Biopolymers
Biopolymers: introduction

Proteins (muscles, skin, hair, nails, enzymes)
DNA (information storage polymer)
Carbohydrates (energy storage, structural components)

**Biopolymers** are polymers that bio-degrade with the action of micro-organisms, heat and moisture. There is no specific standard for biodegradation. Biopolymers can be made using waste starch from a crop that has been grown for food use.
Biopolymers versus man-made polymers

Biopolymers are made from biomass.

Man made polymers are often made from the petroleum feedstock.

Increased use of bio-polymers would reduce the dependence on fossil fuels; another advantage is that biopolymers are easily bio-degradable.
a, Scanning electron micrograph of a dragline. Scale bar, 10 m.
b, The thread's unusual torsional properties prevent an abseiling spider from swinging, a movement that might attract predators.
Condensation and hydrolysis reactions

(a) Condensation

\[
\begin{align*}
\text{H-Monomer-\(\text{OH}\)} + \text{H-Monomer-\(\text{OH}\)} & \rightarrow \text{H-Monomer-Monomer-\(\text{OH}\)} + \text{H-Monomer-\(\text{OH}\)} \\
\text{H-Monomer-Monomer-\(\text{OH}\)} + \text{H-Monomer-\(\text{OH}\)} & \rightarrow \text{H-Monomer-Monomer-Monomer-\(\text{OH}\)} \\
\end{align*}
\]

Water is removed in condensation.

A covalent bond forms between monomers.

(b) Hydrolysis

\[
\begin{align*}
\text{H-Monomer-Monomer-Monomer-\(\text{OH}\)} & \rightarrow \text{H-Monomer-\(\text{OH}\)} + \text{H-Monomer-Monomer-\(\text{OH}\)} \\
\text{H-Monomer-Monomer-\(\text{OH}\)} + \text{H-Monomer-\(\text{OH}\)} & \rightarrow \text{H-Monomer-Monomer-\(\text{OH}\)} + \text{H-Monomer-\(\text{OH}\)} \\
\end{align*}
\]

Water is added in hydrolysis.

A covalent bond between monomers is broken.
Covalent linkages of monomer units in biomacromolecules;

Nucleotide unit  Peptide unit  Hexapyranose unit

The most important torsion angles, which affect the main chain conformations, are indicated.
**Biomacromolecular structural organization**

*Monomers* are the simple building blocks that when polymerized yield a macromolecule.

*Primary structure* is the sequence of monomeric residues in the covalently linked biopolymer. This arrangement is linear for nucleic acids and proteins, but may be branched in polysaccharides.

*Secondary structure* is the local regular structure of a macromolecule or a specific region of the molecule. These are helical, pleated and coil structures.

*Tertiary structure* describes the global three-dimensional fold or topology of the macromolecule, relating the positions of each atom and residue in three-dimensional space.

*Quaternary structure* is the spatial arrangement of multiple distinct polymeric chains (subunits) that form a functional complex.

*Quinternary structure* refers to the association of one class of bio-macromolecules with another class of bio-macro molecules to form complexes of cellular components such as histone (DNA-protein), ribosome (RNA-protein) and glycoprotein (oligo-saccharide-protein).
Nucleotides: constituents of Nucleic acids

The structure and properties of nucleic acids are affected and inherited from the general structure characteristics of their monomer molecules and nucleotides. Nucleotides are the phosphate esters of nucleosides, which are components of both ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). All nucleotides are constructed from three components:

1. a nitrogen base
2. a pentose sugar
3. a phosphate residue
DNA/RNA monomer building blocks

**Nitrogen bases**

- **Purines**
  - Guanine
  - Adenine

- **Pyrimidines**
  - Cytosine
  - Thymine
  - Uracil

**Pentose sugars**

- Nucleoside
- Nucleotide
  - $X = \text{OH}$  Ribose (RNA)
  - $X = \text{H}$  Deoxyribose (RNA)
DNA/RNA monomer building blocks

The base may be either a pyrimidine or a purine.

[Diagram showing the structure of nucleosides and nucleotides]

**Pyrimidines**
- Cytosine (C)
- Thymine (T)
- Uracil (U)

**Purines**
- Adenine (A)
- Guanine (G)

### 3.3 Distinguishing RNA from DNA

<table>
<thead>
<tr>
<th>NUCLEIC ACID</th>
<th>SUGAR</th>
<th>BASES</th>
</tr>
</thead>
<tbody>
<tr>
<td>RNA</td>
<td>Ribose</td>
<td>Adenine, Cytosine, Guanine, Uracil, Thymine</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribose</td>
<td>Adenine, Cytosine, Guanine, Thymine</td>
</tr>
</tbody>
</table>
DNA/RNA

The numbering of ribose carbons is the basis for identification of 5' and 3' ends of DNA and RNA strands.

