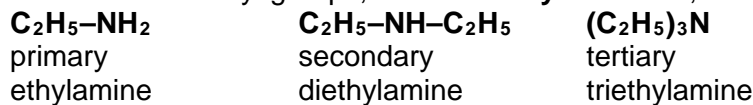


Nitrogen Compounds and Polymerisation

Amines

A **primary amine** is one in which a single alkyl group is attached to the nitrogen, e.g. RNH_2 .

A **secondary amine** has two alkyl groups, and a **tertiary** one three, directly attached to the nitrogen:



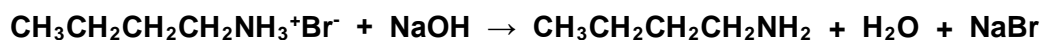
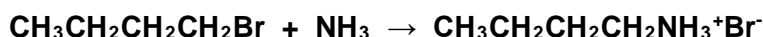
Note - This is a different usage from that employed for alcohols and halogenoalkanes, where it is the number of alkyl groups directly attached to the *carbon* atom bonded to O or Cl which determines primary, secondary or tertiary.

An **aryl amine** has the amine group directly attached to the benzene ring.
e.g. phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$.

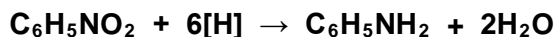
Amine Preparation

Aliphatic (non aryl) amines are produced by heating the appropriate halogenoalkane in a sealed tube with excess ammonia dissolved in ethanol. [See Unit 2].

This initially forms the salt of the amine and the amine can be obtained by adding sodium hydroxide.



Aromatic amines are produced by the reduction of a nitrobenzene. This is carried out by adding concentrated hydrochloric acid to a mixture of nitrobenzene and tin and heating the mixture under reflux.

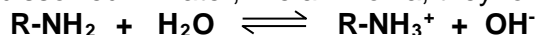


Again in this reaction the amine is actually formed as the chloride salt, so sodium hydroxide has to be added to release the amine which is then extracted from the mixture by steam distillation.

Properties of amines

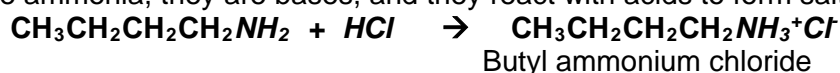
Since amines contain hydrogen atom directly bonded to a nitrogen atom, they can form hydrogen bonds. This enables amines to interact with water molecules and so amines with short carbon chains are miscible with water.

When dissolved in water, like ammonia, they form an alkaline solution.



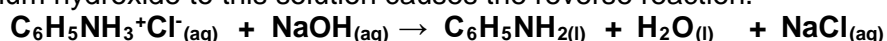
As the carbon chain length increases, the amines become less soluble in water. Phenylamine is only slightly soluble in water because of the large carbon group.

Also like ammonia, they are bases, and they react with acids to form salts.



This ability to react with acids to form salts enables phenylamine to dissolve in a concentrated hydrochloric acid. $\text{C}_6\text{H}_5\text{NH}_{2(l)} + \text{HCl}_{(aq)} \rightarrow \text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-_{(aq)}$

Addition of sodium hydroxide to this solution causes the reverse reaction.

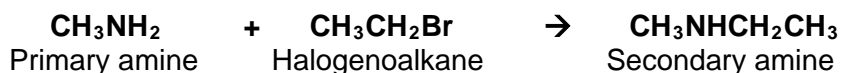


Reaction with halogenoalkanes

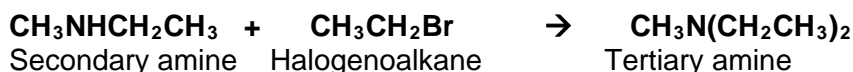
The lone pair on the nitrogen will attack areas of positive charge.

Amines are therefore nucleophiles and will attack the δ^+ carbon in halogenoalkanes.

Primary amines react with halogenoalkanes to form secondary amines and then tertiary amines.

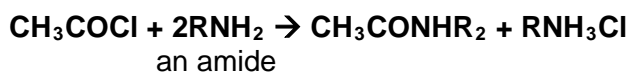


The nitrogen atom in a secondary amine still has a lone pair that can attack the halogenoalkane.

