CIE Chemistry A Level

21 : Polymerisation

(A Level only)

Notes

Condensation polymerisation

Condensation polymerisation is the joining together of **monomers** to form a polymer with the **release of a small molecule** such as water or HCl.

Polyesters

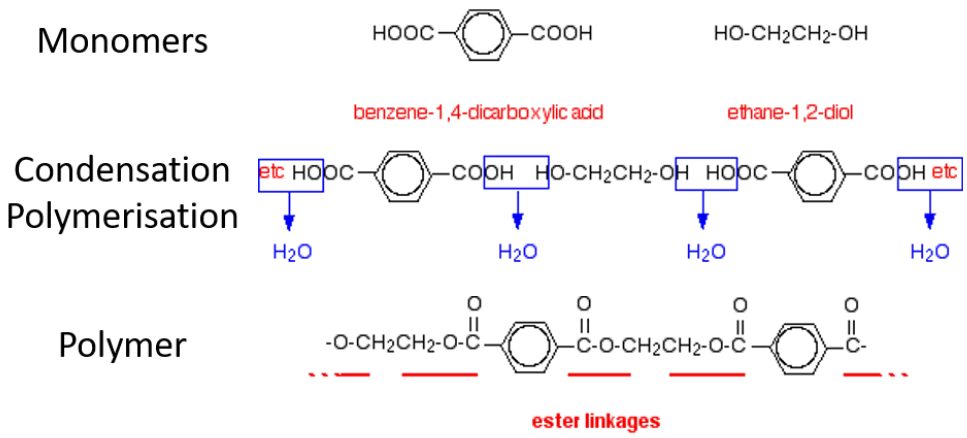
A polyester contains monomers linked with **ester bonds**. For this link to form, either of the following is needed:

- A monomer containing 2 carboxylic acid groups and a monomer containing 2 alcohol groups.
- A monomer containing both an alcohol and a carboxylic acid group.

The ester linkage is formed during a condensation reaction when H is lost from the OH of an **alcohol** and OH is lost from the COOH of a **carboxylic acid**. The H^+ and OH^- combine to form water.

A monomer containing two -COCl (**acyl chloride**) groups may be used instead of the carboxylic acid. The only difference is that **HCl** forms instead of water.

Below is a diagram showing the formation of Terylene:



['Polyesters', Jim Clark, Chemguide](https://www.chemguide.co.uk)

Polyamides

A polyester contains monomers held together by **amide bonds**. For this link to form, either of the following is needed:

- A monomer containing a 2 carboxylic acid groups and a monomer containing 2 amine groups.
- A monomer containing both a carboxylic acid and an amine group.

The amide linkage is formed during a condensation reaction when H is lost from the NH_2 of an **amine** and OH is lost from the COOH of a **carboxylic acid**. Water forms when the H^+ and OH^- combine.

As with ester bond formation, a monomer containing two -COCl (**acyl chloride**) groups can be used instead of the carboxylic acid, forming **HCl** instead of water.

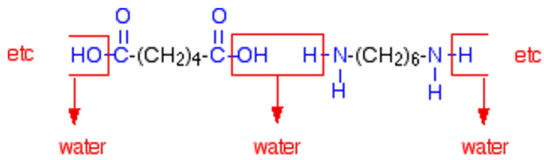
Below are some diagrams showing the polyamides nylon 6,6, nylon 6 and Kelvar (the amide bond is shown in blue in the polymers):

Nylon 6,6

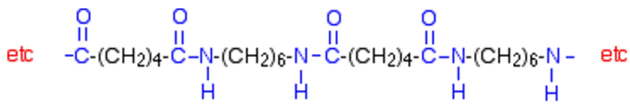
Monomers

$HOOCCH_2CH_2CH_2CH_2COOH$ $\quad$ $H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2$

