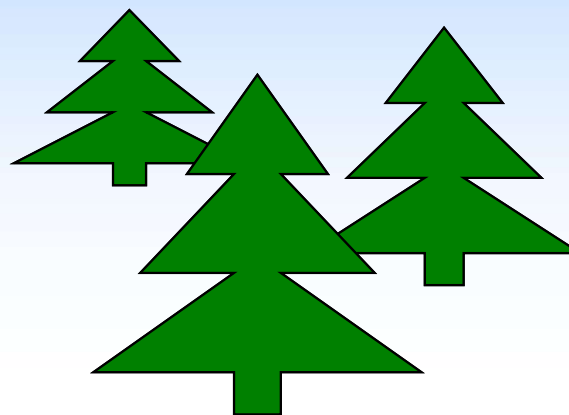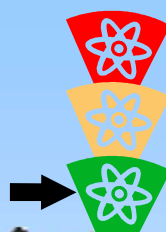

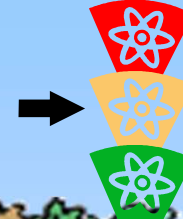**Stone Age**

Iron Age

Timeline

Bronze Age

Polymer time

Polymers are all around us

Properties of molecules

| Low molecular weight	Low molecular weight	Macromolecular
Melting temperature	Precisely defined	Unclear, wider temperature range
Melt viscosity	Low	High
Transition to the gaseous state	Easy, non-destructive	Cannot, decomposition occurs
Mechanical properties	Fragile	Tough, tenacious
Crystallization	Usually easy, fast	Difficult, incomplete
Solution	Dialyzable, low viscosity	Non-dialyzed, high viscosity
Purification	Distillation, crystallisation, sublimation	By precipitation
Composition	Uniform	Polymolecular
Dissolving	Without swelling	after swelling
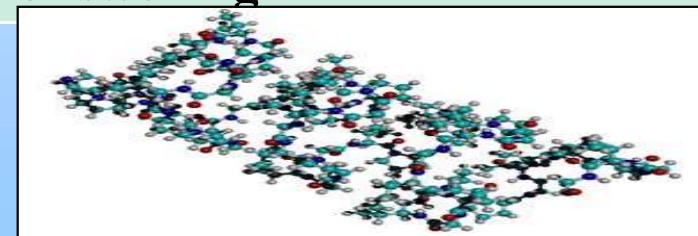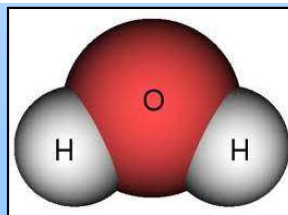
Alkanes - effect of molecule size
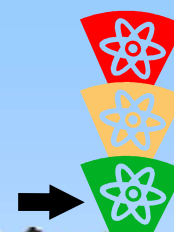
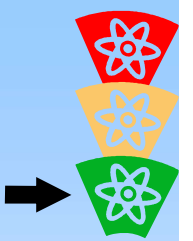**Melting and boiling points as a function of the number of carbons in alkanes**
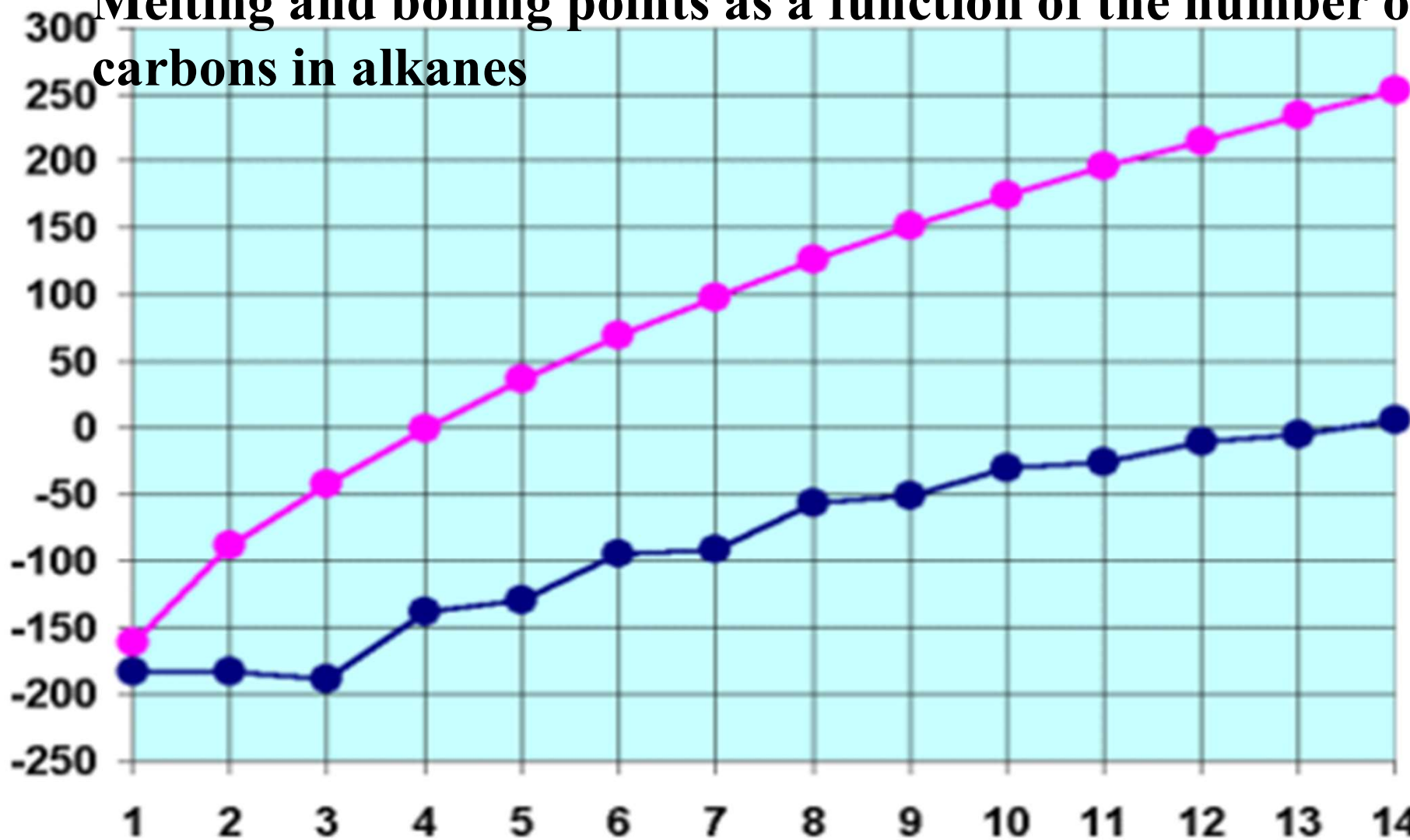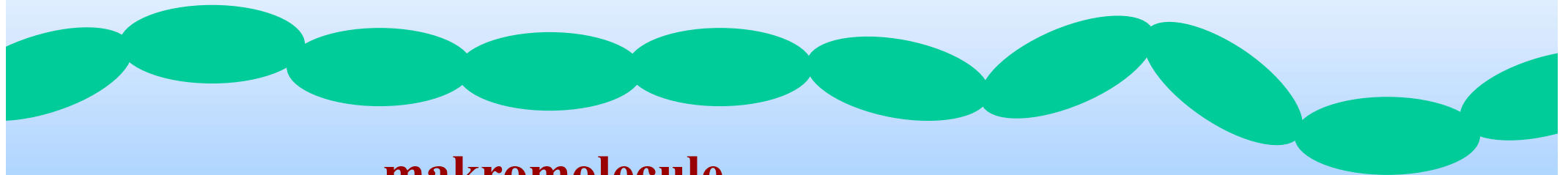

Polyethylene, decomposition at 400 °C
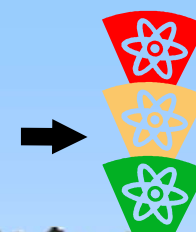
10000

How to make a macromolecule?

from small molecules (monomers) by connecting them

makromolecule

Basic terms

Macromolecular substance = polymer

Polymer chemistry deals with compounds that consist of a large number of identical or similar atomic groups. The groups are linked by covalent bonds.

General formula:

$$\left[\text{repeat unit}\right]_n$$
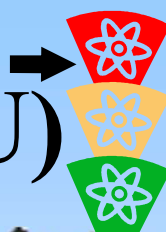
n - number of repeats, degree of polymerization

Monomer - a substance from which a polymer can be prepared by polymerization, a starting substance whose molecules can combine to form macromolecules

Monomer ⟶ **repeat unit (monomer residue, "mer")**

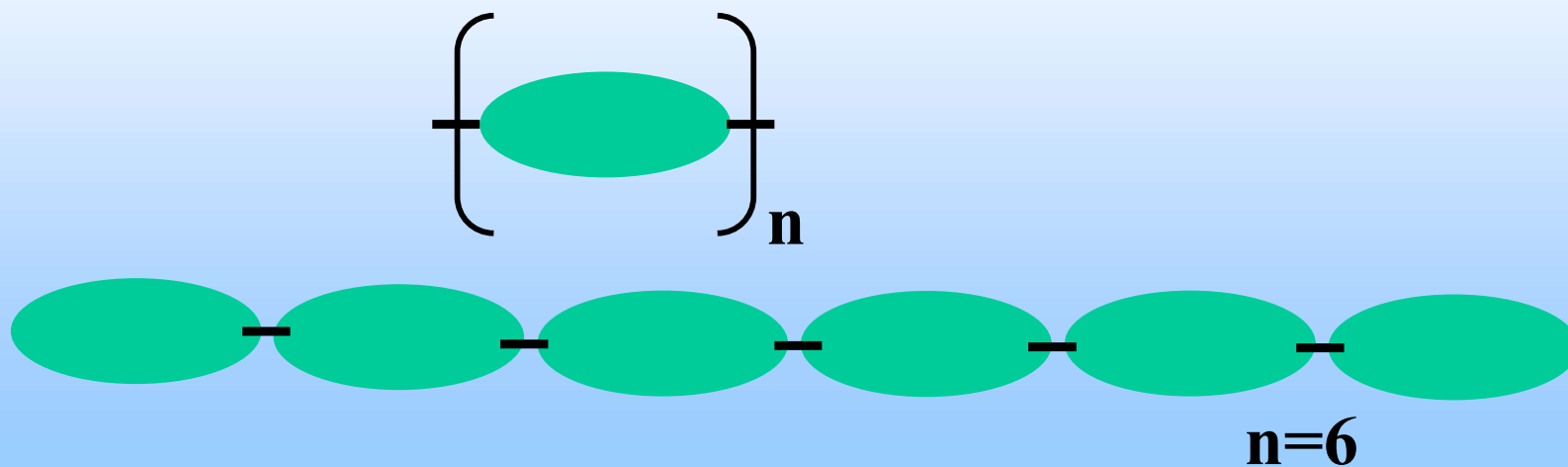"Mer" originates from the Greek word *meros*, which means "a part".

Constitutional repeating unit (CRU)

Constitutional repeating unit (CRU) - the part of the polymer that corresponds to the substance from which it was formed (monomer)

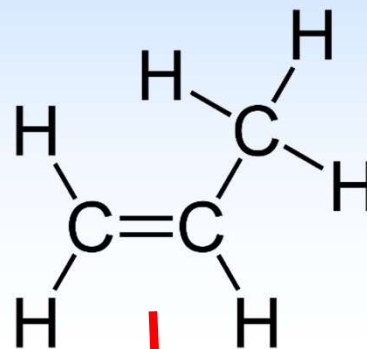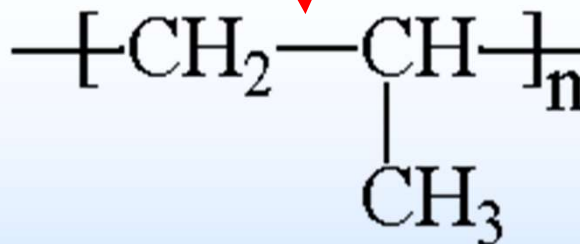**the constitution unit is put in square brackets - it is the part of the macromolecule that repeats regularly**

$$\left[\ \bullet\ \right]_n$$

$n=6$

Constitutional repeating unit (CRU)

propylene

polypropylene

$$-[CH_2-CH]_n-$$

with a CH_3 group

Constitutional repeating unit

Constitutional repeating unit (CRU)

ethylen

$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$
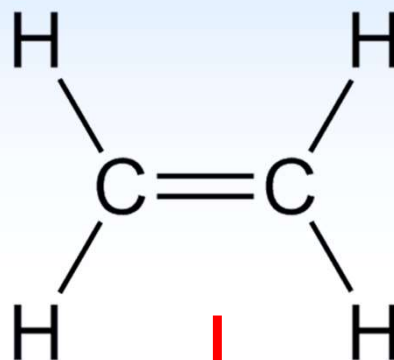
polyethylen

$$\left[CH_2 - CH_2 \right]_n$$
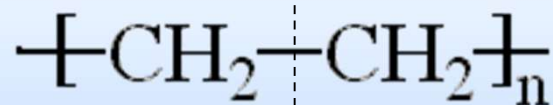
Strukturní jednotka | **Strukturní jednotka**

Stavební jednotka

Constitutional repeating unit (CRU) →

$HOOC - (CH_2)_4 - COOH$ $H_2N - (CH_2)_6 - NH_2$
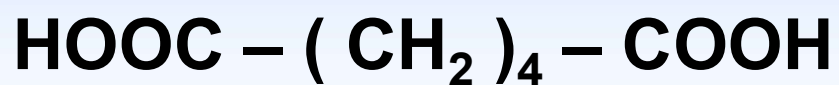
adipic acid   **hexamethylendiamine**