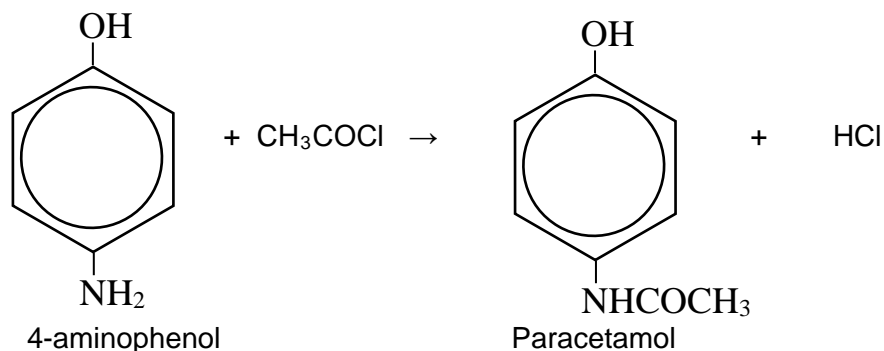
**Reaction with acid chlorides**

The lone pair on the nitrogen will attack areas of positive charge. Amines are therefore nucleophiles.

Amines react with acyl chlorides to form **acid amides**.



An example of this reaction is the formation of paracetamol.

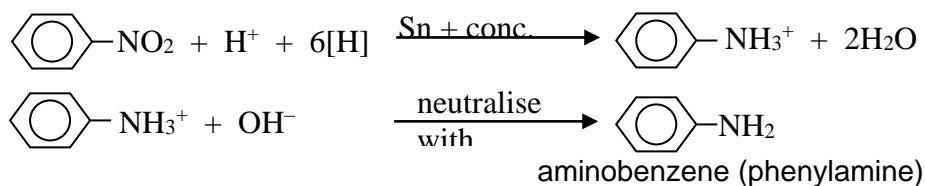
**Reaction with ligands to form complex ions**

The lone pair of electrons on the nitrogen of the amine means that it can form complex ions.

An example of the such a complex is the one formed by the bidentate ligand 1,2-diaminoethane.

Formation of Azo dyes

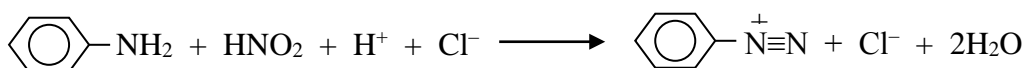
Nitrobenzene is heated under reflux with tin in conc. HCl as a reducing agent.

**Reactions of phenylamine.**

Nitrous acid, HNO_2 , is unstable, so hydrochloric acid and sodium nitrite are used to make it:

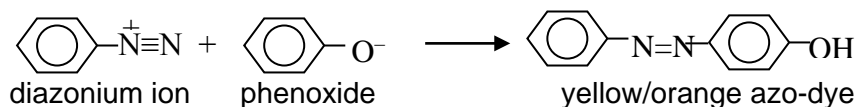


Phenylamine is dissolved in moderately concentrated hydrochloric acid, and cooled to about 5°C . A solution of sodium nitrite, NaNO_2 , is also cooled to 5°C , and added slowly to the phenylamine and acid, cooling to keep the temperature below 10°C . The phenylamine reacts to form benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$:



Benzenediazonium chloride is unstable, and is used, in solution, immediately after it has been prepared – for example, to make an azo-dye.

When cold benzenediazonium chloride solution is added dropwise to a cold solution of phenol in aqueous sodium hydroxide, a yellow/orange precipitate of an azo-dye is obtained:

**Amides**

Amides are unreactive carboxylic acid derivatives.

Amides have the general structure: R-CO-NH_2

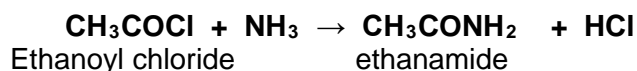
CH_3CONH_2
ethanamide

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$
butanamide

Amide preparation

Amides can be prepared by reacting an acyl chloride with concentrated ammonia.

The reaction occurs vigorously at room temperature forming fumes of HCl and solid amide.

