

# Polymers

There are two **types** of **polymerisation**: **addition** and **condensation**

## Addition Polymers

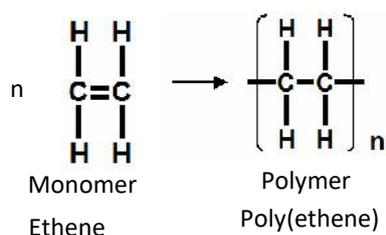
Addition polymers are formed from alkenes. The alkene molecules add to themselves to form long chain molecules. The original alkene molecule is called the monomer. The double bond in the alkene opens to bond to next monomer molecule. Chains form when the same basic unit is repeated over and over.

The simplest addition polymer is made from ethene and is called poly(ethene). Modern naming of polymers is to put the name of the monomer in brackets after the word poly.

e.g. poly(ethene) , poly(chloroethene). Most polymers are still known by their original names or trade names.

Polymer chains can be of various lengths. There are usually between  $10^4$  to  $10^6$  repeating units in a chain

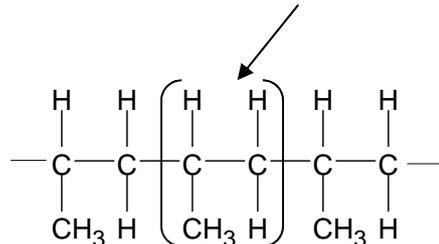
Poly(alkenes) like alkanes are unreactive due to the strong C-C and C-H bonds



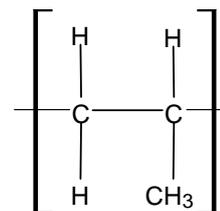
Polymerisation equations are written in the form above showing the formula or one monomer and one repeating unit. The letter n is used to represent the number of repeating units.

The polymer chains consist of strong covalent bonds. Between different polymer chains there are weaker intermolecular forces which can be a mixture of London forces and permanent dipole-dipole forces. Increased chain length leads to increasing density, melting point and hardness.

be able to recognise the repeating unit in a poly(alkene)



If asked to draw **one repeating unit**, don't add the **n** on to your diagram, because n represents a large number

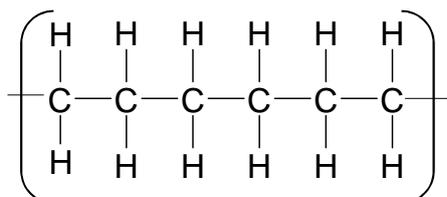


## Poly(ethene) -polythene

Poly(ethene): is used to make plastics bags, buckets, bottles. It is a flexible, easily moulded, waterproof, chemical proof, and a low density plastic.

Poly(ethene) is chemically inert due to the strong C-C and C-H bonds and **non-polar** nature of the bonds and therefore is non-biodegradable.

This shows three repeating units of poly(ethene)

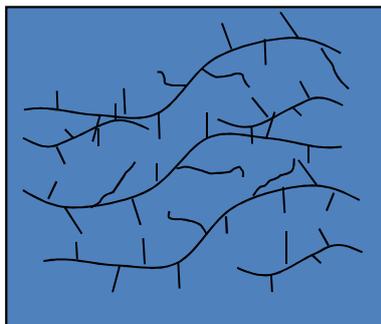


### Different forms of poly(ethene)

Low density (LD) and high density (HD) poly(ethene) are produced from ethene, using different catalysts and reaction conditions.

In HDPE the polymer chains are single strands and can closely line up in parallel (called a crystalline structure). In LDPE, the chains are irregularly packed, branched chain polymers therefore they cannot get as close together. The polymer chains in HDPE can form stronger London intermolecular forces between them.

#### Low Density poly(ethene) LDPE



**Conditions for polymerisation:** high pressure, 1500 atm, 200°C and a free radical organic peroxide initiator.

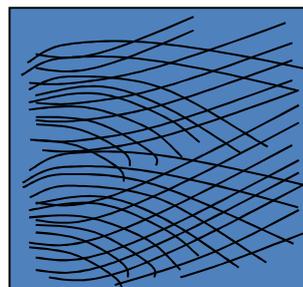
The high pressure compresses the gas molecules together which increases the rate of the reaction

The Structure consists of irregularly packed, branched chain polymers- a more amorphous structure

**Properties:** flexible, low tensile strength and low melting point

**Uses:** plastic bags, wrappers, bottles.

#### High Density poly(ethene) HDPE



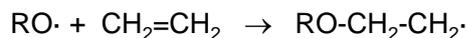
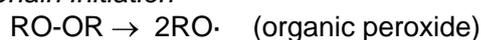
**Condition for polymerisation :** low pressure (2-6 atm), 60°C. Ziegler-Natta Catalyst.

The structure consists of regularly packed, linear polymers chains . This is called a highly crystalline structure. The polymer chains fit closer together.

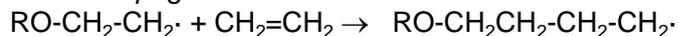
**Uses:** Rigid articles such as ice trays, buckets, bottle crates.

