21. Polymers

There are two **types** of **polymerisation**: **addition** and **condensation**

Addition Polymerisation

An <u>addition polymer</u> forms when unsaturated monomers react to form a polymer
Monomers contain C=C bonds

Poly(alkenes) are chemically inert due to the strong C-C and C-H bonds and **non-polar** nature of the bonds and therefore are non-biodegradable.

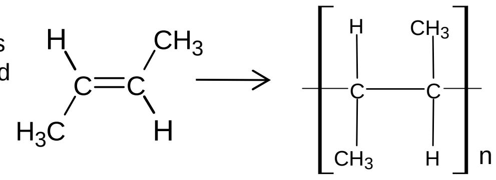
Chain forms when same basic unit is repeated over and over.

You should be able to draw the polymer repeating unit for any alkene

e.g. For but-2-ene

$H_3C-CH=CH-CH_3$

It is best to first draw out the monomer with groups of atoms arranged around the double bond



Condensation Polymerisation

The two most common **types** of condensation polymers are **polyesters** and **polyamides** which involve the formation of an **ester** linkage or an **amide** linkage.

In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g. H_2O or HCl.

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di carboxylic acid, diol, diacyl chloride.

Forming polyesters and polyamide uses these reactions we met earlier in the course

Carboxylic Acid + Alcohol → Ester + water

Acyl chloride + Alcohol → Ester + HCl

Carboxylic Acid + Amine → amide + water

Acyl chloride + Amine → amide + HCl

If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:

dicarboxylic acid + diol → poly(ester) + water

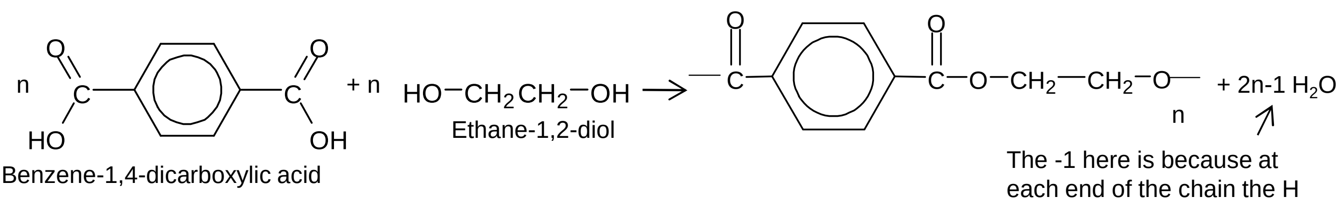
diacyl dichloride + diol → poly(ester) + HCl

dicarboxylic acid + diamine → poly(amide) + water

diacyl dichloride + diamine → poly(amide) + HCl

Using the carboxylic acid to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous HCl fumes.

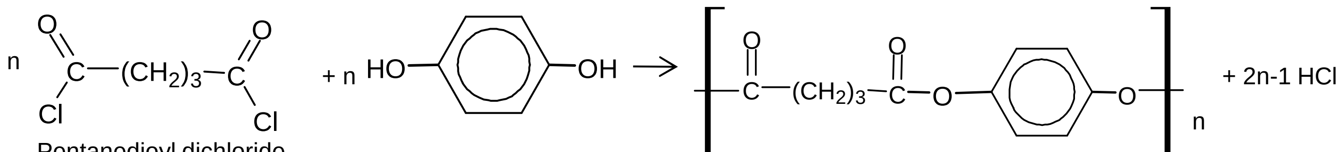
Terylene- a common polyester



Benzene-1,4-dicarboxylic acid

Terylene fabric is used in clothing, tire cords

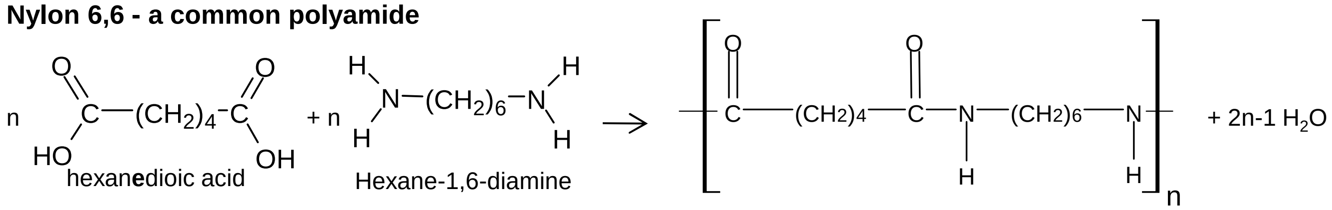
The -1 here is because at each end of the chain the H and OH are still present



