

SEMMELWEIS UNIVERSITY

Dept. of Biophysics and Radiation Biology,  
Laboratory of Nanochemistry



## Water, polymers, macromolecules and biopolymers

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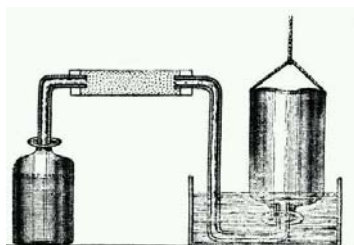
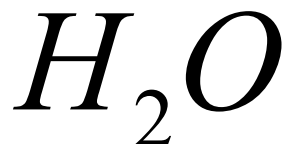


A peculiar liquid: **water**



According to Thales water is the primal element or substance from which all things arose and of which they consist. Water is the the *first principle* of all things.

The chemical composition of water was determined by Henry Cavendish in 1783.



It is essential for all life on Earth

**Naturally occurring** water is almost completely composed of the neutron-less hydrogen isotope proton.

Only 155 ppm include deuterium (D), a hydrogen isotope with one neutron, and fewer than 20 parts per quintillion include tritium (T), which has two neutrons.

**Heavy water** (D<sub>2</sub>O) is water with deuterium content, up to 100%. It is used in the nuclear reactor industry to moderate (slow down) neutrons.

In its pure form, it has a density about 11% greater than water, but otherwise, is physically and chemically similar. (not radioactive)

Water is the only common substance found in all three phases in nature.

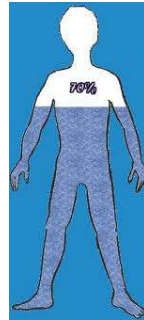
**Water exists in liquid, solid, and gaseous states.**

71% of earth surface is covered by water (mainly salt water).  
70% of fresh water is stored in form of snow and ice.

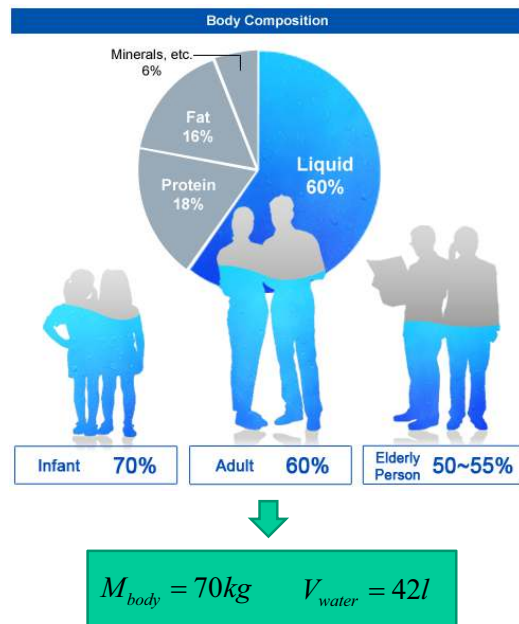
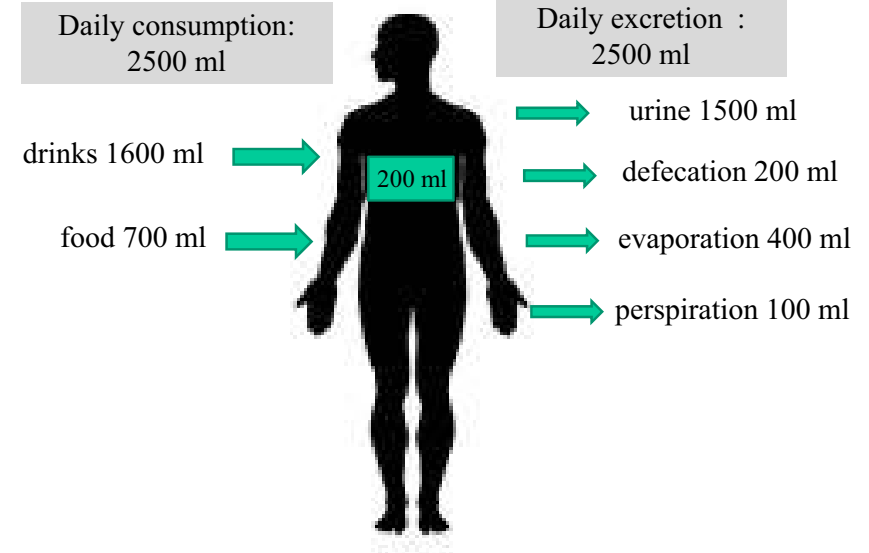
**Water** is the basic component of all living organism.

Water content of Jelly fish 98%,  
three month old embryo 94%,  
a new born child 72%,  
adult 50-60%.

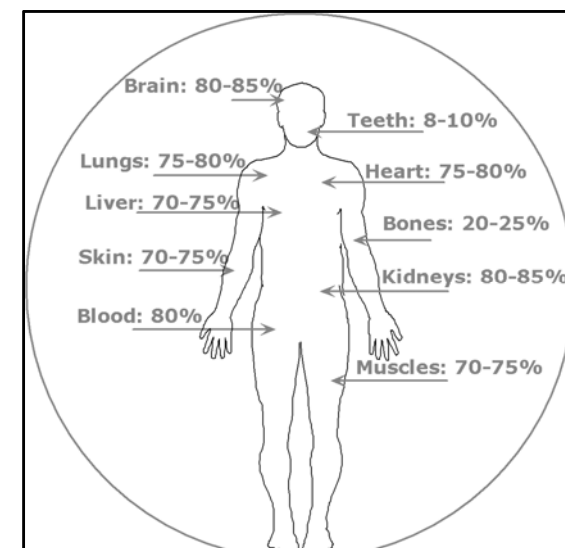
During aging the amount of water in body decreases.

