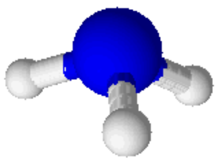
2A - Amines

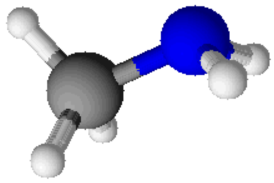
Something fishy about amines:

- Have an **NH_2**, amine group.
- Amines are derivatives of ammonia:



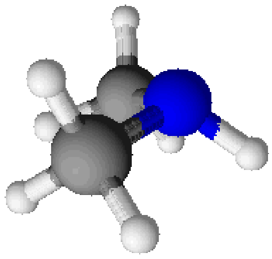
3 H atoms

Ammonia, NH3



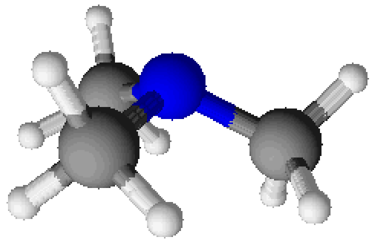
1 H atom replaced: 1 attached C to N

Primary amine



2 H atoms replaced: 2 attached C's to N

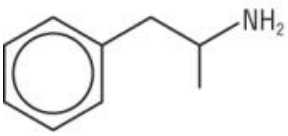
Secondary amine



3 H atom replaced: 3 attached C's to N

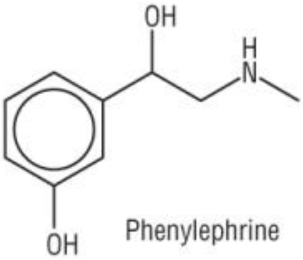
Tertiary amine

- Amines occur in nature and are known for their physiological effects:



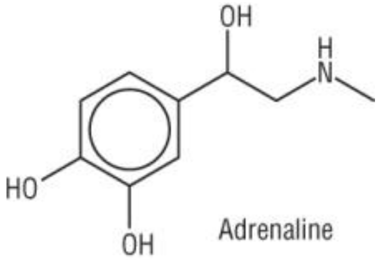
Amphetamine

Treats drowsiness and fatigue syndrome



Phenylephrine

Decongestant



Adrenaline

'Fight or flight' to cope with sudden stress

- Amines are also known for their unpleasant and often fishy smell.

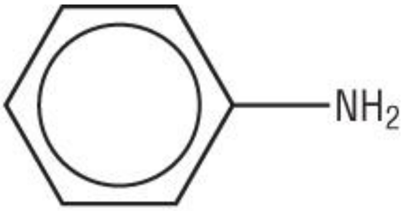
Naming amines:

- To the longest single alkyl chain add the suffix 'amine':

NH_3 — Ammonia

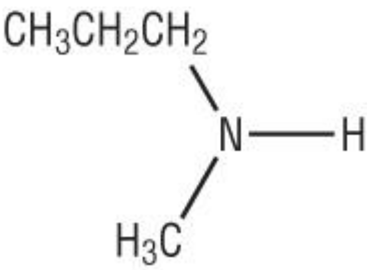
CH_3NH_2 — Methylamine

$CH_3CH_2NH_2$ — Ethylamine



Phenylamine

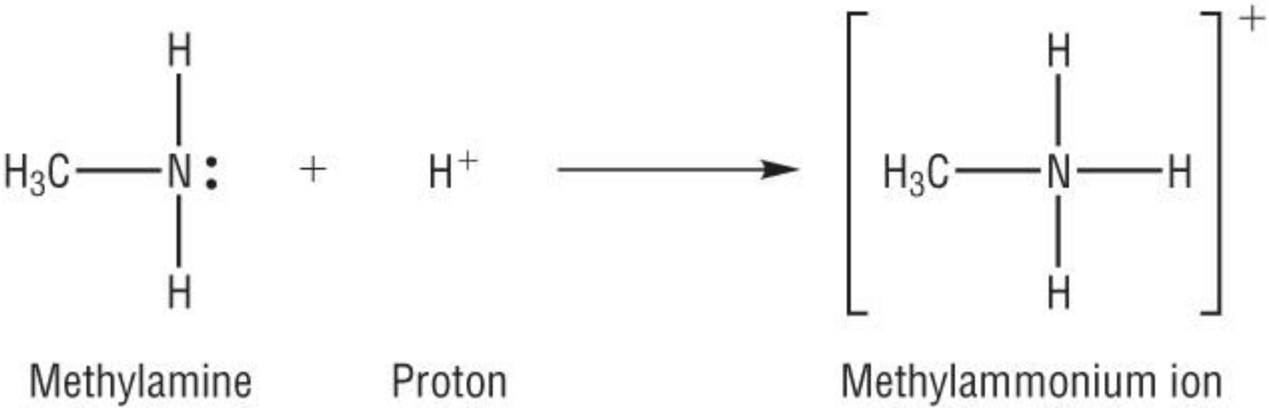
- If there are 2 alkyl groups on the nitrogen:



- Start with the longest alkyl chain - **propylamine**
- The shorter alkyl group is prefixed with 'N' - **N - methyl propylamine**
- The prefix 'N' tells you that the alkyl group comes off the nitrogen atom.
- A tertiary amine would have 2 prefixes of 'N' - N,N - methyl ethyl butylamine (for example)

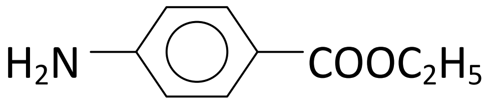
Basicity in amines:

- Amines are weak bases - proton acceptors.
- This is because they have a lone pair of electrons on the nitrogen available to donate in accepting a hydrogen ion:

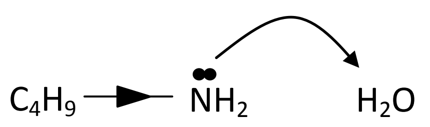
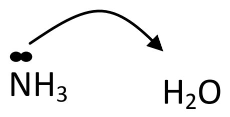
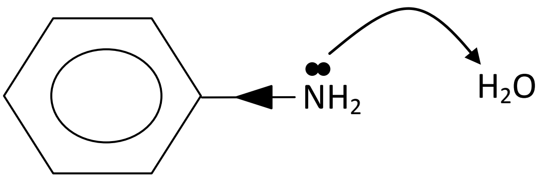
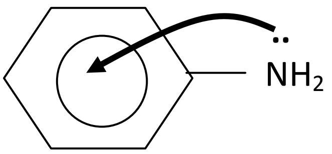


The inductive effect:

- The basic properties of phenylamine are less than that of ammonia.
- The basic properties of amines are greater than that of ammonia.
- This can be explained by the inductive effect:

pH 8	**Phenylamine**	
pH 10	**Ammonia**	NH_3
pH 12	**Butylamine**	$CH_3CH_2CH_2CH_2NH_2$

- Remember a base is a proton acceptor and the proton is accepted using the lone pair of electrons on the nitrogen.
- Groups attached to the functional group can have an effect on how available the lone pair of electrons for accepting a proton:

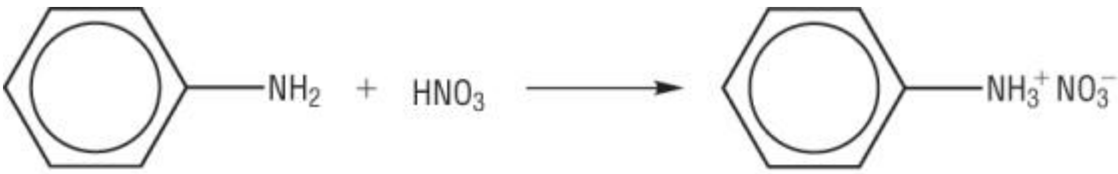
	Alkyl groups have a **positive inductive** effect. This means that they give a small push of electrons towards the neighboring atom (the nitrogen). This gives an increased electrons charge density meaning a better chance of the lone pair being used to accept a proton – **Stronger base**
	Ammonia has no inductive effect as there is nothing attached to the functional group.
 	Benzene rings have a **negative inductive** effect. This means that the benzene ring has a small pull of electrons away from the neighboring atom (the nitrogen). This gives a lower electron charge density making it harder for the lone pair of electrons to be used to accept a proton – **Weaker base** This would be further compounded by the lone pair of electrons on the nitrogen being able to delocalize into the benzene ring.