Pentanedioyl dichloride

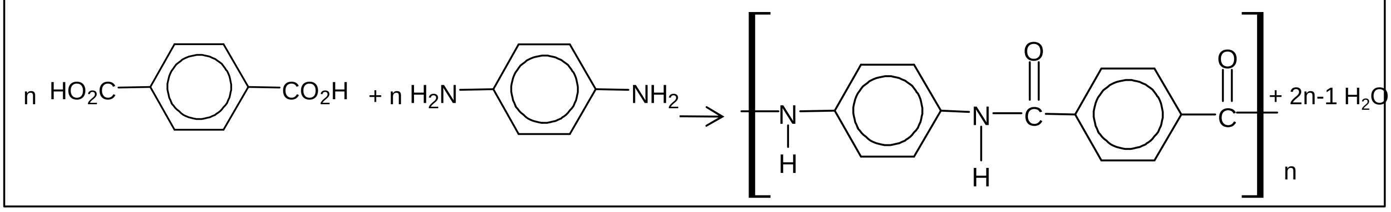
Benzene-1,4-diol

Nylon 6,6 - a common polyamide



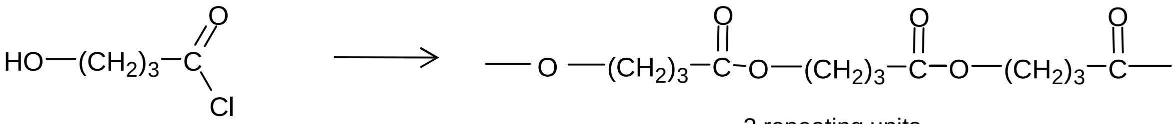
The 6,6 stands for 6 carbons in each of the monomers. Different length carbon chains produce different polyamides

Kevlar- a common polyamide



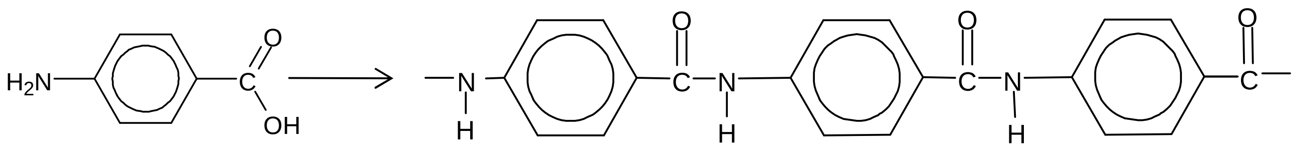
Note on classification for condensation polymers
If asked for **type of polymer**: It is polyamide or polyester
Whereas **type of polymerisation** is **condensation**

It is also possible for polyamides and polyesters to form from **one** monomer, if that monomer contains both the functional groups needed to react

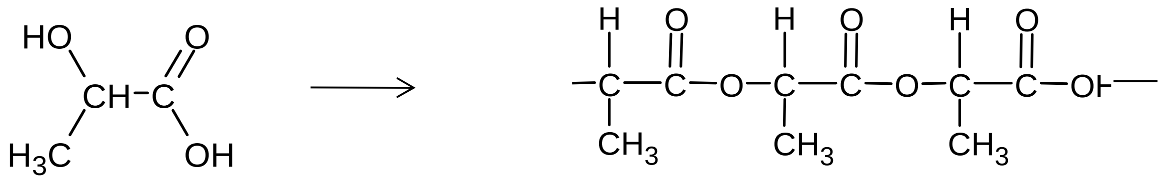


4-hydroxybutanoyl chloride

3 repeating units



3 repeating units

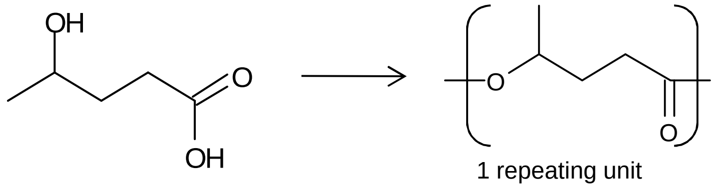


2-hydroxypropanoic acid (lactic acid)