Polyamide 6.6

$$\left[\begin{array}{c} \overset{O}{\overset{\|}{C}} (CH_2)_4 \overset{O}{\overset{\|}{C}} NH(CH_2)_6 NH \end{array} \right]_n$$
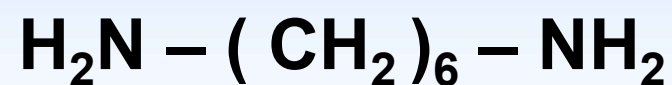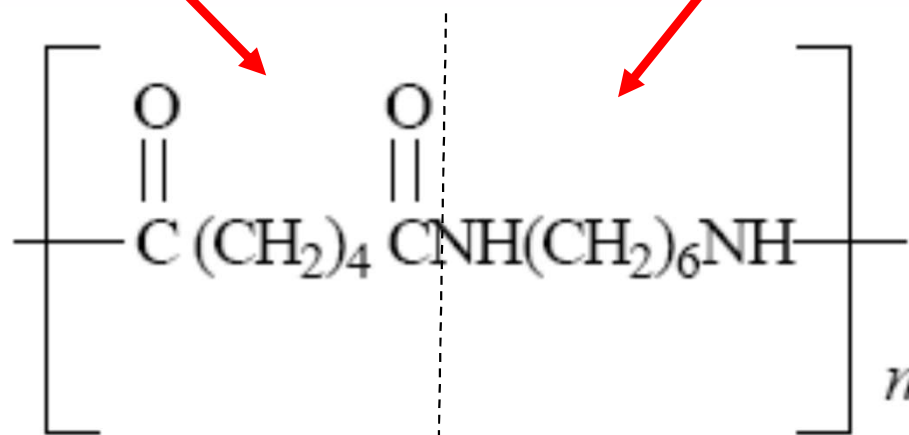
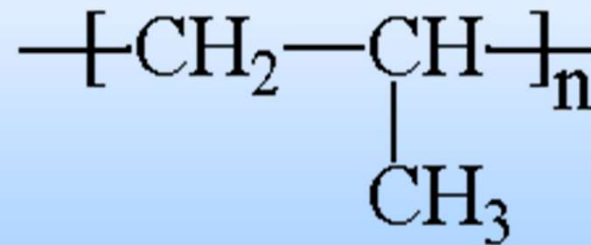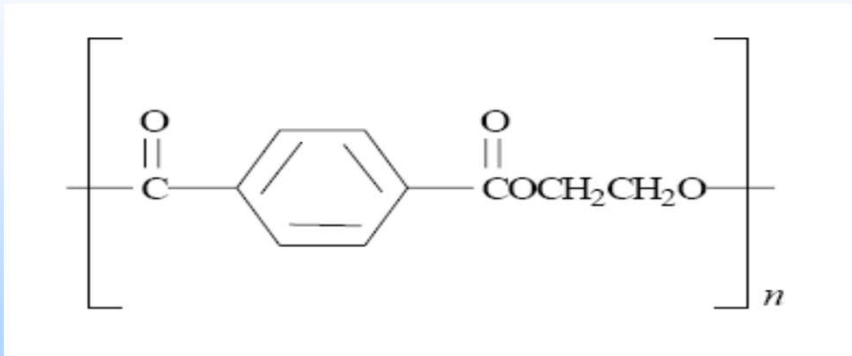**CRU**

Polymerization degree
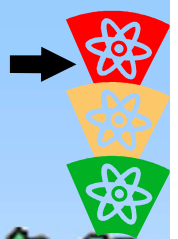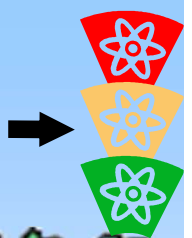
Polymerization degree – number of structural units
                        incorporated into the macromolecule „n"

On the below right, after the square bracket, the structural units

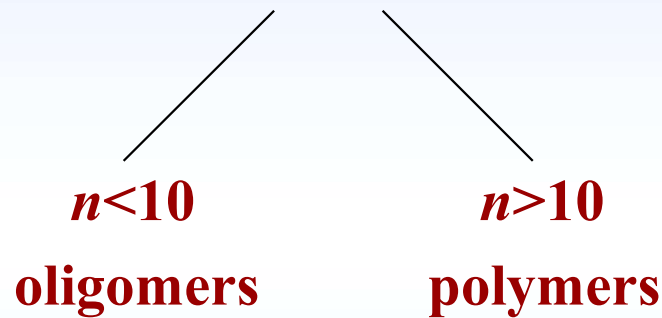For polymers, it takes values from tens upwards (hundreds, thousands, tens of thousands are common...)
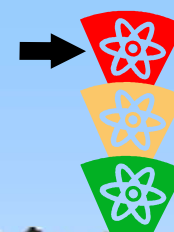
$$\left[\underset{\displaystyle O}{\overset{\displaystyle O}{C}} - \bigcirc - COCH_2CH_2O \right]_n$$

$$-\left[CH_2 - CH \right]_n$$
$$\qquad\qquad\quad CH_3$$

Polymerization degree

Polymerisation degree (n) - indicates the number of structural units bound in the macromolecule

$n<10$

oligomers

$n>10$

polymers

The limiting "n" is a problem, for ethylene it will be more than for polyester (depending on the properties of the structural unit such as size and polarity)
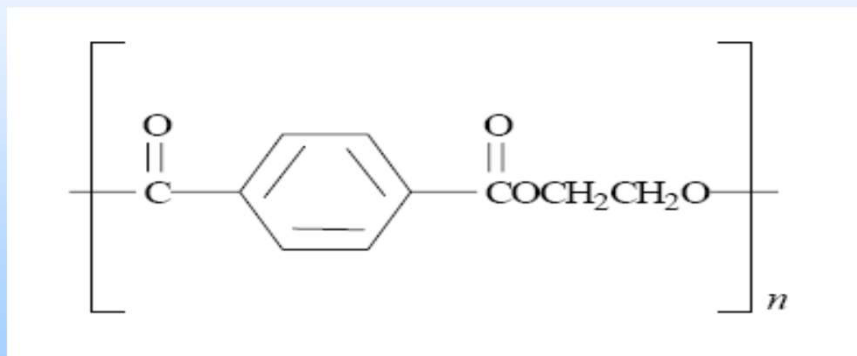
Molar mass

Molar mass is the mass of one mole of a substance (g/mol)

The mass of a polymer molecule is determined by the weight of the structural unit and the polymerization degree

Molar mass of structural unit = …

amount of substance / molar mass
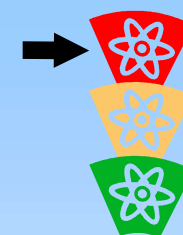
The mole, symbol mol, is the unit of <u>amount of substance</u> in the International System of Units (SI). The quantity amount of substance is a measure of how many elementary entities of a given substance are in an object or sample. The mole is defined as containing exactly 6.02×10^{23} elementary entities.

The number of elementary entities in one mole is known as the Avogadro number. This definition supersedes the previous definition of a mole as the number of elementary entities equal to that of 12 grams of carbon-12, the most common isotope of carbon.

Molar mass = sum (number of atoms in a molecule x their atomic mass)

Example: CH4 ... 12 + 4x1 ... 16 g/mol

C ... 12 g/mol, H ... 1 g/mol, O ... 16 g/mol, N ... 12 g/mol

Molar mass
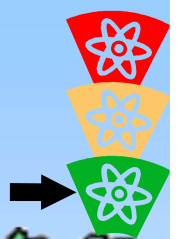
The amount of substance in low molecular weight substances is easily detectable/calculable.

For macromolecules it is different: they are usually a mixture of substances with very similar properties. Therefore, a "distribution curve" has to be considered.
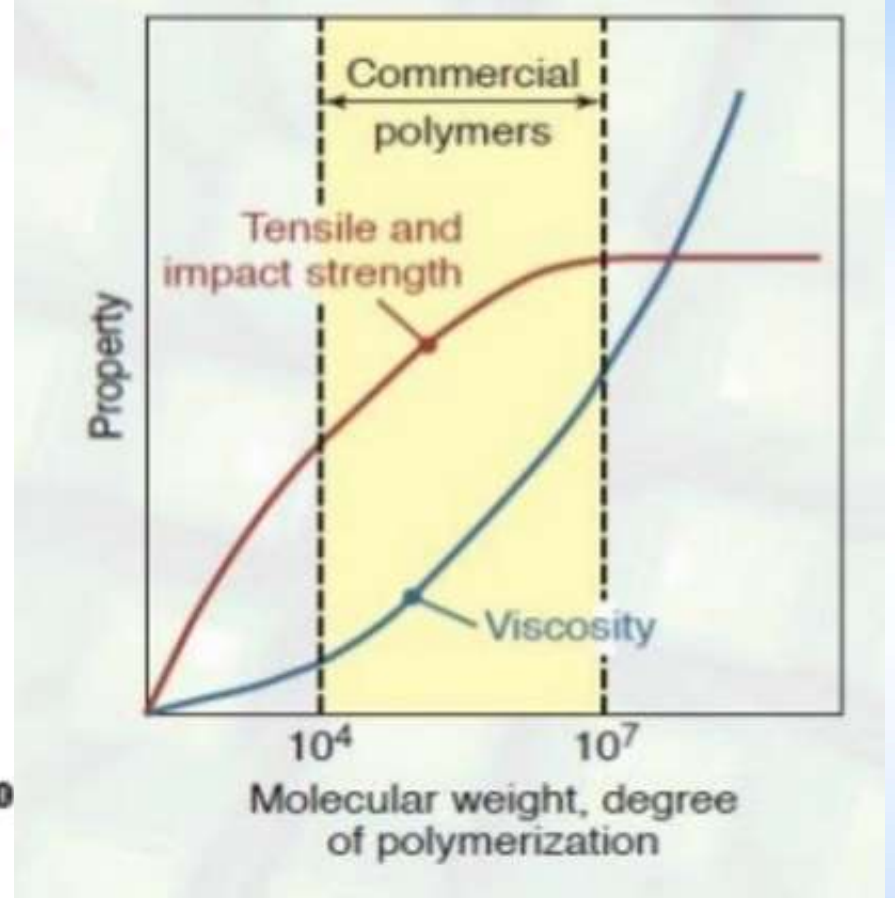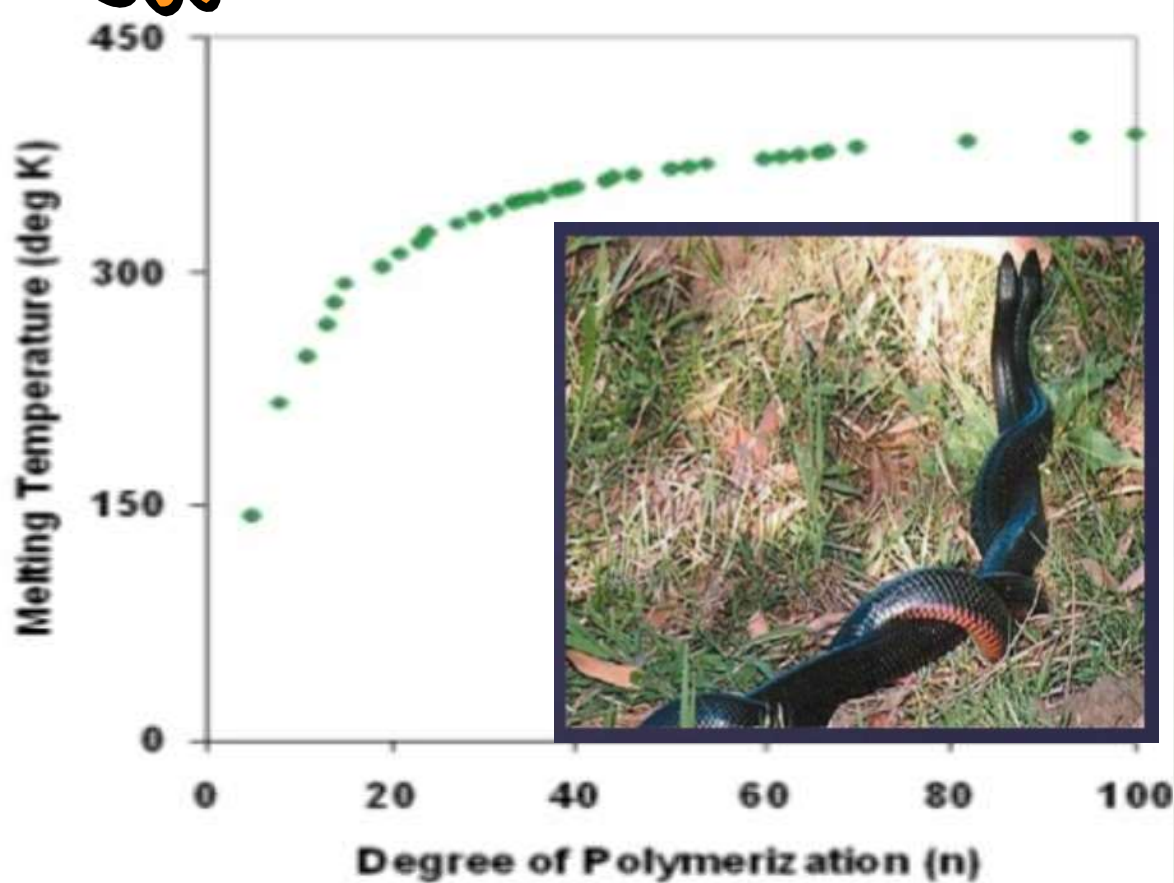
mass fraction
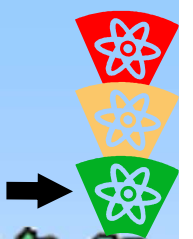
M_n

M_w
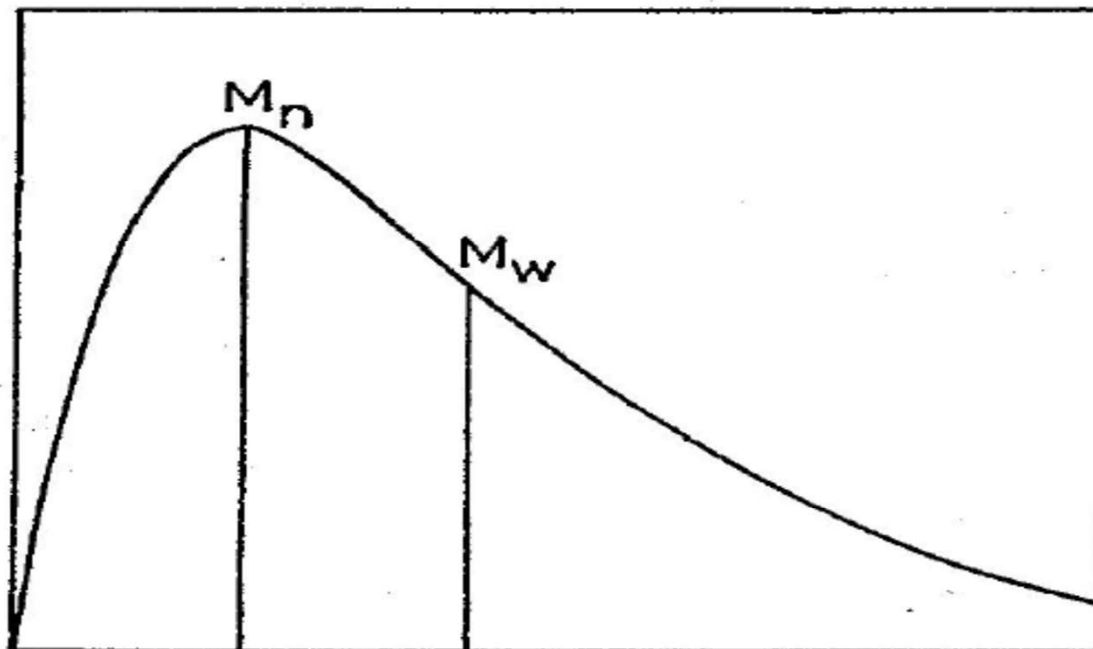
Molar mas

Molar mass and polymer properties

small macromolecules (= lower values of (n) and (Mr) = shorter chains): sticky, low melting points, more soluble

large macromolecules (= higher values of (n) and (Mr)= longer chains): Non-sticky, higher melting points, higher strength, better solvent resistance