Base reactions of amines:

- Just as ammonia forms salts with acids so do amines:

Base	**+**	**Acid**	**→**	**Salt**
$NH_{3(aq)}$	+	$HCl_{(aq)}$	→	$NH_4^+Cl^-_{(aq)}$
$C_4H_9NH_{2(aq)}$	+	$HCl_{(aq)}$	→	$C_4H_9NH_3^+Cl^-_{(aq)}$
$C_6H_5NH_{2(aq)}$	+	$HCl_{(aq)}$	→	$C_6H_5NH_3^+Cl^-_{(aq)}$

- Phenylamine reacts with nitric acid:



Phenylammonium nitrate

Questions 1 - 2 P37

<u>Amines and their reactions</u>

Preparation of primary aliphatic amines:

- These are made by warming halogenoalkanes with excess ammonia:

$$CH_3CH_2CH_2Cl \quad + \quad NH_3 \quad \rightarrow \quad CH_3CH_2CH_2NH_2 \quad + \quad HCl$$

- The excess ammonia reacts with the HCl formed:

$$NH_3 \quad + \quad HCl \quad \rightarrow \quad NH_4Cl$$

Preparation of secondary / tertiary aliphatic amines:

- Propylamine can react further (like the ammonia) with more chloropropane:

$CH_3CH_2CH_2Cl$ + $CH_3CH_2CH_2NH_2$ → $(CH_3CH_2CH_2)_2NH$ + HCl

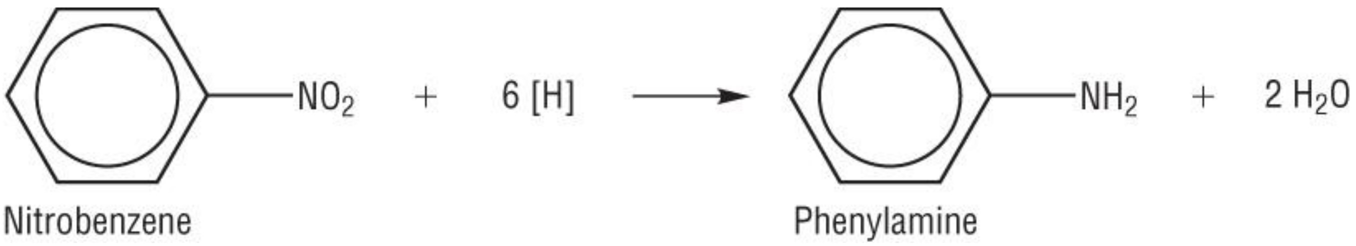
- And dipropylamine can react even further again:

$CH_3CH_2CH_2Cl$ + $(CH_3CH_2CH_2)_2NH$ → $(CH_3CH_2CH_2)_3N$ + HCl

- **Multiple substitution is avoided by having ammonia in excess. This minimises the 'chance' of further substitution.**

Preparation of aromatic amines:

- Nitrobenzene (and other nitroarenes) can be reduced using a **mixture of tin and concentrated hydrochloric acid:**



- The excess HCl is neutralised at the end of the reaction.
- This is an important reaction as it is used in the manufacture of dyes.

Synthesis of dyes from phenylamine:

- There are 2 stages in this process:

1) Diazotisation
2) Coupling reactions

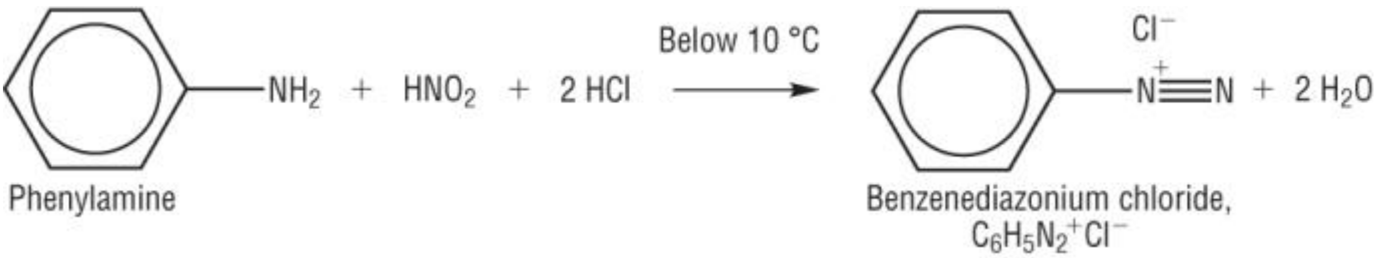
1) Diazotisation:

a) Making Nitrous acid:

- Nitrous acid is unstable so must be made when needed.

$NaNO_2$ + HCl → HNO_2
Sodium nitrite Hydrochloric acid **Nitrous acid**

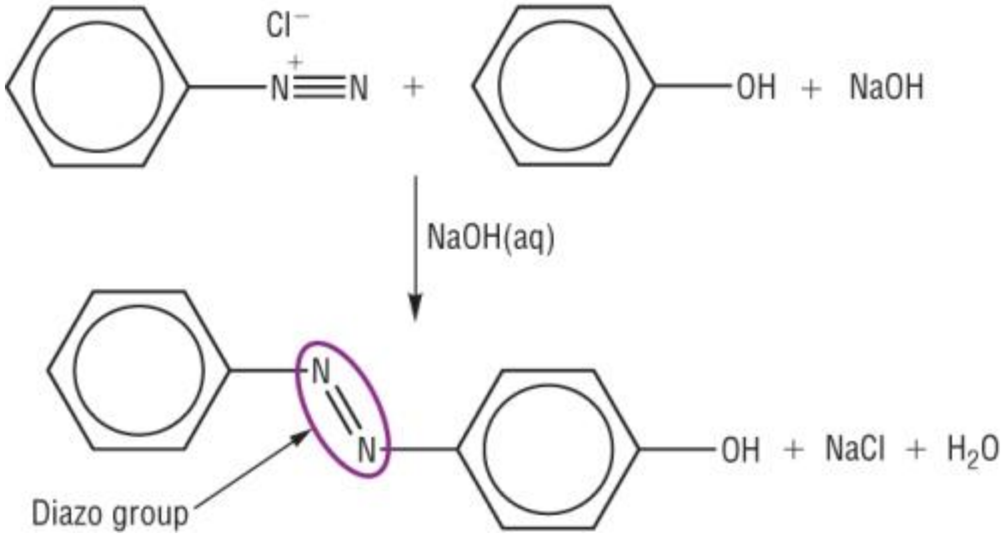
b) Diazotisation reaction:



- The diazonium ion, N_2^+ is unstable and decomposes releasing nitrogen, this is why it needs to be kept below 10°C.

