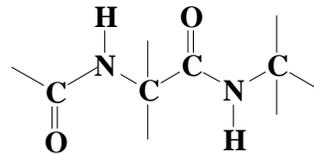


BIOPOLYMERS

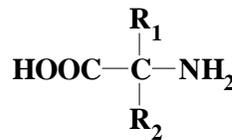
- aminoacids (chemical constituent units of proteins) have intrinsic handedness (*chirality*, lack of plane of symmetry) - hence helical handedness is predetermined.

- polypeptides:

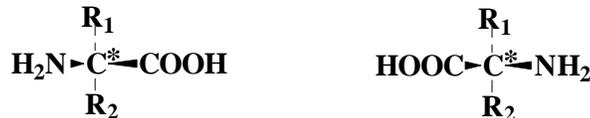
Polypeptides are short proteins, i.e. chains of aminoacids. This portion of a polypeptide chain shows 2 aminoacid monomer units.



There are 30+ aminoacids in nature, all with the same basic formula



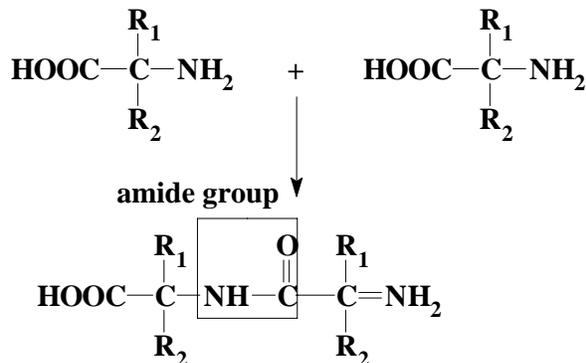
If R_1 and R_2 are different, all four substituents are different and the central C-atom is the *asymmetric centre* (labeled by asterisk). The molecule has no mirror plane and is said to be *chiral*.



The two aminoacids above are *stereoisomers* or *enantiomers*, one right-handed and one left-handed. They are related by mirror symmetry. All natural aminoacids are left-handed.

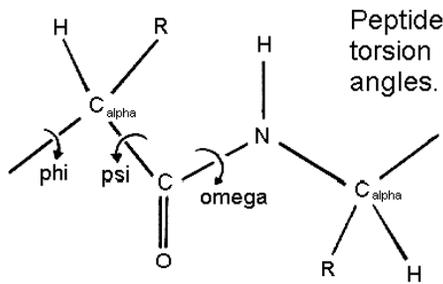
Two aminoacids form a **peptide link**, containing an amide group

(carboxylic acid + amine = amide + H_2O):

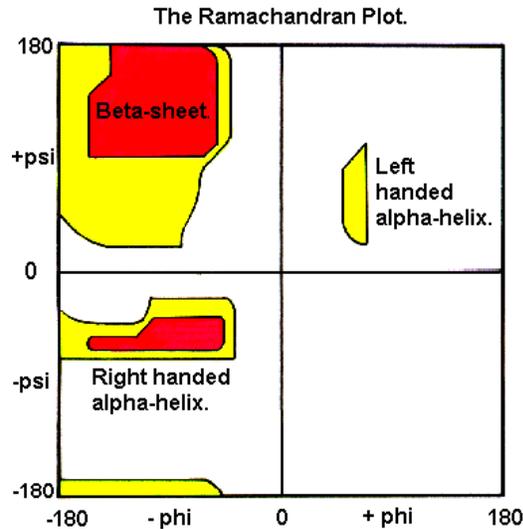


R_1 and R_2 represent different substituents, including H. Different aminoacids are distinguished by different substituents.

Aminoacids make up all the proteins in nature. Proteins are aperiodic macromolecules, but they all have the same polypeptide backbone



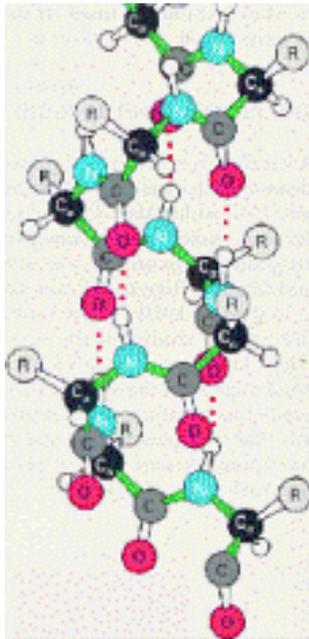
Calculating the energy of a peptide monomer unit as a function of torsion angles ϕ (phi) and ψ (psi), we obtain the conformational energy map below. Red areas are the lowest energy, i.e. the most stable states; white areas have high energy.