3 repeating units

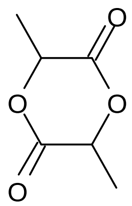
poly(lactic acid)

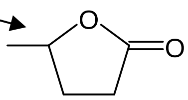
2 lactic acid molecules can also form a ring diester



4-hydroxypentanoic acid

1 repeating unit

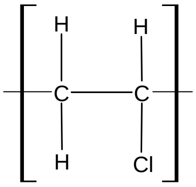




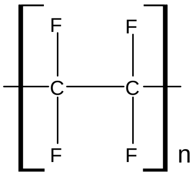
It is possible for some of these compounds to form various cyclic esters under different conditions from forming the polymer.
You do not need to learn these but may be asked to deduce structures from information given

Properties of polymers

Low density (LD) and high density (HD) poly(ethene) are produced from ethene, using different catalysts and reaction conditions. In HDPE the polymer chains are single strands and can closely line up in parallel (called a crystalline structure). In LDPE, the chains are irregularly packed, branched chain polymers therefore they cannot get as close together. The polymer chains in HDPE can form stronger van der waals forces between them.



Poly(chloroethene) is a polymer that is water proof, an electrical insulator and doesn't react with acids.
In its pure form it is a rigid plastic. The strong permanent-dipole intermolecular bonding between polymer chains prevents them moving over each other. In this un-plasticised form it is used make uPVC window frame coverings and guttering.

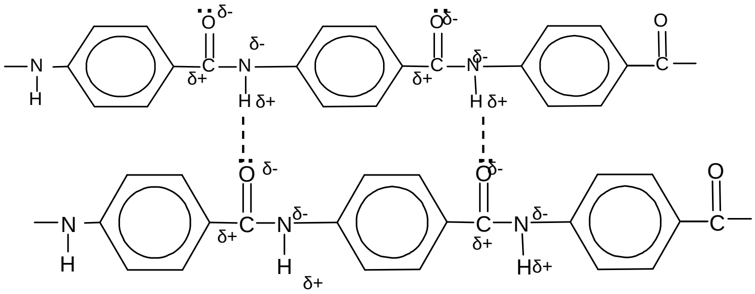


Polytetrafluoroethene (PTFE, or "Teflon") is very resistant to heat and chemical corrosion. It is used on nonstick cookware. It has strong van der waals forces between chains

Intermolecular bonding between condensation polymers chains

Polyesters have permanent dipole forces between the $C^{\delta+}=O^{\delta-}$ groups in the different chains in addition to the instantaneous temporary dipole forced between the chains.

Polyamides (and proteins) have **hydrogen bonding** between the lone pairs on oxygen in $C^{\delta+}=O^{\delta-}$ groups and the H in the $N^{\delta-}-H^{\delta+}$ groups in the different chains.
There are also **instantaneous temporary dipole forces** which are large because there are many electrons in the molecule
Polyamides will therefore have higher melting points than polyesters.



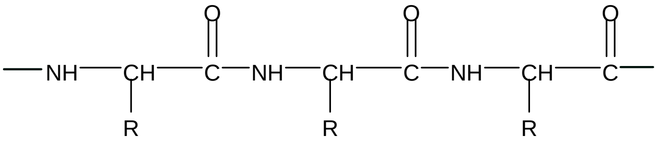
Hydrogen bonding between Kevlar chains causes chains to line up into very strong sheets.
It is used to make bullet proof clothing.

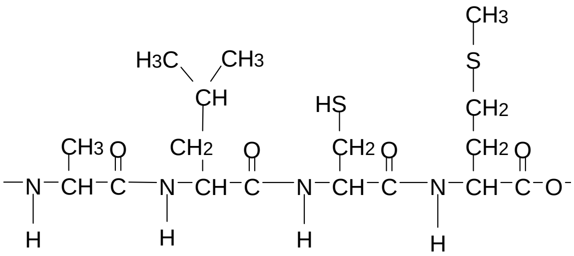
Proteins

Primary Structure of Proteins

Proteins are polymers made from combinations of amino acids.
The amino acids are linked by peptide links, which are the amide functional group.