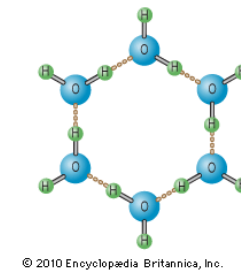
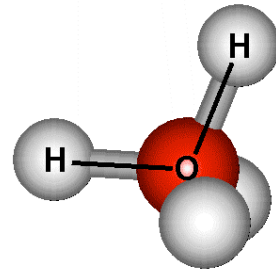
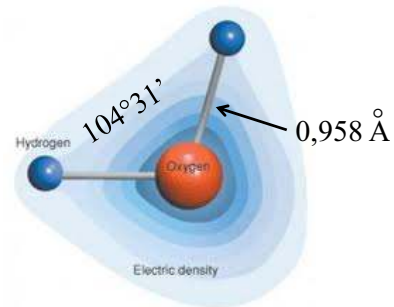
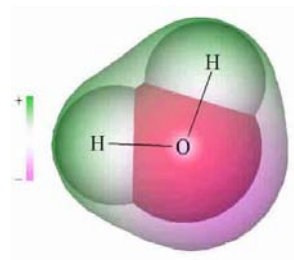
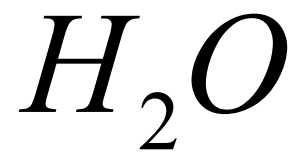


Age dependent water content of a body: 45m% - 75m% (65m%)

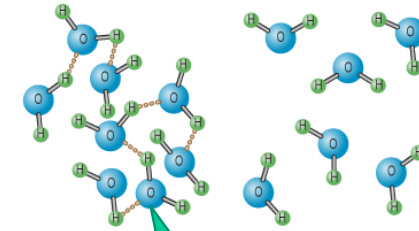


**Water content of different parts of body**



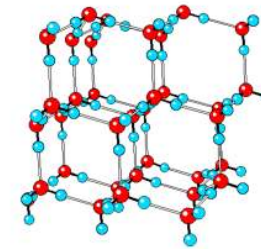


ice

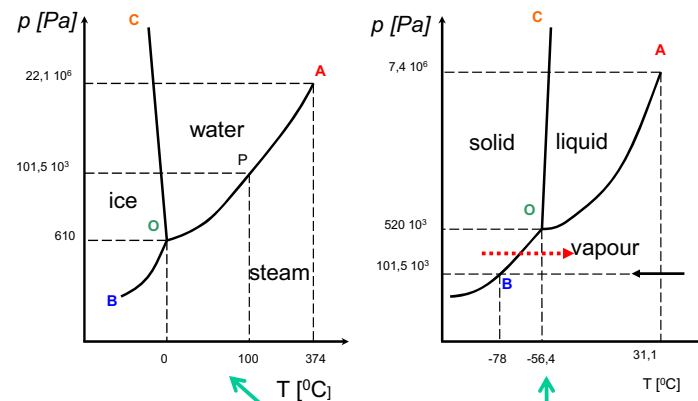


water

steam

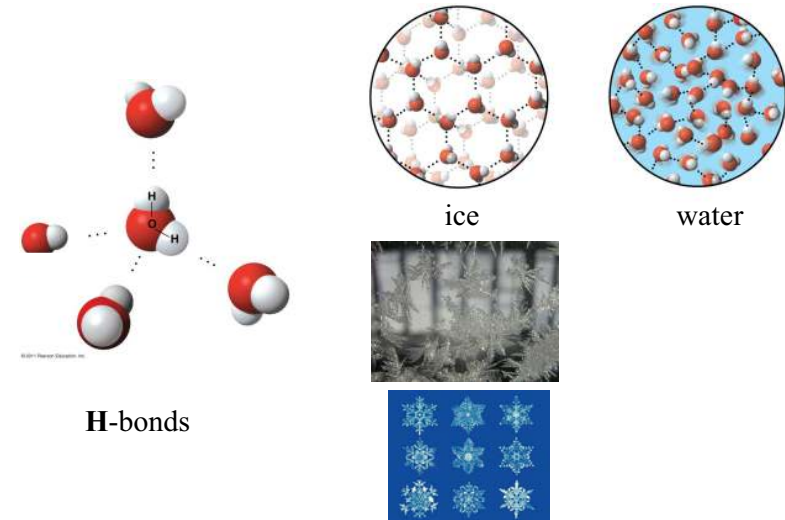


The molar volume of water at 4 C° is minimal, accordingly the density is maximal.

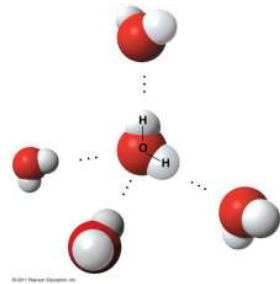
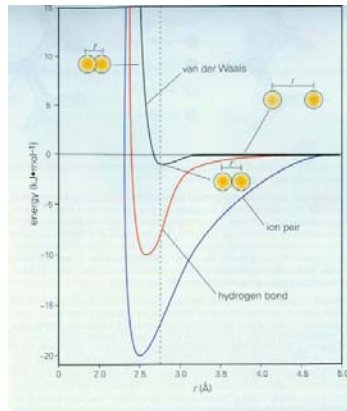


Phase diagram of water and carbon-dioxide

The molar volume of most substances in solid state is smaller than in liquid state. Exception: **water**



## Hydrogen bond



$$E_H = 4 - 40 \text{ kJ / mol}$$

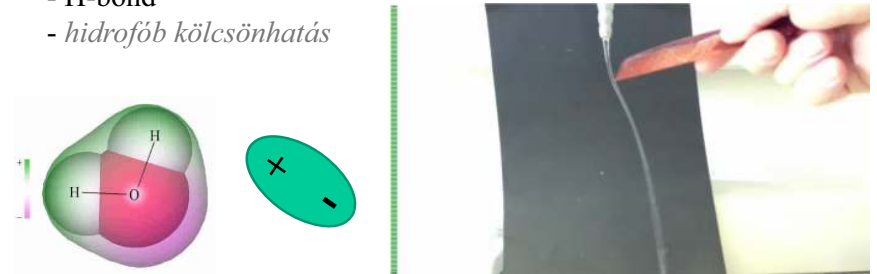
Hydrogen bonds are very common in biological macromolecules

## Basic intermolecular interactions

- ion – permanent dipole
- ion – induced dipole
- permanent dipole – permanent dipole
- permanent dipole – induced dipole
- induced dipole – induced dipole
- H-bond
- *hidrofób kölcsönhatás*

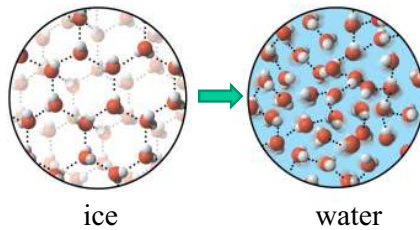


van der Waals



During melting the molar volume of water decreases by 8%.