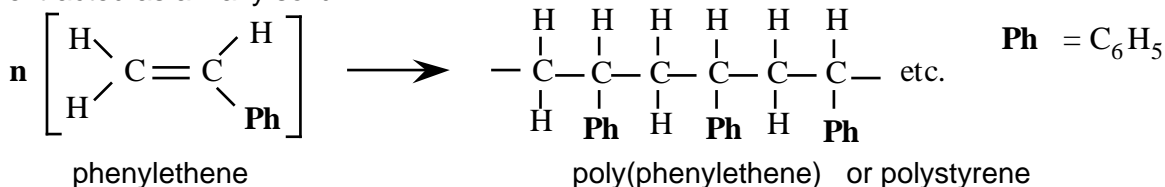


Polymerisation

Addition polymerisation

The process of **polymerisation** is the building up of long-chain molecules from small molecules, which are called the **monomers**. In **addition polymerisation** there are no other products, while in **condensation polymerisation** a small molecule such as water or HCl is ejected every time a link is made. Addition polymers are normally made from compounds containing carbon-carbon double bonds, so that the process is essentially similar to the formation of poly(ethene).

Phenylethene (styrene) can be heated in an inert solvent (paraffin) under reflux, with a small amount of a peroxide compound as initiator. It gradually forms the polymer, which can be extracted as a waxy solid:

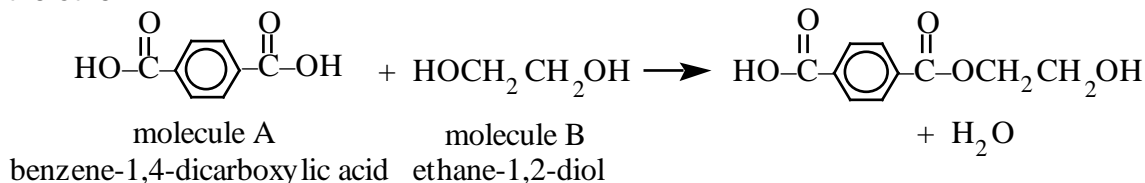


Condensation polymerisation

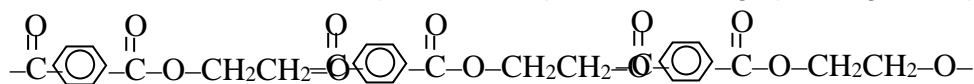
As explained above, **condensation polymerisation** is the process by which long-chain molecules are formed by reaction between bifunctional monomer molecules, with the loss of one small molecule (such as water or HCl) for each link which is formed. Normally there are two different monomer molecules, as in the case of the diacid and diol in (a) below, but sometimes both the types of reactive group may be contained within the same molecule.

(a) Polyesters

If molecule A contains two carboxylic acid groups, and molecule B contains two alcohol groups, when they react to form an ester the product will have an acid group at one end and an alcohol at the other:



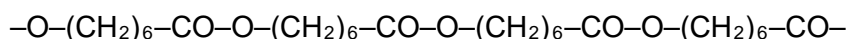
The left hand carboxyl can then react with the OH of another molecule B, while the righthand OH can react with another molecule A. This process is repeated, building up a long chain polymer:



Note that each time an ester group is formed a water molecule is lost. This type of polymer is known as a polyester, and this particular example, made from benzene-1,4-dicarboxylic acid (A) and ethane-1,2-diol (B), is marketed by ICI as Terylene[®].

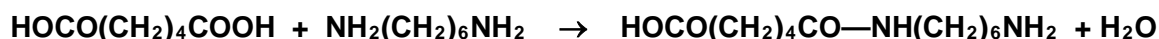
Polyesters are suitable for fibres, and are widely used for modern crease-resistant synthetic materials, for ropes and sails. Since they contain ester links, they will be slowly hydrolysed by acids, and more rapidly by alkalis.

If both the alcohol and the acid groups are in the same monomer, it may polymerise with itself. For example, the molecule HO-(CH₂)₆-COOH might form:



(b) Polyamides

When a compound containing two acid groups, e.g. $\text{HOCO}(\text{CH}_2)_4\text{COOH}$, reacts with another compound containing two amine groups, e.g. $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$, an amide is formed with loss of H_2O :



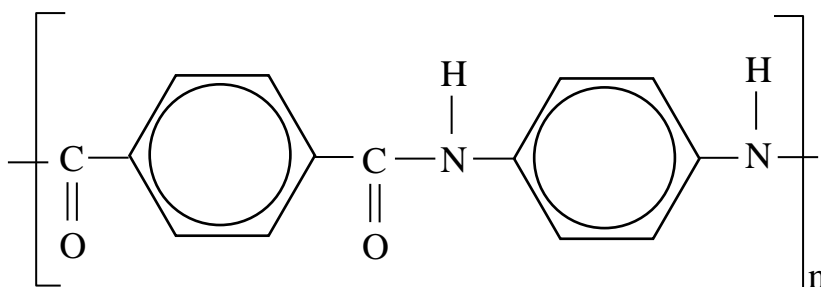
The amide produced still has reactive groups at either end, and can react with another diamine on the left, and a diacid on the right, to form a chain four units long. The process is repeated giving the polymer called **nylon-6,6** (because there are 6 carbon atoms in each monomer unit):