The primary structure of proteins is the sequence of the 20 different naturally occurring amino acids joined together by condensation reactions with peptide links



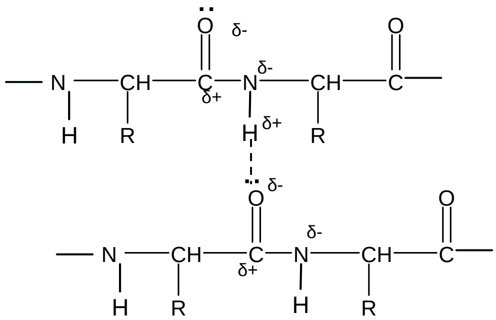


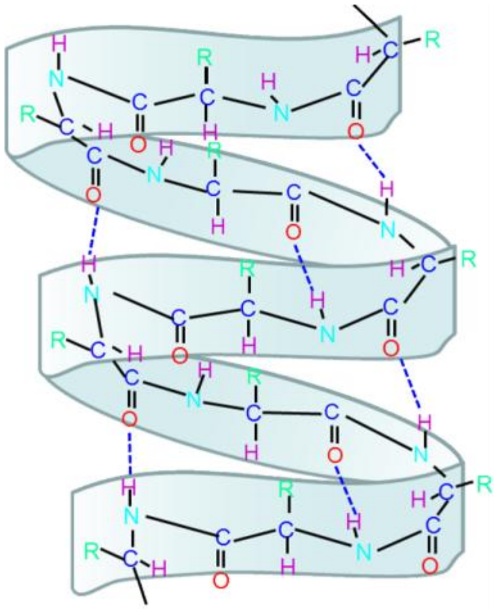
Secondary Structure of a Protein.

Secondary Structure: α-helix

The 3D arrangement of amino acids with the polypeptide chain in a corkscrew shape is held in place by Hydrogen bonds between the H of $–N^{\delta-}—H^{\delta+}$ group and the –O of $C^{\delta+}=O^{\delta-}$ of the fourth amino acid along the chain

The R-groups on the amino acids are all pointed to the outside of the helix



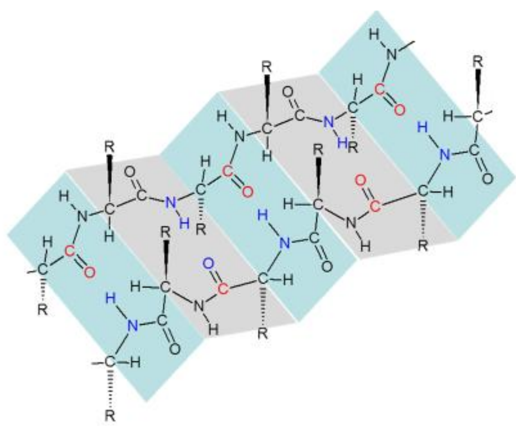


Secondary Structure: β-Pleated Sheet Structure of Proteins

The secondary structure can also take the form of a β–pleated sheets

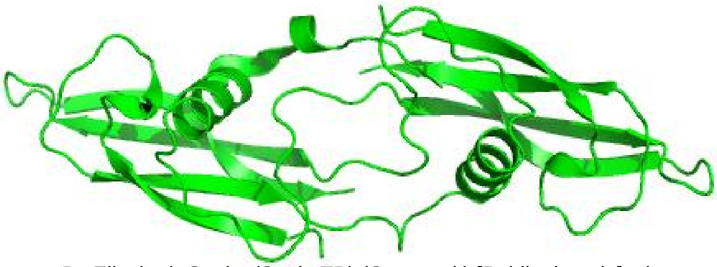
The protein chain folds into parallel strands side by side

The protein chain is held into a the pleated shape by Hydrogen bonds between the H of –N-H group and the –O of C=O of the amino acid much further along the chain in the parallel region .



Tertiary Structures of Proteins

The tertiary structure is the folding of the secondary structure into more complex shapes. It is held in place by interactions between the R- side groups in more distant amino acids . These can be a variety of interactions including hydrogen bonding, sulphur-sulphur bonds and ionic interactions



