

# POLYMERS

If two or more molecules of the same compound join the product is known as *polymer*. Examples of naturally occurring macromolecules are proteins and starch. Some times a molecule formed by two smaller ones are called a *dimer*, by three a *trimer*.

Polymers are long chains of repeating structural units, called *monomers*.

**Polymerisation** is the process whereby these small units are joined together to form the polymer.

There are **two types of polymerisation--addition polymerisation and condensation polymerisation.**

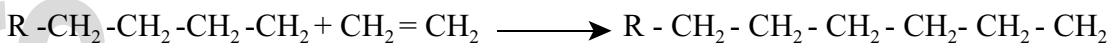
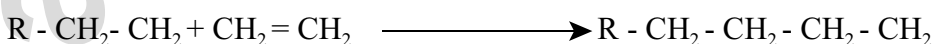
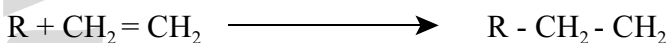
## ADDITION POLYMERIZATION

These are based on **addition reactions** such as those undergone by ethene. A common factor in these reactions is the removal of the double bond. Addition polymerisation involves a series of addition reactions such as those in polyethene, (trade name polythene), under high P and T and in the presence of catalyst, ( $E_A$  for polymerisation is high), ethene molecules join together...

The number of repeating ethene unit(-CH<sub>2</sub> CH<sub>2</sub>-) in the complete molecule is 'n' plus the two end groups. The value of 'n' is usually greater than 100 and often exceeds 1000. Generally some hundreds or even thousands, of units are joined together in a single molecule of the polymer. Polymers are generally used as "**plastic**".

A monomer that contains a double bond often reacts in a process called an **addition reaction.**

Special catalysts start the reaction by forming free radicals, and more free radicals are then produced in a chain reaction. The net result is that the double bond opens ( $\pi$  - bond), and then reforms with two adjacent molecules. This kind of chain reaction depends on the presence of an initiator which is nucleophilic. A peroxide such as dibenzoylperoxide splits up into free radicals. If the free radical is represented by R, then the following steps in the reaction occur...



The reaction may be terminated when (i) two chains add to each other (ii) another free radical adds to chain, or (iii) two free radical, R, recombine.

The length of the chains and the degree to which the chain is branched can be controlled by varying the conditions of the polymerisation and using different catalysts. Thus polyethenes with a variety of different properties can be obtained- they may be viscous liquids or solids of varying degree of hardness. Addition polymers of this type have a wide range of uses.

Some familiar polymers and the monomers from which they are made are listed below...

Name	Monomer	Typical Uses
Polyethylene	$\text{CH}_2 = \text{CH}_2$	Bottles, plastic gloves, food wrap + bags, garment bags
Polypropylene	$\text{CH}_2 = \text{CHCH}_3$	Indoor /outdoor carpeting
Polyvinyl chloride "(PVC)	$\text{CH}_2 = \text{CHCl}$ (chloroethene)	Credit cards, pipes, records
Polystyrene	$\text{CH}_2 = \text{CHC}_6\text{H}_5$	Foamed beads, packaging blocks, ceiling tiles
Teflon (PTFE)	$\text{CF}_2 = \text{CF}_2$ (tetrafluoroethene)	Non stick surfaces

As can be seen from the above table, one of the hydrogen atoms of ethene molecule may be replaced by any of a number of other atoms or groups of atoms - on polymerisation a correspondingly modified product will be obtained.

Polyethene can be manufactured in two forms by the use of different catalyst and different reaction conditions...

i) **Low Density** polyethene

This is cheap to produce and is often used for materials where great strength is not necessary, have more branched chains.

ii) **High Density** polyethene

This is more expensive to produce but, in this form, the polyethene is much stronger. The linear chains are more tightly packed (hence higher density). This form is used for making milk crates, bleach bottles etc.

The importance of these addition polymers often depends upon their lack of chemical reactivity. Where the alkene monomer is of the form  $\text{CH}_2 = \text{CHX}$  ( where X is  $\text{CH}_3$  -,  $\text{C}_2\text{H}_5$ -, Cl-, etc) when polymerisation occurs, the X can be situated:

- i) on the same side of the chain, called **isotactic**
- ii) on the alternate side of the chain, **syndiotactic**
- iii) randomly, **atactic**.

The type of polymer determines the properties. In isotactic polymers the chains can approach more closely. This increases the crystallinity of the polymer.

Polymers can also be classified as **thermosetting** and **thermoplastic**.