Polymerization degree

orientation values ! Only for fibres

polymer	Polymrization degree	Molar mass of repeating unit	Molar mass of polymer	Polarity of polymer
Polyethylene	10 000	28	280 000	low
polypropylene	5 000	43	200 000	low
Polyetylenglykolterefta late	100	192	19 000	medium
Polyamide 6.6	200	240	50 000	medium
Polyamide 6	100	113	11 000	medium
akrylonitril	2000	53	106 000	medium
Cellulose (viscose)	300	162	52 000	high

shape of a macromolecule
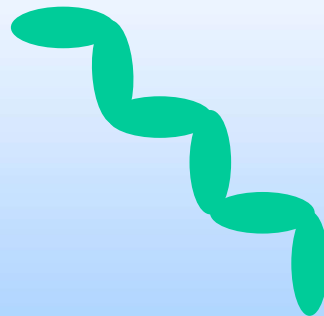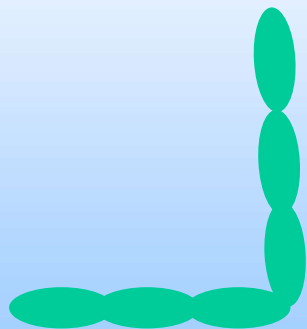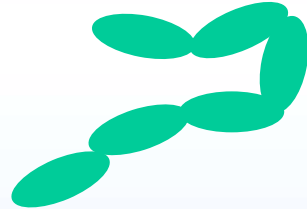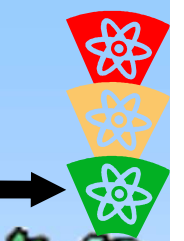
Anything is possible if the geometry of the system allows it

The probability of a particular possible arrangement is related to its energy efficiency

shape of a macromolecule
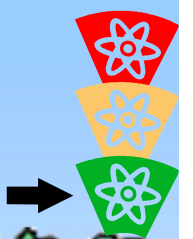
Each individual chain changes its size and shape with time, so that at any given time in the system different chains vary in size and shape
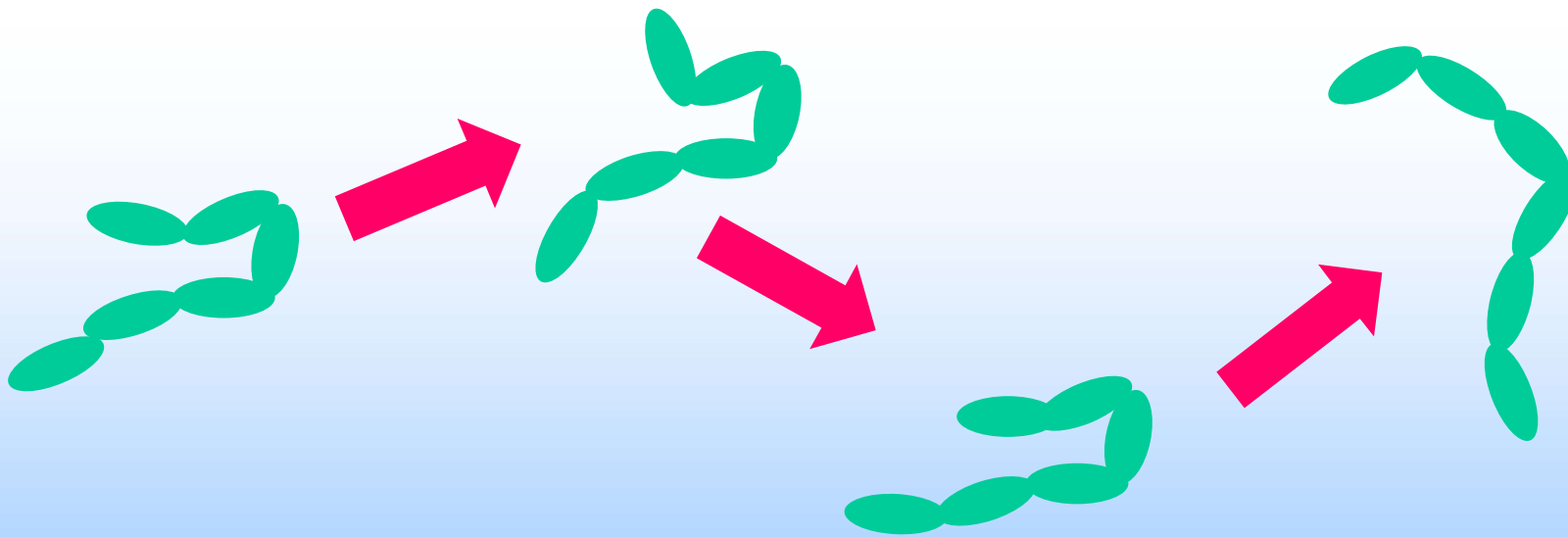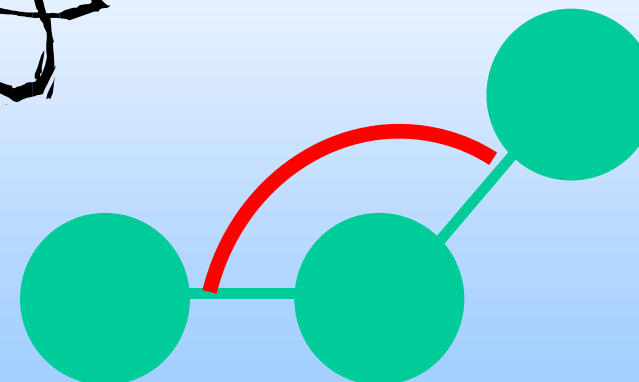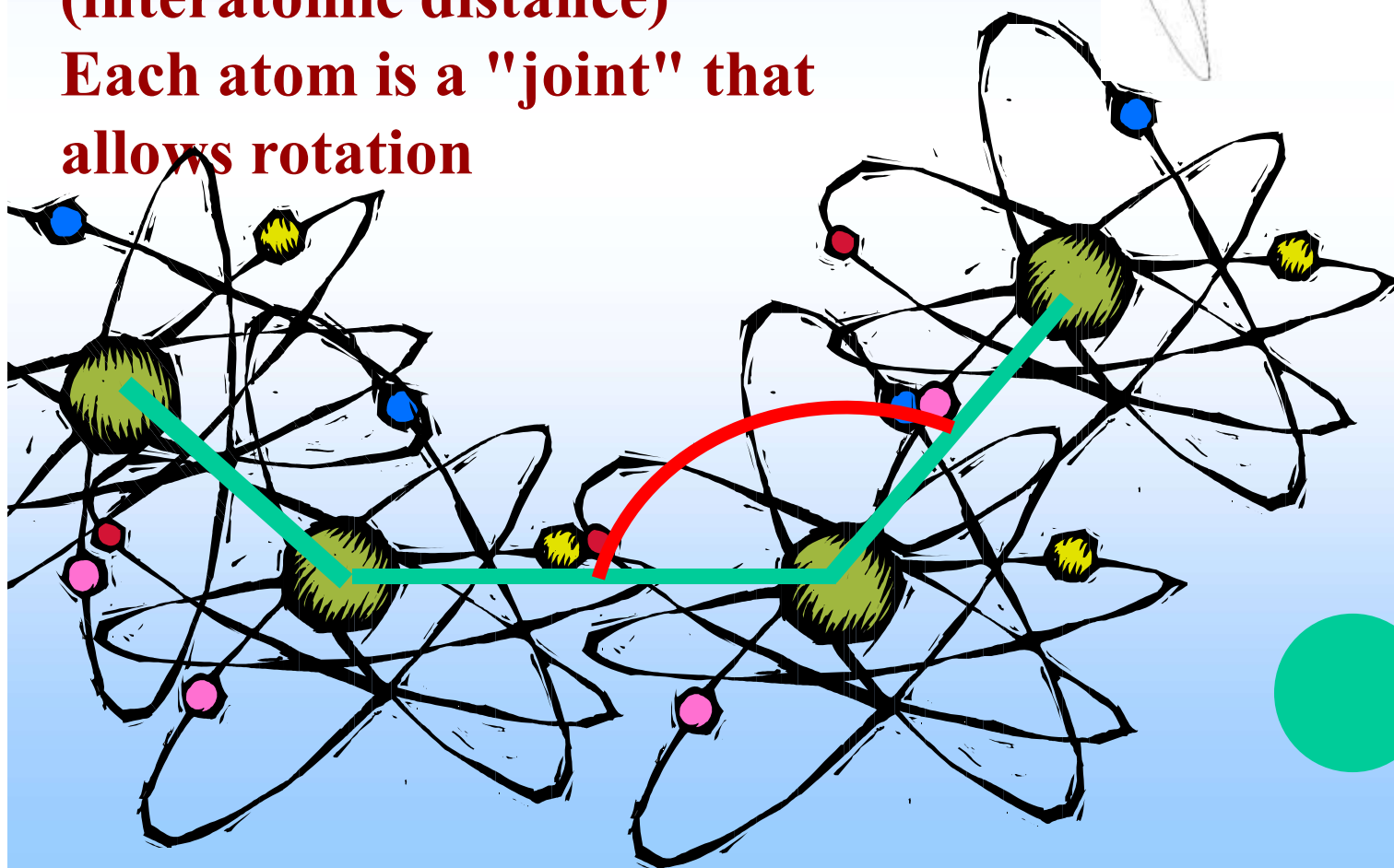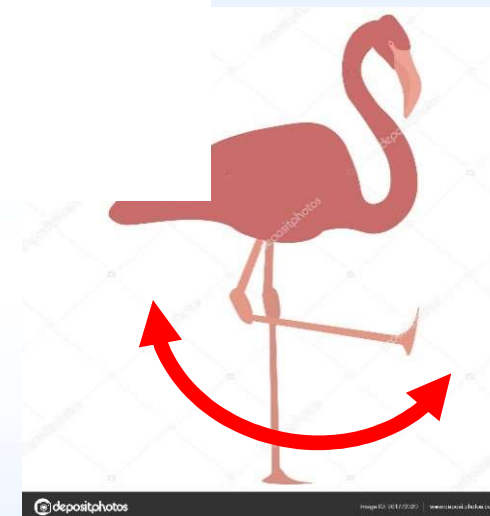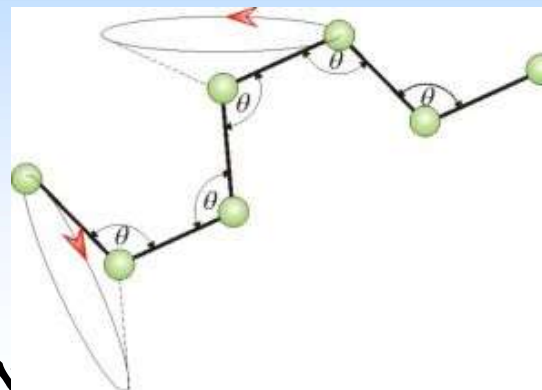
The changes are rapid (order 10^{-12}s)