### Free radical Polymerisation mechanism

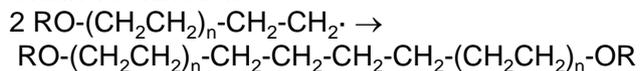
#### Chain Initiation



#### Chain Propagation

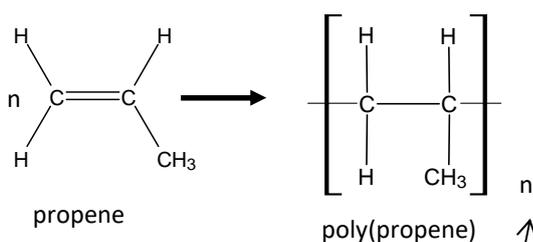


#### Chain Termination



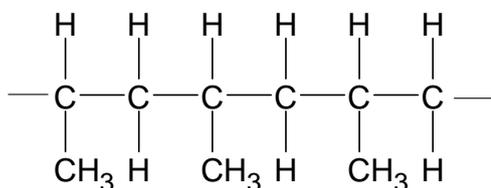
The mechanism for the formation of HDPE using the Ziegler-Natta catalyst is different from the free radical mechanism above.

**Poly(propene)** is a stiffer polymer, used in utensils and containers and fibres in rope and carpets.



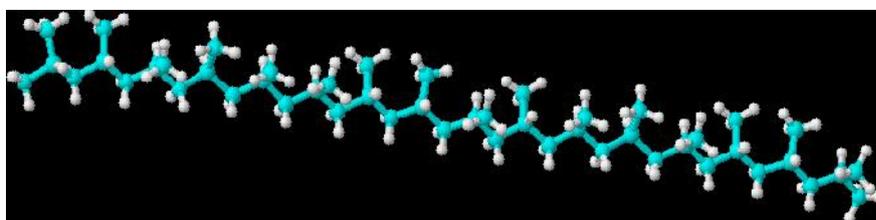
Poly(propene) is recycled

Add the **n**'s if writing an equation showing the reaction where '**n**' monomers become '**n**' repeating units

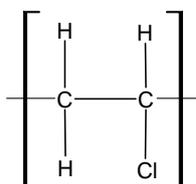


This shows three repeating units of poly(propene)

Poly(propene) has stronger London intermolecular forces between chains than poly(ethene) because it has more electrons in its structures.



## Poly(chloroethene) also known as PVC



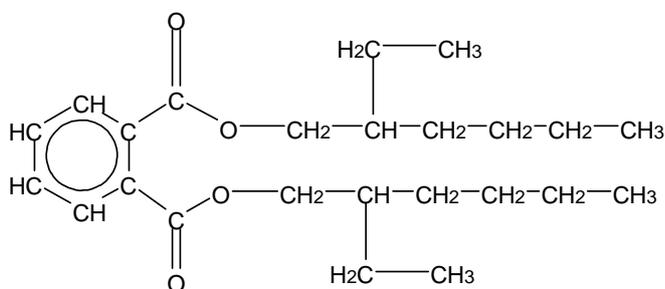
Poly(chloroethene) is a polymer that is water proof, an electrical insulator and doesn't react with acids.

In its pure form it is a rigid plastic. The strong permanent-dipole intermolecular bonding between polymer chains prevents them moving over each other. In this unplasticised form it is used to make uPVC window frame coverings and guttering.

If a plasticiser is added the intermolecular forces are weakened which allows the chains to move more easily resulting in more flexibility in the polymer. In this form PVC is used to make insulation on electrical wires, and waterproof clothing.

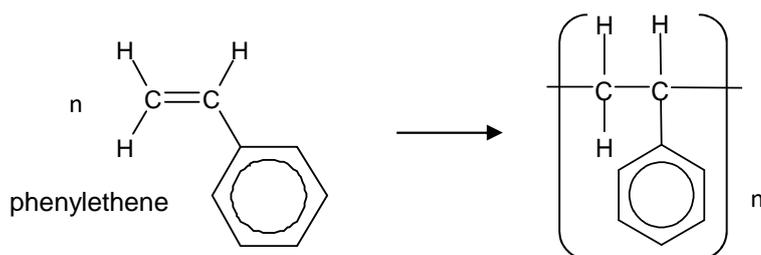
To make PVC 'mock leather' material up to 50% by weight plasticiser may be added.

The plasticiser may evaporate over time making the plastic more brittle as it ages. There are health concerns over the use of some phthalate plasticisers as some with lower molecular weights are potentially toxic.



A common ester phthalate plasticiser

## Poly(phenylethene) also known as polystyrene



The phenyl group is  $-C_6H_5$

See chapter 6.9 on benzene for more detail on its structure

Polystyrene in its unexpanded form is a clear, relatively stiff and brittle plastic used in toys, plastic cups, CD cases, and moulded electronic equipment.



## Expanded polystyrene

Expanded or extruded polystyrene foams are produced by mixing blowing agents with the polymer during its production. The blowing agents evaporate to form bubbles and expand the foam. The blowing agents are usually volatile organic liquids such as pentane or hydrofluorocarbons.

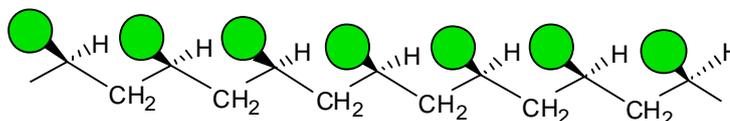
In its expanded form it is commonly used in packaging, and for heat insulation. It has good insulating properties and is a good shock absorber



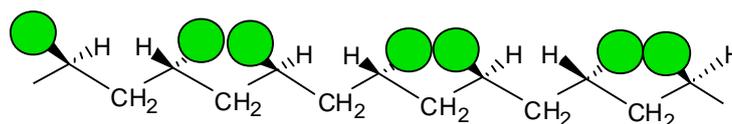
## Isotactic, syndiotactic and atactic forms of polymer chains

The properties of polymers can also be affected by the positioning of the substituent side group (eg  $-Cl$ ,  $-CH_3$  or phenyl group)

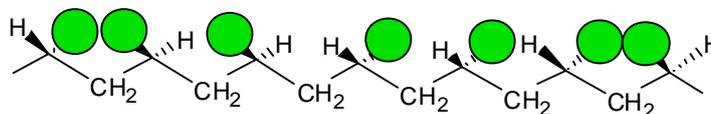
In the **isotactic form** the substituent groups are all on the same side of the polymer chain in a regular arrangement.



