

Condensation polymerization

We have previously seen addition polymerization, where a double bond in a monomer is broken and used to form connect one monomer to another, progressively forming very long chain molecules.

Definition: **Condensation** is a reaction in which two small molecules react together to form a larger molecule, with the elimination of a small molecule such as water.

Condensation polymerisation is therefore a reaction in which many monomers join together to form a polymer, with the elimination of a smaller molecule such as water each time a monomer joins the chain.

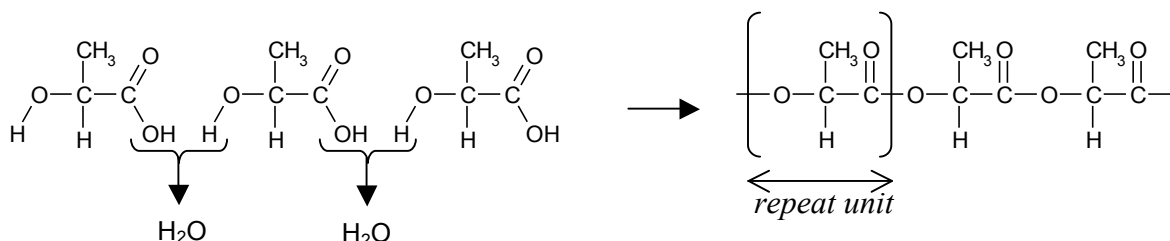
Polyesters

Recall that an ester can be made from the reaction of a carboxylic acid (or an acyl chloride) with an alcohol. An ester linkage (-COO-) is formed and water (or hydrogen chloride) is eliminated.

i) using one monomer

The monomer must have both a carboxylic acid or an acyl chloride functional group, and an alcohol functional group. The monomers can then react with themselves, forming a chain.

e.g. poly(lactic acid), PLA, formed from the monomer lactic acid (2-hydroxypropanoic acid).



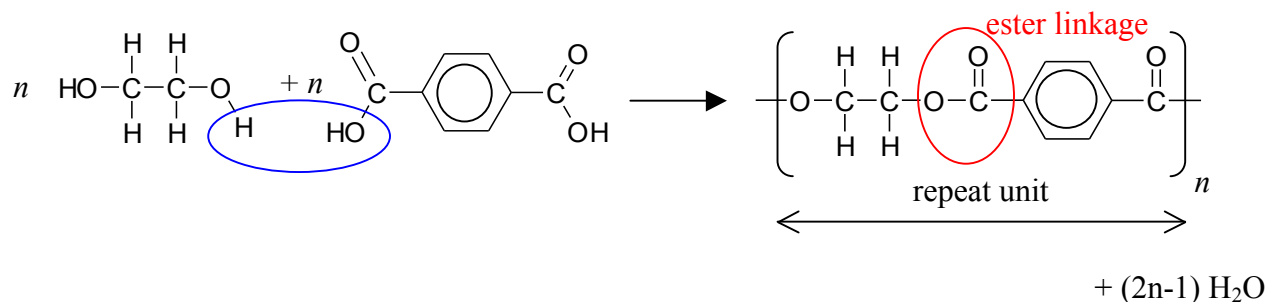
Preventing the monomers from reacting until they are required to can be problematic with monomers of this kind, so the alternative is to form the polyester using two monomers which are combined to form the polymer.

ii) using a pair of monomers

One monomer has two alcohol functional groups - a diol. The other monomer has two carboxylic acid or acyl chloride groups. The monomers alternate forming the polymer chain.

e.g. Terylene (when a fibre), also known as PET (when solid e.g. in bottles)