The **repeat unit** here is: $\text{—CO}(\text{CH}_2)_4\text{CO—NH}(\text{CH}_2)_6\text{NH—}$

The product, a polyamide, is useful for making fibres, since the long chains can be drawn out into filaments, which causes them to line up, and is also a hard-wearing solid polymer (e.g. the cases of d-i-y tools, like electric drills, are made of nylon, as are curtain hooks).

Kevlar® is made from benzene-1,4-diamine and benzene-1,4-dicarboxylic acid, and the repeat unit is:



Kevlar is an extremely tough fibre, and is used in e.g. bullet-proof vests.

For a cable of a particular diameter Kevlar has the same strength as steel, but is five times lighter. It is used in bullet-resistant clothing and in aircraft wings. It is used to some extent in tyres for HGVs where it can make the tyre 9kg lighter. Introduction for this purpose has been slow as tyre manufacturers have invested heavily in the use of steel for reinforcing tyres.

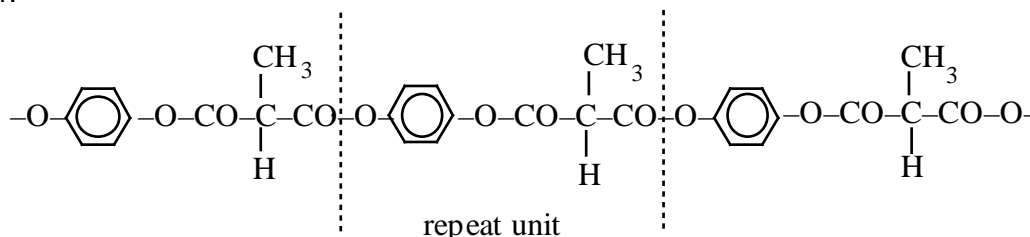
Drawing polymers and finding repeat units

You need to be able to predict the repeat unit of a polymer from a given set of monomers, or to be able to identify the monomers from a given length of polymer.

e.g. Draw a section of polymer which might be obtained from the molecules



Answer:



Draw the two repeat unit lines in so that the same groups occur either side, in the same order.

Note that, when an alkene is symmetrical, like $\text{CF}_2=\text{CF}_2$, the minimum needed to specify the polymer chain is $-(\text{CF}_2)_n-$. Arguably, therefore, this is the repeat unit, though some examiners favour showing the monomer unit in the brackets, i.e. $-(\text{CF}_2-\text{CF}_2)_n-$. In the unlikely event of your getting such a simple question, explain the situation and put both down:

e.g. Give the repeat unit from polymerisation of tetrafluoroethene.

Answer: the chain formed is $-(\text{CF}_2-\text{CF}_2)_n-$, though the minimum repeat unit is $-(\text{CF}_2)_n-$

To work out the monomer units from polymer chains:

Does it contain ester ($-\text{CO}_2-$, also written $-\text{O}-\text{CO}-$, or $-\text{COO}-$) groups in the chain? if so, it is a polyester, and each group splits into $-\text{COOH}$ and $\text{HO}-$ when identifying the monomer units.

Does it contain amide ($-\text{CONH}-$) groups in the chain? if so, it is a polyamide, and each group splits into $-\text{COOH}$ and NH_2- when identifying the monomer units.

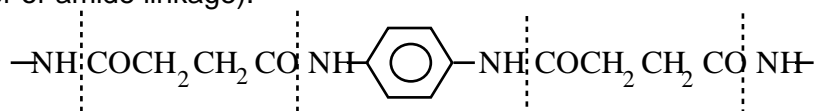
If it contains neither, but has a continuous carbon chain, it is probably an addition polymer, and each pair of C atoms in the chain originally had a double bond between them.

For a polyamide it is best to draw lines between the CO and the NH, and make the CO into COOH, and the NH into NH_2 :

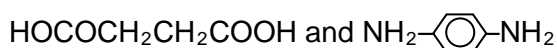
e.g. What are the monomer units of the following polymer?



