

# Polymers

A polymer is a long chain molecule that is composed of a large number of repeating units of identical structure. Polymers may be naturally occurring like proteins, cellulose and silk or synthetic like polyethylene, polystyrene and nylon. In some cases, naturally occurring polymers can also be produced synthetically. An important example is natural rubber, which is known as polyisoprene in its synthetic form.

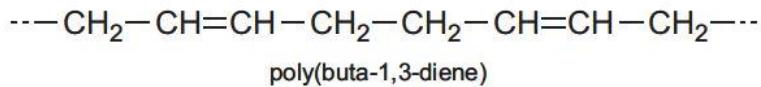
Polymers that are capable of high extension under ambient conditions find important applications as elastomers. In addition to natural rubber, there are synthetic elastomers such as nitrile and butyl rubber. Other polymers may have characteristics that permit their formation into long fibers suitable for textile applications. The synthetic fibers, principally nylon and polyester, are good substitutes for the naturally occurring fibers such as cotton, wool and silk.

In contrast to the usage of the word polymer, those commercial materials, other than elastomers and fibers that are derived from synthetic polymers are called plastics. A commercial plastic resin may contain two or more polymers in addition to various additives and fillers. These are added to improve some property such as the processability, thermal or environmental stability and mechanical properties of the final product.

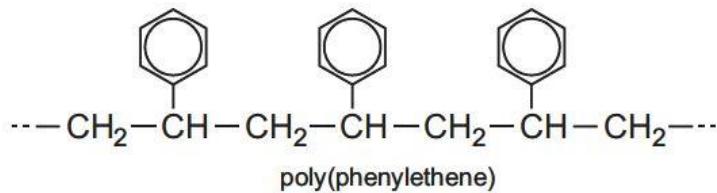
Today, polymeric materials are used in nearly all areas of daily life and their production and fabrication are major worldwide industries. As a group, plastics accounted for over 75% of their production, while synthetic fibers (15%) and elastomers (10%) made up the rest.

Molecules with fewer than ten repeating units are termed oligomers and exhibit quite different thermal and mechanical properties compared to the corresponding high molecular weight polymer. For example, oligomeric styrene having only seven repeating units is a viscous liquid at room temperature while commercial grade high-molecular weight polystyrene is a brittle solid that does not soften until it is heated to above approximately 100°C.

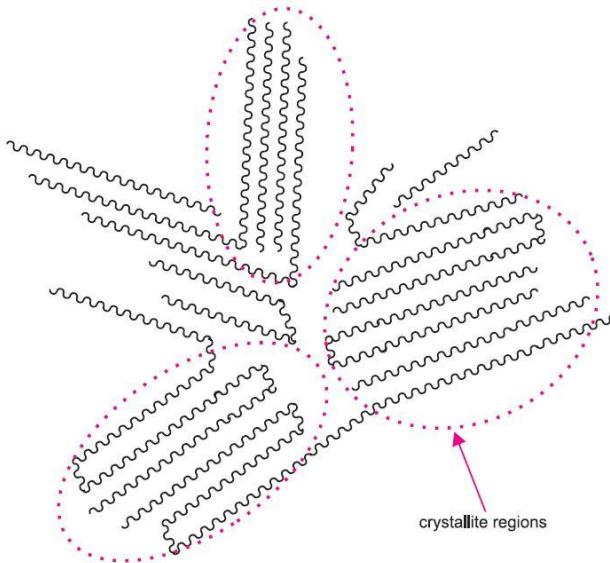
Polymers are large molecules, a type of macromolecule. Their chemical properties are similar to those of simple molecules. For example, if the polymer contains a carbon-carbon double bond, as in poly(but-1,3-diene), it will undergo additions reactions with, say hydrogen or bromine.



If it contains an aromatic ring, as in poly(phenylethene) (often known as polystyrene), it will undergo substitution reactions, say with nitric acid.



The major differences between smaller molecules and polymers lie not with their chemical properties but with their physical ones. Their larger sizes lead to much stronger intermolecular forces leading in turn to much higher melting points, and the characteristic properties of hardness and flexibility. These intermolecular forces are even stronger when the polymer chains pack together in a regular way as in HDPE (high density poly(ethene)) and have regions of crystallinity. When heated, it melts and the crystallinity is lost. As it does not have a sharp melting point, the temperature at which this occurs is termed the *melt transition temperature*,  $T_m$ . Above this temperature, the polymer is amorphous. Some polymers are hard and amorphous, having no regions of crystallinity, for example, poly(methyl methacrylate). The temperature at which they become soft and pliable is termed the *glass transition temperature*,  $T_g$ .