In the **syndiotactic form** the substituent groups are regularly alternate from one side of the polymer chain to the other.



In the **atactic form** the substituent groups are randomly arranged on alternate sides.

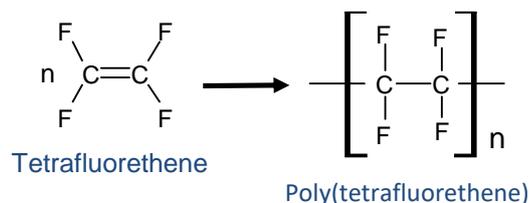


These different forms can have different properties. Often the isotactic form can fit closer together and have stronger intermolecular forces between chains so have higher melting points.

The isotactic form of polystyrene is produced using a Ziegler-Natta catalyst and the atactic form is produced using the free radical mechanism

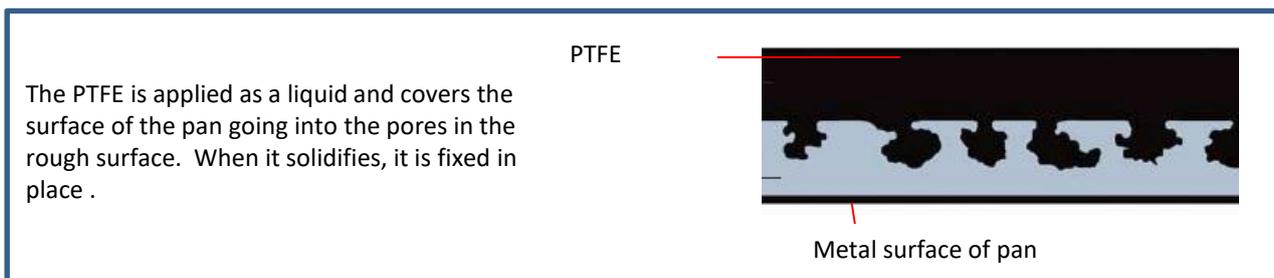
## Polytetrafluoroethene

Polytetrafluoroethene (PTFE, or "Teflon") is very resistant to heat and chemical corrosion. It is used on nonstick cookware and coatings on bearings.



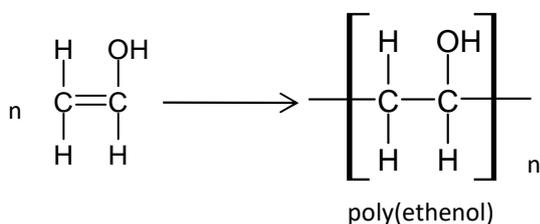
### How is it non stick?

Sticking is caused by chemical bonds forming between the food and the metal pan. These bonds may be relatively weak London forces or covalent bonds. Protein-rich foods are particularly sticky because they can form complexes with the iron atoms in the steel pan.



The PTFE has a high melting point so will not melt when the pan is heated. Food can not bond with the smooth inert surface of the PTFE. It has a high melting point because it has strong London forces and permanent dipole forces between chains.

## Poly(ethenol)



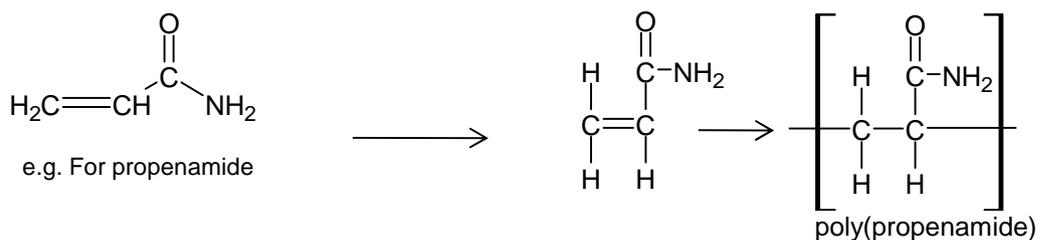
The addition polymer poly(ethenol) has good solubility in water because it can form many strong hydrogen bonds with water. This makes it a useful polymer for uses such as soluble laundry bags and liquid detergent capsules.

You should be able to draw the polymer repeating unit for any alkene

e.g. For but-2-ene  $\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3$

It is best to first draw out the monomer with groups of atoms arranged around the double bond

$$\begin{array}{c} \text{H} & & \text{CH}_3 \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H}_3\text{C} & & \text{H} \end{array} \longrightarrow \left[ \begin{array}{cc} \text{H} & \text{CH}_3 \\ | & | \\ -\text{C} & - & \text{C}- \\ | & | \\ \text{CH}_3 & \text{H} \end{array} \right]$$



## Condensation Polymerisation

The two most common **types** of condensation polymers are **polyesters** and **polyamides** which involve the formation of an **ester** linkage or an **amide** linkage.