All of the *addition polymers are thermoplastic*. This means that on heating they will soften and melt. As a result they can be remoulded or reformed, hence recycled easily.

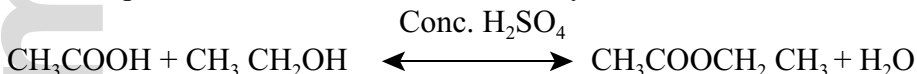
*Thermosetting polymers (i.e. condensation polymers)* do not melt on heating; they are permanently hardened when formed. When heated they decompose and, therefore, cannot be worked in the same way.

# CONDENSATION POLYMERIZATION

A **condensation reaction** is a reaction in which two molecules join together to form a larger molecule with the loss of a smaller molecules such as  $H_2O$ ,  $HCl$ ,  $NH_3$ .

This process is based on nucleophilic attack on a carbonyl group and the subsequent breaking of the  $\pi$  -bond of  $C=O$  to join molecules together. Some condensation polymerisations require two different molecules; reactions that form esters and peptide bonds are examples.

An example of a condensation reaction that you have encountered before is esterification.



Also the reaction of an alkanolic acid with an amine  $\rightarrow$  amide, has been encountered previously. Another example is ...

Each monomer may contain an acid and a basic functional group, as shown above, in which case there is only one reactant.

Another method of producing a condensation polymer involves using one monomer that contains two acid groups and another monomer that contains two basic groups. An equal molar mixture of these two monomers is used to form the polymer...

Starch and cellulose are both condensation polymers of glucose. The different physical and chemical properties are due to the different arrangements of the bonds in these two polymers. Some common condensation polymers and their uses are listed below...

Name	Monomer(s)	Typical Uses
Terylene	Ethanel, 2-dio +dimethylbenzene -1, 4-dicarboxylate	Fibres, fabric
Nylon	1, 6-hexanedicarboxylic acid + 1, 6-diaminohexane	Fibres, fabric
proteins	Amino acids	Biological reactants, food
starch		

Condensation polymerisation often results in cross-linking, under suitable conditions, thus making the product thermosetting. These polymers are fusible at some stage of their production but become permanently hard under the influence of heat and pressure.

Crosslinking alters the physical properties of the polymers. It increases the effective molecular mass of the polymer and affects its solubility. It also prevents the movement of the chain relative to nearby chains. Cross-linking of some kind is essential if the polymer is to act as a fibre.

Natural rubber is a natural addition polymer. It is unsuitable for use in making rubber tyres unless it is treated with sulphur. Treatment with 30% sulphur hardens the rubber by forming cross-links between chains. This process is called **vulcanisation**.

Polyamide chains are cross linked by hydrogen bonding.

In terylene, chains are linked by weaker dipole-dipole attractions. This takes place because carbonyl groups are polarized.

In chains of addition polymers such as polyethene, the only crosslinking is by van-der-Waals' forces.

# POLYMER PROPERTIES

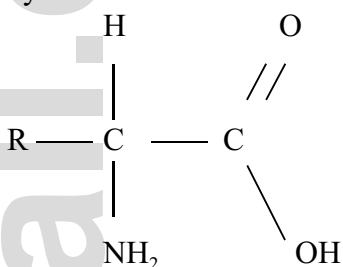
Polymers with polar, hydrogen-bonding functional groups may be soluble in water despite their tremendous size. This fact explains the solubility of proteins and polyvinyl alcohols. Most other polymers, however, are insoluble. The length of these polymers allows them to align with each other, thereby generating substantial London forces of attraction.

Although addition polymers are prepared from monomers with double bonds, the finished polymer has no double bonds. As a result, these polymers are fairly inert. The most inert is Teflon, in which the very strong C-F bond cannot be broken easily.

Polymers have distinct properties which depend on the method used to manufacture the polymer. Branched chain polymers have different properties than linear polymers.

## AMINO ACIDS AND PROTEINS

Amino acids are obtained by hydrolysis of proteins. The amino acids can be represented by...

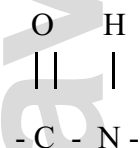


The simplest amino acids are :

- i) aminoethanoic acid (glycine)
- ii) 2-aminopropanoic acid (alanine)

All amino acids except aminoethanoic acid contain an asymmetric carbon atom and exhibit **optical isomerism**.

Amino acids are linked together by *peptide linkages* ...



Amino acid polymers are called polypeptides (molar mass < 1000), those with larger molecular masses are called proteins (test:  $\text{CuSO}_4(\text{aq}) + \text{NaOH}(\text{aq})$ , using ninhydrin produces pink/purple spots on a chromatogram if amino acids are present).