shape of a macromolecule
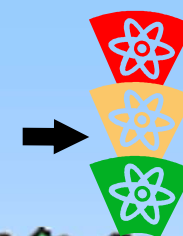
"fixed" is the bond angle (valence angle) between the atoms and the bond length (interatomic distance)
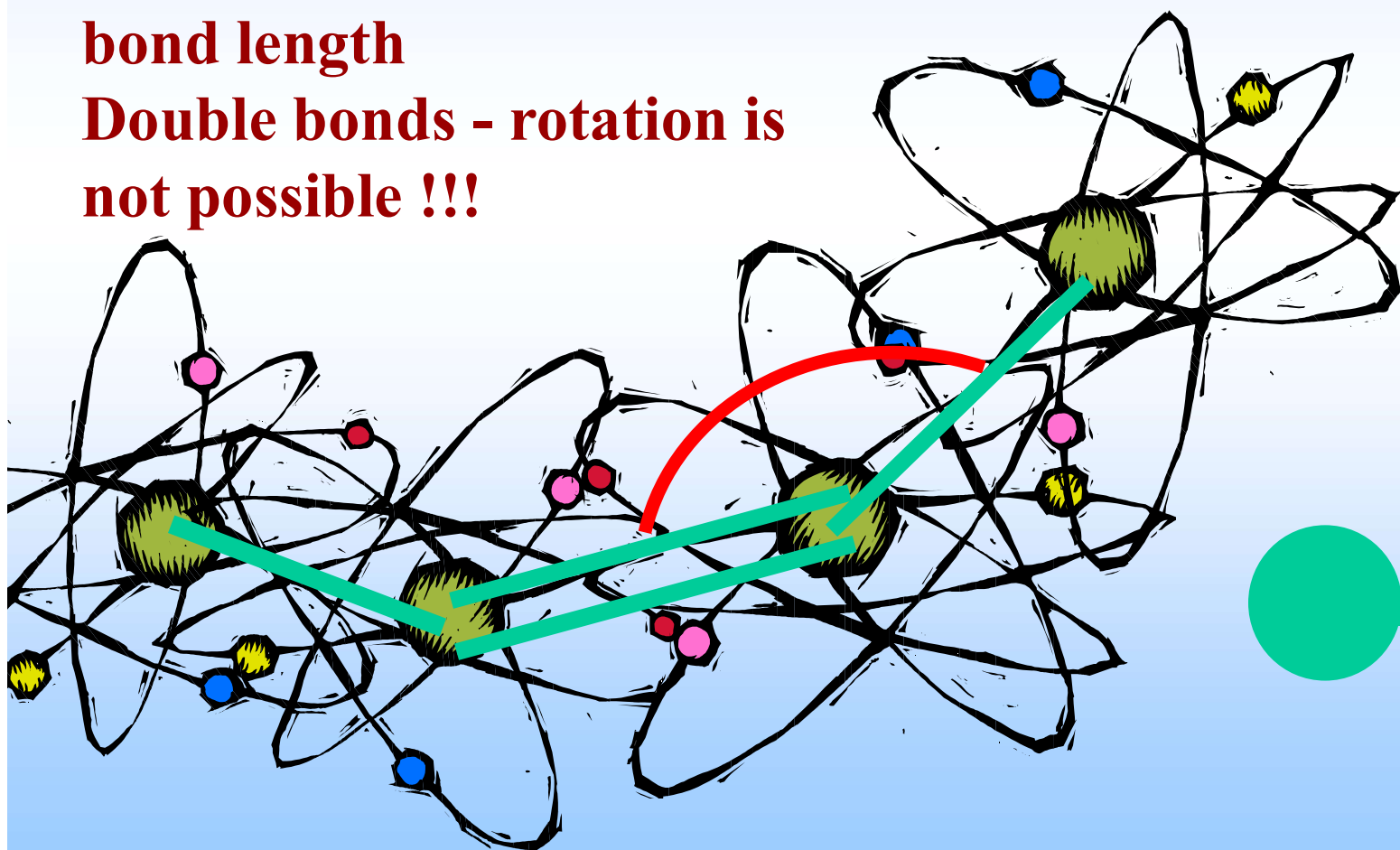Each atom is a "joint" that allows rotation
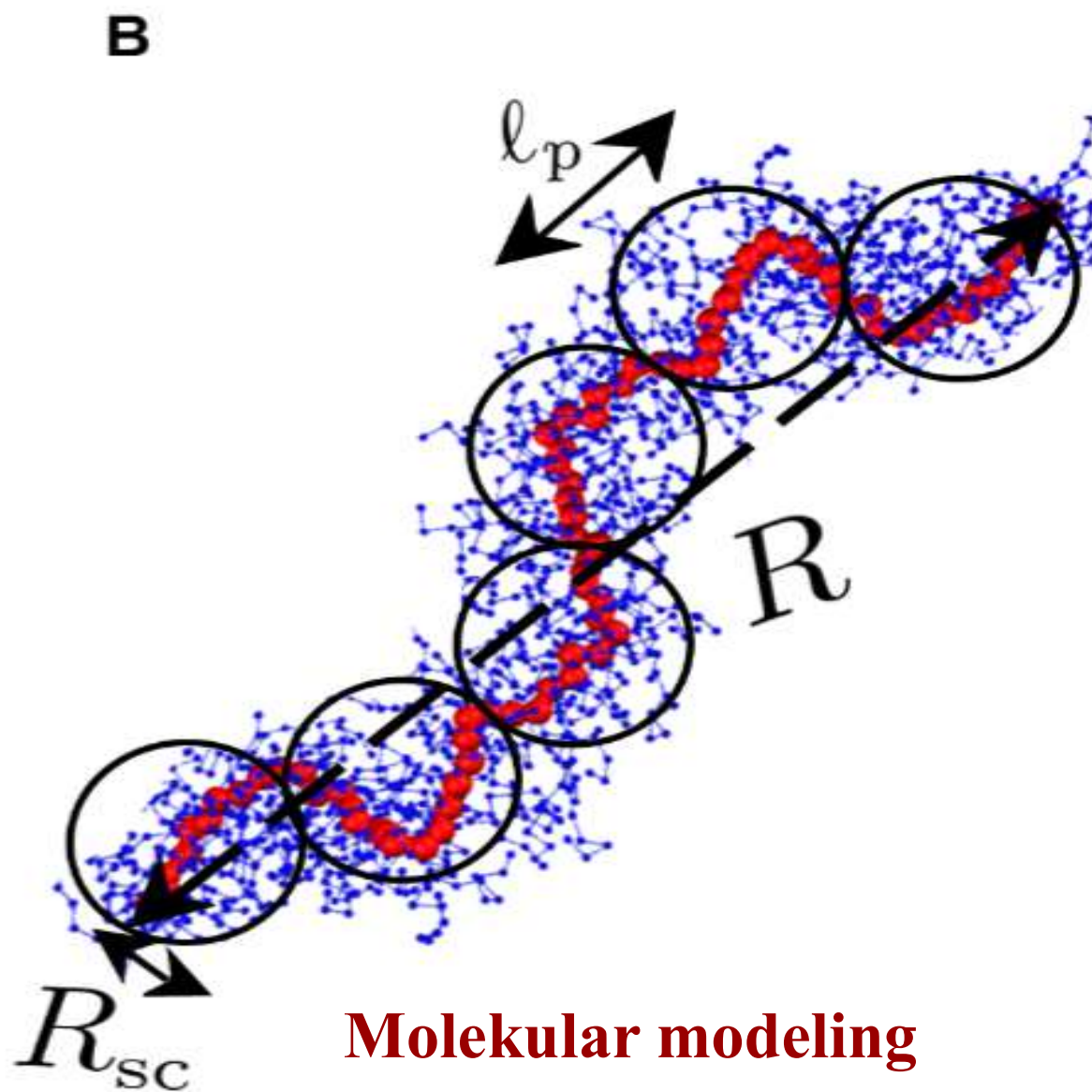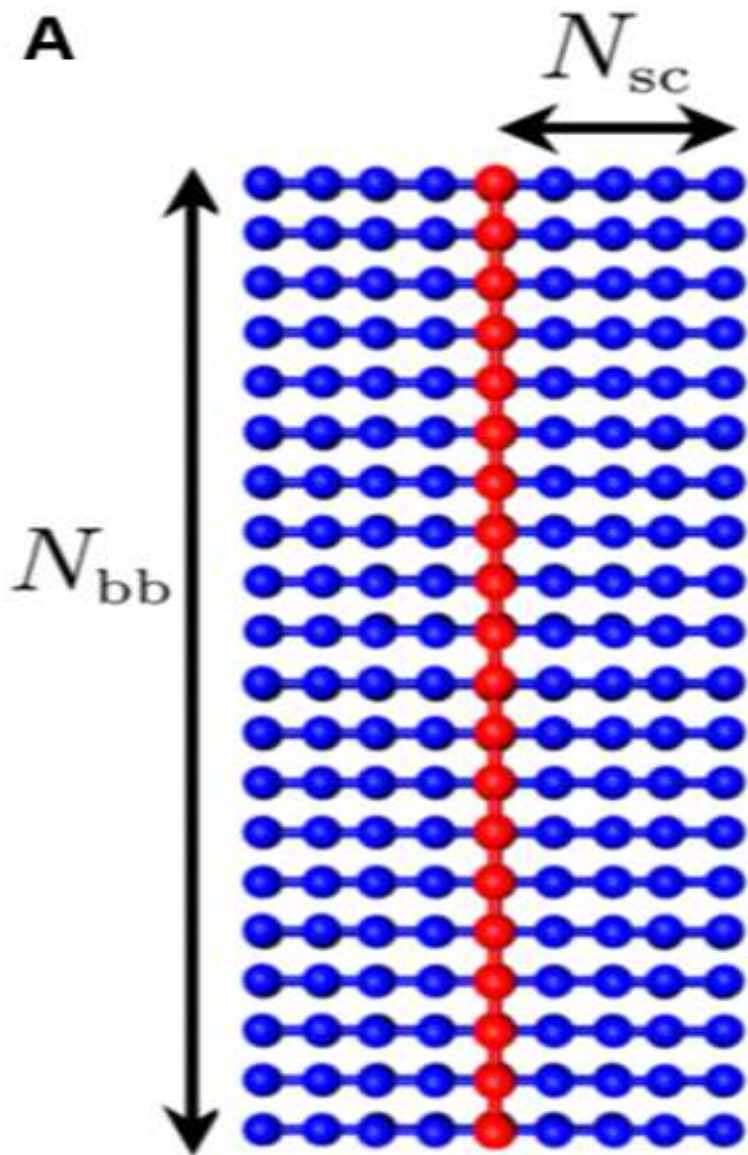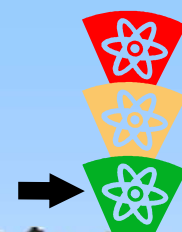
shape of a macromolecule
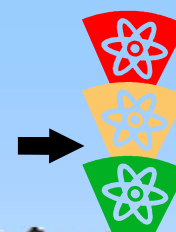
"fixed" is the bond angle
between the atoms and the
bond length
Double bonds - rotation is
not possible !!!

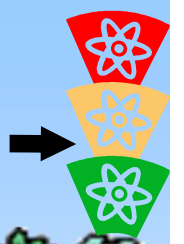# shape of a macromolecule

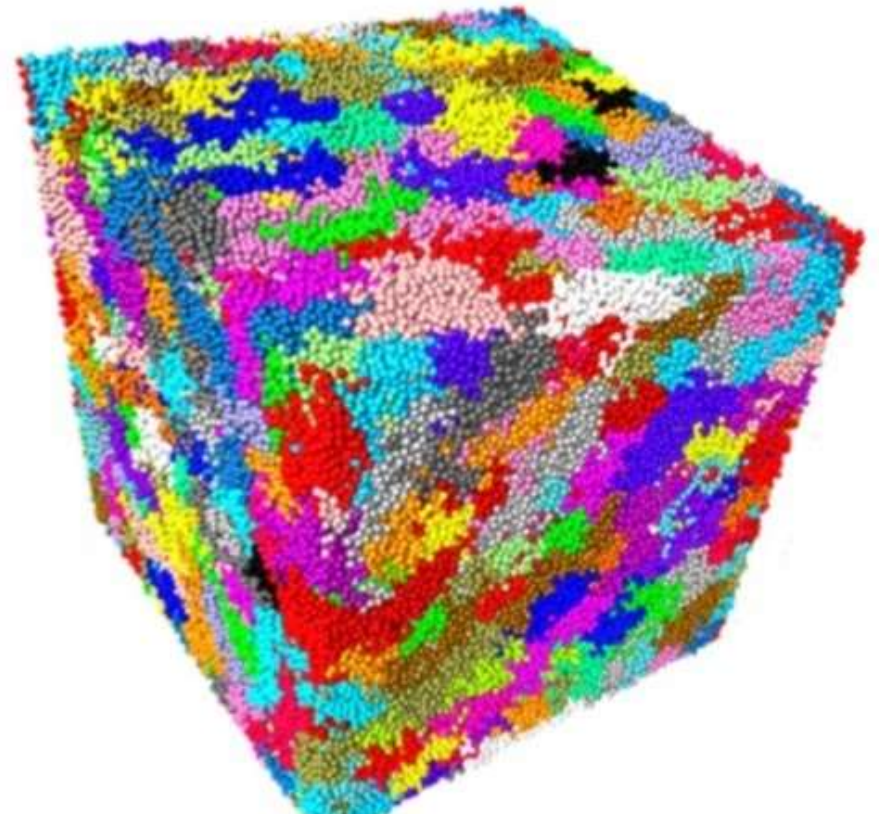**A** N_{sc} N_{bb} R_{sc}

B ℓ_p R
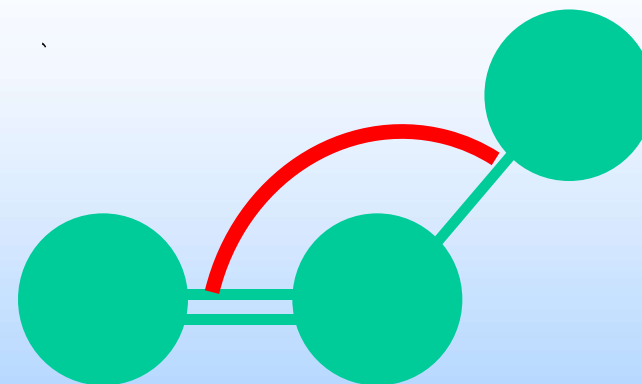
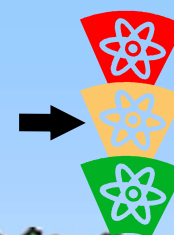**Molekular modeling**

shape of a macromolecule

The free mobility of the segments is preserved in solution or melt - there they form so-called statistical balls, after solidification their shape remains typically preserved
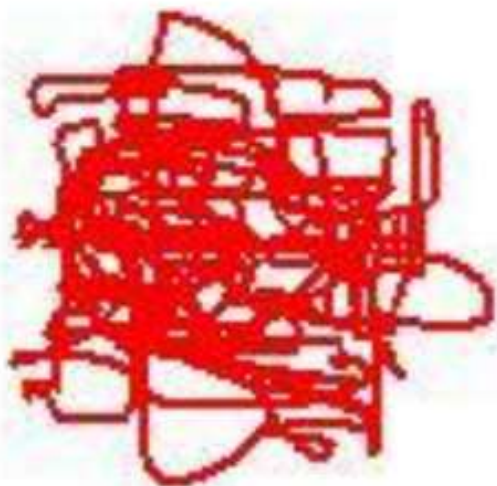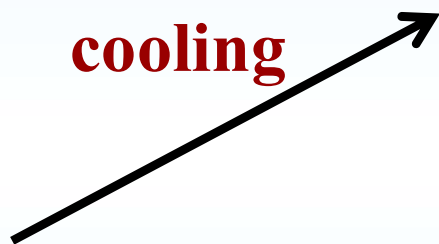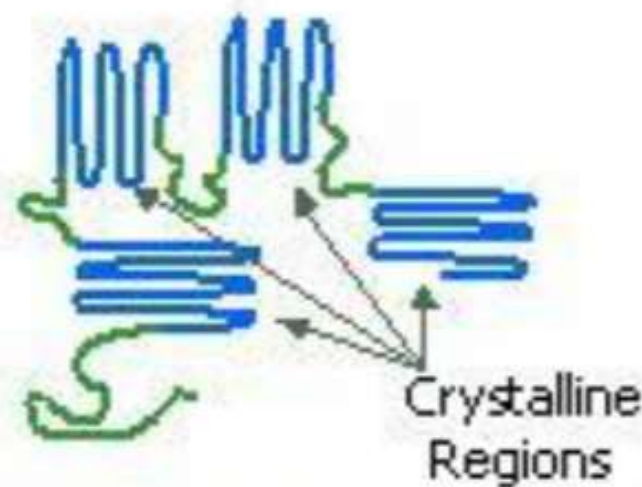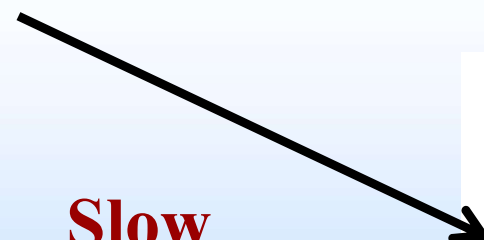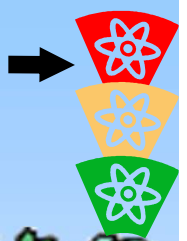
Supramolecular structure, Crystallinity

Melt

Fast cooling

Slow cooling, (not always)