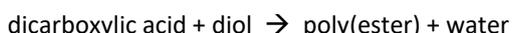
In condensation polymerisation there are two different monomers that add together and a small molecule is usually given off as a side-product e.g.  $\text{H}_2\text{O}$  or  $\text{HCl}$ .

The monomers usually have the same functional group on both ends of the molecule e.g. di-amine, di carboxylic acid, diol, diacyl chloride.

Forming polyesters and polyamide uses these reactions we met earlier in the course

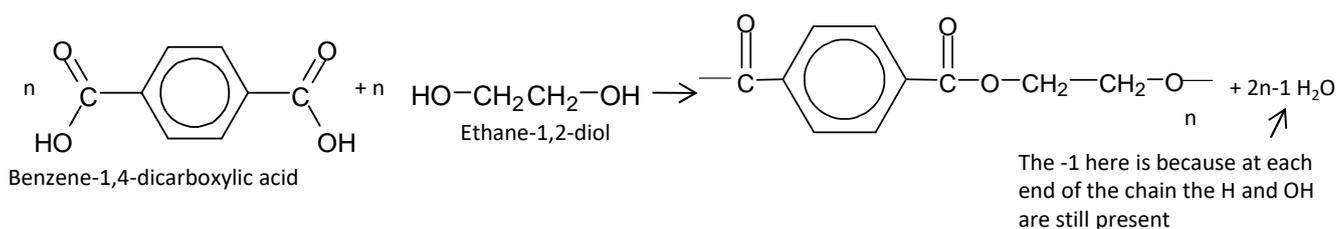


If we have the same functional group on each end of molecule we can make polymers so we have the analogous equations:



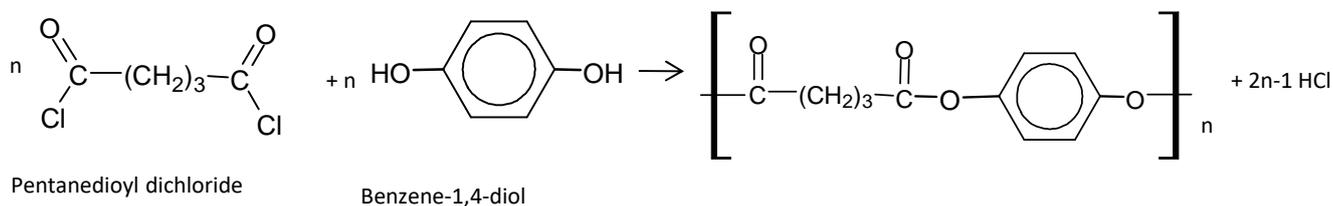
Using the carboxylic acid to make the ester or amide would need an acid catalyst and would only give an equilibrium mixture. The more reactive acyl chloride goes to completion and does not need a catalyst but does produce hazardous  $\text{HCl}$  fumes.

### PET- Terylene- a common polyester



This condensation polymer is commonly known as PET or PETE (short for polyethylene terephthalate). It is the most widely used polyester. It is often used to produce fizzy drink bottles. It can also be drawn into filaments and blown into films. In its fibre form, known as Terylene in the UK, it can be used to produce textiles.

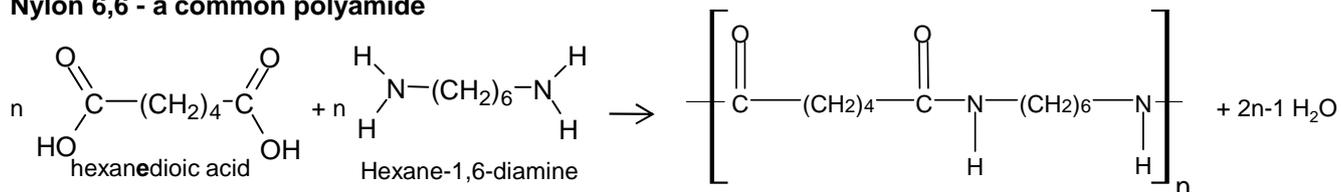
Terylene fabric is used in clothing, tire cords



Polyesters have permanent dipole forces between the  $\text{C}^{\delta+}=\text{O}^{\delta-}$  groups in the different chains in addition to the London forces between the chains.

The stronger intermolecular forces in polyesters mean they can form strong fibres that can be woven into clothes