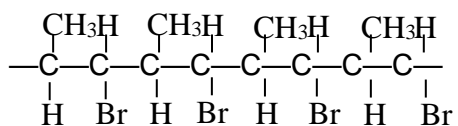
First, sketch in dotted lines to identify the repeat unit(s): make sure they go in sensible positions (i.e. at an ester or amide linkage):



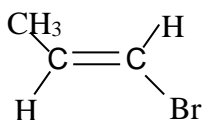
In this case, note that the repeat unit for the polymer contains two of these sections. The monomer units are:



e.g. What is/are the monomer unit(s) of the following polymer?

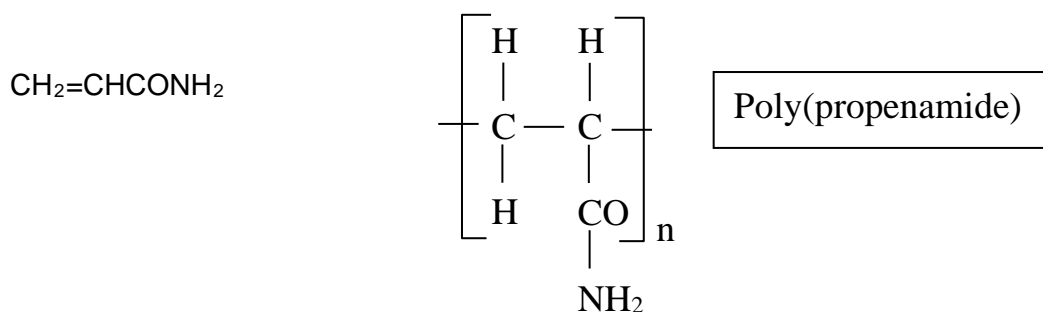
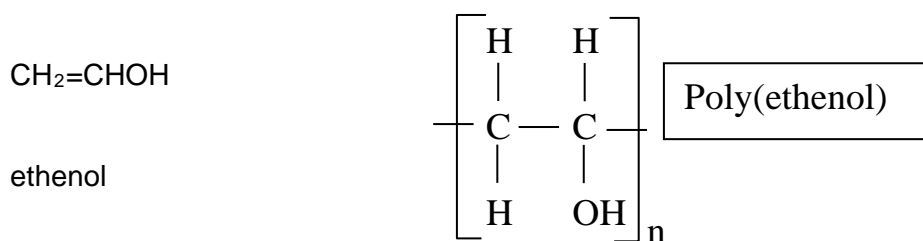


Answer:



Water Attracting Addition Polymers

Addition polymers can be made from ethenol and propenamide.



The alcohol group and the amide groups in these polymers allows them to form hydrogen bonds and so interact with water.

Poly(ethenol) dissolves in water. It is used in dissolving laundry bags. These are used in hospitals where soiled laundry can be moved without being handled directly and when placed in a washing machine the plastic dissolves away.

It is also used for detergent capsules which are placed in washing machines, the plastic dissolves in the water and releases the detergent.

Poly(propenamide) does not dissolve in water, but can absorb water molecules and so becomes softer in water, so it is used to make soft contact lenses.

Amino acids

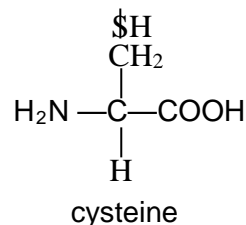
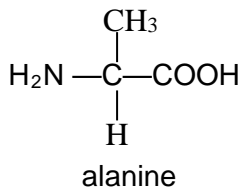
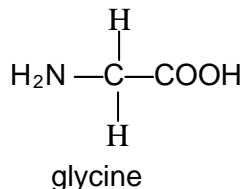
Amino acids contain both an amine (NH_2) and a carboxylic acid group (CO_2H).

Their general formula is $\text{RCH}(\text{NH}_2)\text{COOH}$, where R represents a side-chain (not just an alkyl group).

There are about twenty amino acids which are found in nature, and which combine to make up the proteins found in living organisms.

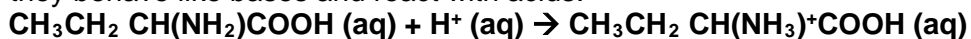
They are all α -amino acids, i.e. the NH_2 and the COOH groups are attached to the same carbon atom.