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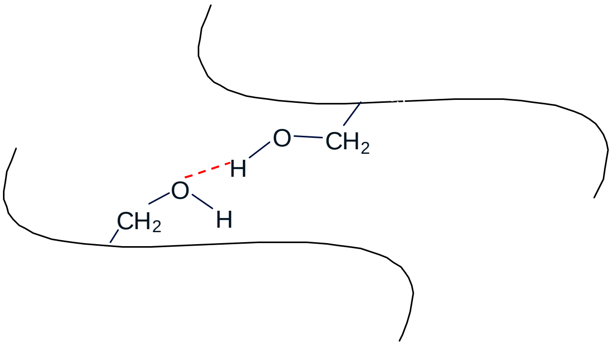
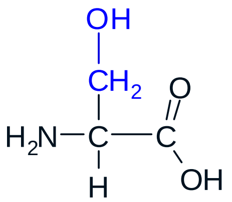
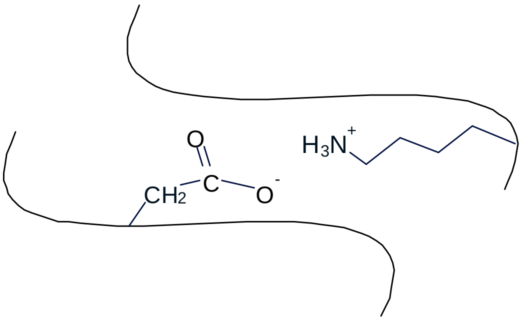
Hydrogen bonds





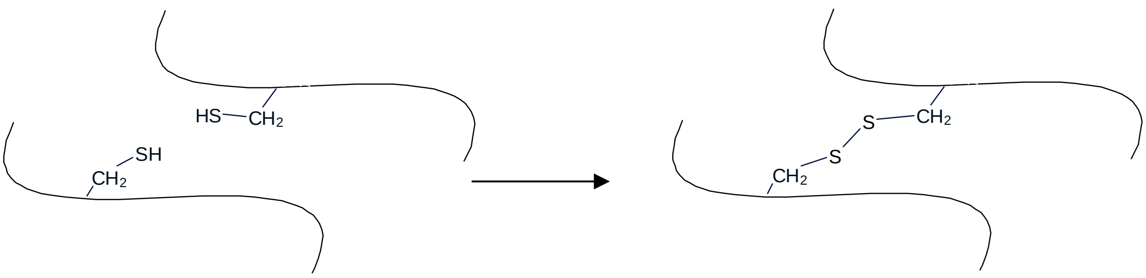
Hydrogen bonds could form between two serine side chains in different parts of the folded chain. (Other amino acids chains can also hydrogen bond)

ionic interactions

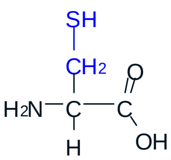


Ionic interactions could form between acidic amino acids such as aspartic acid and basic amino acids such as lysine. There is a transfer of a hydrogen ion from the -COOH to the -NH_2 group to form zwitterions just as in simple amino acids.

Sulphur bridges



If two cysteine side chains end up near each other due to folding in the protein chain, they can react to form a ***sulphur bridge***, which is a covalent bond.

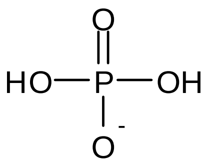


cysteine (cys)

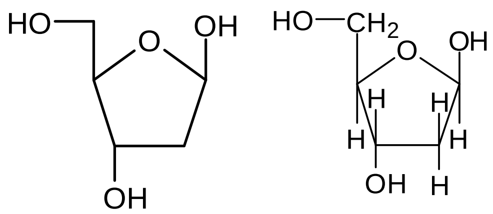
You don't need to learn the details of these interactions on this page but understand the principles of how the tertiary structure is held in place.

DNA

Key molecules in DNA

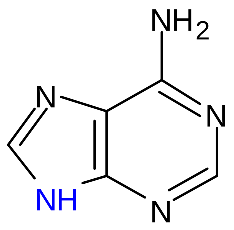


phosphate ion

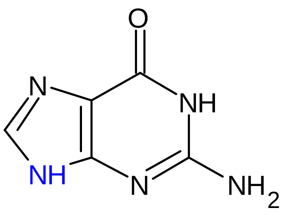


2-deoxyribose (a pentose sugar)

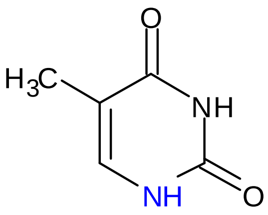
The 4 bases



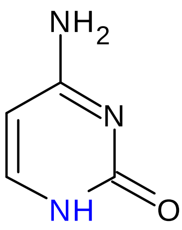
Adenine (A)



Guanine (G)



Thymine (T)