### Nylon 6,6 - a common polyamide



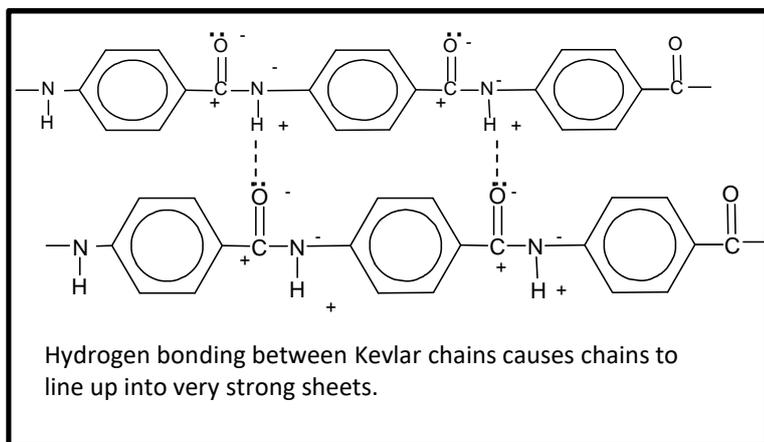
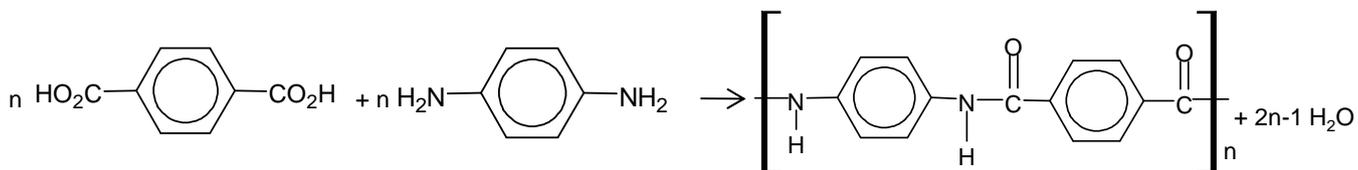
The 6,6 stands for 6 carbons in each of the monomers. Different length carbon chains produce different polyamides

Polyamides (and proteins) have **hydrogen bonding** between the lone pairs on oxygen in  $\text{C}^{\delta+}=\text{O}^{\delta-}$  groups and the H in the  $\text{N}^{\delta-}-\text{H}^{\delta+}$  groups in the different chains.

There are also **Permanent dipole-permanent dipole forces** because the polar C=O bond and polar C-N bond

There are also **London forces** which are large because there are many electrons in the molecule  
Polyamides will therefore have higher melting points than polyesters.

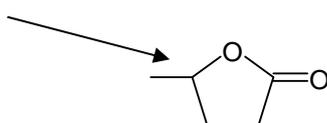
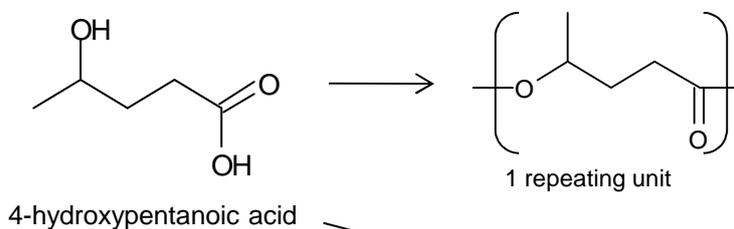
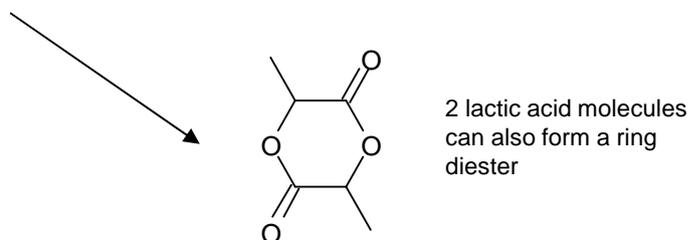
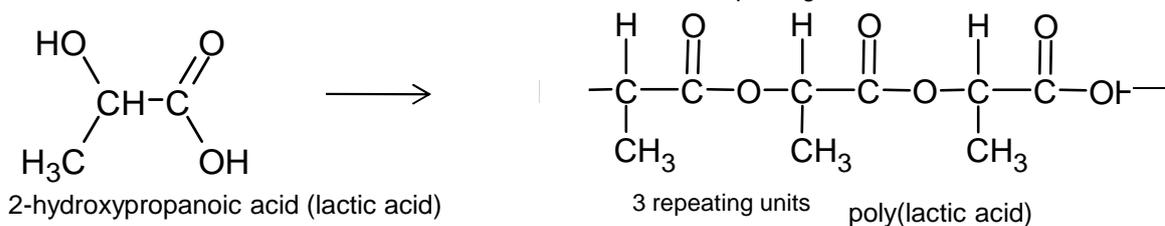
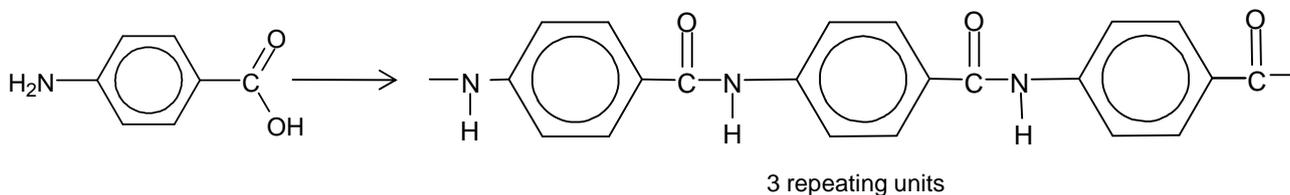
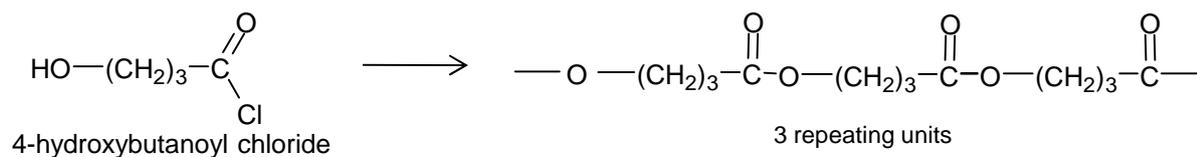
### Kevlar- a common polyamide



Kevlar is a polyamide with a strong and ordered structure.  
It is used to make bullet proof clothing and reinforcing tyres.