Condensation Polymerisation



Polymer

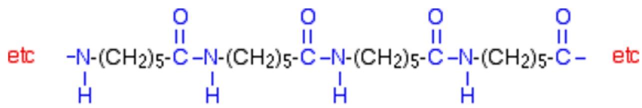


Nylon 6

Monomer

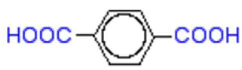
$H_2NCH_2CH_2CH_2CH_2CH_2COOH$

Polymer

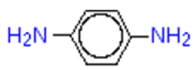


Kevlar

Monomers

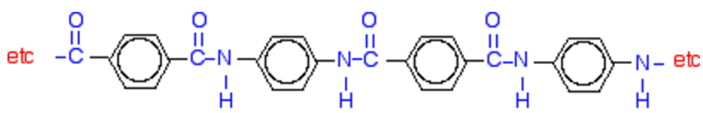


benzene-1,4-dicarboxylic acid



1,4-diaminobenzene

Polymer

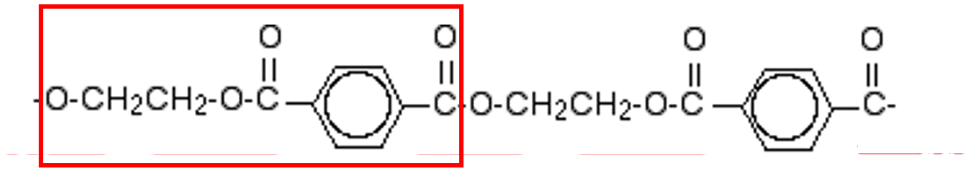


['Polyamides', Jim Clark, Chemguide](https://www.chemguide.co.uk/)

Repeat Units

A **repeat unit** is a structure that **occurs in a molecule many times**. Sometimes the repeat unit is made up of one monomer, sometimes it contains a pair of monomers. On the following page, there are examples of repeat units in polymers:

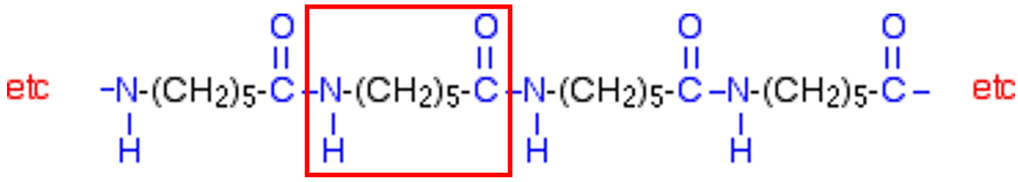
Terylene



Repeat unit

['Polyesters', Jim Clark, Chemguide]

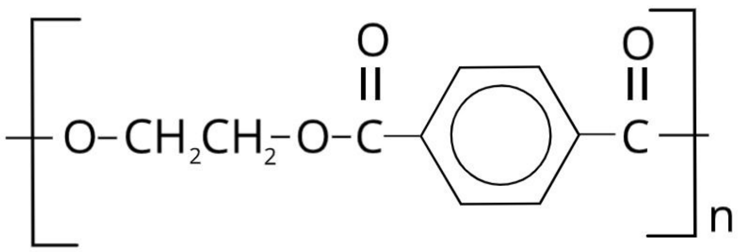
Nylon 6



Repeat unit

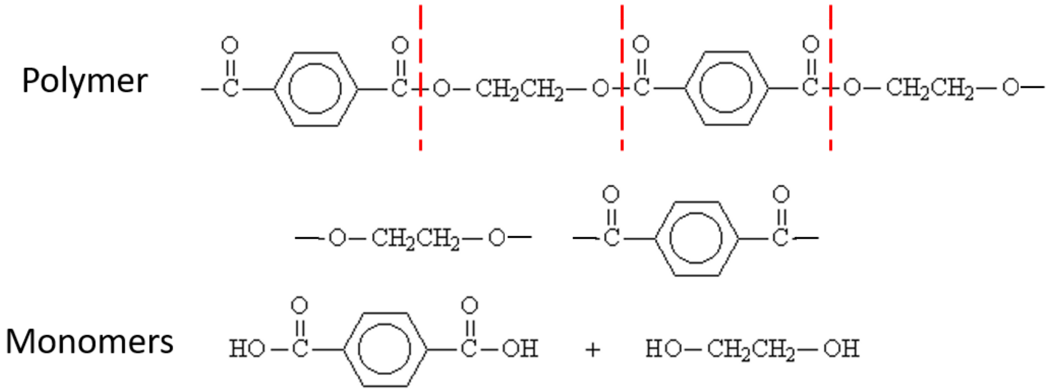
['Polyamides', Jim Clark, Chemguide]

Polymers can also be represented using their repeat unit and square brackets. The **'n'** is the diagram of **Terylene** below is used to show that there are many repeat units in the polymer.



Monomers

To identify the monomers in a polymer, draw a line through the ester or amide linkages. Add OH or H to create the monomers.