Segments of natural protein have 2 basic minimum energy conformations: right-handed “ α -helix” and “ β -sheet” (L. Pauling).

α -helix is a **18/5 helix**.

β -sheet is a **planar zig-zag** conformation (similar to polyethylene but with an amino acid group instead of the CH_2 group as repeat unit).



These conformations are stabilised by **hydrogen bonds** acting between O and N atoms. Intramolecular H-bonds stabilize regular helical conformations of biopolymers even in the absence of crystallisation. Half the period of an α -helix (9 out of 18 amino acid residues) is shown on the left. Dashed lines indicate H-bonds.

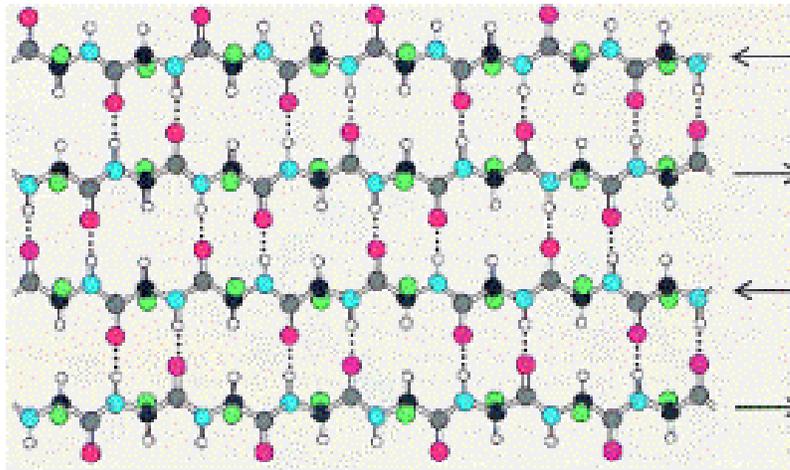
A right-handed α -helix is more stable than the left-handed one (the potential energy minimum is deeper - see the conformational energy diagram above). The energies of right and left-handed helices are different because the constituent amino acids are chiral (left-handed).

In contrast, right- and left-handed helices in synthetic polymers have equal energies because the monomers are normally achiral. Handedness of a helical conformation of a synthetic polymer is therefore determined **at the crystallization stage** by the best fit to the surrounding chains. The net chirality of a crystal unit cell of a synthetic polymer is usually zero, i.e. there is equal number of right- and left-handed chains.

A 4-strand antiparallel β -sheet of a protein is shown below. Here H-bonds are intermolecular.

α -helix, β -sheet and folds between the segments represent the **secondary structure** of proteins.

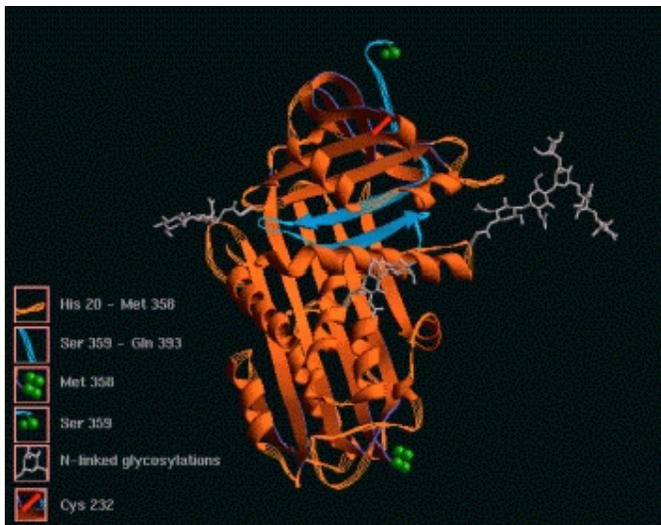
A complete protein is made up of more or less straight sections of α -helix and β -sheet, with folds between them (**tertiary structure**).