RNA (single-stranded)
- Phosphate
- Ribose
- Pyrimidine base

DNA (double-stranded)
- Hydrogen bond
- Purine base

In RNA, the bases are attached to ribose. The bases in RNA are the purines adenine (A) and guanine (G) and the pyrimidines cytosine (C) and uracil (U).

In DNA, the bases are attached to deoxyribose, and the base thymine (T) is found instead of uracil. Hydrogen bonds between purines and pyrimidines hold the two strands of DNA together.
Base pair stacking energies in DNA

Complementary base pairing $A = T$ and $C = G$

<table>
<thead>
<tr>
<th>base pair</th>
<th>Hydrogen bonds</th>
<th>London</th>
<th>Total energy (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A:T</td>
<td>-26.0</td>
<td>+1.0</td>
<td>-25.0</td>
</tr>
<tr>
<td>G:C</td>
<td>-40.0</td>
<td>-16.3</td>
<td>-56.3</td>
</tr>
</tbody>
</table>
Some advantages of using DNA in nano-engineering

The enormous specificity of the A:T and G:C base pair interaction allows the convenient programming of designed DNA receptors.

The great versatility to synthesize DNAs of desired sequence, and the possibility to amplify any sequence from microscopic to macroscopic quantities by PCR.

DNA displays a relatively high physicochemical stability

The availability of specific enzymes allows for processing of DNA materials

\[ \text{J. Am. Chem. Soc., 2004, 126, 5932.} \]
Amino acids: constituent of proteins

Twenty standard Amino Acids

Nonpolar, aliphatic R groups
- Glycine
- Alanine
- Valine
- Leucine
- Methionine
- Isoleucine

Aromatic R groups
- Phenylalanine
- Tyrosine
- Tryptophan

Polar, uncharged R groups
- Serine
- Threonine
- Cysteine

Positively charged R groups
- Lysine
- Arginine
- Histidine

Negatively charged R groups
- Aspartate
- Glutamate
Formation of peptide bonds

The amino and carboxyl groups of two amino acids react to form a peptide linkage. A molecule of water is lost (condensation) as each linkage forms.

Repetition of this reaction links many amino acids together into a polypeptide.
Secondary structures and motifs of proteins

- **Primary structure:** Amino acid monomers are joined, forming polypeptide chains.

- **Secondary structure:** Polypeptide chains may form α helices or β pleated sheets.
  
- **Tertiary structure:** Polypeptides fold, forming specific shapes. Folds are stabilized by bonds, including hydrogen bonds and disulfide bridges.

- **Quaternary structure:** Two or more polypeptides assemble to form larger protein molecules. The hypothetical molecule here is a tetramer, made up of four polypeptide subunits.
Conformational map for protein

The plots show allowed $\phi$ and $\psi$ angles.

White areas show sterically unfavourable conformations.
Denaturation of proteins

**Denaturing** agents can disrupt the tertiary and secondary structure of a protein and destroy the protein's biological functions.

**Renaturation** (reassembly into a functional protein) is sometimes possible, but usually denaturation is irreversible.
Amyloid formation

**Figure 1.** The formation of amyloid fibrils. A natively folded monomer undergoes a conformational transition into a β-sheet-rich state, usually through a partial unfolded state. Self-assembly of these intermediates into ladders of β strands results in the formation of ordered filaments that aggregate into the well-known amyloid fibrils.
Integration of semiconducting oligoelectrolytes within amyloidogenic proteins

Monosaccharides: constituents of glycans

α-D-glucose

β-D-glucose

D-ribose

2-Deoxy-D-ribose

Glycosidic bond
Oligosaccharides

(a) Molecular structure

Cellulose

Starch and glycogen

Hydrogen bonding to other cellulose molecules can occur at these points.

Glycogen and starch are polymers of glucose with α,1,4 glycosidic linkages. α,1,6 glycosidic linkages produces branching at carbon 6.

(b) Macromolecular structure

Linear (cellulose)
Branched (starch)
Highly branched (glycogen)

Parallel cellulose molecules from hydrogen-bonds, resulting in thin fibrils.

Branching limits the number of hydrogen-bonds that can form in starch molecules, making starch less compact than cellulose.

The high amount of branching in glycogen makes its solid deposits more compact than starch.

(c) Polysaccharides in cells

Layers of cellulose fibrils, as seen in this scanning electron micrograph, give plant cell walls great strength.

Dyed purple in this micrograph, starch deposits have a large granular shape within cells.

Colored pink in this electron micrograph of human liver cells, glycogen deposits have a small granular shape.
Oligosaccharides: importance of configuration at the anomeric centre

\[ \alpha \text{-configuration} \]

\[ \beta \text{-configuration} \]

amylose (component of starch)

Cellulose