- made from the monomers ethane-1,2-diol and benzene-1,4-dicarboxylic acid

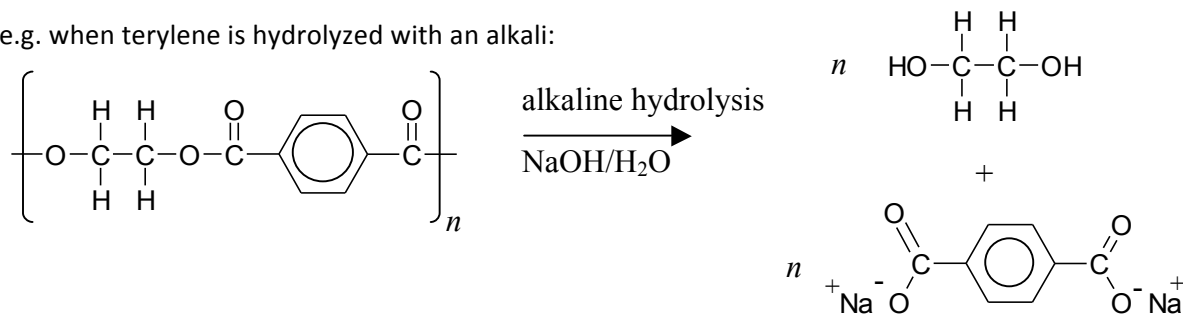


Breaking down polyestersAlkaline hydrolysis

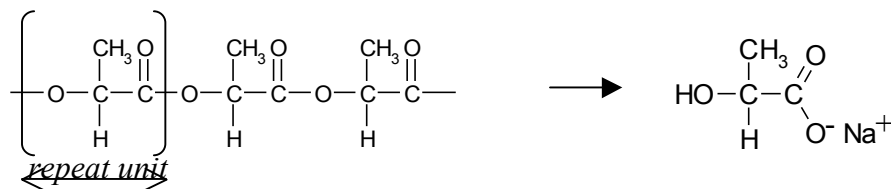
Polyesters, like esters, are hydrolysed by hot aqueous alkalis such as sodium hydroxide solution. Each ester linkage is hydrolysed to:

- the sodium salt of a carboxylic acid, $\text{-COO}^-\text{Na}^+$
- a hydroxyl group, -OH

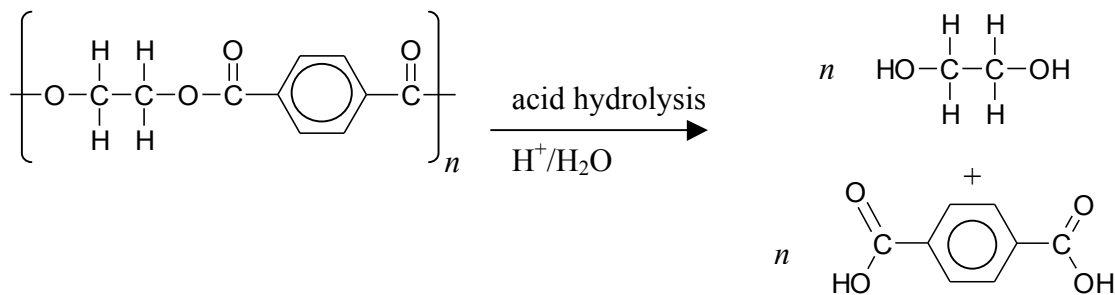
e.g. when terylene is hydrolyzed with an alkali:



e.g. when PLA is hydrolysed with an alkali:

Acid hydrolysis

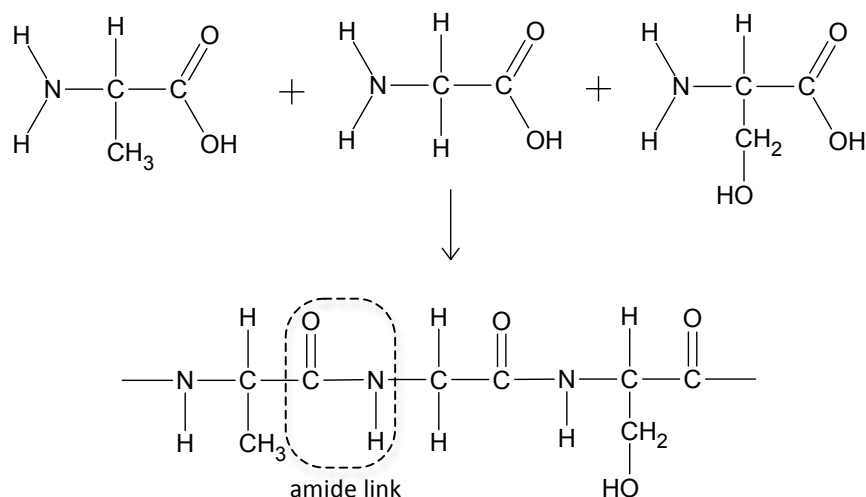
Polyesters can also be hydrolysed with hot aqueous acid, such as hydrochloric acid. The monomer units of the polyester are produced.