An increase of pressure promotes melting



## If the water behaved like any other liquids

- we would not have mountain springs,
- the ice would sediment in water,
- the rivers would be completely frozen,
- we could not skate.
- .....

### Heat capacity of water

$$Q = C(T)m\Delta T$$

Due to its extensive hydrogen bonds, water has a very high heat capacity.



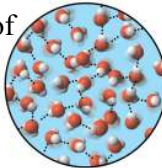
Large amount of heat is needed to raise the temperature of aqueous solution.



Important to regulate the heat generated by metabolic processes.



The ability of water to absorb a lot of heat with little temperature increase is greatly influences the earth's climate.



water

$$E_H = 4 - 40 \text{ kJ / mol}$$

The specific heat capacity of water at room temperature: 4.18 J/gK

The specific heat capacity of steam at 100 C temperature: 2.08 J/gK

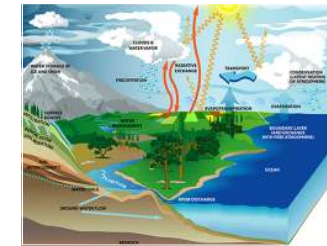
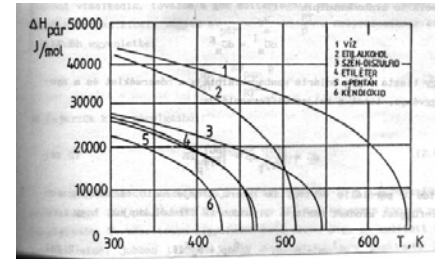
### Heat of evaporation of water

$$Q_{\text{vap}} = 2.3 \cdot 10^3 \text{ kJ / kg}$$

$$Q_{\text{molar}} = 41 \text{ kJ / mol}$$

Sweating is an effective way to regulate body temperature

Water can store more energy in unit volume than any other liquid.



### High surface tension

$$\gamma = 72,7 \text{ mN / m at } 25^\circ \text{C}$$

Strong intermolecular interactions due to H-bonds gives water a high surface tension.

Strong wetting due to hydrophilic interaction  
(capillary rise)



It does not wet hydrophobic surfaces  
(e.g. teflon)

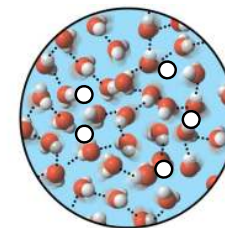






### Good solvent

Due to its loose structure water dissolves several gases ( $O_2, CO_2, \dots$ )

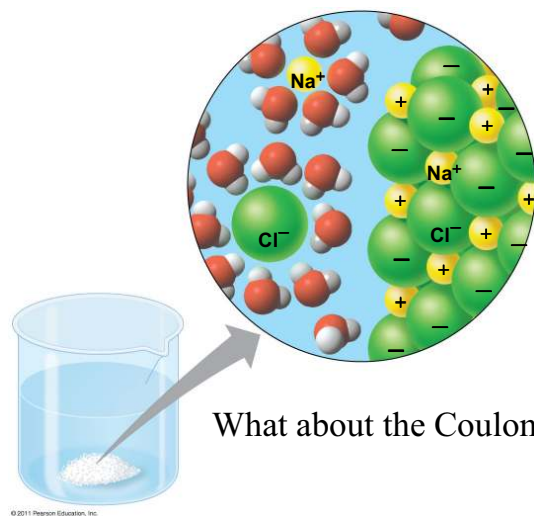


Good miscibility with several components ( $CH_3CH_2OH$ )

*Patented by Mengyelejev*



### Good solvent for salts



What about the Coulombic law?

### Good solvent for ions

Strong attraction between ions of different charge?

Coulombic law

$$U_{elstat} = \frac{1}{4\pi\epsilon_o} \frac{q_i \cdot q_j}{r_{ij}}$$

$\epsilon_o$  is the electric permittivity of vacuum:  $\epsilon_o = 8.85 \cdot 10^{-12} C^2 N^{-1} m^{-2}$

Let us express the charge in terms of **elementary charges**, instead of Coulomb:

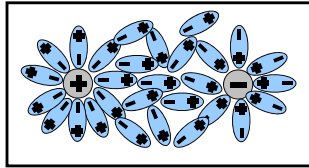
$$U_m = \frac{q_i \cdot q_j}{r_{ij}} \cdot 1391 \text{ kJ/mol}$$

Example:

$q_i = 1(+)$  and  $q_j = 1(-)$  then  $U_m = -347.81 \text{ kJ/mol}$  *in vacuum!*

Thermal energy at room temperature  $k_B T = 2.5 \text{ kJ/mol}$

## What is the role of water?



← hydration

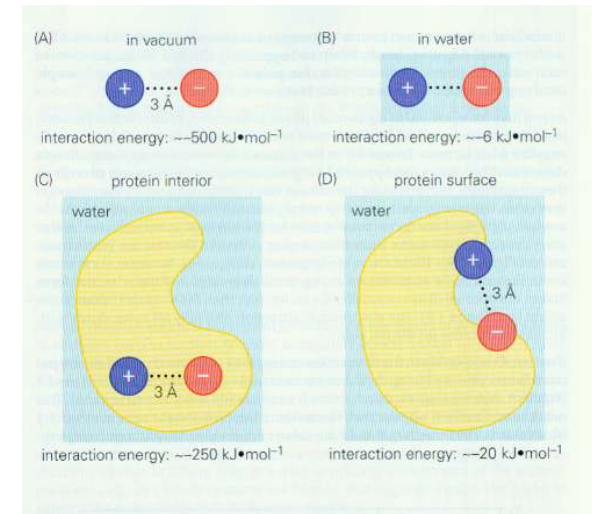
$$U_{elstat} = \frac{1}{4\pi\epsilon_o\epsilon_{rel}} \frac{q_i \cdot q_j}{r_{ij}}$$

The **dielectric constant** is a scale factor that reduces the magnitude of electrostatic energy. It weakens the interactions between charges.