4-stranded antiparallel β -sheet

Problem: Label the chain conformation in a β -sheet in terms of helical (m/n) notation.

The reason that nearly all of the huge number of different proteins adopt just two chain conformations is their common polypeptide backbone. The differences are in side-groups which have only a minor effect on the conformation.

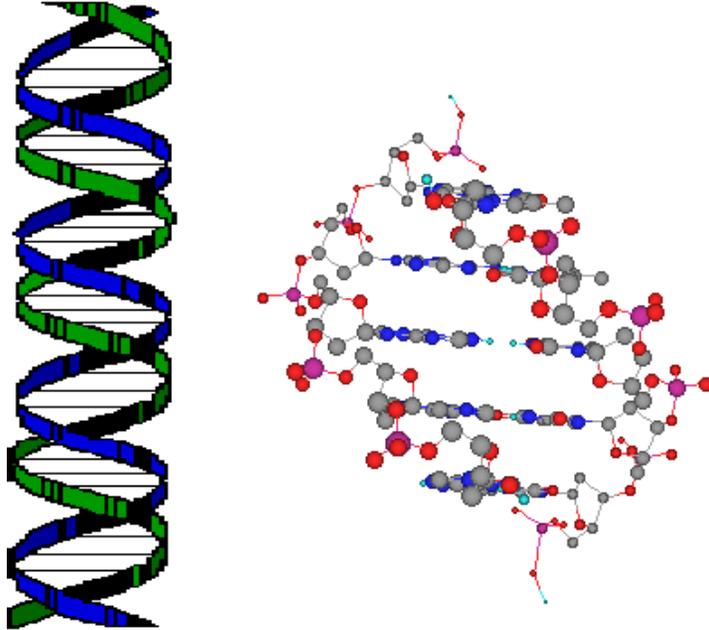


3-d tertiary structure of a typical protein (serine protease inhibitor), showing sections of α -helix (coiled tape) and β -sheet (flat tape). Two overlaying β -sheets at 90° to each other (“ β -sandwich”) are visible in the upper half.

Note that silk fibres are β -sheets of relatively simple proteins.

DNA double helix

Desoxy ribonucleic acid forms a double-stranded helix held by H-bonds. H-bonds form between each pair of “bases” (heterocyclic units, i.e. with rings containing atoms other than carbon, e.g. N). The bases pair up like lock and key (“molecular recognition”), and this is how DNA replicates producing exact copies of itself. (Note that DNA is not a protein). The handedness of DNA is again predetermined by the chirality of the monomer units.



Collagen



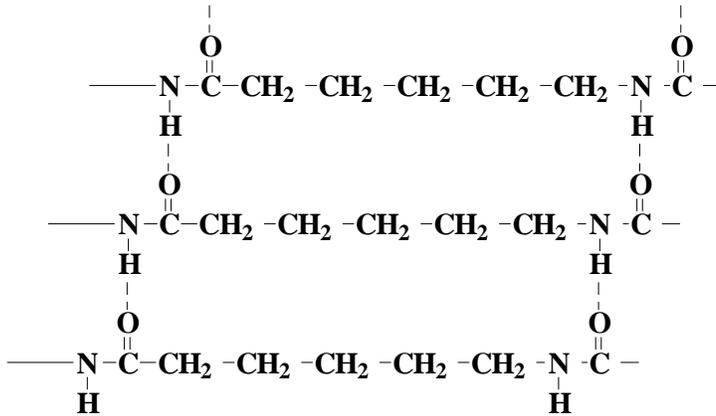
Collagen is a very versatile protein (in fact it is a group of similar proteins). It can be found in many animal and human organs, ranging from cornea of the eye to tendon tissue. The high modulus and impact resistance required by tendons is achieved by the molecules forming triple helices joined by H-bonds.