Solid

Crystalline Regions

Crystallinity = percentage of crystalline phase in the polymer

crystalline regions

amorphous regions

Amorphous and Crystalline Areas of Polymers
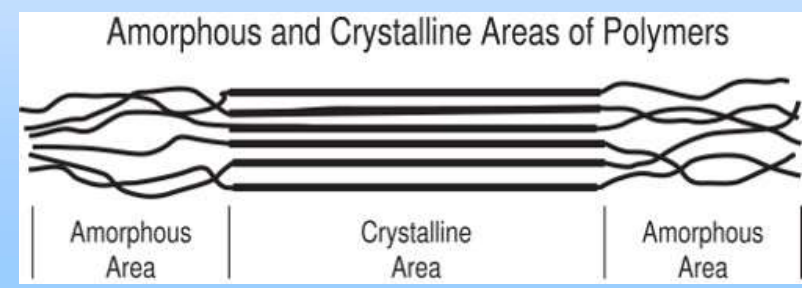
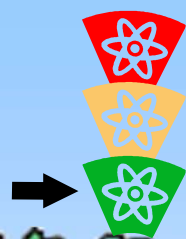| Amorphous Area | Crystalline Area | Amorphous Area |
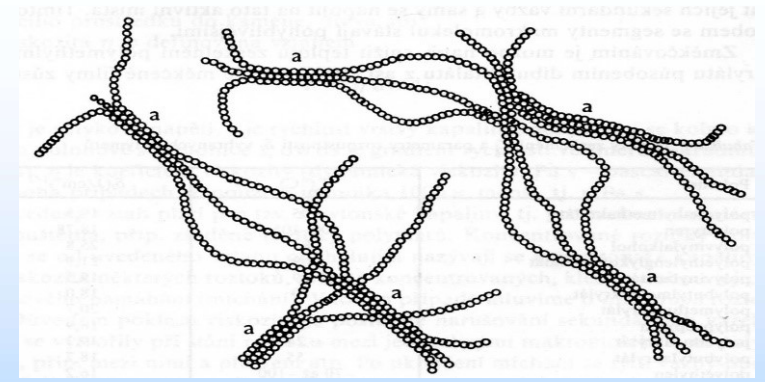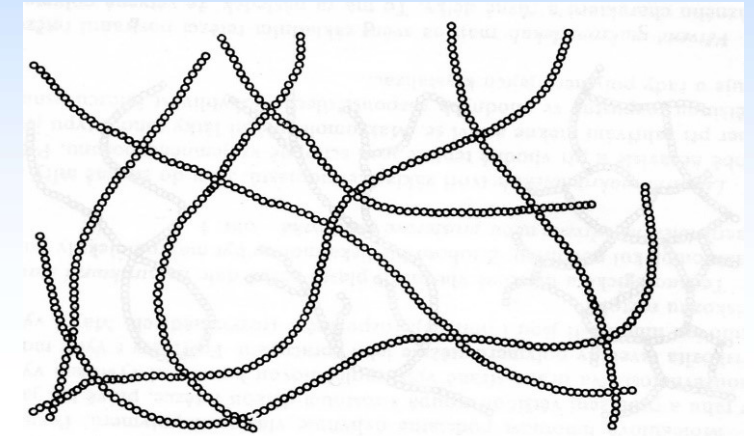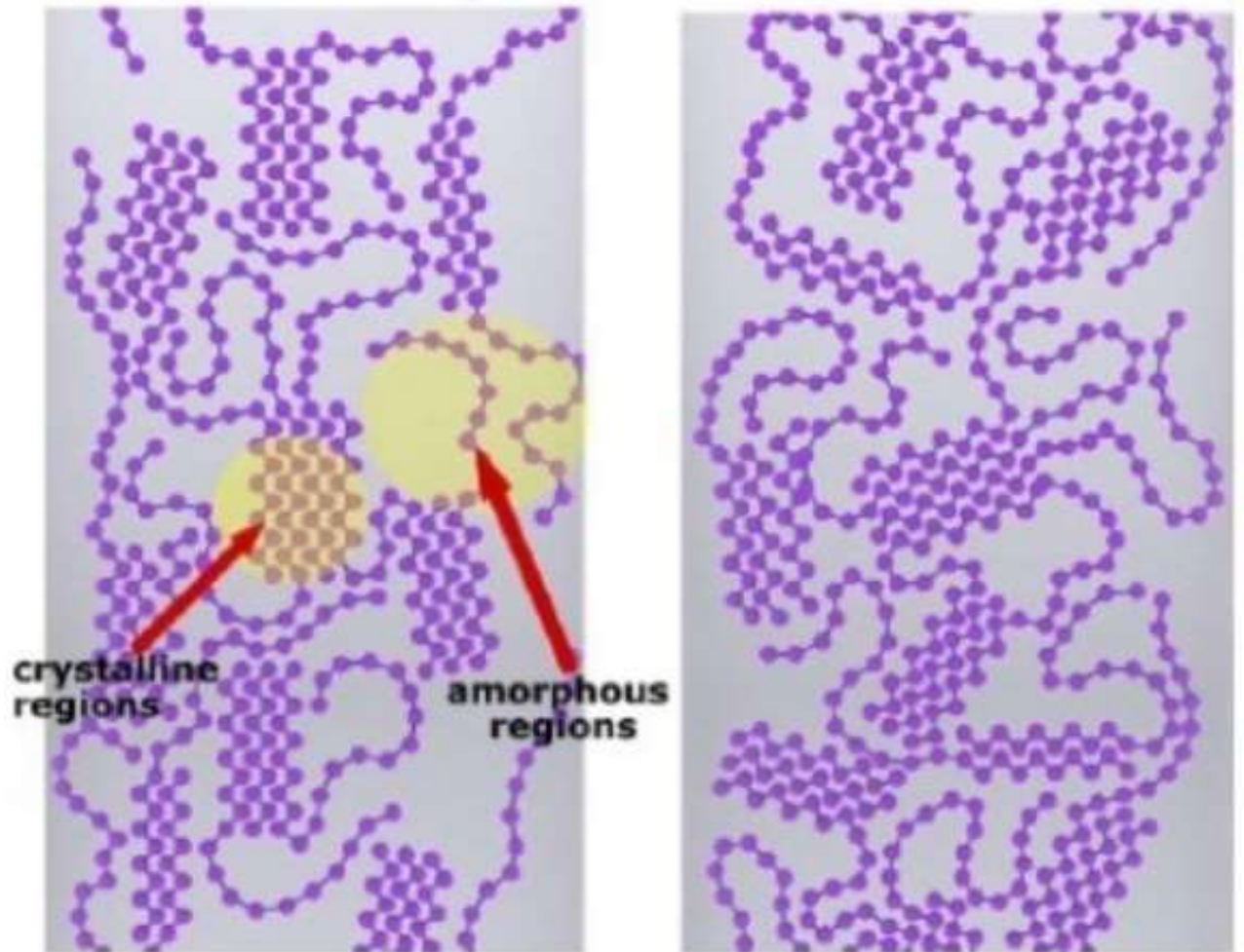
Supramolecular structure, Crystallinity

| Polymer	Crystallinity %	Density of crystalline phase g/cm3	Density of amorphous phase g/cm3
Polyamide 6.6 (PA66)	35–45	1.24	1.08
Polyoxymetylen (POM)	70–80	1.54	1.28
Polyethylentereftalate	30–40	1.50	1.33
Polytetraflourethylene	60–80	2.35	2.00
Polypropylene	70–80	0.95	0.85
Highdensity polyethylen	70–80	1.0	0.85
Lowdensity polyethylen	45–55	1.0	0.85

formation of crystals in polymers
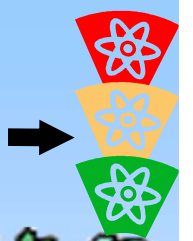
- **Sterically regular structure (tacticity)**
- **Linear unbranched macromolecules (large substiutents prevent crystals)**
- **Suitable conformation**
- **Sufficiently strong secondary bonds (between segments)**
- **Sufficiently flexible chains (placement in crystal regions)**
- **Suitable preparation conditions (cooling rate, temperature)**
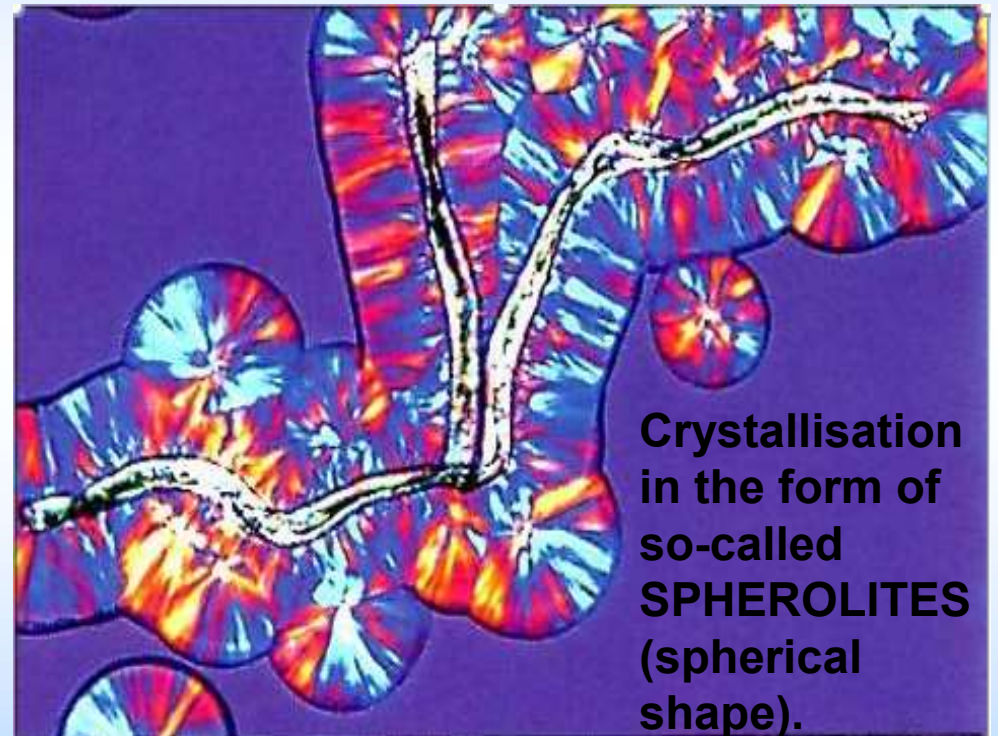
How to influence crystallinity
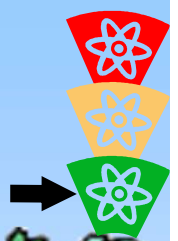
Cooling speed
Nucleation
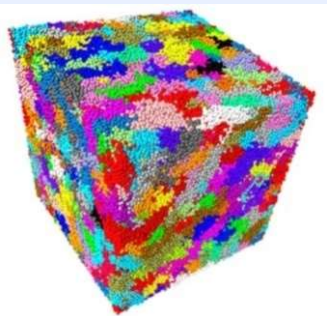**Arrangement and deformation of chains**
Heating
Increase the mobility of macromolecules (intermolecular "lubricants")

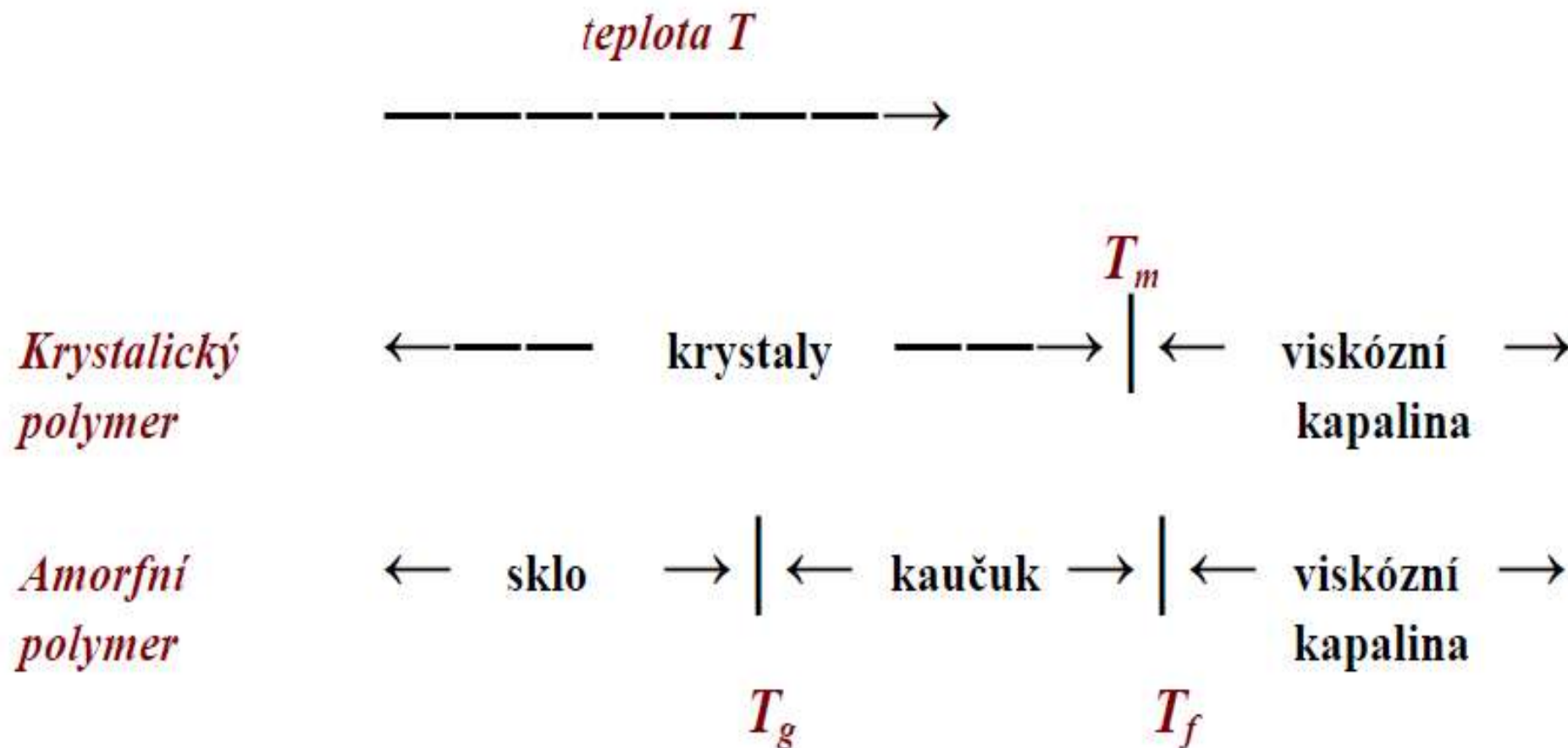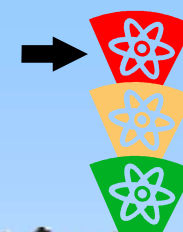Nucleation - PP crystal growth on cotton fibre at 130°C

Crystallisation in the form of so-called SPHEROLITES (spherical shape).