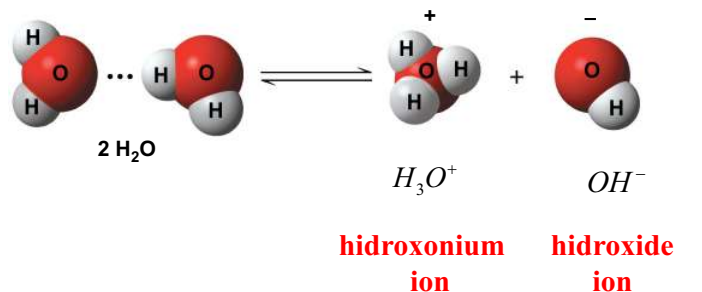
The dielectric constant of bulk water is **78.54** at 25 C°.

The dipole momentum is **1.82 D**.

Water has one of the **highest dielectric constant** of all liquids.  
Excellent solvent for ionic compounds



## Autoprotolysis

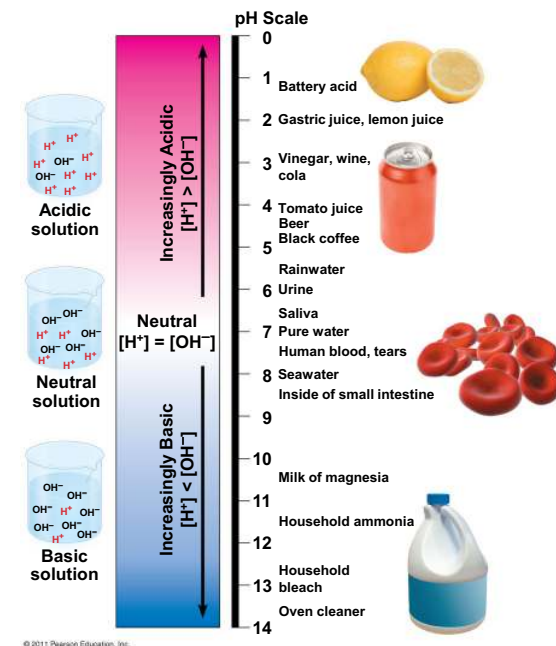


$$10^{-7} \text{ mol} / \text{dm}^3 \quad 10^{-7} \text{ mol} / \text{dm}^3$$

$$K_v = 10^{-14}$$

→ pH

$$pH = -\log[H^+]$$



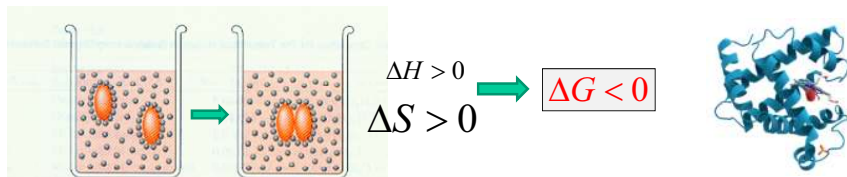
## Hydrophobic interactions

Hydrophobic interaction describes the influences that causes nonpolar substances to cluster together to minimize their contact with water.

$$\Delta G = \Delta H - T\Delta S$$



Basis for many important chemical and biological phenomena



As a result of hydrophobic interactions the nonpolar molecules come together, releasing some of the ordered water molecules in the clathrate structure, thus increasing entropy.



W. Kauzman

## Macromolecules

Aggregates or giant molecules?



**Hermann Staudinger** (1881- 1962)

The Nobel Prize in Chemistry 1953

## Bond energy and stability

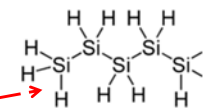
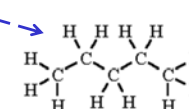
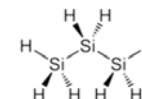
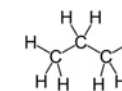
Single Bonds												
H	C	N	O	F	Si	P	S	Cl	Br	I		
436	415	390	464	569	395	320	340	432	370	295	H	
	345	290	350	439	360	265	260	330	275	240	C	
		160	200	270	—	210	—	200	245	—	N	
			140	185	370	350	—	205	—	200	O	
				160	540	489	285	255	235	—	F	
					230	215	225	359	290	215	Si	
						215	230	330	270	215	P	
							215	250	215	—	S	
								243	220	210	Cl	
									190	180	Br	
										150	I	

Multiple Bonds									
C=C,	611	C=N,	615	C=O,	741	N=N,	418	O=O,	498
C≡C,	837	C≡N,	891	C≡O,	1080	N≡N,	946		

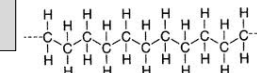
## Organic and inorganic polymers

Bond energy; kJ/mol

bond	Energy kJ/mol
C-C	345
C-O	350
C-N	290
C-P	265
Si-Si	230



Higher bond energy  
↓  
More stable compound



polysilane  
explosive!