Three examples are given below:



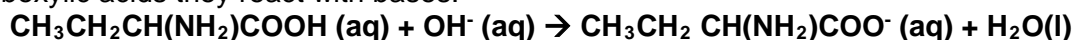
Reaction with acids

Like amines they behave like bases and react with acids.



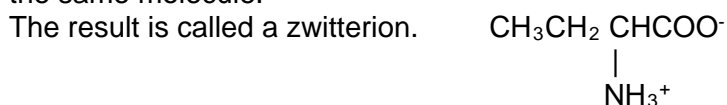
Reaction with bases

Like carboxylic acids they react with bases.



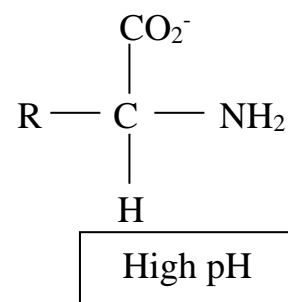
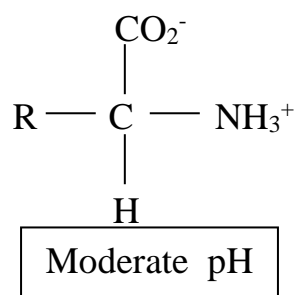
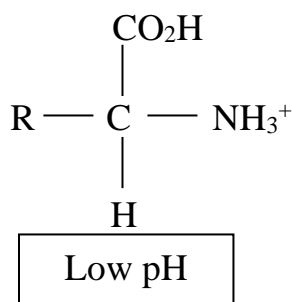
Zwitterion ion structure

In solution the acidic hydrogen of the amino acid is lost and can attach itself to the nitrogen atom in the same molecule.

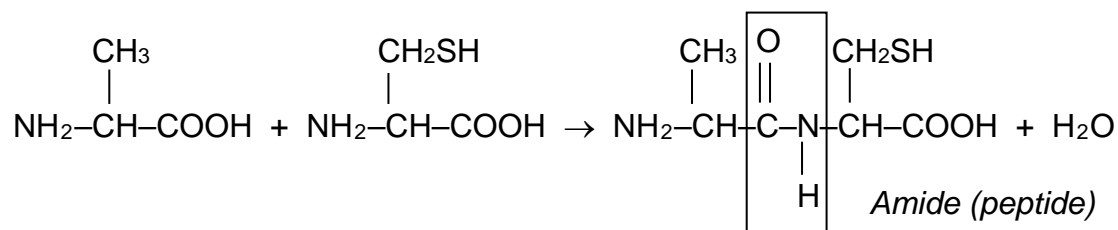


The species formed contains a cation and an anion group. The groups which are ionised will depend upon the pH of the solution in which they are dissolved.

In a solution of low pH, where there is a high concentration of hydrogen ions, the acid group will tend to accept a proton. In a solution of high pH, where there is a low concentration of hydrogen ions, the amine group will tend to release a proton. This means that a particular amino acid can be found in three forms according to the pH.



When two amino acid units join together via an amide link, they form a dipeptide. This is a condensation reaction.



By convention the amino acid with the unbonded NH_2 group is shown on the left.

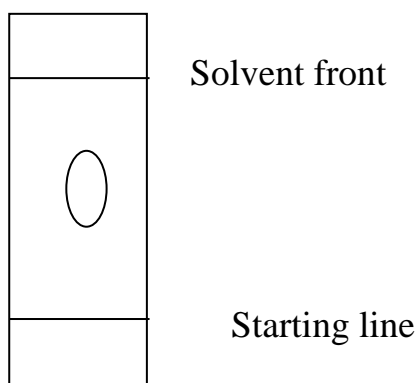
When amino acids are joined in this way the amide link is called a peptide bond. It is possible for many amino acids to join in this way to produce a polypeptide. A protein is made up of one or more polypeptide chains.

The amino acid present in a protein can be investigated by

- first hydrolysing the protein using concentrated hydrochloric acid
- then by separating the various amino acids and identifying them using chromatography.

Since amino acids are colourless, they cannot be seen on the paper or thin layer and so a material is used which reacts with them forming a coloured product; such a material is known as a locating agent.

Once the chromatography has been carried out, the paper will be sprayed with **ninhydrin** and placed in an oven at about 100°C . The amino acids are shown up as purple spots (although turn brown with time). The various amino acids can then be found from their R_f value.



$$R_f = \frac{\text{Distance moved by compound}}{\text{Distance moved by Solvent front}}$$