Deformation 300% - change in shape of molecules - orientation

Polymer phase states

teplota T

Krystalický polymer $\quad\leftarrow$ — — — krystaly — — — $\rightarrow$ | $\leftarrow$ viskózní $\rightarrow$ kapalina $\quad T_m$

Amorfní polymer $\quad\leftarrow$ sklo $\rightarrow$ | $\leftarrow$ kaučuk $\rightarrow$ | $\leftarrow$ viskózní $\rightarrow$ kapalina $\quad T_g \quad T_f$

Obr. 20. Schematické rozdělení jednotlivých fází v krystalickém a amorfním polymeru v závis-losti na rostoucí teplotě. T_g – teplota skelného přechodu, T_m – teplota tání krystalického podílu, T_f – teplota plastického toku
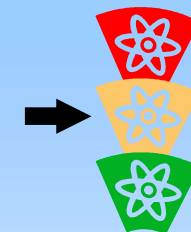
intermolecular forces
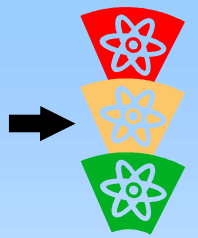
A strong chemical bond can form between atoms - this creates molecules (a molecule is made up of atoms joined by a chemical bond)
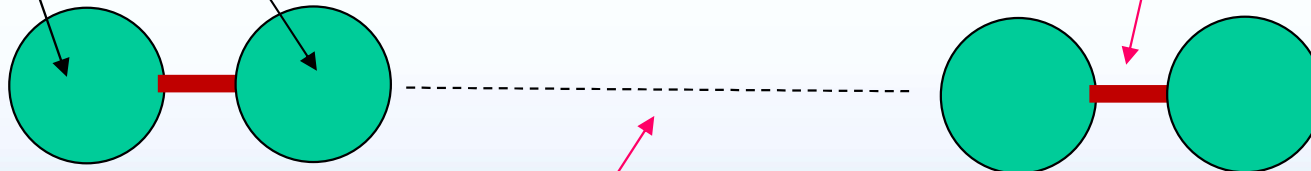
intermolecular forces - There are also weaker forces between atoms or molecules - weak intermolecular interactions - this causes clumping of particles (liquids, solids)

Bond strength

Bond strength - Expressed in terms of the energy required to break (cleave) the bond

- is of the same magnitude as the energy released in the formation of the same bond

is the binding energy per 1 mol of bond,

i.e. molar binding energy in units of J. mol-1 or kJ . mol-1
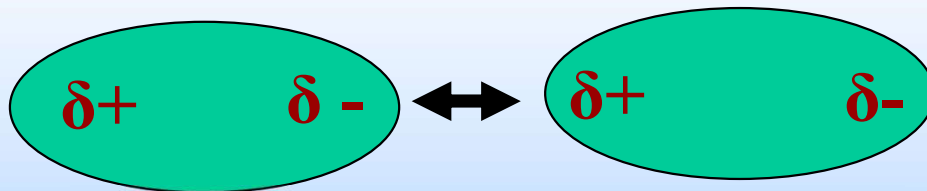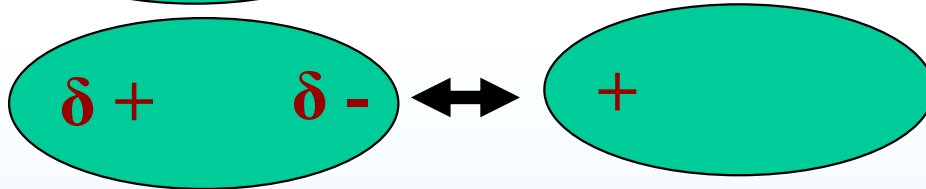

We must supply energy to break bonds
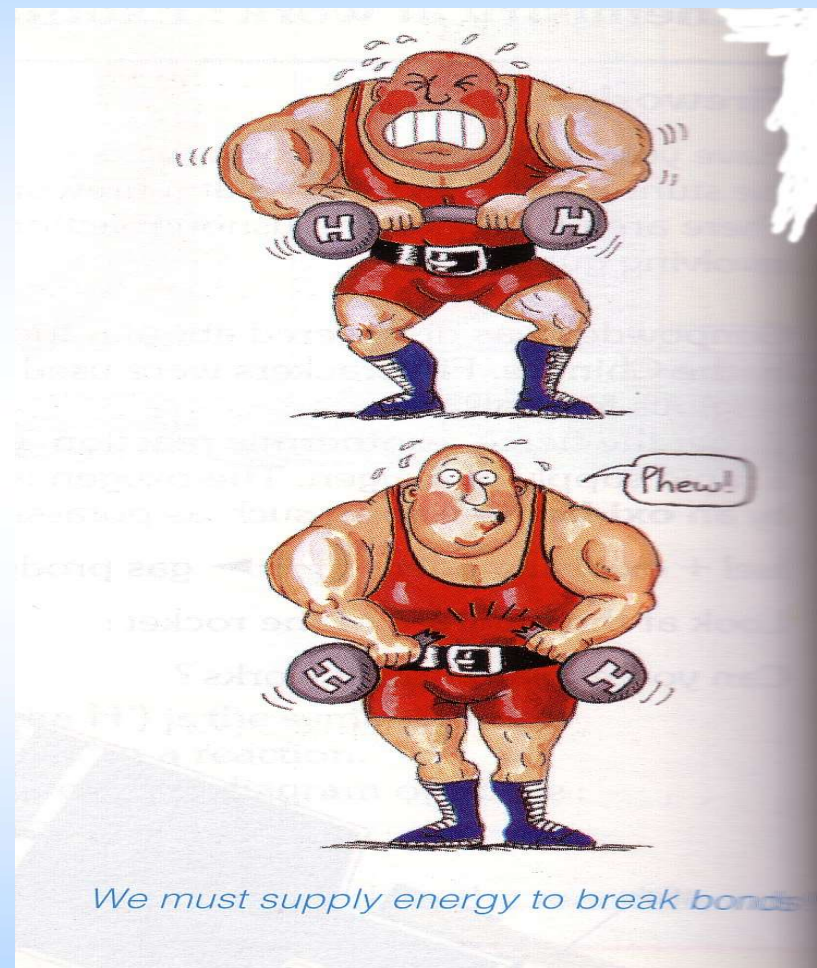
A stable bond is formed only if energy is released during its formation

v.d.Waals Coulombic interactions
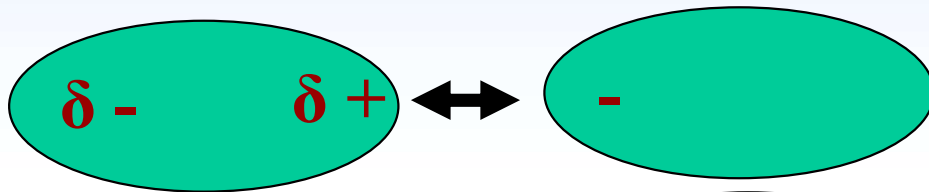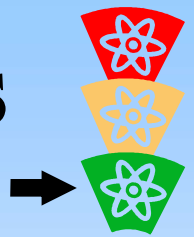
Dipole-ioné forces

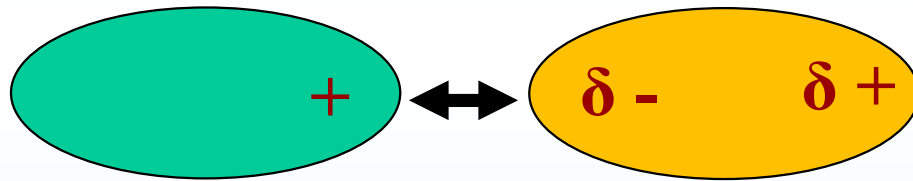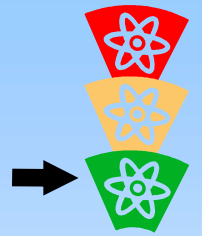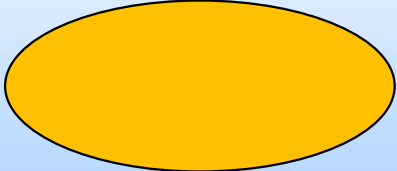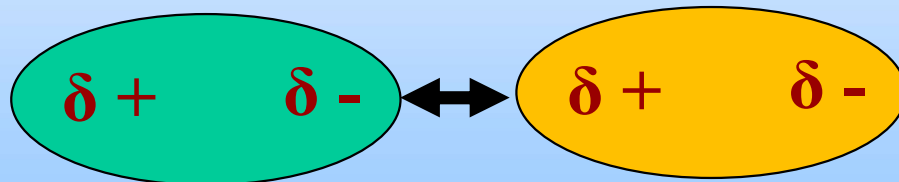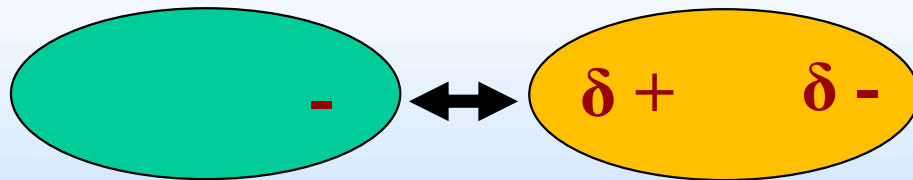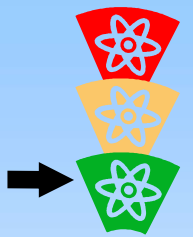Dipole-Dipole forces
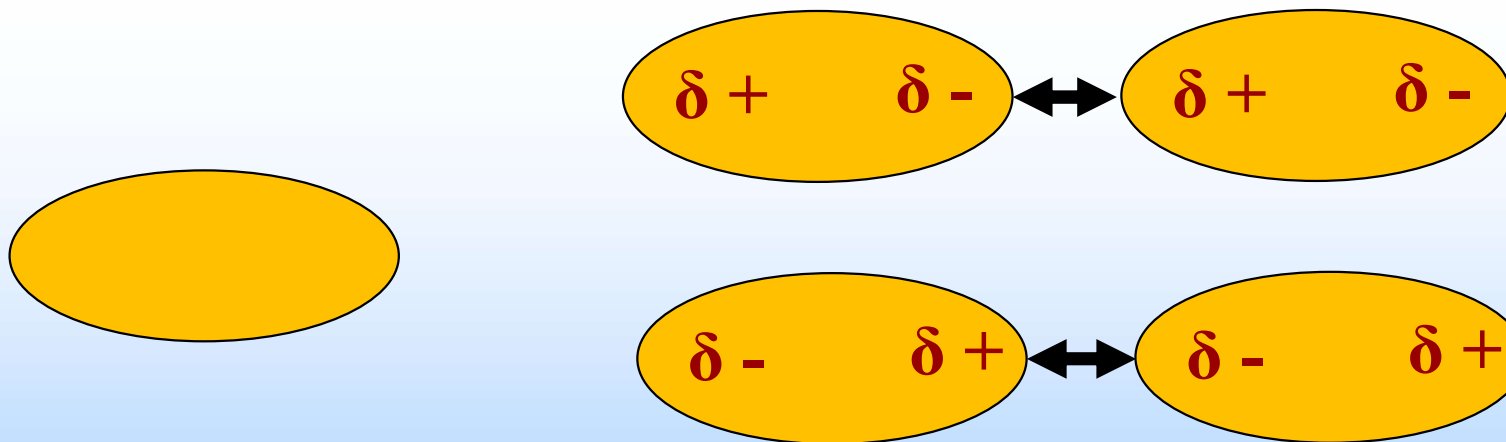
v.d.Waals Induction forces

Dipole - induced dipole

Particles without charge
even without partial
charges

v.d.Waals - Dispersion forces

Dispersion forces = partial charges (dipole) in non-polar molecules quickly arise and disappear due to the movement of electrons in the orbital, between particles that do not have a permanent dipole


Frequency of occurrence is high, binding energy is low: 0.1 to 4 kJ.mol^{-1}. It acts up to a distance of 0.4 nm (i.e. about twice the length of a covalent bond!), but the bond strength decreases very strongly with distance (with the sixth power of the distance!).

Hydrogen bonding (hydrogen bridge)

This is an important - relatively strong - physical interaction between hydrophilic sections of molecules, which is also of considerable importance in fibre dyeing. Also, the sorption of water molecules during the swelling of fibres by water takes place via these hydrogen bridges
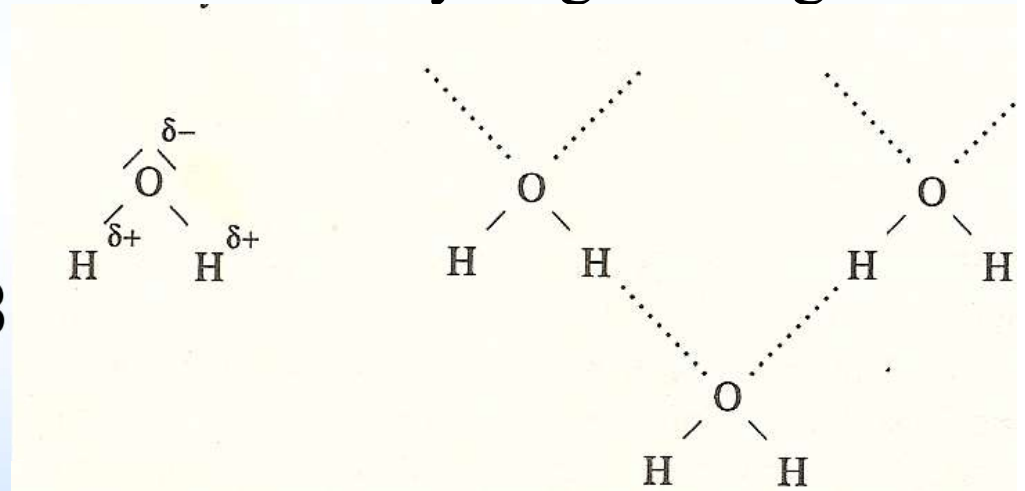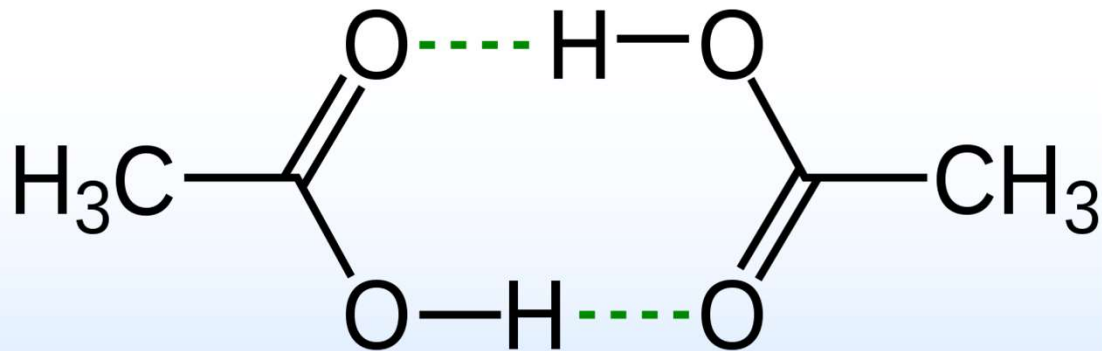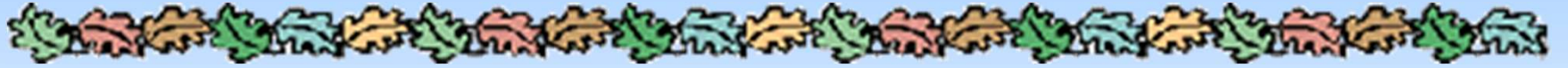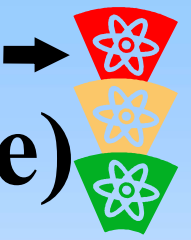
It occurs mainly in compounds of H with F, O and N. It is explained by   by the strong polarity of the HF, OH and NH bonds.