← collagen triple helix - natural high-strength / high-modulus fibre

HYDROGEN BONDING IN SYNTHETIC POLYMERS

H-bonds stabilise crystals of some synthetic polymers:

- aliphatic polyamides (Nylons)
- aromatic polyamides - Kevlar, Nomex



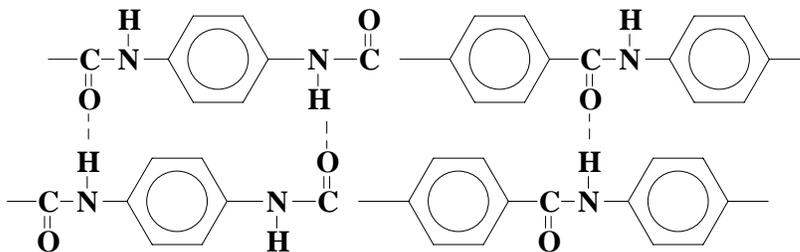
Nylon-6

Nylon forms H-bonded sheets inside the crystals. This increases its strength, modulus, abrasion resistance and melting point. The extra cohesive energy of H-bonds causes the melting point of Nylon-6 to increase from 130°C (polyethylene) to 250-260°C. Since

$$T_m = \frac{\Delta H_f}{\Delta S_f}$$

(ΔH_f and ΔS_f are enthalpy and entropy of fusion), breaking H-bonds on melting significantly increases T_m through increasing ΔH_f . H-bonds (3-15 kcal/mol) are strong compared to van der Waals bonds (the only interchain bonds in PE; $E_{vdW} \leq 1$ kcal/mol), but weak compared to covalent bonds ($E_{C-C} \approx 100$ kcal/mol) (1 kcal = 4.185 kJ).

(Note that Nylon-2 is a polypeptide)

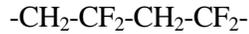


Kevlar

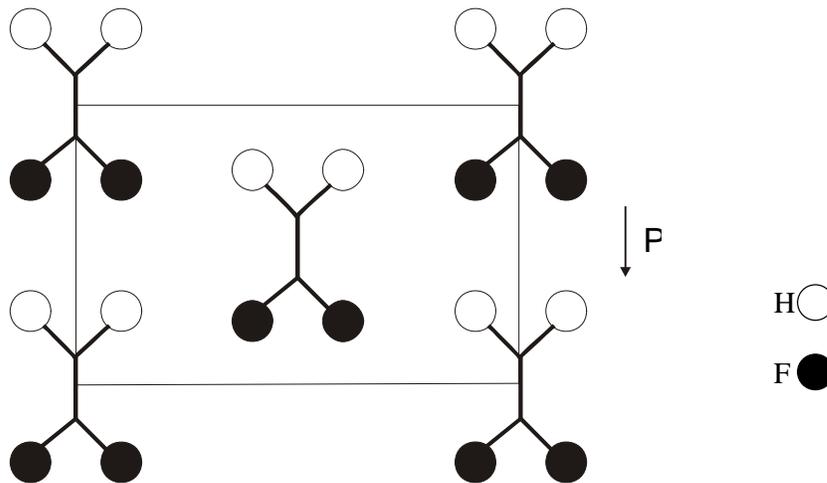
Kevlar has an extremely high melting point, partly due to its H-bonds, and partly due to the rigidity of its chains (more on Kevlar next semester).

PIEZOELECTRIC POLYMERS

Poly(vinylidene fluoride)



- Crystals are non-centrosymmetric. If molecules have a dipole moment, then:
 - ferroelectric (spontaneously polarize, have net electric dipole)
 - piezoelectric (change polarization under pressure)
 - pyroelectric (generates electric potential when heated)



A unit cell of PVDF (β -form) viewed along chain axis

C-F bond is highly polarised, with F negatively charged. Each unit cell is an electric dipole, because it lacks centre of symmetry. If it had a centre of symmetry, each unit dipole pointing in one direction would be cancelled by another unit dipole pointing in opposite direction. The value of the unit cell dipole is $D = lq$, where q is the net electric charge and l the separation between the centres of + and - charges. Pressure changes l , hence changes D . \mathbf{P} , the net polarization, is the vector sum of all dipoles.

In order to obtain net alignment in the polymer film, the polymer must be *poled*, i.e. annealed (at 70-100°C) in a strong electric field. PVDF pads, placed between electrodes, are used in computer keyboards. Some IR sensing cameras use PVDF as thermal sensor.

- Compare the unit cell of PVDF with that of polyethylene. Is polyethylene unit cell centrosymmetric? How would you describe the conformation of PVDF chains, using helical notation?