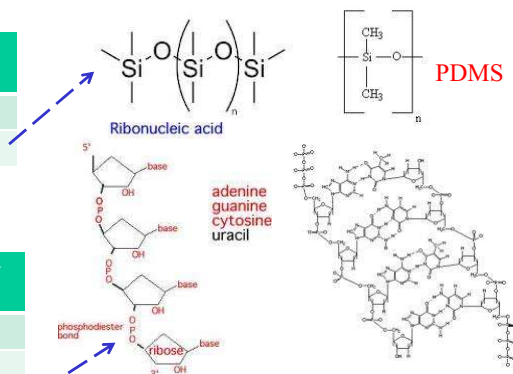
Bond	Energy kJ/mol
C-C	345
Si-H	395
Si-Si	226

$SiH_4$  stable

$\rightarrow Si_5H_{12}$  **explosive**

Bond	Energy kJ/mol
C-C	345
Si-O	370

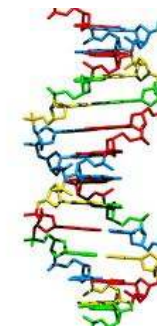
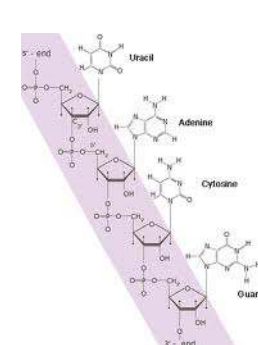
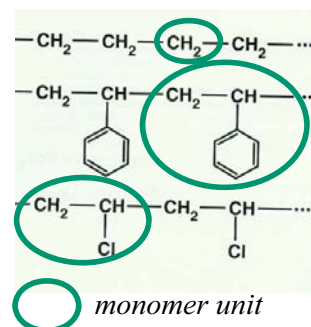
Bond	Energy kJ/mol
C-O	350
C-N	290
P-O	350



Polymers and macromolecules are **giant molecules!**

synthetic

biopolymers



Number of monomer units:  $N$

RNA

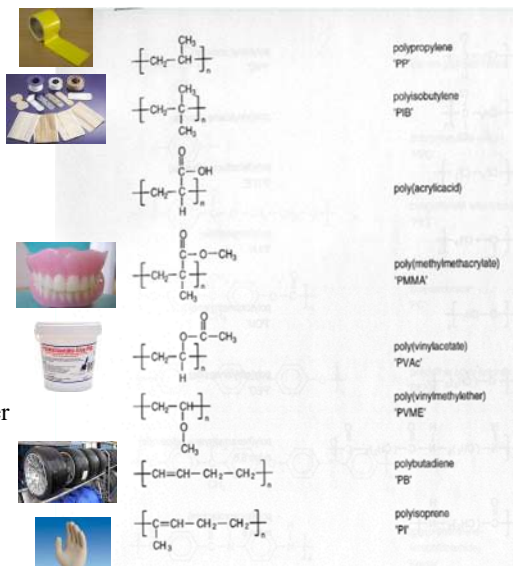
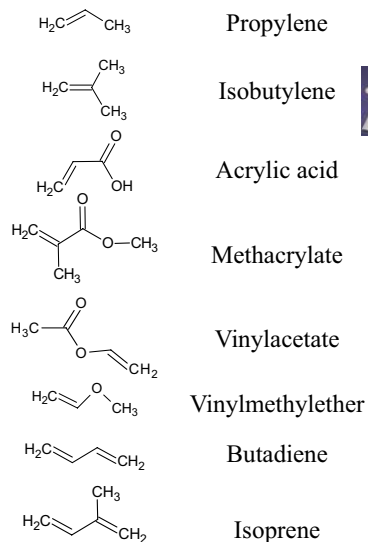
DNA

The longest macromolecule **DNA** :  
several meter!

$$10^9 < N < 10^{10}$$

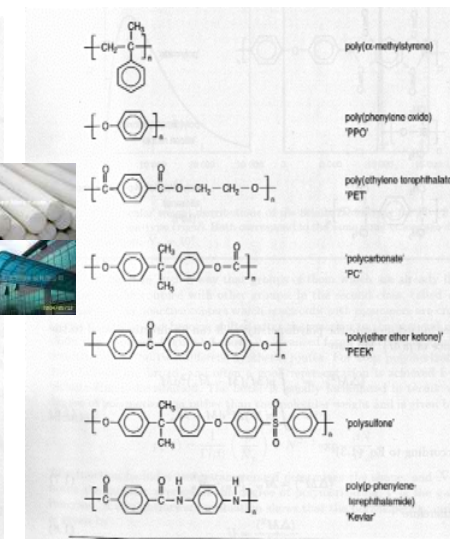
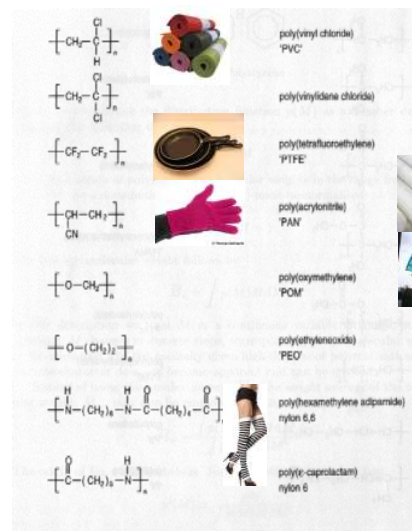
Monomers