Kevlar is insoluble in most solvents except concentrated sulfuric acid  
The hydrogen bonds between O and N can be broken with the use of concentrated sulfuric acid.

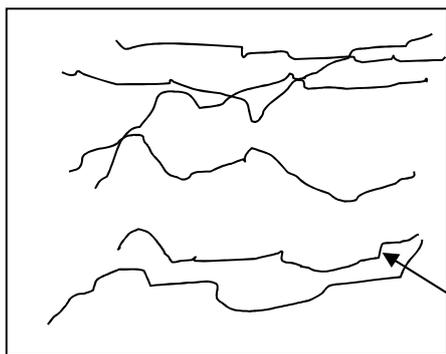
It is also possible for polyamides and polyesters to form from **one** monomer, if that monomer contains both the functional groups needed to react



It is possible for some of these compounds to form various cyclic esters under different conditions from forming the polymer. You do not need to learn these but may be asked to deduce structures from information given

## Thermoplastic/Thermosoftening polymers

Thermoplastic polymers soften on heating and can be re-shaped. In general they have low melting points. Most polymers met in this chapter are classed as thermoplastic polymers.

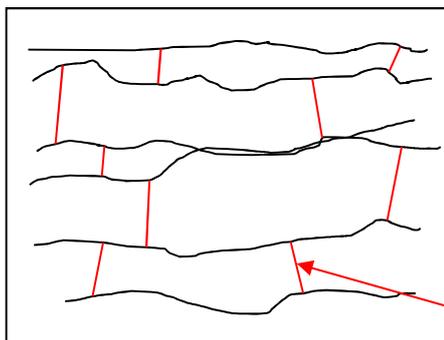


There are weak inter-molecular forces between the chains holding them together. The chains can slide over each other and this creates the flexibility often found in polymers.

On heating the weak forces between the chains are broken and the object can be reshaped.

overlapping chains of polymers in thermoplastic polymers with only intermolecular forces between chains

## Thermosetting polymers



The chains are held together by strong covalent bonds called crosslinks. These bonds cannot be broken easily; this makes the polymers rigid because the polymer chains are fixed.

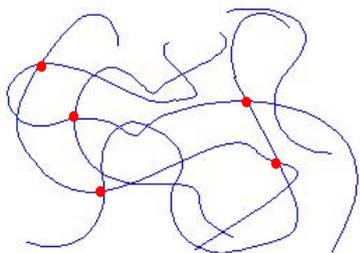
The cross-links do not break on heating and so the polymer cannot be reshaped once it is made.

Thermosetting polymers include epoxy glues and bakelite ( which is used in light fittings and saucepan handles because they do not soften on heating.)

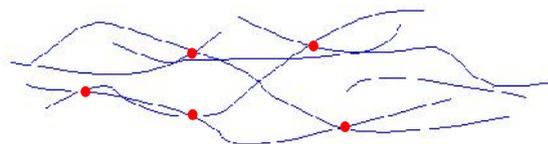
Polymer chains held together by cross links. The amount of crosslinks and regularity of the structure may vary between different thermosetting polymers

## Elastomers

Elastomers can be stretched to many times their original length, and then return to their original shape without permanent deformation.



This is what the polymer chains look like in a piece of un-stretched rubber. It has high entropy.

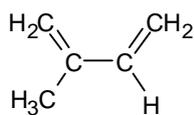


This is what the polymer chains look like in a piece of stretched rubber. The chains are stretched out and have lower entropy as they have a more ordered arrangement.

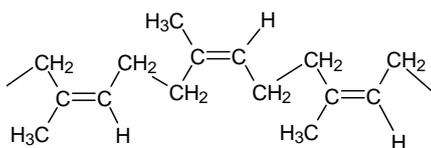
When released the elastomer returns to the original point of high entropy and the polymer reforms its original shape.

Limited cross linking of chains can help the elastomer 'remember' its original state and return to it.

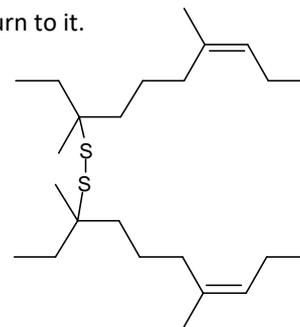
Vulcanising Rubber with sulfur is an example of this cross linking in an elastomer



Monomer unit for rubber  
2-methylbuta-1,2-diene



Polymer chain for rubber  
Poly(2-methylbuta-1,2-diene)



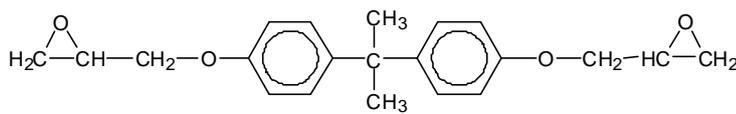
Sulfur cross links between polymer chains.