The bonding electron pair is to that extent shifted to the more electronegative atom that a hydrogen atom can form a weak bond with a free bond to a free electron pair on an atom of another molecule.
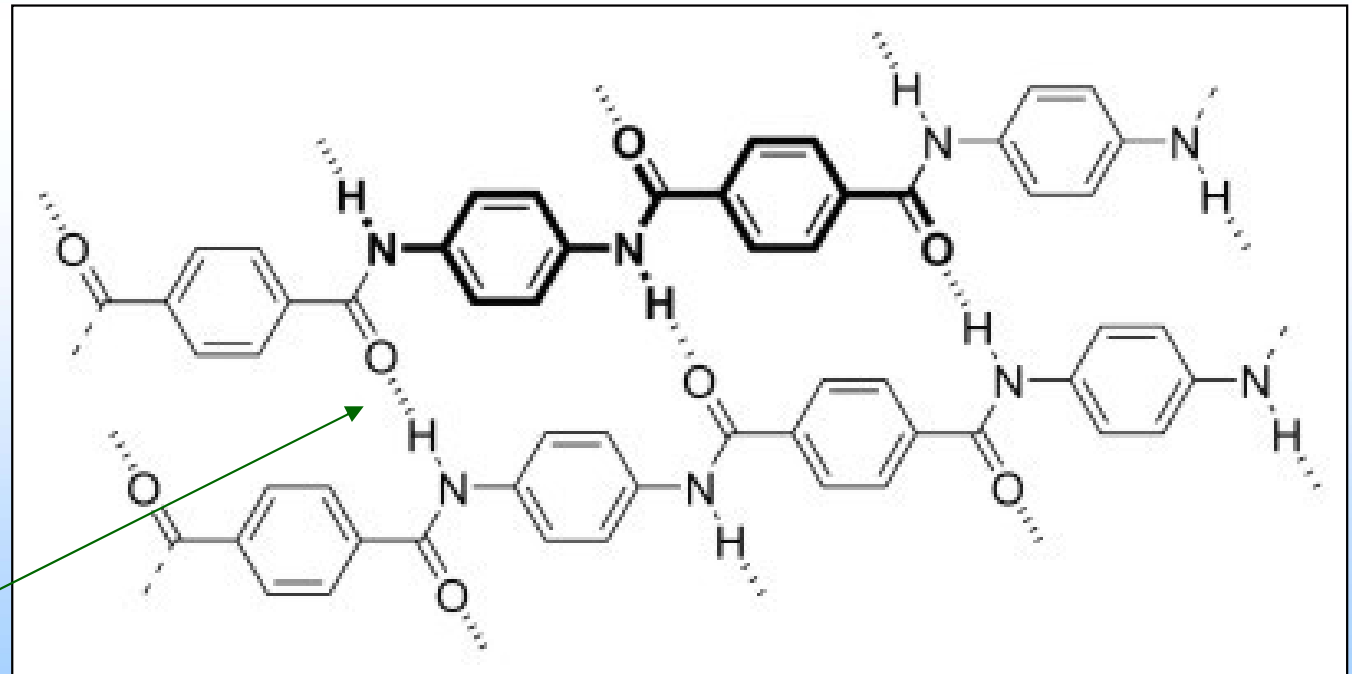
Hydrogen bonding (hydrogen bridge)

Key interactions in many threads

E.g. cotton, kevlar

increase the cohesiveness of the polymer, strength, melting point or solvent resistance
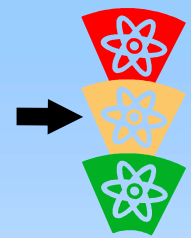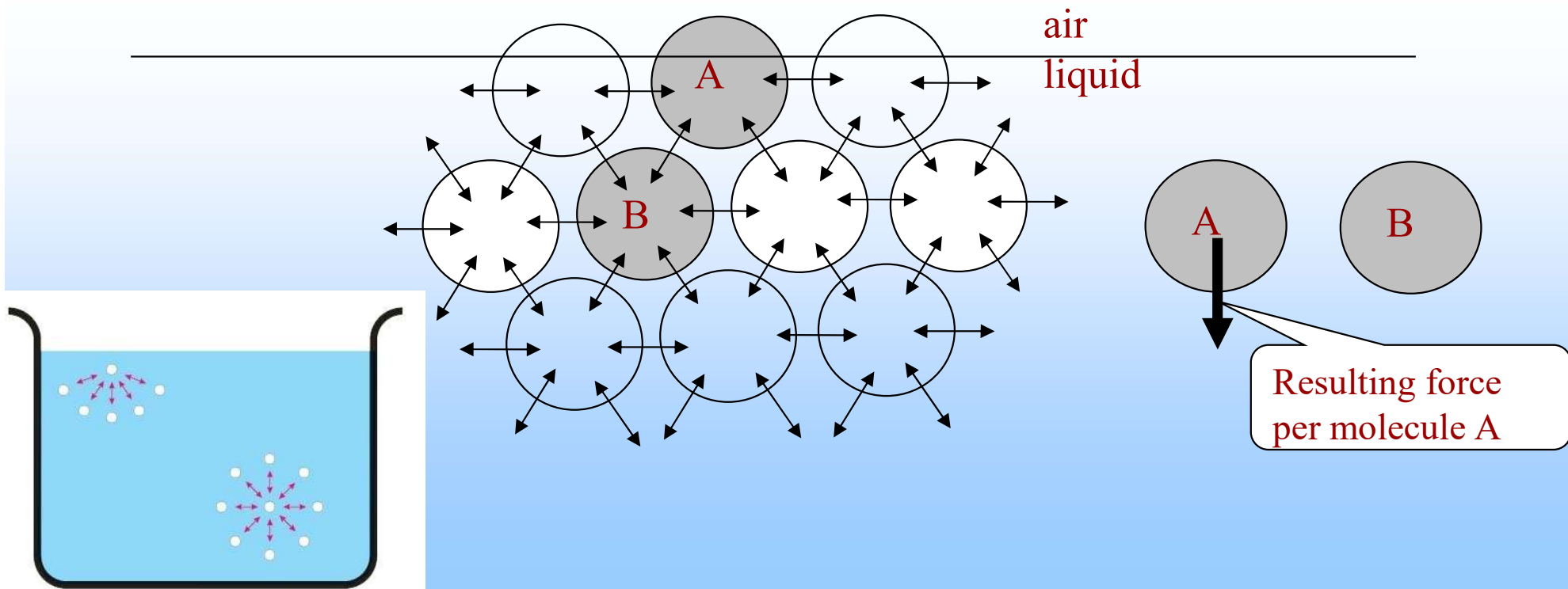

Hydrogen bond

Kevlar (polyamide)
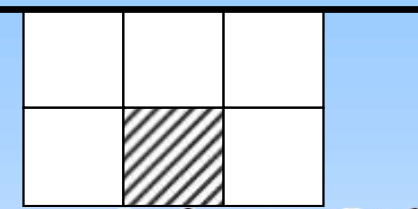
Forces between particles - surface tension

There are attractive forces between the molecules of the liquid (or solid), only the forces towards the liquid act on the molecules in the surface, as shown in the following figure

air
liquid

A B

Resulting force per molecule A

Phase surface

Matter is composed of cubic particles with edge A. The value of A is related to the molar volume V (cm3.mol-1) through the number of particles in one mole (NA):

$$V = N_A.A^3 \qquad A = \sqrt[3]{\frac{V}{N_A}}$$

The interfacial area between the particles (cubes) in one mole of matter is S, based on the geometry of the cube:

The contact of the cube below the surface of the substance with the surrounding particles has area 6A2. S is the surface area of all the cubes (particles) in volume V.

$$S = N_A.6.A^2 \qquad\qquad \delta^2.V = \gamma.S$$

The surface energy density on surfaces between cubic particles can be considered equal to the surface tension of the phase surface. Based on this consideration, the dependence of the surface phase on the cohesive energy can be derived. After substituting for NA ($6{,}023.10^{23}$) and including the dimensional constants, we obtain:

$$\gamma = \delta^2.\sqrt[3]{\frac{V}{N_A}}.\frac{1}{6} \qquad \gamma = 0{,}019.\partial^2.\sqrt[3]{V}$$

$V \dots cm^3.mol^{-1}$

$\gamma \dots mJ.m^{-2}$

$\delta^2 \dots J.cm^{-3}$

Polymers - Physical classification
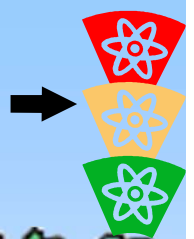
Plastics are polymers that are usually hard and often brittle under normal conditions. At elevated temperatures they become plastic and mouldable:

If the change from plastic to rigid is reversible, these polymers are called thermoplastics - they soften with heating, become plastic and can be repeatedly shaped (e.g. polyethylene, polyvinyl chloride). Linear polymers are soft at higher temperatures and soluble in most organic solvents.

If the change is irreversible (non-repeatable, permanent), because it results in a chemical reaction between molecules, usually at elevated temperatures, we speak of reactive plastics (thermosets, resins). Branched and spatially cross-linked polymers change chemically on heating and only swell in solvents.

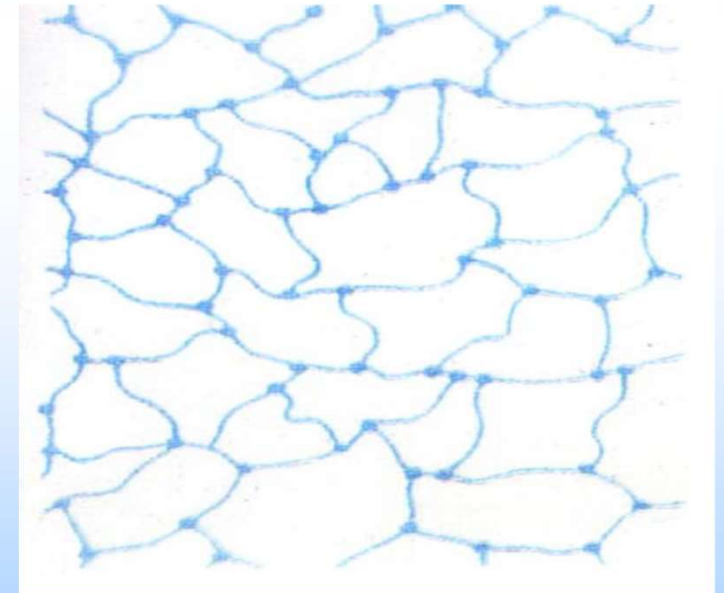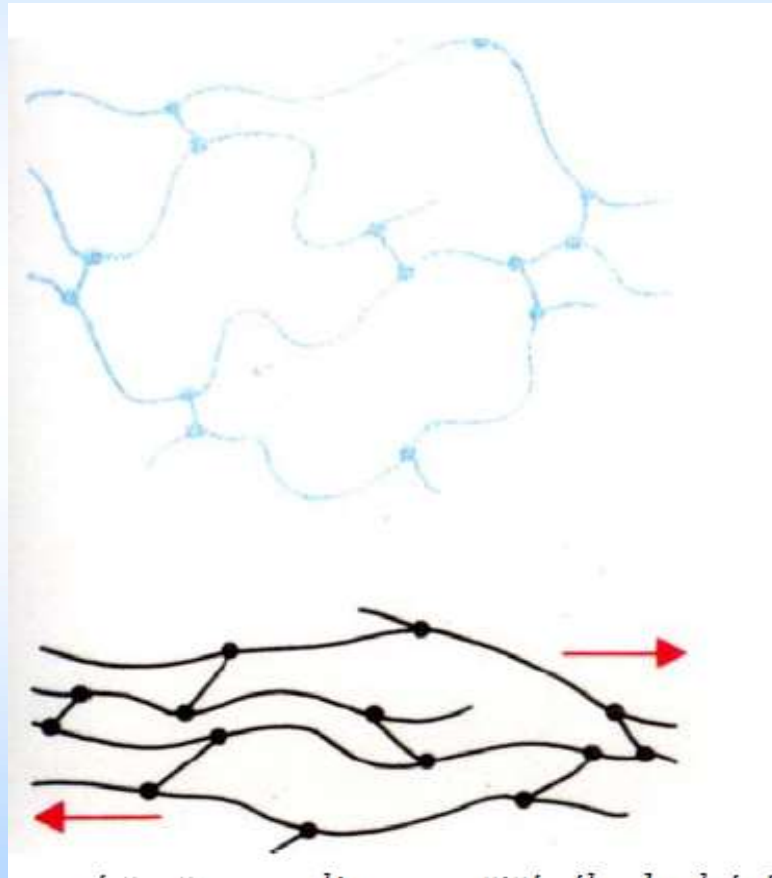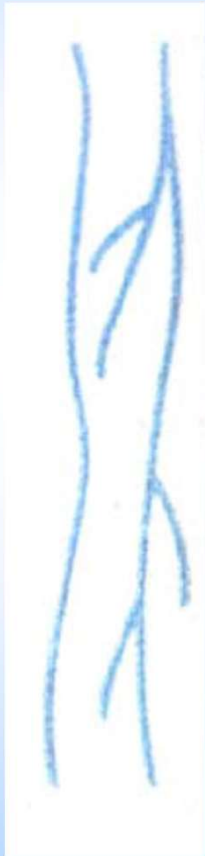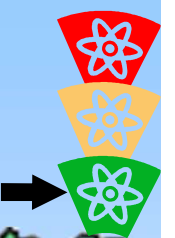# Polymers - Physical classification
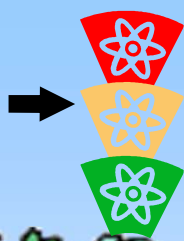
Elastomer

is a highly elastic polymer that can be deformed considerably under normal conditions with little force without breaking. This deformation is mostly reversible. The dominant group of eleastomers are rubbers, from which rubbers ('rubber') are made.

Elastomers - elastic, deform under the action of an external force and then resume their original shape, softening on heating; they have long and very weakly linked chains (e.g. synthetic rubber).

HELLO, NOVELTY SHOP.
ABOUT THAT RUBBER
KNIFE YOU SOLD ME.