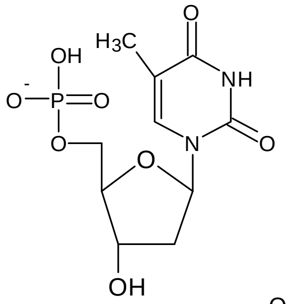


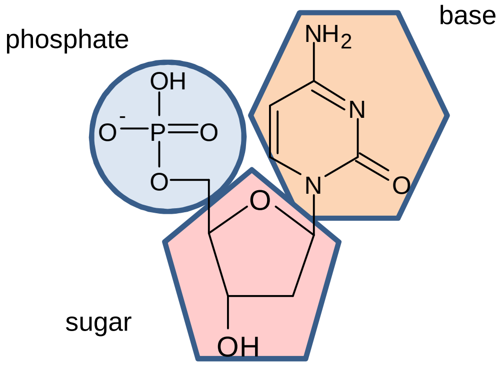
Cytosine (C)

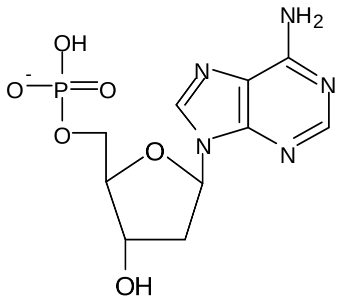
The structures of these substances are given in the Chemistry Data Booklet.

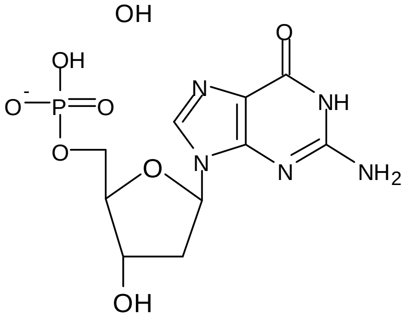
Nucleotides

A nucleotide is made up from a phosphate ion bonded to 2-deoxyribose which is in turn bonded to one of the four bases adenine, cytosine, guanine and thymine



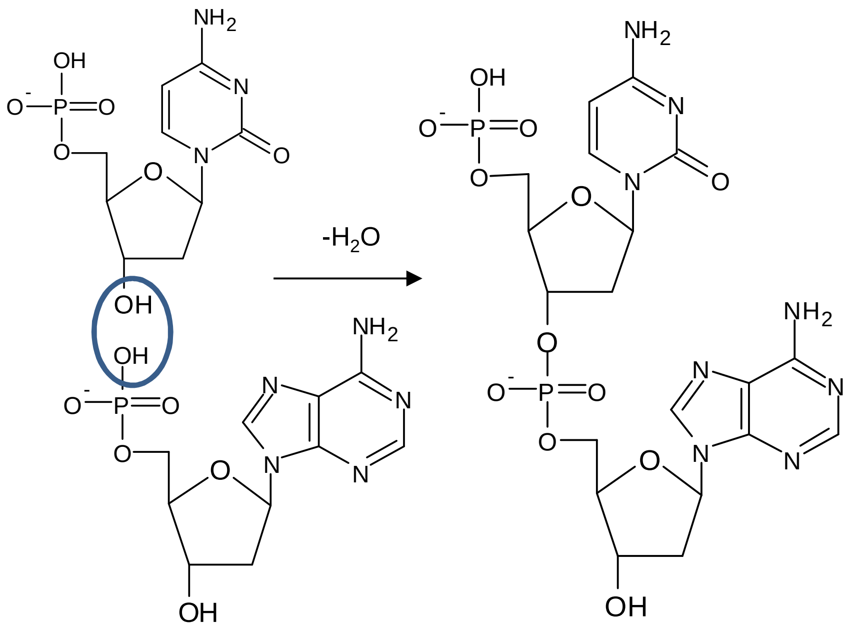






Although the structures will be given in the data sheet you need to learn which atoms on the base joins on to the sugar and how the sugar attaches to the phosphate ions

Sugar- phosphate chain

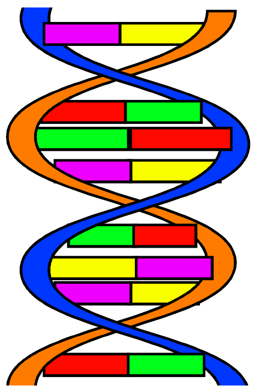


A single strand of DNA (deoxyribonucleic acid) is a polymer of nucleotides linked by covalent bonds between the phosphate group of one nucleotide and the 2-deoxyribose of another nucleotide.