**Polyamides**

Polyamides are condensation polymers, with the amide linkage being formed by reaction of an -NH_2 group with a -COOH (or -COCl group) and the elimination of water (or hydrogen chloride).

i) using one monomer

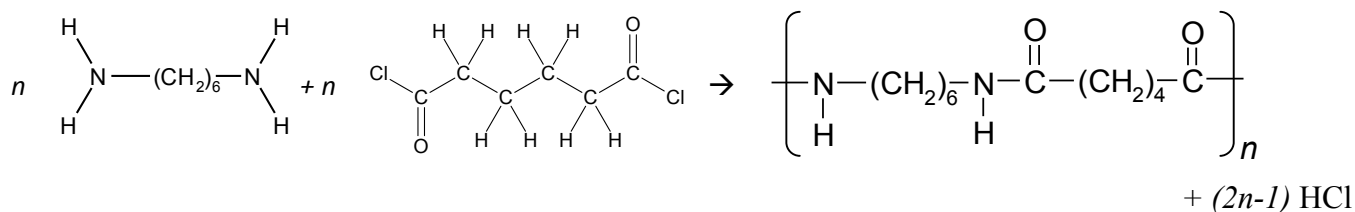
The monomer must have an amine group and a carboxylic acid (i.e. an amino acid) or acyl chloride group. The polymer formed in this way is called a polyamide or polypeptide. Proteins are very long polypeptides containing many different amino acids polymerised into a chain and linked by amide bonds.



ii) using a pair of monomers

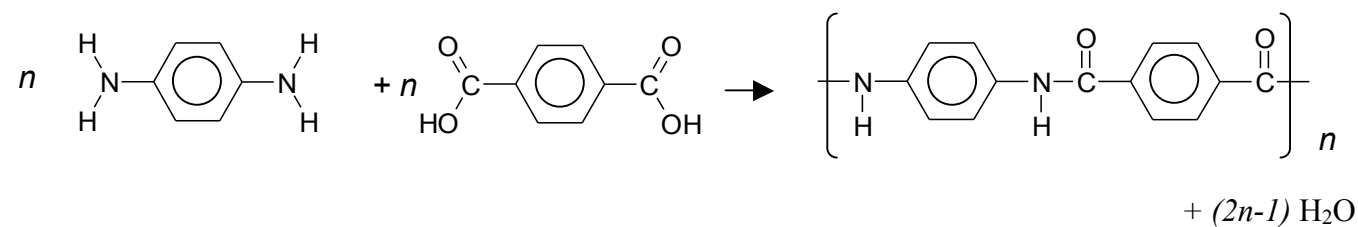
The monomers are a diamine with two -NH_2 groups, and a dicarboxylic acid or acyl chloride with two -COOH groups or -COCl groups.

e.g. Nylon-6,6 can be made from 1,6-diaminohexane and hexanedioyl chloride.



The '6,6' comes from the number of carbon atoms between the NH_2 groups of the diamine, and in the dicarboxylic acid (including those of the COOH). Other nylons can be made by varying the numbers of carbons in either monomer.

e.g. Kevlar is formed from benzene-1,4-diamine and benzene-1,4-dioic acid.



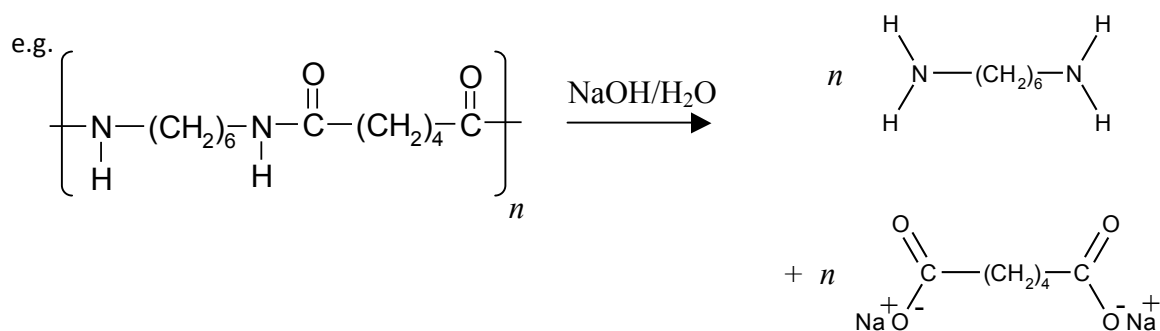
Kevlar has some remarkable properties – fire resistant, and a higher strength than steel. It is used to make protective clothing e.g. for firefighters and in bullet-proof vests.