**Figure 1:** These crystallites have order in which the zigzag polymer chains are held together in a regular pattern by intermolecular forces

There are many examples of polymers that occur naturally, for example, starch, cellulose and proteins. Over the last 70 years, synthetic polymers have been invented, often mimicking nature and they are now manufactured in millions of tonnes a year and are one of the most essential materials we use. Many are used as fibres. Others are moulded into required shapes and when they are used in this way, they are often termed plastics.

## Molecular Weight Distribution

A typical synthetic polymer sample contains chains with a wide distribution of chain lengths. This distribution is seldom symmetric and contains some molecules of very high molecular weight. The exact breadth of the molecular weight distribution depends upon the specific conditions of polymerization. For example, polymerization of some polyolefins results in a molecular-weight distribution that is extremely broad, while it is possible to polymerize some polymers, such as polystyrene with nearly monodisperse distribution under laboratory conditions. Therefore, it is necessary to define an average molecular weight to characterize an individual polymer sample as detailed below.

The molecular weight of polymers is commonly expressed in two ways: by number average ( $\bar{M}_n$ ) and by weight average ( $\bar{M}_w$ ). The number average is obtained by adding the molecular weights of all the molecules and dividing by the number of molecules. If we have  $n_1$  molecules of molecular weight  $M_1$ ,  $n_2$  of molecular weight  $M_2$  and  $n_x$  of molecular weight  $M_x$ , then

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \dots + n_x M_x + \dots}{n_1 + n_2 + \dots + n_x + \dots} \text{ or, } \bar{M}_n = \frac{\sum_{i=1}^N n_i M_i}{\sum_{i=1}^N n_i}$$

The weight average molecular weight is calculated according to weight of all the molecules at each molecular weight. Let  $w_1$  be the weight (in molecular weight units) of molecules of molecular weight  $M_1$ ,  $w_2$  the weight of molecules of molecular weight  $M_2$  and so on, then

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + \dots + w_x M_x + \dots}{w_1 + w_2 + \dots + w_x + \dots}$$

But, the total weight of all the molecules with molecular weight  $M_1$  is  $n_1M_1$ , so we can substitute  $w_1 = n_1M_1$ ,  $w_2 = n_2M_2$ ,  $w_x = n_xM_x$ , and so on in the above equation, whence

$$\bar{M}_w = \frac{n_1M_1^2 + n_2M_2^2 + \dots + n_xM_x^2 + \dots}{n_1M_1 + n_2M_2 + \dots + n_xM_x + \dots}$$

$\bar{M}_n$  tells us where most of the polymer molecules are relative to the molecular weight distribution. The parameter  $\bar{M}_w$ , on the other hand, tells us where most of the weight is regardless of the molecular weight distribution. Because  $\bar{M}_w$  is biased towards molecules with higher molecular weight, it will be larger than  $\bar{M}_n$ .

A measure of the breadth of the molecular weight distribution is given by the ratios of molecular weight averages. For this purpose, the most commonly used ratio is  $\bar{M}_w/\bar{M}_n$ , which is called the polydispersity index or PDI. If PDI is unity then all the molecules have the same molecular weight, and as the distribution of molecular weights becomes wider, this ratio increases.

Boling point elevation, freezing point depression, osmotic pressure, and end group analysis give number average molecular weight; light scattering and sedimentation methods give weight averages. Viscosity measurements give a value somewhat between the two.

The molecular weight profile of a polymer can be determined only by fractionation. Cumbersome solvent precipitation techniques give numerous fractions, and the molecular weight of each is determined. The fractions must be so narrow that for each of them  $\bar{M}_w/\bar{M}_n$  is effectively unity.

## Degree of Polymerization

The degree of polymerization (DP) is the number of repeat units in an average polymer chain at time  $t$  in a polymerization reaction. The length is in monomer units. The degree of polymerization is a measure of molecular weight. For most industrial purposes, lengths in the thousands or tens of thousands are desired.

$$DP = \text{Total MW of the polymer} / \text{MW of the repeating unit}$$

## Polymerization Procedures

Polymerizations are carried out by four different procedures – bulk, solution, suspension and emulsion polymerizations.

In bulk polymerization, the monomer and the initiator are combined in a vessel and heated to the proper temperatures. This procedure, although the simplest, is not always the best. The polymer that forms may dissolve in the monomer to give a viscous mass and heat transfer becomes difficult. Heat cannot escape, and the polymer may char or develop voids. If the exotherm gets out of hand, the system may explode.