Monomer units

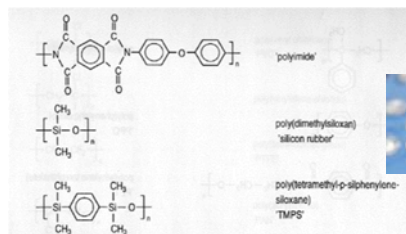


Monomers

Monomer units



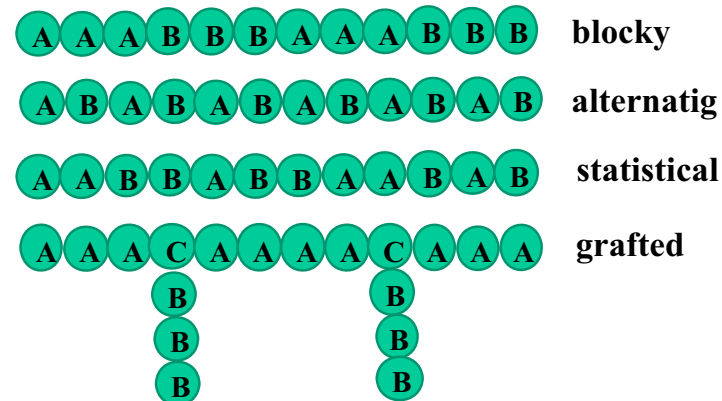
## Monomer units



## Homopolymer

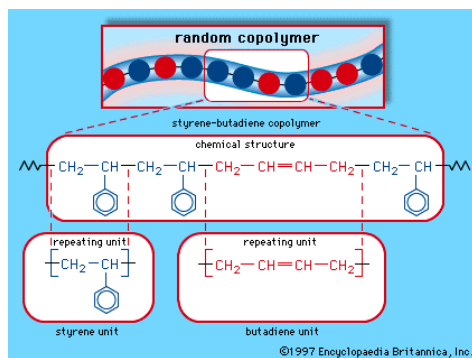


## Copolymer nomenclature



## Copolymer examples

### Synthetic polymers



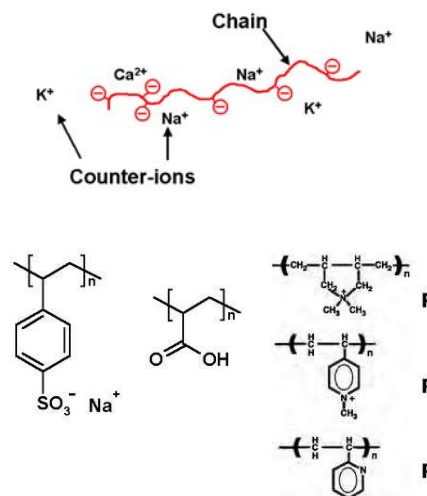
### Biopolymers

**DNA:**  
four different monomer units

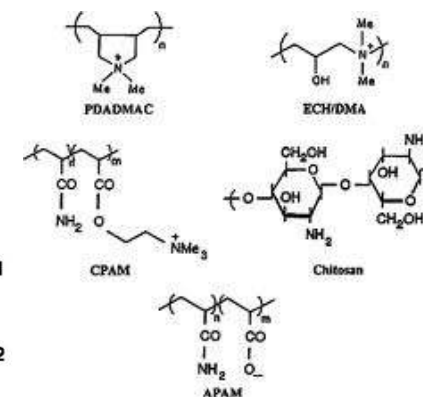
**proteins:**  
20 different amino acid units

## Polyelectrolytes

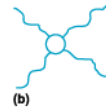
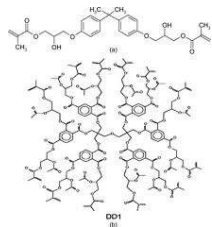
### Anionic



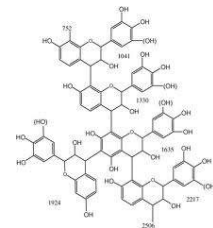
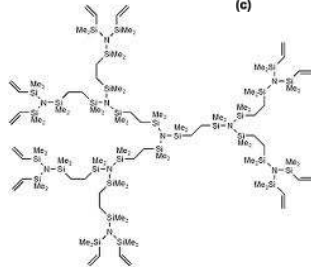
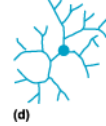
### Cationic



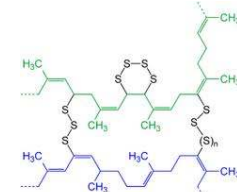
## Macromolecules with branching



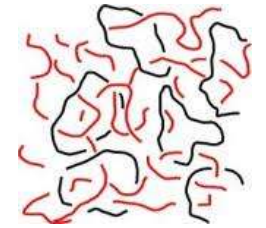
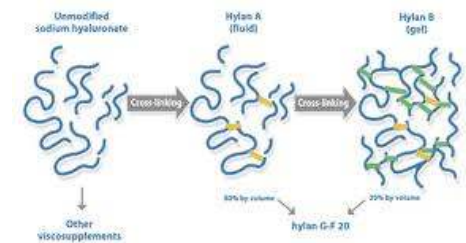
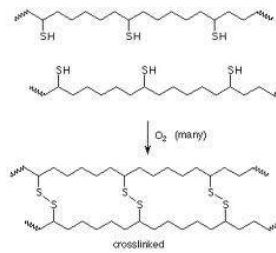
brush or comb like architecture



## Cross-linked polymers



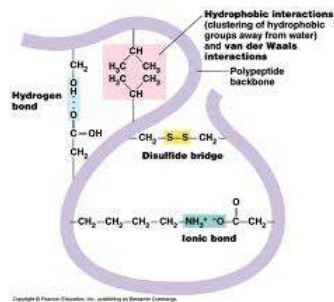
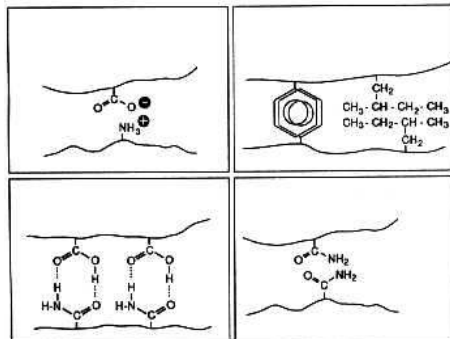
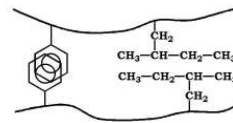
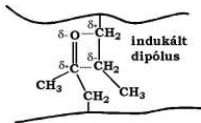
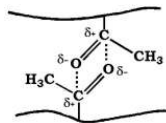
Vulcanised rubber