- The benzene ring in benzenediazonium salts allow the π electrons from the diazonium functional group to be delocalised over the benzene ring.
- This stabilises the benzenediazonium salts enough to be used at low temperatures.

2) Coupling reaction:

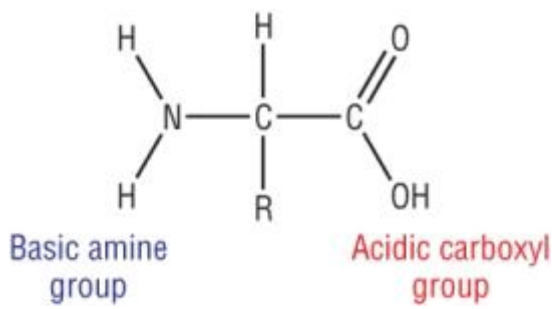


- The benzenediazonium salt is reacted with phenol under alkaline conditions.
- As the 2 molecules are now '**coupled**' together we call it a **coupling** reaction.
- The Azo dye is now stable as there is extensive delocalisation over both arenas via the azo group, -N=N-.
- An everyday use of azo dyes is methyl orange indicator.

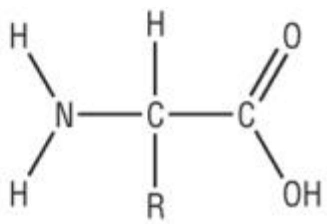
Questions 1 - 3 P39 Qu 9 P41 Qu 2a (ii) (iii) P42 Qu 11-13 P44,45

<u>**Amino acids**</u>

- Have an **NH_2**, amine and a **COOH**, carboxylic acid group:

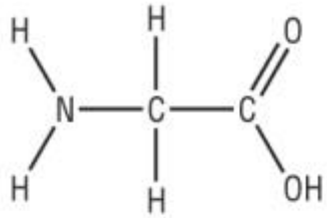


- They are the building blocks for proteins which are held together by peptide links.
- The body has 20 different amino acids which, as proteins can be enzymes, hormones, antibodies.
- These proteins are responsible for body functions such as carrying oxygen in the blood, formation of bones etc.
- The 20 Naturally occurring amino acids have the general formula of:



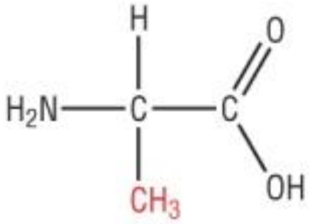
- This arrangement is called α amino acids due to its optical isomerism (covered later)

- The R group can contain OH, SH, COOH or NH_2 group.
- Glycine is the simplest amino acid which means it will not contain an R group:

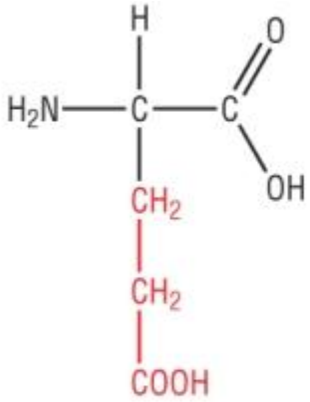


Glycine

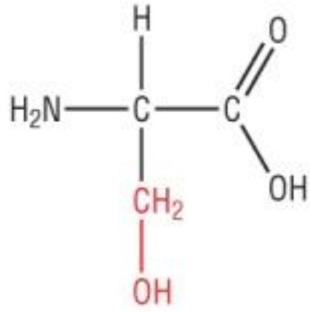
- Other examples of α amino acids are shown below with different R groups attached:



2-aminopropanoic acid (alanine)



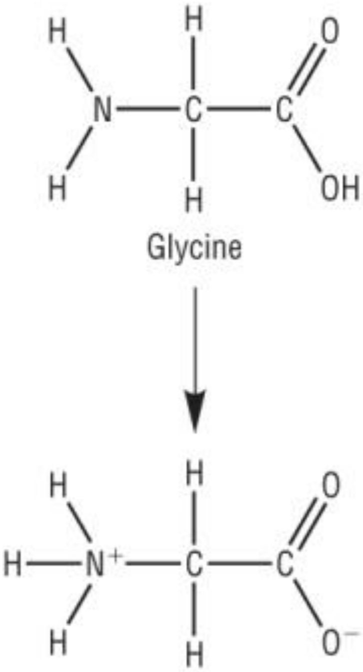
2-aminopentanedioic acid (glutamic acid)



2-amino-3-hydroxypropanoic acid (serine)

Zwitterion and the isoelectric point:

- Amino acids contain an acidic carboxylic acid group and a basic amine group.
- These can interact with each other to form a **zwitterion**:



Zwitterion

- A proton is transferred from the **COOH** to the $\mathbf{NH_2}$
- The **zwitterion** has no overall charge as the $\mathbf{COO^-}$ cancels out the $\mathbf{NH_3^+}$
- The **isoelectric point** is the pH at which there is no 'net' electric charge.
- This **+ / -** charge increases the intermolecular forces between amino acids considerably.
- They are often described as having **unusually high melting points**.
- You may expect this to be pH7. In actual fact is is usually around the **pH6** region.
- This is due to the fact that the **COOH** is actually slightly more acidic than the $\mathbf{NH_2}$ is basic.
- The rest of the molecule also has an influence on how acidic and how basic the **COOH** and $\mathbf{NH_2}$ are which means that every amino acid will have a slightly different **isoelectric point**.

Comparison of melting points:

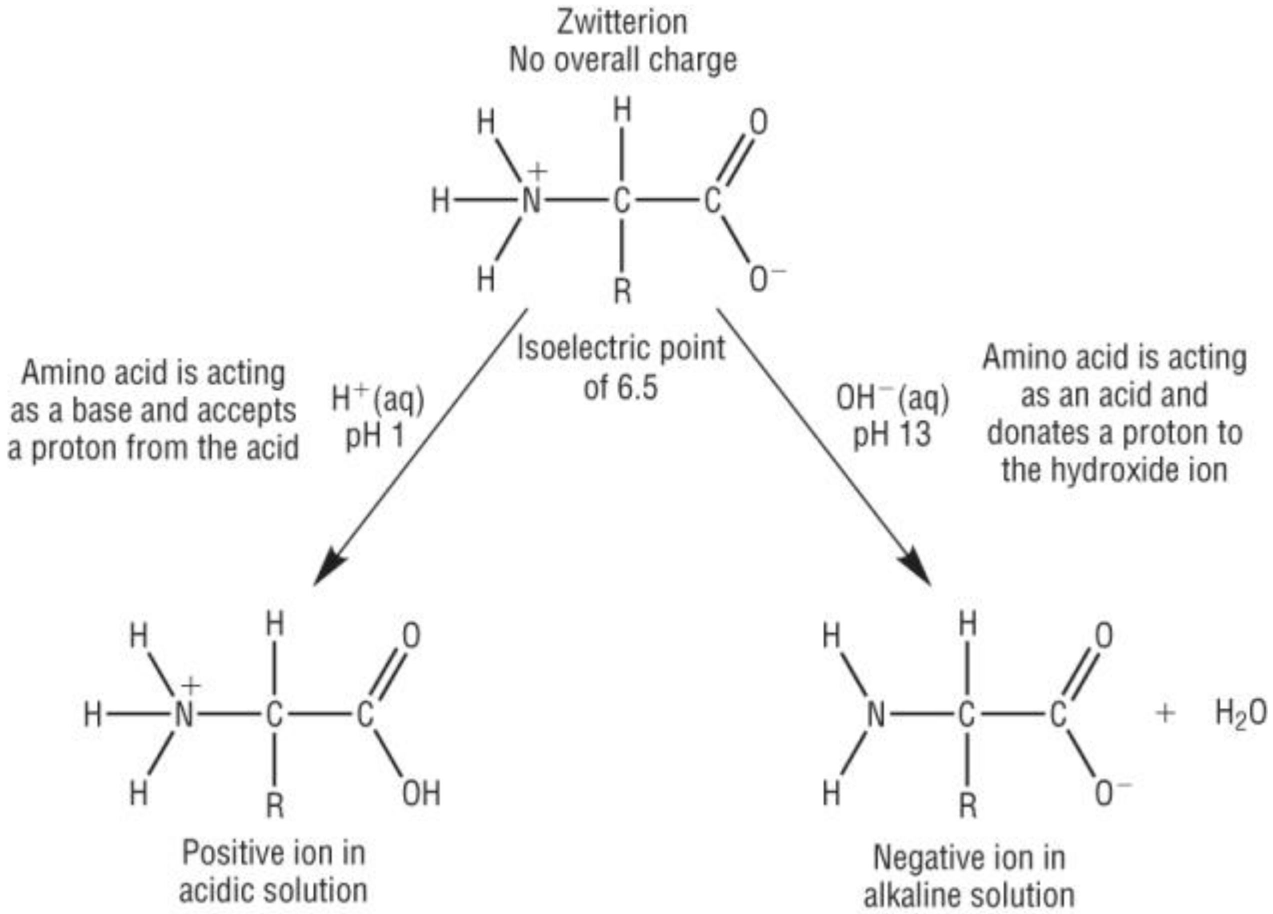
Molecule		Melting point
Glycine,	NH_2CH_2COOH	262°C
Propanoic acid	CH_3CH_2COOH	-21°C

Acid and base properties of amino acids:

- Amino acids are **amphoteric**.
- This means that they will react with both:

Acids: Due to the basic **NH_2** present.
Alkalis: Due to the acidic **COOH** present.

pH < Isoelectric point: **pH > Isoelectric point:**



- **pH < Isoelectric point:**
- **In acidic conditions there is an abundance of H^+ions.**
- **The amino acid acts as a base and accepts as many H^+ions as possible.**

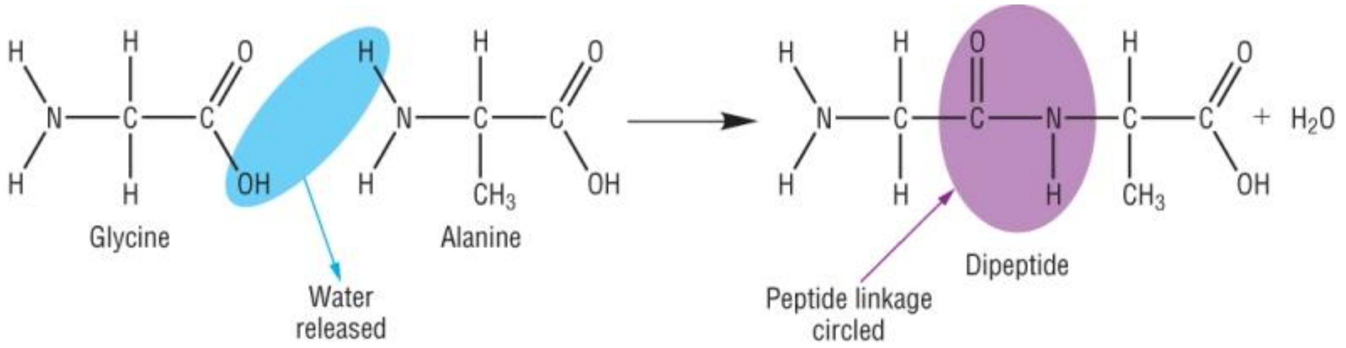
- **pH > Isoelectric point:**
- **In Alkaline conditions there is a defficit of H^+ions.**
- **The amino acid acts as an acid and donates as many H^+ions as possible.**

Qu 1 - 3 P51

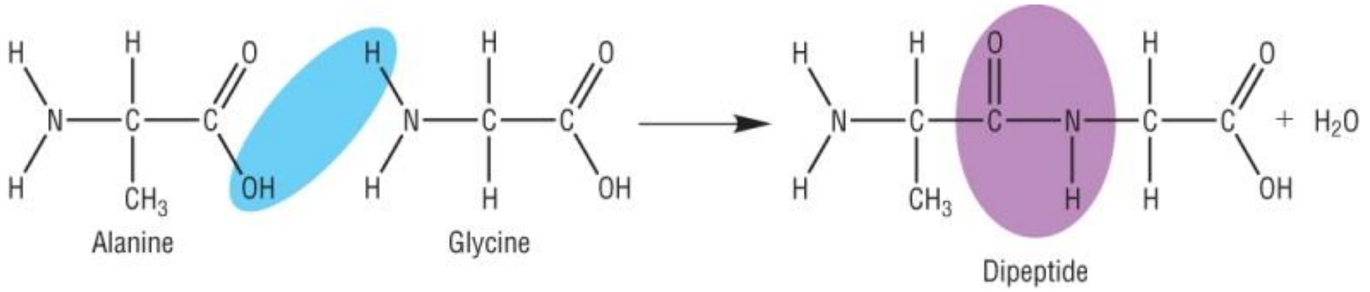
<u>**Polypeptides and proteins**</u>

Amino acids and condensation reactions:

- When 2 amino acids join together we call it a dipeptide.
- When 3 amino acids join together we call it a tripeptide.
- When many join together we call it a polypeptide.
- Polypeptides are synthetic.
- Proteins are natural and are usually larger than polypeptides.
- The term ‘Peptide linkage’ (or bond) is the name for the amide link which in poly peptides or proteins.
- The reaction is called a condensation reaction as water is given off:

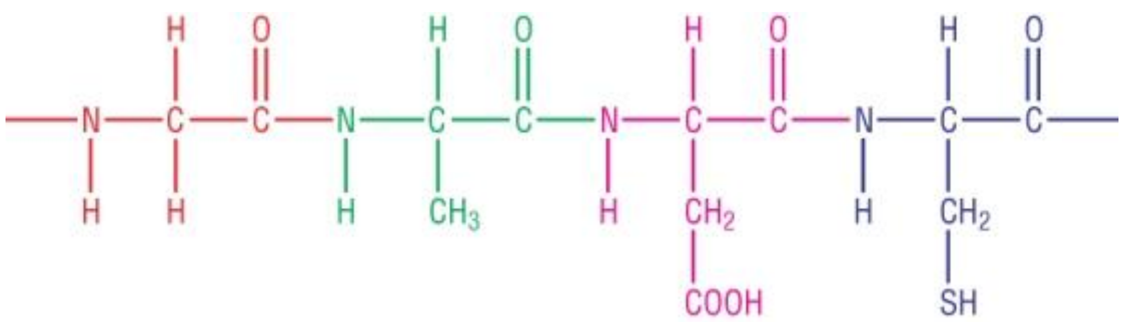


- The functional group (in purple) is an amide group (CONH)
- A different dipeptide can be made by joining them the other way round:



Forming polypeptides and proteins:

- This is a long chain of amino acids joined by peptide linkages:



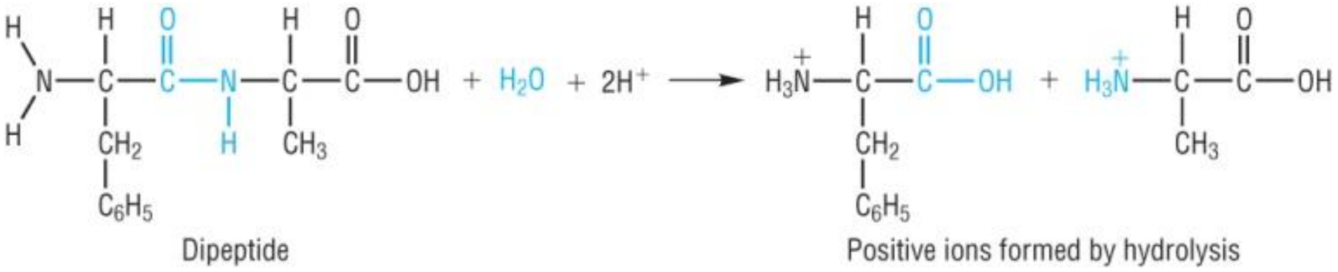
- Each linkage forms a molecules of water.
- A polypeptide generally has >50 amino acids.

Hydrolysis of polypeptides and proteins:

- Polypeptides and proteins can be hydrolysed back into their constituent amino acids.
- This is the reverse of the reaction above.
- This is done by using an acid or alkaline catalyst. (like ester hydrolysis).

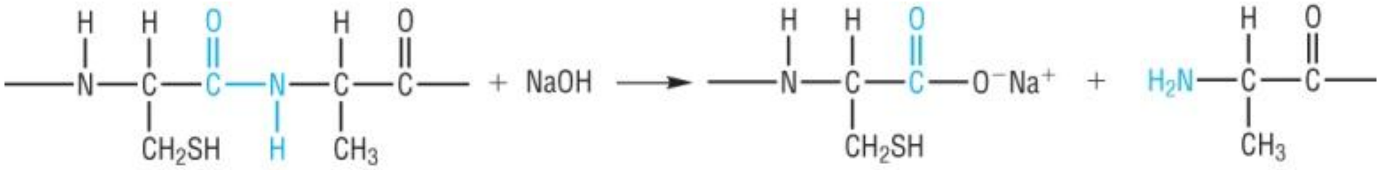
Acid hydrolysis:

- **Heat under reflux with 6M HCl fro 24hrs**
- As this is in acidic conditions, the acid amino acid ion is formed:



Alkali hydrolysis:

- **Solution of aq NaOH above 100^{o}C**
- As this is in alkaline conditions, the alkali amino acid ion (salt) is formed:



Qu 1 - 3 P51

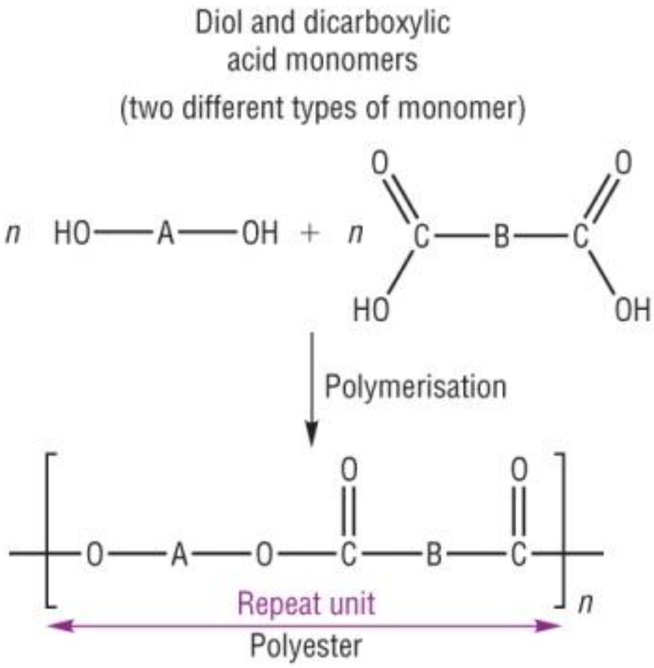
Condensation polymerisation: 1) Polyesters

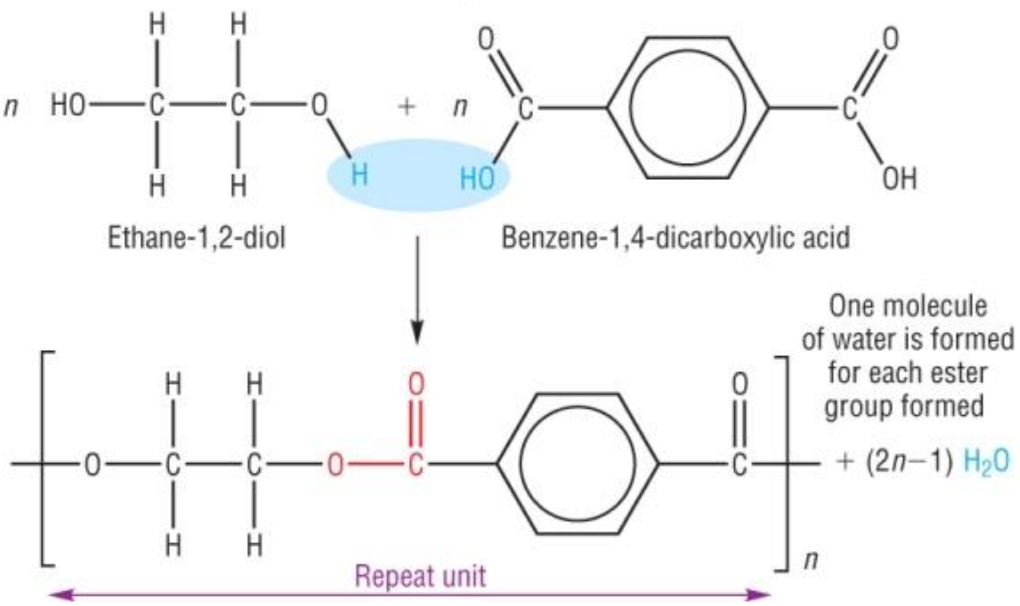
- This is the joining of s monomers while eliminating a small molecule - H_2O or HCl
- The functional group on one monomer joins with a different functional group in another molecule.
- There are 2 types of condensation polymerisations covered
- **Polyesters - from alcohols and carboxylic acids**
- **Polyamides - from amines and carboxylic acids**

1) polyesters:

- A polyester is made by condensing an alcohol and carboxylic acid.
- The joining link is an **ester** functional group, hence poly**ester**.
- A polyester is can be made in one of 2 ways:

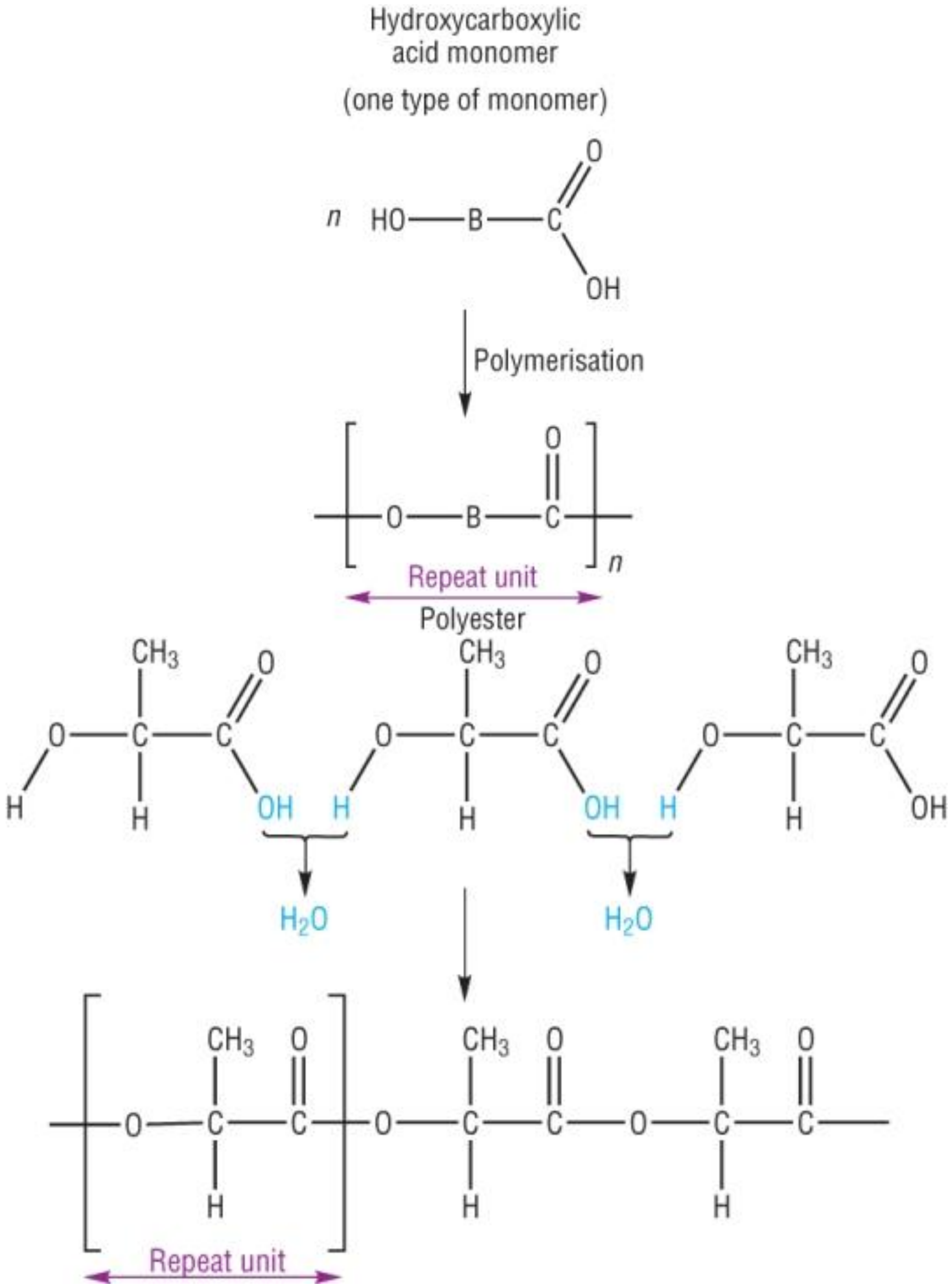
a) 2 monomers: Diol and Dicarboxylic acids-





- Terylene is made from the reaction between the monomers ethane-1,2-diol and benzene-1,4-dicarboxylic acid.
- It is described as a **condensation reaction** as **water** is eliminated as the **ester link** is formed.
- Used in the manufacture of carpets.

b) 1 monomer: Hydroxycarboxylic acid

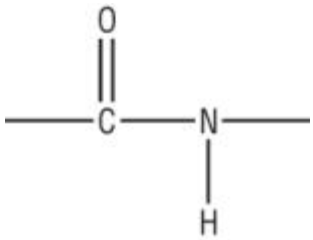


- Poly(lactic acid), PLA is made from the reaction between the same monomer containing an **OH** and a **COOH** group.
- It is described as a **condensation reaction** as **water** is eliminated as the **ester link** is formed.

Qu 1-3 P55

Condensation polymerisation: 2) Polyamides:

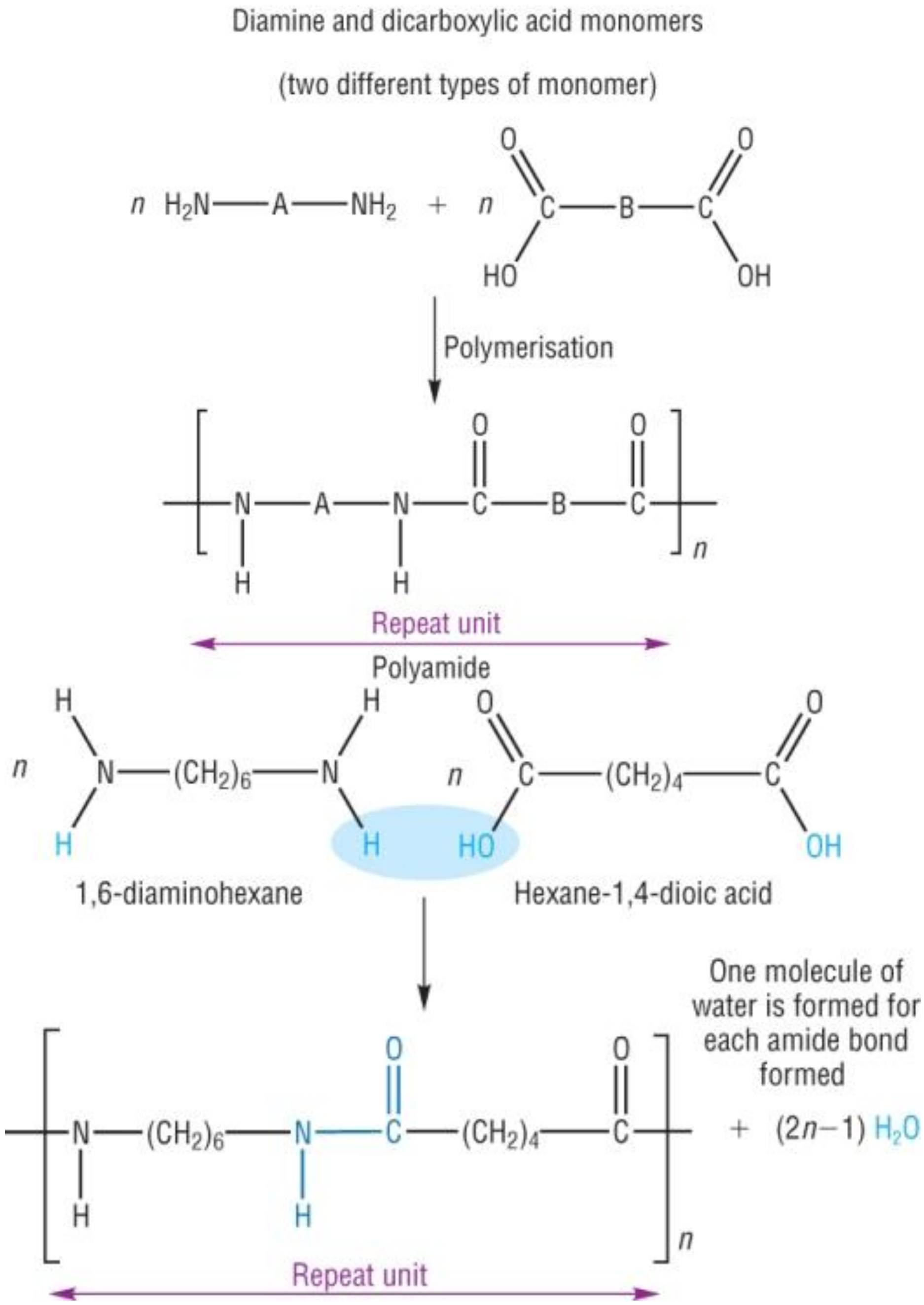
- **Polyamides** are made by an **amine / carboxylic acid** condensation reaction.
- The resulting link is an **amide**:



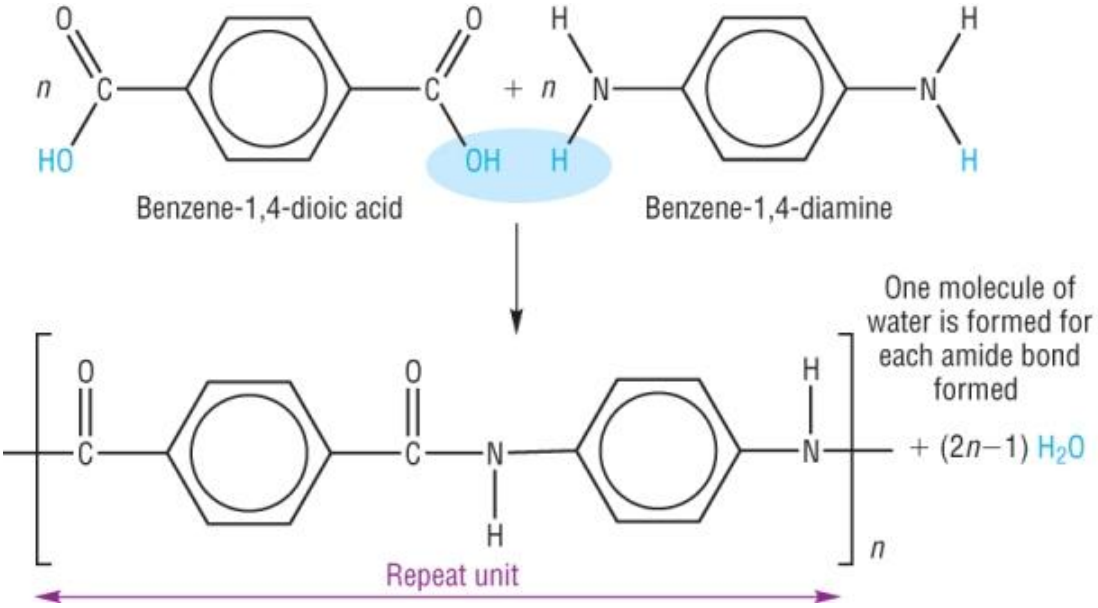
- A polyester is can be made in one of 2 ways:

a) 2 monomers: Diamine and Dicarboxylic acids-

- Formed from the reaction between the 2 monomers containing 2 **NH_2** and 2 **COOH** groups.

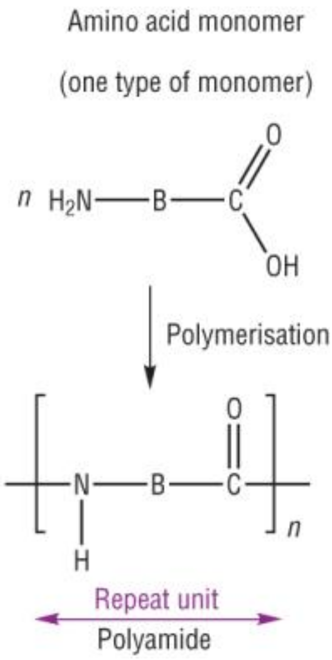


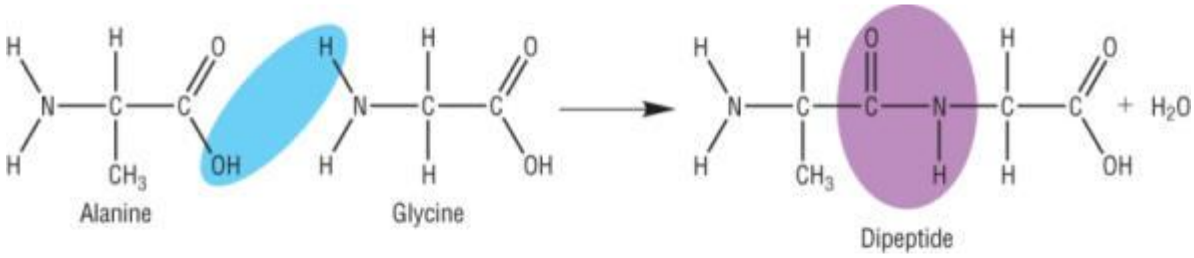
- Nylon is made from the reaction between the monomers 1,6-diaminohexanel and hexane-1,4-dioic acid.
- It is described as a **condensation reaction** as **water** is eliminated as the **amide link** is formed.
- Used in the manufacture of clothing.
- Another is **kevlar** - very strong polymer used in fire and bullet proof vest and crash helmets:



b) 1 monomer: Hydroxycarboxylic acid

- A monomer with an amine group at one end and a carboxylic acid group at the other.





Polypeptides and proteins - from the reaction between the same monomer containing an **NH_2** and a **COOH** group.

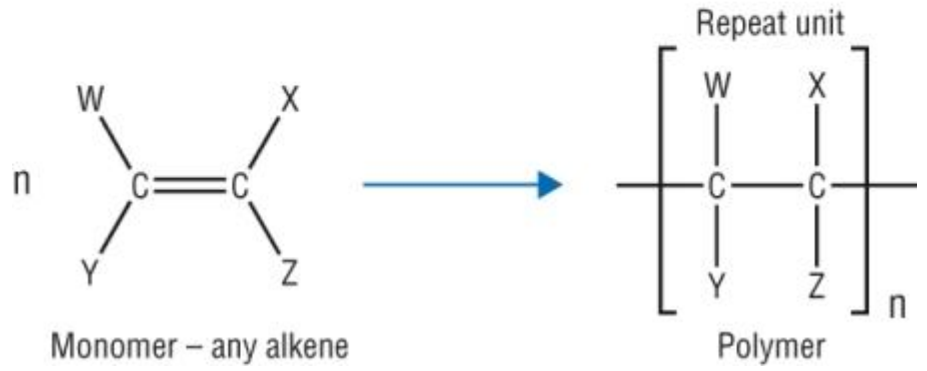
- It is described as a **condensation reaction** as **water** is eliminated as the **amide link** is formed.