'Polymer Chemistry: Polymerization Reactions', Engineering LibreTexts, CC BY-NC-SA 3.0 US

Predicting types of polymerisation

Addition polymerisation	Condensation polymerisation
Monomers contain C=C double bonds.	Monomers contain -OH and -COOH or -COCl for polyesters. Monomers contain $-NH_2$ and -COOH or -COCl for polyamides.
Main chain of the polymer only contains C-C single bonds.	Main chain contains nitrogen or oxygen atoms as well as carbon atoms.
The polymer is the only product of the reaction.	The polymer and a small molecule like water or HCl are formed during the reaction.

Properties of polymers

- **Thermoplastics** soften and eventually melt meaning they can be remelted and reshaped. This is because when they are heated, enough energy is supplied to overcome the intermolecular forces of attraction between the molecules meaning the chains can move.
- **Thermosetting plastics** have covalent bonds between polymer chains so a large amount of energy is needed to overcome the forces of attraction between the chains. These polymers tend to remain solid when heated.

Side chains and intermolecular forces

The presence of side chains in polymers such as **poly(alkenes)** prevents the molecules packing together meaning that these polymers have **lower densities**. This also means that there are few points of contact between the molecules so the **van der Waals forces** are weaker and less energy is needed to overcome these forces. As a result, these polymers will have **lower melting and boiling points**.

PTFE (teflon) has a **high melting point** because although **van der Waals forces** as relatively weak, there are no side branches so the molecules can pack closely together. This means there are more points of contact between the molecules so lots of van der Waals forces form between the chains. As a result, more energy is needed to overcome these forces to melt the polymer.

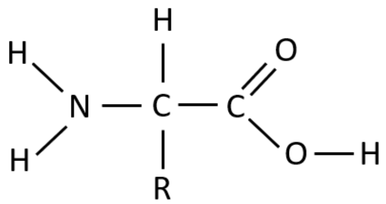
Kevlar is **very strong** because the molecules line up in a sheet with **hydrogen bonds** between the strands (between the O in C=O and the H in N-H).

Hydrogen bonding and DNA

DNA is a polymer made up of **nucleotide monomers**. DNA is described as a double stranded helix and it contains 4 different bases: A, C, T and G. Monomers in each strand are joined together with a phosphate backbone. The two strands are held together with **hydrogen bonds** between the bases. **A always pairs with T and C always pairs with G**. This complementary base pairing occurs due to the hydrogen bonding that forms between the base pairs and this is important to ensure that **an identical strand of DNA is produced after replication**.

Proteins

Proteins are polymers made from **amino acids**. Amino acids contain an **amine** group ($-NH_2$) and a **carboxylic acid** group (-COOH). The general structure of an alpha amino acid is shown below (where R represents any group):



A **dipeptide** contains 2 amino acids joined together with an amide bond. A **polypeptide** contains many amino acids bonded together in a chain by amide bonds.

Below is a description of the structure of proteins:

- **Primary structure** - the sequence of amino acids.
- **Secondary structure** - amino acid chains are held by **hydrogen bonds** in structures called α-helices and β-sheets. The hydrogen bonds form between a lone pair of electrons on oxygen in C=O and the hydrogen in N-H. An α-helix looks like a loosely coiled spring and a β-sheet looks like a zig-zag of parallel strands.
- **Tertiary structure** - the final 3D shape of the protein (includes the primary and secondary structure). This is held together with **interactions between R groups** such as:
    - Ionic interactions (may be due to transfer of H^+ from -COOH to $-NH_2$ to form $-COO^-$ and $-NH_3^+$).

- Hydrogen bonds between R groups.
- Van der Waals forces (due to temporary dipoles).
- Disulfide bridges (the amino acid cysteine contains 2-SH groups in its R group. If the hydrogen is lost from the -SH group (oxidation), covalent bonds form between sulfur atoms in the R groups of adjacent cysteines).