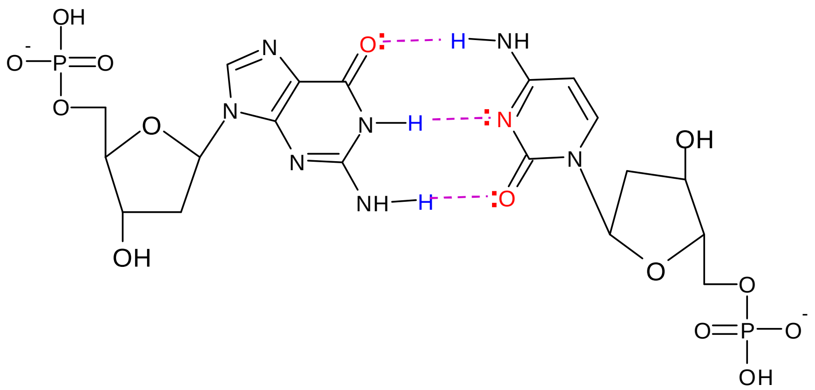
This results in a sugar-phosphate-sugar- phosphate polymer chain with bases attached to the sugars in the chain.

Carefully learn how these join together

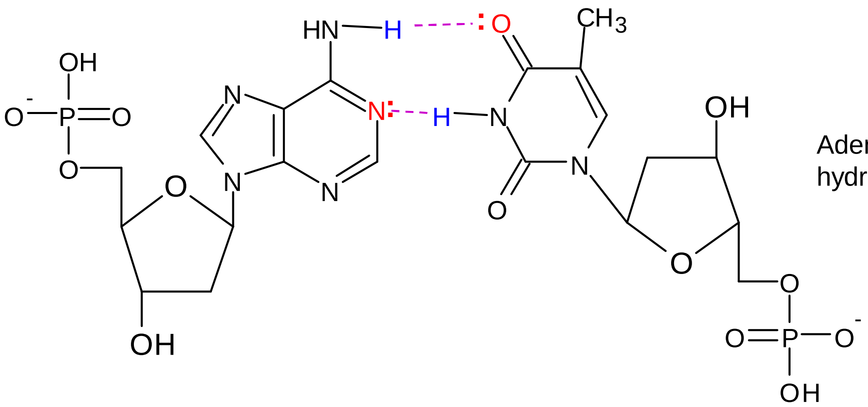
DNA exists as two complementary strands of the sugar phosphate polymer chain arranged in the form of a double helix.



Hydrogen bonding between base pairs leads to the two complementary strands of DNA.



Guanine pairs with cytosine by 3 hydrogen bonds



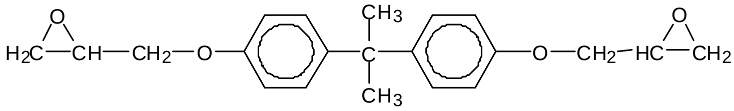
Adenine pairs with thymine by 2 hydrogen bonds

Non-solvent based adhesives

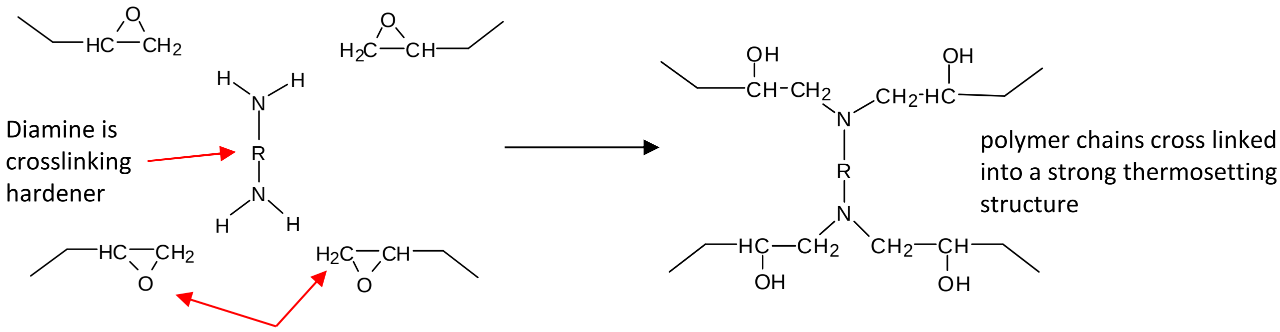
Most adhesives are solvent based. They harden when the solvent evaporates. The following harden in a different way.