Qu 1-3 P57

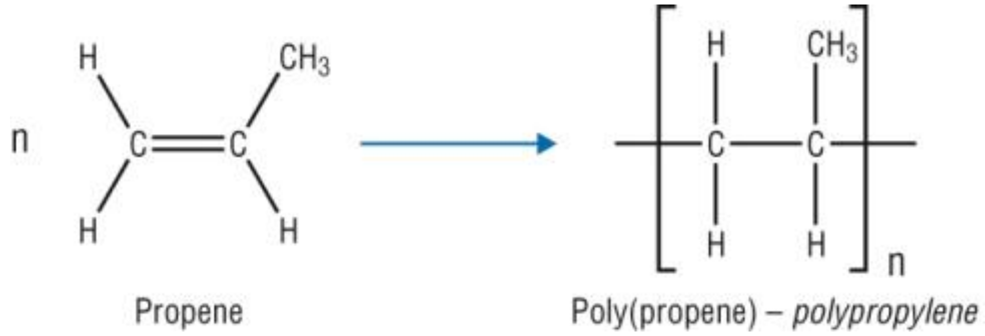
Addition and condensation polymerisation

Addition polymers:

- This was covered in AS under the alkenes chapter:



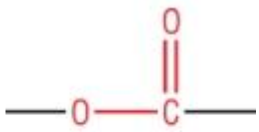
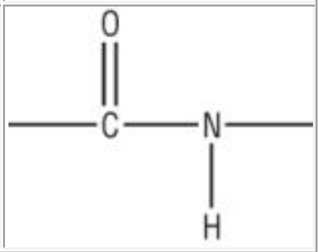
- These are made from one monomer only - containing a C=C
- Only one product is formed.
- Using different alkene molecules, different addition polymers can be made:



Condensation polymerisation:

- These polymers are when monomers are joined with the elimination of a small molecule, H_2O or HCl.
- The monomers must have 2 functional groups.

Comparison of addition and condensation polymers:

	Addition polymerisation	Condensation polymerisation	
		Polyester	Polyamide
Functional groups	**C=C**	**COOH / OH**	**COOH / NH_2**
No monomers	**1**	**1 or 2**	**1 or 2**
Products	**poly(alkene)**	**polyester + water**	**polyamide + water**
linkage	**C-C**		

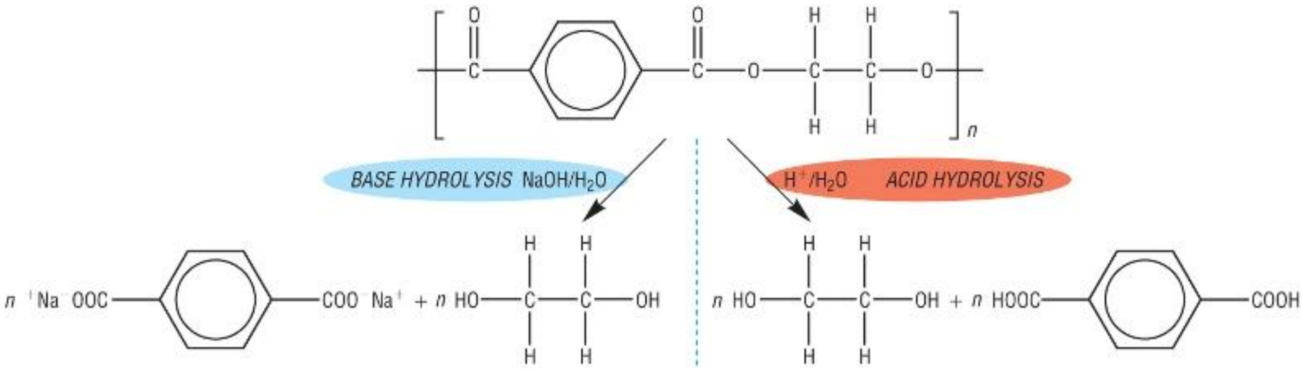
Qu 1,2 P59

<u>Breaking down condensation polymers</u>

- If condensation **polymerisation eliminates water** then they can be **hydrolysed with the addition of water** (acid / base)
- 2 condensation polymers have been covered and both can be hydrolysed:

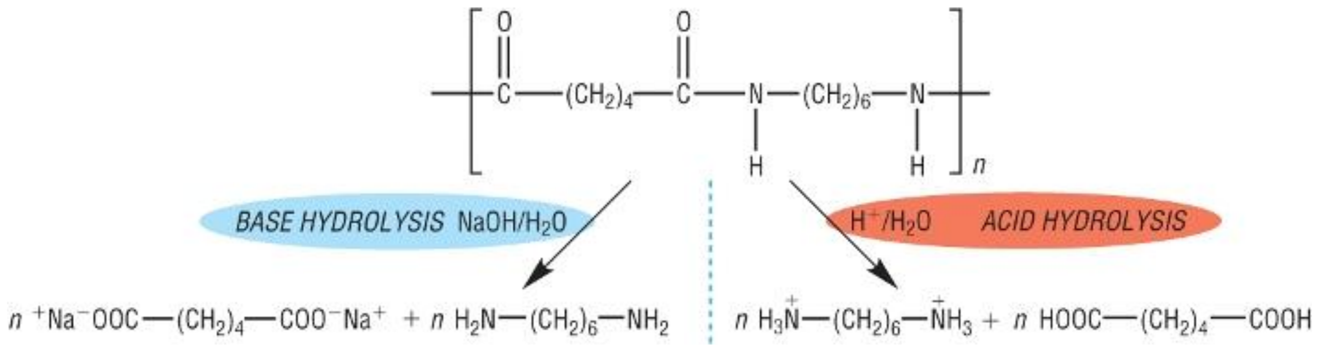
1) Hydrolysis of polyesters:

- In carbonyl compounds we saw that esters can be hydrolysed in acidic or basic conditions.
- This gave the corresponding alcohol and carboxylic acid (or salt of acid - base)
- **Polyesters** can be hydrolysed in exactly the same way with **hot aqueous acid / aqueous alkali**.
- The monomers making up the polymer are produced (or salt if base hydrolysis used):



2) Hydrolysis of polyamides:

- **Polyesters** can also be hydrolysed with **hot aqueous acid / aqueous alkali**.
- The monomers making up the polymer are produced - ammonium in acidic conditions - carboxylate salts in basic:



Degradable polymers:

- Most plastic packaging is addition polymers which will not degrade in landfill sites.
- Environmental demand has produced biodegradable plastics.
- These have chemical bonds that will hydrolyse similar to polyesters and polyamides.
- A polymer based on tapiocha starch will decompose in 28 days when buried.

Photodegradable polymers:

- These become weak and brittle when exposed to light.
- The polymers are blended with light sensitive catalysts which will catalyse the decomposition of the polymer.
- Another way is to encorperate C=O bonds within the polymer structure.
- These absorb UV light and break.
- Photodegradable plastics break to form waxy shorter hydrocarbon molecules before bacteria breaks them further into CO_2 and H_2O.

Qu 1-3 P61
Qu 9 P41 Qu 2a (ii) (iii) P42 Qu 11-13 P44,45
Qu 1,2,4,5,6 P 69 / Qu 1a,2,3,4,5,6,9,10,11,12 P70-73