Even so the polymerization of ethylene by high-pressure method is a bulk polymerization and is one of the polymerizations carried out on the largest scale. Fortunately, the polymer does not dissolve in the monomer. Instead it collects at the bottom of the reactor and is drawn off. The exotherm still presents a problem, and the strictest possible control of temperature and heat transfer is necessary. The polymerization of methyl methacrylate to “Lucite” (Plexiglass, Perspex) is also carried out in bulk.

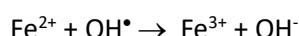
Fluid bed processes are essentially bulk polymerizations and represent one way of handling the exotherm. They have become popular because they provide an economical way to make many grades of high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and polypropylene (PP). The fluid bed comprises small particles of the preformed resins, fluidized by inert gas. The gaseous monomer and catalyst are injected into the fluid bed and the polymer forms around the nuclei provided by the particles of preformed resin. Conversion is only 2% but ethylene is easily recycled.

The other polymerization procedures are all designed to solve the problem of heat transfer. In solution polymerization, the reaction is carried out in a solvent that acts as a heat sink and reduces the viscosity of the reaction mixture. The snags with the solution polymerization are first, it is frequently difficult to remove the last traces of solvent from the polymer, and second, the solvent participates in chain transfer reactions so that low molecular weight polymers result. Solution polymerization is useful if the product is to be used in solvent. Solvent-based poly (vinyl acetate) adhesive is an example. Slurry polymerization is a variant of solution polymerization and is used for the important polymerizations of ethylene to high-density (low-pressure) polyethylene, and propylene to polypropylene. A small amount of solvent is combined with the monomer and the catalyst in the reactor. The solvent forms slurry with the catalyst and aids in its distribution throughout the reaction mixture. At the same time, it helps to remove exotherm. Initially, it was necessary to separate the catalyst by a cumbersome process. This has led to the development of catalysts that separate more readily. Also, catalysts are now available that give such high yields, and thus are present in low concentrations, that they can be left in the polymer without affecting its properties.

In suspension polymerization, the monomer and catalysts are suspended as droplets in a continuous phase such as water. These droplets have a high surface/volume ratio so heat transfer to the water is rapid. The droplets are maintained in suspension by continuous agitation and also, if necessary, by addition of a water-soluble polymer such as methyl cellulose that increases viscosity of the water. Finely divided inorganic materials such as clay, talc, aluminum oxide and magnesium carbonate have a similar stabilizing effect on the suspension. The need to remove these materials is one of the disadvantages associated with their use. Poly (vinyl chloride) is frequently made by suspension polymerization.

The final procedure is emulsion polymerization, a technique that was developed as part of the synthetic rubber program during World War II. The products are particularly useful for the formulation of water-based paints. As its name implies, it uses an emulsifying agent, usually various kinds of soap. In solution, this forms micelles in which the nonpolar hydrophobic ends of the soap molecules point inward and the polar hydrophilic groups point outward and interact with the water. If monomer is added, that can be absorbed, in the micelles, a separate monomer droplet phase may form that is also stabilized by the soap molecules, the droplets being a micron or more in diameter.

A water-soluble composite initiator called a “redox” catalyst is then added. This consists of a mixture of a reducing agent and an oxidizing agent. An example is the ferrous ammonium sulfate and hydrogen peroxide. In the absence of monomer, the former would reduce the latter in a two-stage process:



If monomer is present, however, the hydroxyl free radical can initiate polymerization.

These polymerizations must be carried out with rigorous exclusion of oxygen, which is an inhibitor in this case, although an initiator in low-density polyethylene production.

The free radicals diffuse into the micelles, and polymerization takes place within them. Diffusion into the droplets also occurs but, since they have a far lower surface/volume ratio than the micelles, virtually none of the polymerization takes place within them. As polymer is formed, the micelles grow by diffusion of monomer from the droplets into the micelles. Rather than providing a site for polymerization, the droplets serve as reservoirs for monomer that will later react in the micelles.

Polymerization within a micelle may take as long as 10s. Very high molecular weights are produced, higher than by any of the three other procedures. The product is a latex, a dispersion of solid particles in water, which is frequently a desirable form for a polymer. For example, poly(vinyl acetate) or polyacrylate lattices are used as such for “emulsion” paints. On the other hand, if solid polymer is required, the dispersion must be broken and the polymer precipitated.

There are two important differences between emulsion and suspension polymerization. In emulsion polymerization, the catalyst or the initiator is in the aqueous phase, not dissolved in the monomer. Also, the particles produced are at least an order of magnitude smaller than those obtained from suspension polymerization.