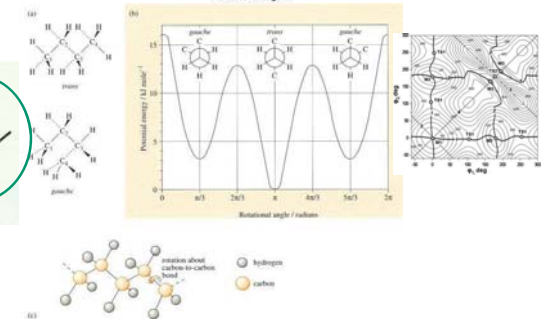
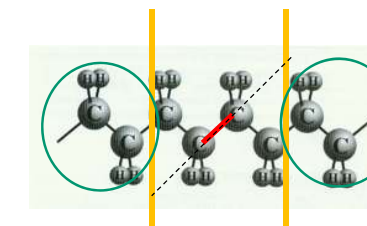
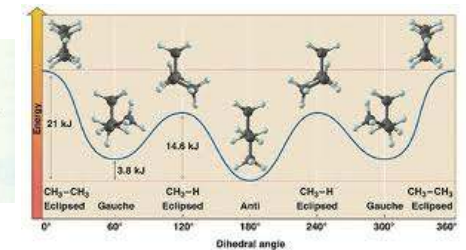
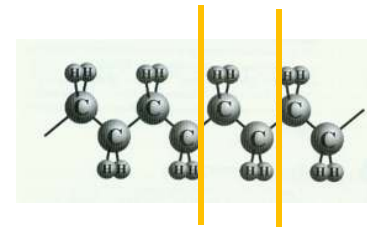
IPN

Interpenetrated network

## Intermolecular interactions



## Flexibility of macromolecules





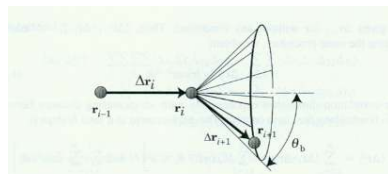
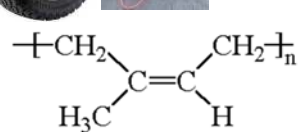
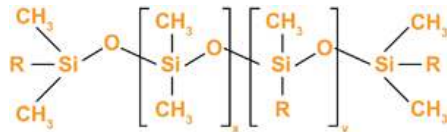


Figure 1.23. Bond vectors in the bead-stick model with a fixed bond angle.

### Flexible polymers



india-rubber,  
polyisoprene



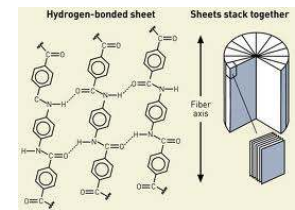
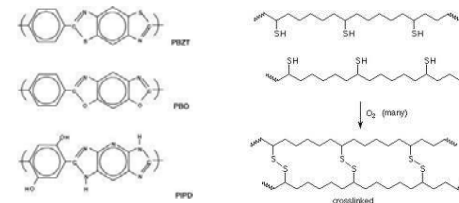
R =  $-\text{OH}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{CH}_3$ , or another alkyl or aryl group

silicon rubber,  
poly(dimethyl-siloxane)

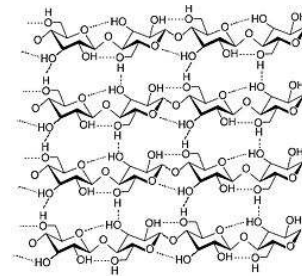
**Enlarged distance between rotating units increases the flexibility!**



### Rigid polymers



Formation of intra- and intermolecular  
H-bonds enhances rigidity.



### Highly flexible polymers

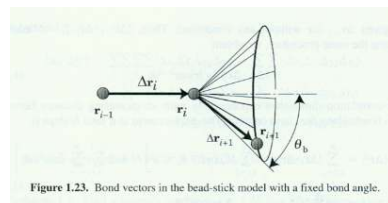
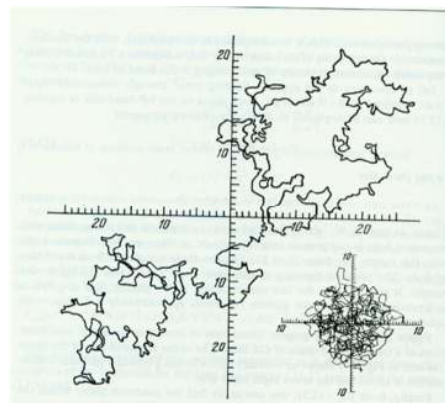


Figure 1.23. Bond vectors in the bead-stick model with a fixed bond angle.

Free rotation around C-C bond



**Random coil.**

### Models of flexible polymers

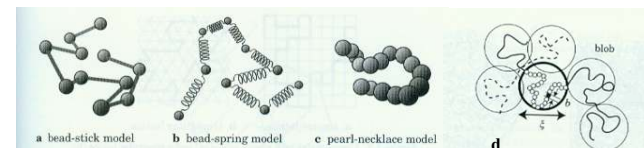
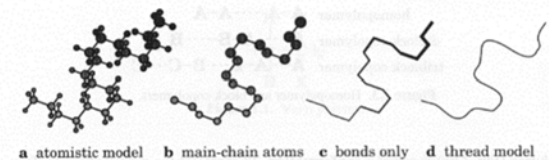


Figure 1.6. Various models for a linear chain molecule in a continuous space.

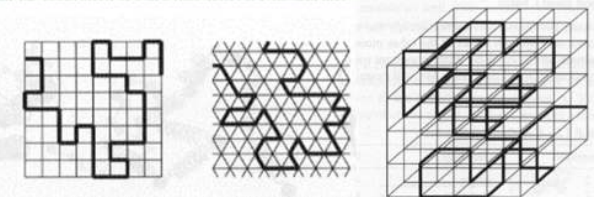
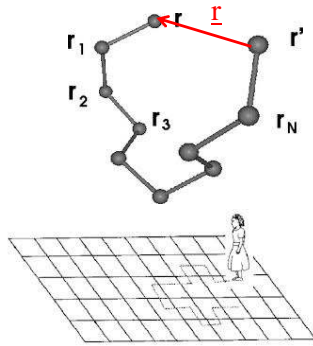


Figure 1.8. Linear chain on a cubic lattice.