## Non-solvent based adhesives

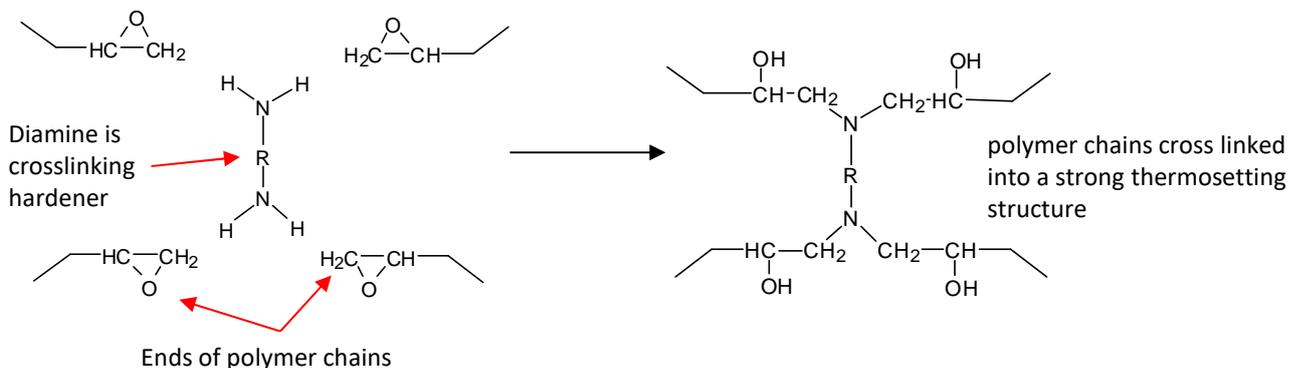
Most adhesives are solvent based. They harden when the solvent evaporates. The following harden in a different way.

### Epoxy resin glues

The glues have two components: one containing polymer chains and the other a hardener (which is a cross-linking agent). They are mixed together when the glue is applied. As the glue sets the hardener forms cross links between the polymer chains forming a strong thermosetting structure.



pre-polymer with epoxy group

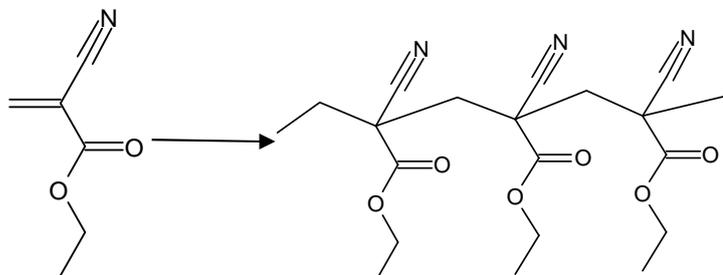


Cross links in **thermosetting** polymers tend to be covalent bonds which are strong and not easy to break. Once formed the polymer cannot be melted

You don't need to remember the details of the substances here- just the process of crosslinking.

### Superglue

The monomer in superglue polymerises on exposure to moisture in the atmosphere to form a strong addition polymer



monomer  
ethyl 2-cyanoprop-2-enoate

You don't need to remember the details of the substances here

### Conducting polymers –poly(ethyne)

Ethyne has a triple bond. It can form an addition polymer that has alternate double single bonds.



Poly(ethyne) also known as polyacetylene

Poly(ethyne) conducts electricity. It conducts through its long chain of delocalised electrons. It can delocalise because the polymer chain is planar so the  $\pi$  bonds overlap with each other.

### Chemical reactivity of condensation polymers

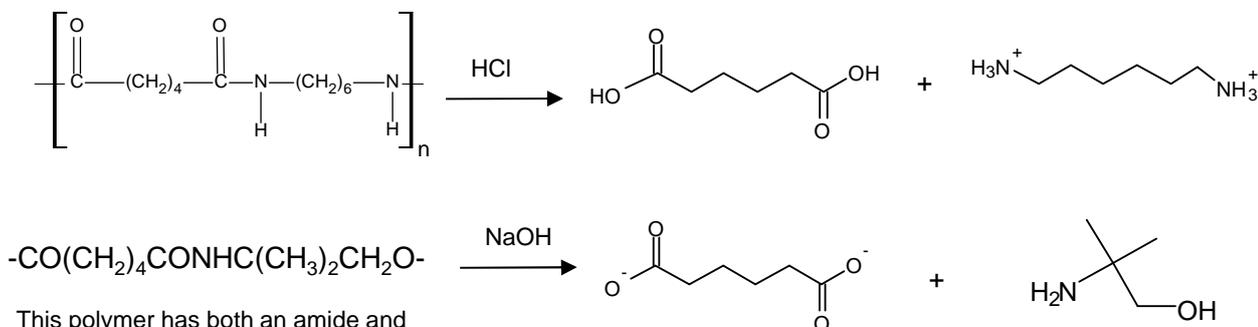
polyesters and polyamides can be broken down by **hydrolysis** and are, therefore, biodegradable

The reactivity can be explained by the presence of **polar bonds** which can attract attacking species such as nucleophiles and acids

### Hydrolysis

Polyesters and polyamides can be hydrolysed by acid and alkali

The hydrolysis will result in the original monomers forming- although the carboxylic acid or amine group will be in salt form depending on whether the conditions are alkaline or acidic



**Dealing with waste polymers** Waste polymers can be processed in several ways.

### Landfill

The most common method of disposal of waste in UK. Many are now reaching capacity.

European regulations will mean councils are charged much more for using landfill.

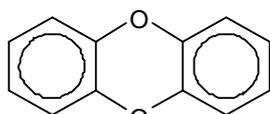
Most polymers (polyalkenes) are non-biodegradable and take many years to break down. One solution to this problem is to more biodegradable plastics, e.g. Polyamides and cellulose and starch based polymers to improve rates of decomposition

### Incineration

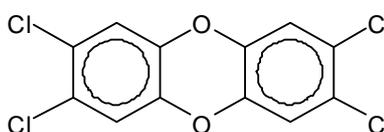
Rubbish is burnt and energy produced is used to generate electricity.