Epoxy resin glues

The glues have two components: one containing polymers chains and the other a hardener (which is a cross-linking agent). They are mixed together when the glue is applied. As the glue sets the hardener forms cross links between the polymer chains forming a strong thermosetting structure.



pre-polymer with epoxy group



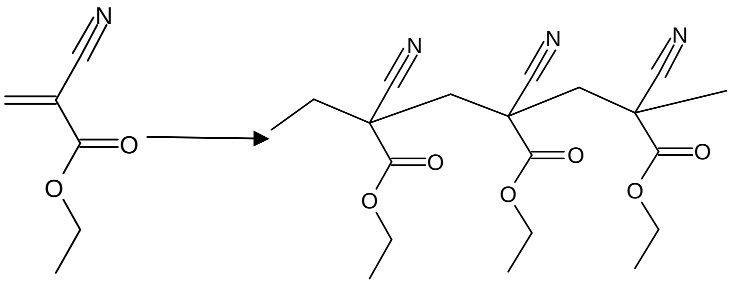
You don't need to remember the details of the substances here- just the process of crosslinking.

Cross links in **thermosetting** polymers tend to be covalent bonds which are strong and not easy to break. Once formed the polymer cannot be melted

Polymers with only weaker intermolecular forces between chains can generally be heated up to melt and change their shape. These are called **thermosoftening** polymers.

Superglue

The monomer in superglue polymerises on exposure to moisture in the atmosphere to form a strong addition polymer

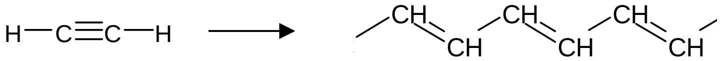


monomer
ethyl 2-cyanoprop-2-enoate

You don't need to remember the details of the substances here

Conducting polymers –poly(ethyne)

Ethyne has a triple bond. It can form an addition polymer that has alternate double single bonds.



Ethyne

Poly(ethyne) also known as polyacetylene

Poly(ethyne) conducts electricity. It conducts through its long chain of delocalised electrons. It can delocalise because the polymer chain is planar so the π bonds overlap with each other.

Degradable polymers

Poly(alkenes) are chemically inert and can therefore be difficult to biodegrade

Poly(alkenes) are chemically inert due to the strong C-C and C-H bonds and **non-polar** nature of the bonds and therefore are non-biodegradable.

Some condensation polymers may be photodegradable as the C=O bond absorbs radiation.

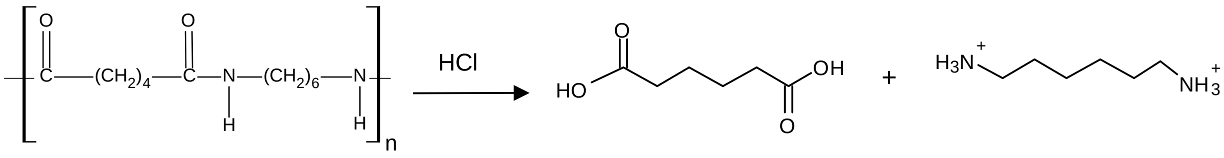
Chemical reactivity of condensation polymers

polyesters and polyamides can be broken down by **hydrolysis** and are, therefore, biodegradable

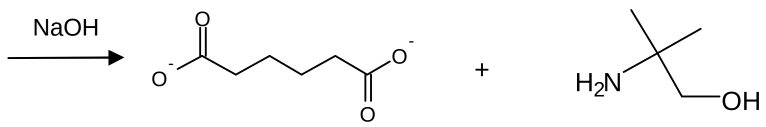
The reactivity can be explained by the presence of **polar bonds** which can attract attacking species such as nucleophiles and acids

Hydrolysis

Polyesters and polyamides can be hydrolysed by acid and alkali
The hydrolysis will result in the original monomers forming- although the carboxylic acid or amine group will be in salt form depending on whether the conditions are alkaline or acidic



$-CO(CH_2)_4CONHC(CH_3)_2CH_2O-$



This polymer has both an amide and ester link

Hydrolysis of di-peptides/proteins

If proteins are heated with dilute acid or alkali they can be hydrolysed and split back into their constituent amino acids.

The composition of the protein molecule may then be deduced by using TLC chromatography