### Ideal flexible macromolecule

Random walk  $\rightarrow$  Conformation



$$\underline{r} = \sum_{i=1}^{N_s} \underline{r}_i \quad \langle \underline{r} \rangle = 0$$

$$\langle \underline{r}^2 \rangle \neq 0$$

$$r^2 = \sum_{i=1}^{N_s} \sum_{j=1}^{N_s} \underline{r}_i \cdot \underline{r}_j = \sum_{i=1}^{N_s} r_i^2 + 2 \sum_{i < j} \underline{r}_i \cdot \underline{r}_j = N a_s^2 + 2 \sum_{i < j} a_s^2 \cos \alpha_{ij}$$

$$R_o \equiv \langle r^2 \rangle^{1/2}$$

$$R_0 = a_s N_s^{1/2}$$

### Short range interactions (constitution)

Valence angle  $\rightarrow R_\vartheta = 1 \left( \frac{1 + \cos \vartheta}{1 - \cos \vartheta} \right)^{1/2} \cdot N^{1/2}$

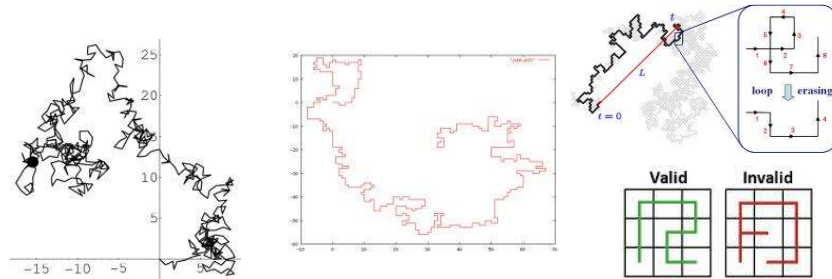
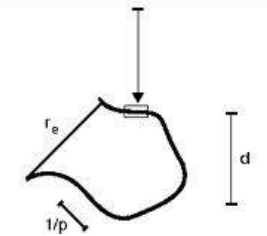
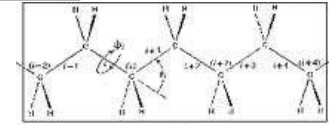
Valence angle + Rotation energy  $\rightarrow R_{\vartheta, \varphi} = 1 \left( \frac{1 + \cos \vartheta}{1 - \cos \vartheta} \frac{1 + \langle \cos \varphi \rangle}{1 - \langle \cos \varphi \rangle} \right)^{1/2} N^{1/2}$

$$\langle \cos \varphi \rangle = \int_{-\pi}^{\pi} \cos \varphi \cdot e^{-\frac{U(\varphi)}{RT}} d\varphi$$

Ideal macromolecule

$$R_\Theta = \ell \cdot C_\infty \cdot N^{1/2} = C_\infty R_0 \rightarrow R_\Theta = \ell \cdot C_\infty \cdot N^{1/2} = a_s N_s^{1/2}$$

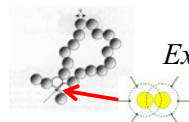
Characteristic ratio



random walk (RW)  $\rightarrow$  self avoiding walk (SAW)

$$R_0 = a_s N_s^{1/2}$$

$$R_0 = a_s N_s^\nu \quad \nu = 0.588 \approx 3/5$$



Excluded volume effect!

### Macromolecules of life

Proteins

Nucleic acids

Glycans

Poly(amino acids)

RNA and DNA

Glycans are sugar or sugar polymers

## Structure of macromolecules

constitution    configuration    conformation

### Primary structure:

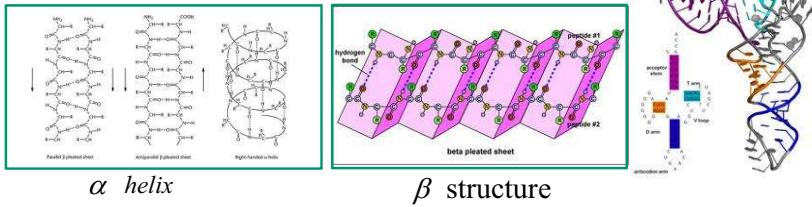
**Human's genom project:** complete primary structure of a human's DNA molecule

if  $N \sim 10^2$  and 20 different monomer units, then  $20^{100}$  different molecules!

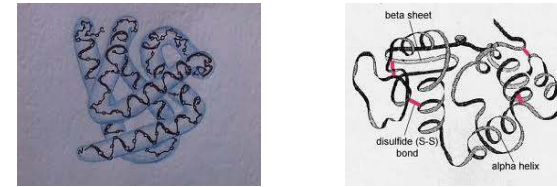
### Secondary structure:

Long range order of monomer units

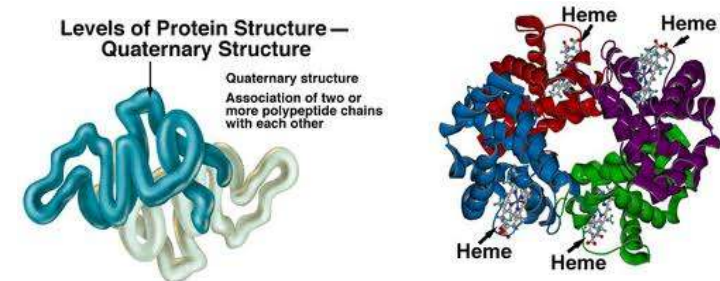
*Pl. ceratine,                      fibroin*



### Tertiary structure (globular proteins):



### Quaternary structure ( association of several chains):



## Polymer biomaterials

Structures display a hierarchial organisation