Polymer uses

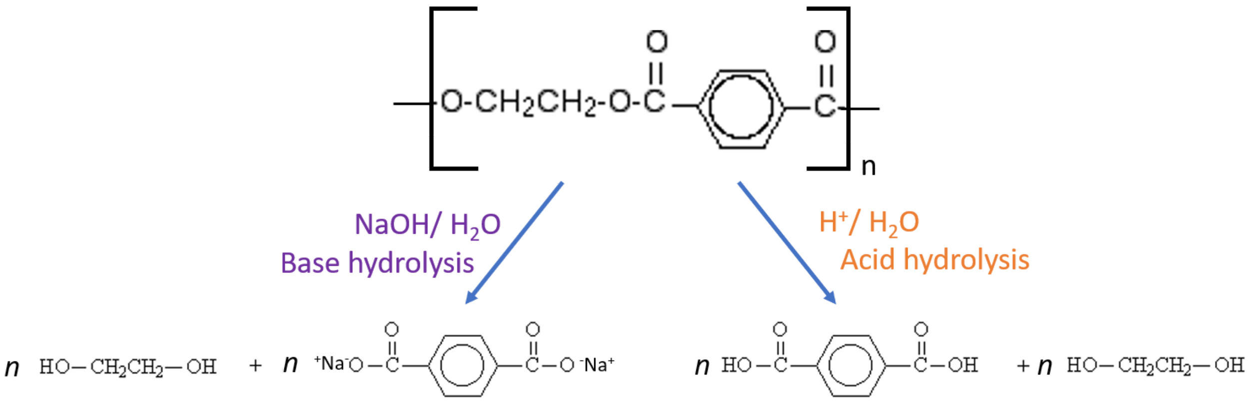
- Non-solvent based adhesives:
    - **Epoxy resins** - contain a cross-linked thermosetting polymer which sets into a shape that can't be changed.
    - **Super Glues** - water vapour in the air triggers the polymerisation of monomers in the glue.
- Conducting polymers (e.g. **polyacetylene**): polyacetylene contains alternating double and single bonds. When a double bond forms, p orbitals overlap sideways. As this happens along that whole chain, all the p orbitals overlap to create a delocalised system of electrons. This means that the polymer can conduct electricity.

Degradable polymers

Poly(alkenes) are chemically **inert** (very unreactive) meaning they are **difficult to biodegrade**.

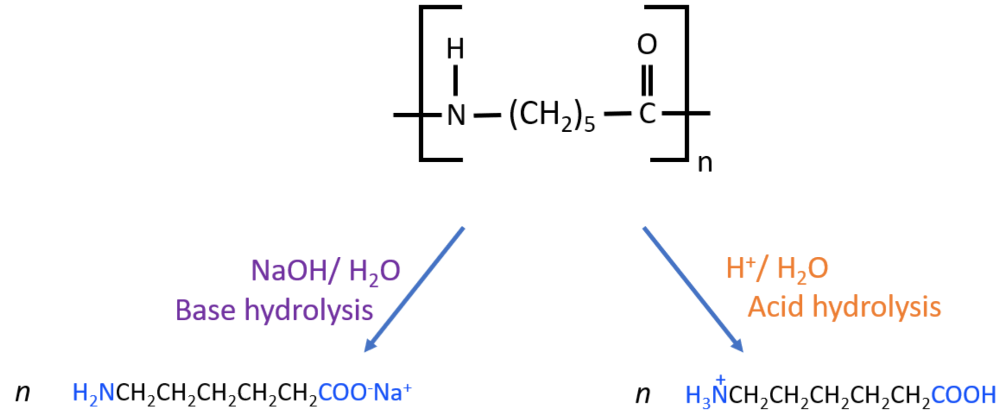
Some polymers, such as LDPE, can be **degraded using light**. Light (typically **UV**) causes the polymer chains to break so the material crumbles.

Polyesters are **biodegradable** and can be **hydrolysed** using dilute acids or alkalis (slower hydrolysis with acids). Below is an example of hydrolysis of the polyester Terylene:



'Polyesters', Jim Clark, Chemguide (image modified from original)
'Polymer Chemistry: Polymerization Reactions', Engineering LibreTexts (image modified from original), CC BY-NC-SA 3.0 US

Polyamides are also **biodegradable** and can be **hydrolysed** using dilute strong acids or alkalis (slower hydrolysis with alkalis). Below is an example of hydrolysis of the polyamide nylon 6:



The **acid hydrolysis** of proteins is very similar to the acid hydrolysis of polyamides. There are two ways to complete this reaction:

- Heat protein at 110°C with 6 mol dm^{-3} hydrochloric acid for 8 hours (slow method).
- Place protein in a sealed tube containing 6 mol dm^{-3} hydrochloric acid and an atmosphere of nitrogen. Place in a microwave for 5-30 minutes (dependant on the protein), using temperatures up to 200°C. Faster method for small samples of protein during analysis.

When proteins are hydrolysed using acid, amino acids are formed, however the **amine group accepts a proton** to become **$-NH_3^+$**. The general structure of the product of protein hydrolysis is shown below (where R represents any group):