Why is Kevlar so strong ?

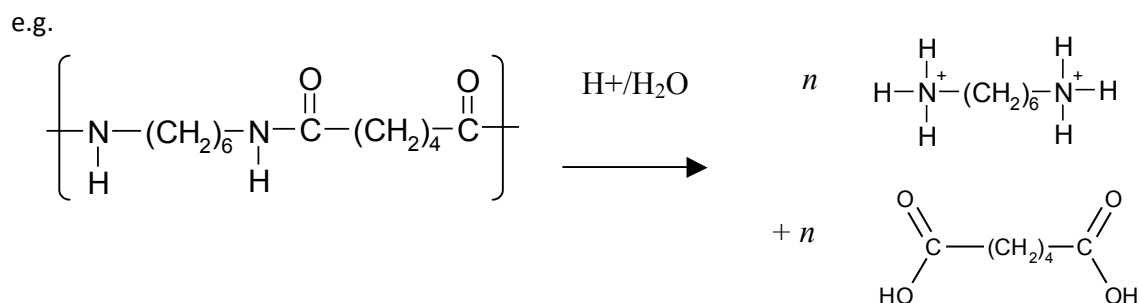
In part because the polar C=O groups along one chain has a δ^- oxygen atom and will align exactly with the polar N-H groups in another chain which has a δ^+ H atom. Extensive hydrogen-bond cross linking of chains is therefore possible.

Hydrolysis of polyamides

Like polyesters, polyamides can be hydrolysed by hot aqueous alkali, e.g. $\text{NaOH}_{(\text{aq})}$. Each amide linkage is hydrolysed producing an $-\text{NH}_2$ group and the sodium salt of the acid, $-\text{COO}^-\text{Na}^+$



Alternatively polyamides can be hydrolysed using hot aqueous acid, such as $\text{HCl}_{(\text{aq})}$. The dicarboxylic acid is produced, along with the ammonium salt of the diamine.

**Comparing addition and condensation polymerisation**

Addition polymerisation	Condensation polymerisation
One monomer	One or two monomers
Monomer functional group: $\text{C}=\text{C}$	Monomer functional groups: $-\text{COOH}$ and $-\text{OH}$ $-\text{COCl}$ and $-\text{OH}$ $-\text{COOH}$ and $-\text{NH}_2$ $-\text{COCl}$ and $-\text{NH}_2$
No additional product other than polymer	H_2O or HCl eliminated
Polymer chain continuous $-\text{C}-\text{C}-\text{C}-\text{C}-$	Polymer chain contains $-\text{COO}-$ or $-\text{CONH}-$ links
Polymer chain not easily broken down	Polymer can be hydrolysed

Identifying types of polymerisation

For addition polymerisation, look out for:

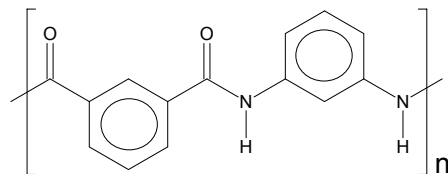
- monomer has a double bond
- polymer backbone is continuous chain of C atoms

For condensation polymerisation, look out for

- two monomers, each with two functional groups
- one monomer with two different reacting functional groups
- *polymer contains ester or amide linkages*

Practice:

Nomex is a synthetic heat resistant and fire resistant polyamide with the structure shown:



- i) identify the monomer(s) from which it is formed
- ii) write the structures of the products of acid hydrolysis of nomex using hydrochloric acid
- iii) write the structures of the products of alkaline hydrolysis of nomex using potassium hydroxide solution