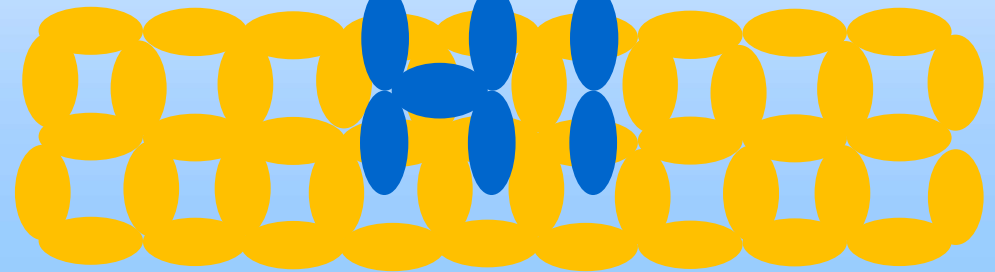CARTOONSTOCK

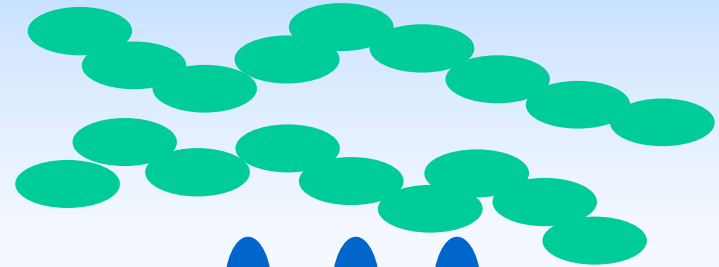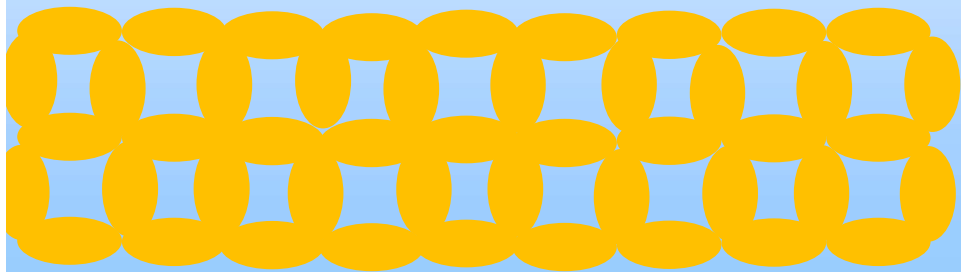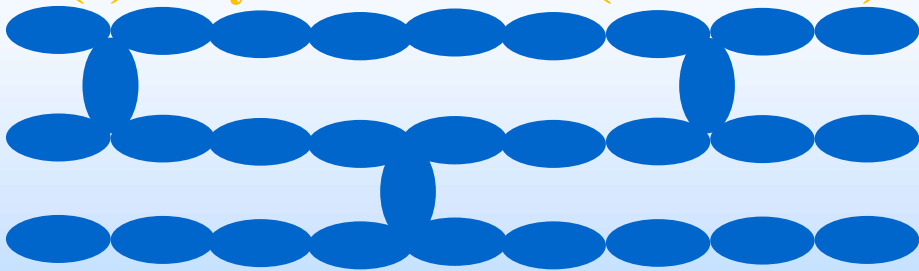Search ID: mfln3332

Polymers – Physical classification

thermoplastic   elastomer

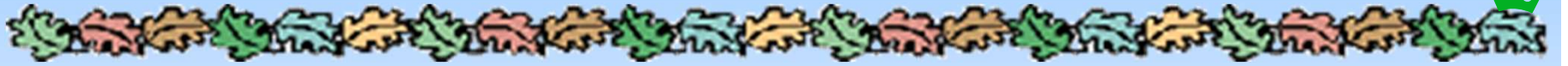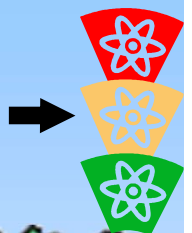Thermosets/reacto
plastics

deformation polymers - flexibility
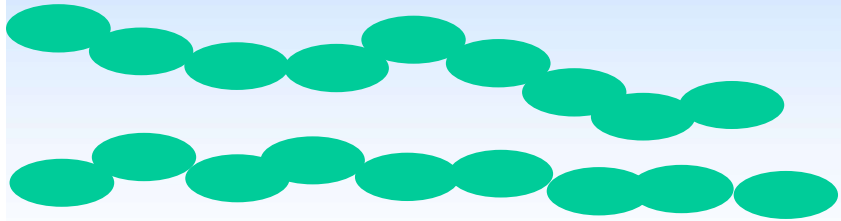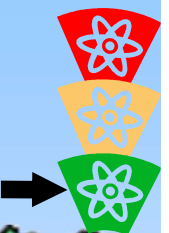
- Three forms of monomer crosslinking:
- a) Non-crosslinked - linear (thermoplastic)
- (b) point cross-linked (elastomer)
- (c) fully cross-linked (thermoset)

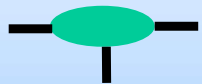Acting force

How to build a macromolecule

Monomers:

mono-functional   *__Cannot__*
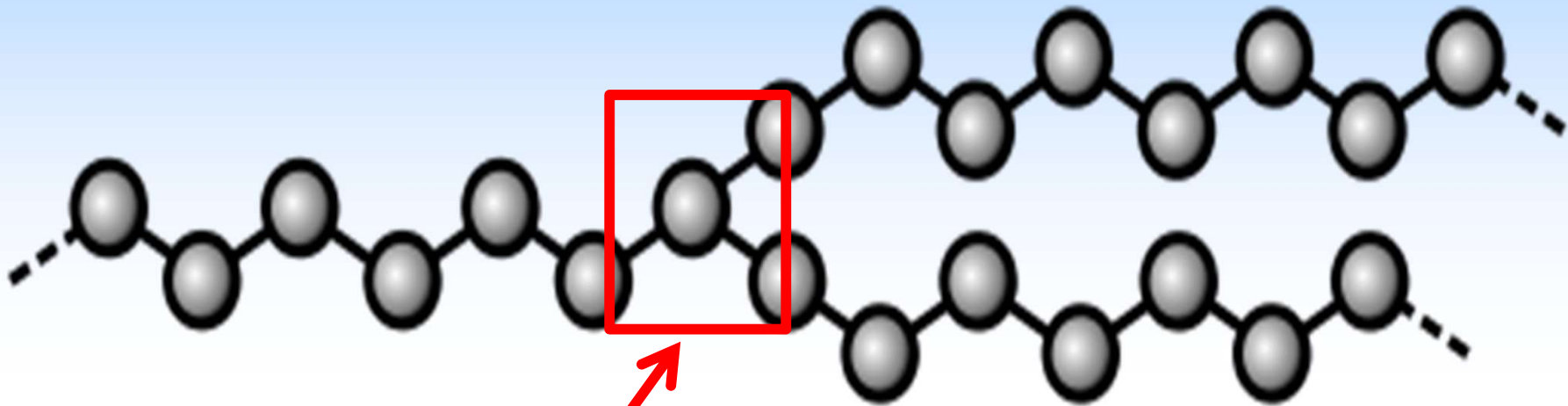
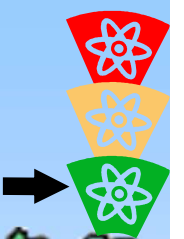Bi-functional   Linear macromolecules

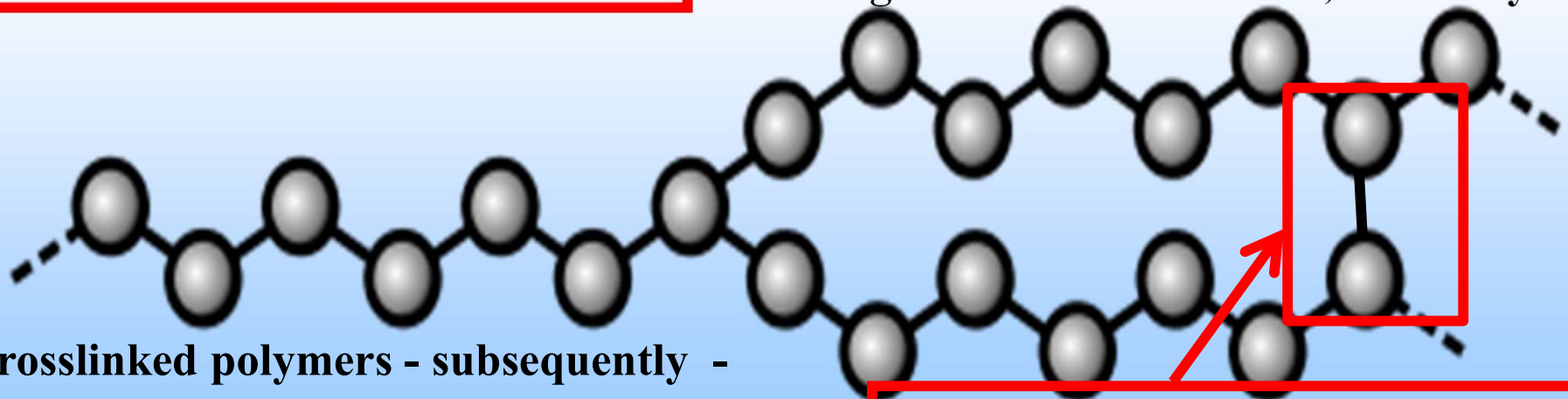three-functional   Branched macromolecules

Branched polymers X crosslinked polymers

Branched polymers

Branched polymers - during production, impact on flow properties, spatial arrangement of the molecule, solubility ....
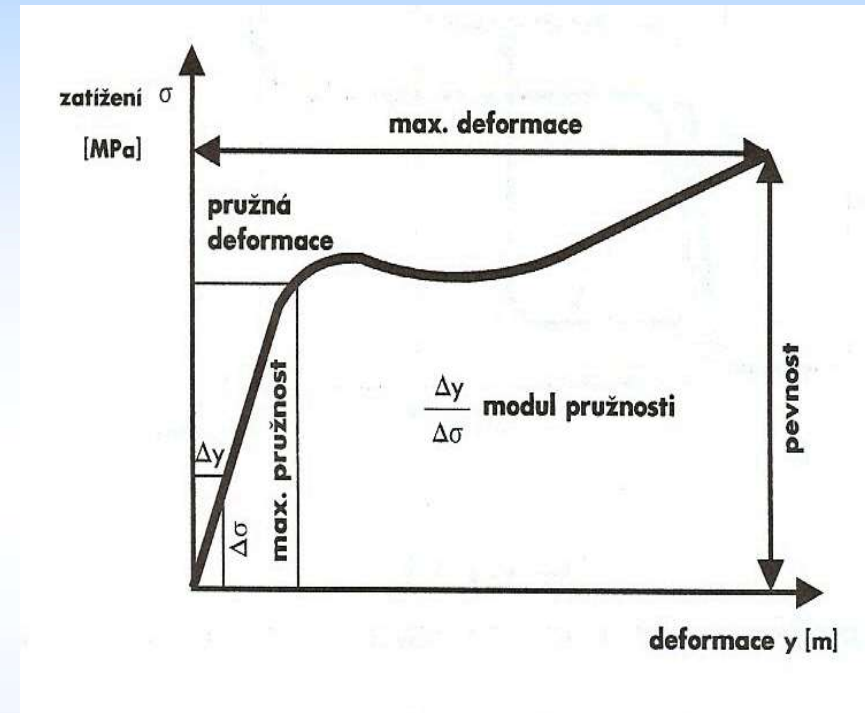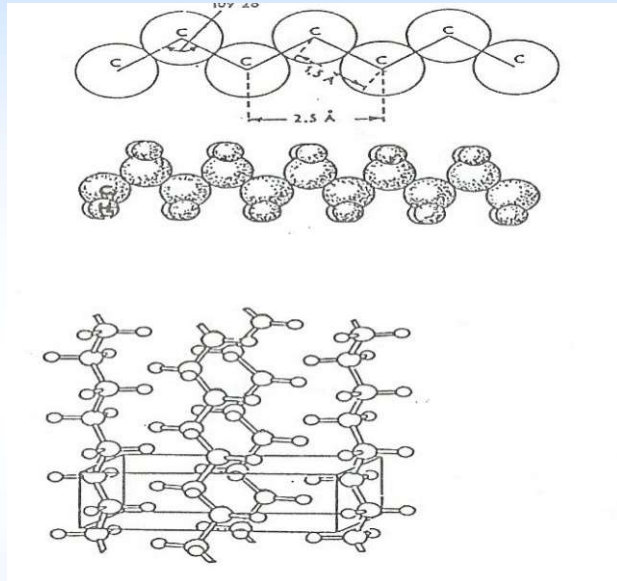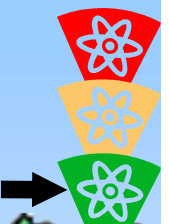
crosslinked polymers - subsequently - impact on flow properties, spatial arrangement of the molecule, solubility ....
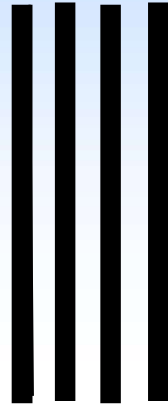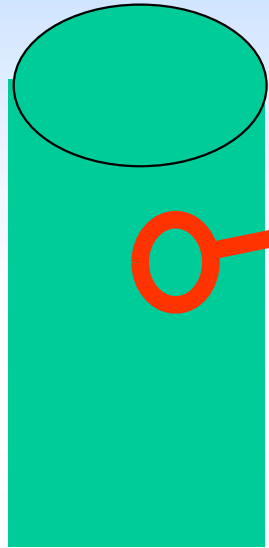
crosslinked polymers

The properties of polymers are determined by: chem. composition, shape of molecular units, length of macromolecule and mobility of macromolecular chains

Typical deformation diagram of macromolecular substances

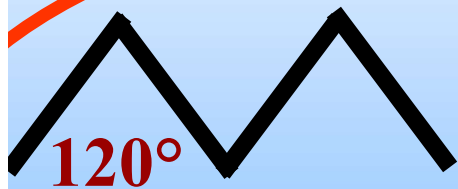# Indication of the calculation of the limiting theoretical strength of fibres

-CH2-CH2-CH2-

Strength of bonds... 347 kJ/mol

... 5 . 10^{-19} J /

Uspořádané makromolekuly

vlákno

1m =

= 5 . 10^{-19} J

= 1,7 . 10^{-13}g ... 1,7 . 10^{-10} tex

120°

Molar mass „-CH2-" = 14g/mol

Length of bond C-C 0,154 nm

n > 100 000   Dyneema

mez pevnosti: 3,5 GPa
hustota: 970 kg m^{-3}

...the strength of polymer fibres is also important to us textiles...