This will result in large amounts of greenhouse gases such as carbon dioxide being produced. They can also produce the products of incomplete combustions such as toxic carbon monoxide.

Combustion of halogenated plastics (ie PVC) can lead to the formation of toxic and acidic waste products such as HCl and various dioxins.



dibenzodioxin



A PCDD tetrachlorodibenzodioxin

Dioxins are highly toxic compounds that consist of two benzene rings connected by two oxygen atoms. They are often carcinogenic. Burning PVC has a potential risk of producing dioxins such as a polychlorinated dibenzodioxins. Dioxins do not decompose in the environment and can be passed on in the food chain.

Modern incinerators can burn more efficiently and most toxins and pollutants can be removed. Greenhouse gases will still be emitted though. The volume of rubbish is greatly reduced.

House fires can release many toxins due to plastics in things like shower curtains burning. Low smoke zero halogen cabling is now often used in wiring to prevent these hazards.

**Polychlorinated biphenyls**, PCBs are a group of manufactured organic chemicals containing carbon, hydrogen and chlorine atoms

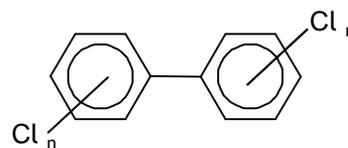
PCBs were manufactured in the twentieth century but are now banned. They are often highly toxic.

Their properties include non-flammability, chemical stability, high boiling point and electrical insulating properties.

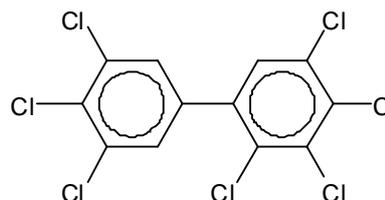
PCBs were therefore used in many applications including:

- Electrical and heat transfer equipment
- Plasticisers in paints and plastics.

Disposal of old products containing PCB's can still be an issue as they are stable and do not break down in the environment. Burning of plastics containing PCB's can be a problem.



General structure of PCB's can be shown like this. The hydrogens on the benzene rings are replaced with chlorine atoms. Different PCB's have different numbers of chlorine atoms. One example below.



## Recycling

Plastics require more processing to be recycled than other materials.

The waste is sorted into each different type of polymer (ie PTFE, PVC, PET) based on different resin types codes. Then each type of thermoplastic polymers can be recycled by melting and remoulding.

Recycling saves raw materials. Nearly all polymers are formed from compounds sourced or produced from crude oil. Recycling saves precious resources.

The collecting and sorting can be an expensive process in terms of energy and manpower.

Polymers can only be recycled into the same type, so careful separation needs to be done.

### Resin identification codes



polyethylene terephthalate



high-density polyethylene

HDPE



polyvinyl chloride

PVC



low-density polyethylene

LDPE



polypropylene

PP



polystyrene

PS



OTHER

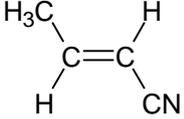
other

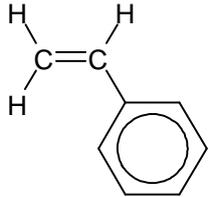
## Feedstock for Cracking

Waste polymers can be used as a feedstock for the cracking process allowing for the new production of plastics and other chemicals.

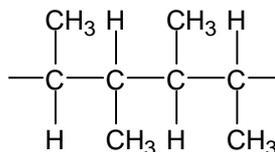
## Addition Polymers

- Propene polymerises to form poly(propene). Draw 3 repeating units of poly(propene)
- Write an equation, using displayed formulae, for the formation of poly(tetrafluoroethene) from its monomer.
- Compound chloroethene,  $\text{CH}_2=\text{CHCl}$ , forms an addition polymer.
  - Draw the repeating unit of the polymer formed and name the polymer
  - This polymer is rigid. Explain why in terms of intermolecular bonding
  - The use of plasticisers can be used to modify the properties of this polymer and make the polymer more flexible. Explain how this works in terms of intermolecular forces.

4. The monomer  can be used to make a polymer. Name the monomer (including appropriate E-Z terminology) Draw one repeating unit of the polymer formed.

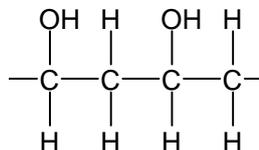
5. Draw two repeating units of the polymer formed from  phenylethene.

6. The following diagram shows a portion of a polymer chain  
Draw and name the monomer that forms this polymer.



7. Draw and name the monomer that makes poly(ethanol)

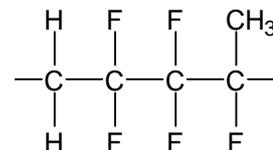
.Why does this polymer dissolve in water?



- Draw one repeating unit of the polymer formed from but-1-ene.
- 2-methylbut-2-ene forms an addition polymer. Draw one repeating unit of the polymer formed.
- Pent-2-ene forms an addition polymer. Draw two repeating units of the polymer formed.
- Cyclopentene can be polymerised to form poly(cyclopentene). Draw two repeating units of this polymer.

12. The following figure shows one repeating unit of a polymer made from two monomers by addition polymerisation.

Draw and name the two monomers.



13. The compound ethyl 2-cyanoprop-2-enoate can polymerise by addition polymerisation to form a strong glue. Draw 3 repeating units of the polymer formed.