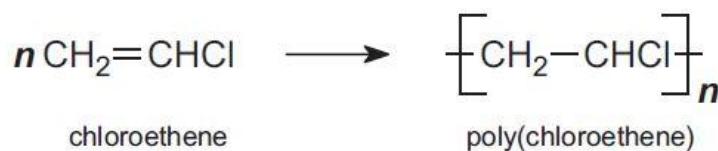
# Characterising polymers

There are several ways in which polymers can be characterised:

- a) how they are made, by addition or by condensation
  - b) whether they are homopolymers or heteropolymers (co-polymers)
  - c) whether they are thermoplastics, thermosets, elastomers or fibres
  - d) by their steric structure

### *(a) Addition and condensation polymers*

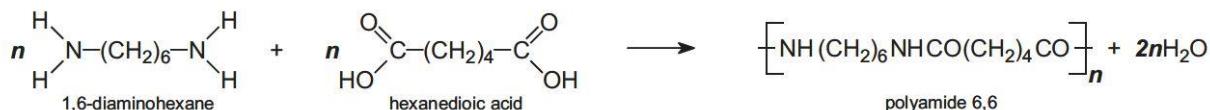
In **addition polymerization**, the polymer has the same empirical formula as the monomer but a higher molecular mass (Table 1). An example is the polymerization of chloroethene (vinyl chloride) to form poly(chloroethene), PVC:



**Table 1: Some addition polymers**

Monomer	Formula	Polymer	Trivial name	Structure
Ethene	$\text{H}_2\text{C}=\text{CH}_2$	LDPE <u>Low density poly(ethene)</u>	Low density polythene	$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$
Chloroethene	$\text{H}_2\text{C}=\text{CHCl}$	<u>Poly(chloroethene)</u>	Polyvinyl chlorine, PVC	$-\text{CH}_2-\overset{\text{Cl}}{\underset{\text{CH}}{\text{CH}}} \text{CH}_2-\overset{\text{Cl}}{\underset{\text{CH}}{\text{CH}}}-$
Propene	$\text{H}_2\text{C}=\text{CH-CH}_3$	<u>Poly(propene)</u>	Polypropylene	$-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}}{\text{CH}}}\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}}{\text{CH}}}-$
Propenonitrile	$\text{H}_2\text{C}=\text{CH-CN}$	<u>Poly(propenonitrile)</u>	Polyacrylonitrile	$-\text{CH}_2-\overset{\text{CN}}{\underset{\text{CH}}{\text{CH}}}\text{CH}_2-\overset{\text{CN}}{\underset{\text{CH}}{\text{CH}}}-$
Methyl 2-methyl propenoate	$\text{H}_2\text{C}=\overset{\text{CO}_2\text{CH}_3}{\underset{\text{C}}{\text{C}}}\text{CH}_3$	<u>Poly(methyl 2-methylpropenoate)</u>	Polymethyl methacrylate	$-\text{CH}_2-\overset{\text{CO}_2\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{CH}_2-\overset{\text{CO}_2\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-$
Styrene	$\text{H}_2\text{C}=\text{CH-}\text{C}_6\text{H}_5$	<u>Poly(phenylethene)</u>	Polystyrene	$-\text{CH}_2-\text{CH-}\text{C}_6\text{H}_5-\text{CH}_2-\text{CH-}\text{C}_6\text{H}_5-$
Tetrafluoroethene	$\text{F}_2\text{C=CF}_2$	<u>Poly(tetrafluoroethene)</u> (PTFE)	Polytetrafluoroethylene, PTFE	$-\text{CF}_2-\text{CF}_2-\text{CF}_2-\text{CF}_2-$

In **condensation polymerization**, polymerization of one or more monomers is accompanied by the elimination of small molecules (such as water or ammonia) (Table 2). For example, in producing polyamide 6,6 (Nylon 6,6), two monomers are used.



Another type of condensation polymer is said to be formed if the polymer chain contains (rather than appended to the chain) a functional group such as an ester, amide or urethane (Table 2).

**Table 2: Some condensation polymers**

Polymer	Monomer	Formula
<u>Polyesters</u>	$\text{HO}-(\text{CH}_2)_x-\overset{\text{O}}{\underset{\text{OH}}{\text{C}}}$	$\left[ (\text{CH}_2)_x-\overset{\text{O}}{\underset{\text{O-H}}{\text{C}}-\text{O}} \right]_n$
<u>Polyamides</u>	$\begin{matrix} \text{H} & & \text{H} \\ & \diagdown & \diagup \\ \text{H}-\text{N}-(\text{CH}_2)_x-\text{N}-\text{H} \\ & \diagup & \diagdown \\ & \text{O} & \\ & \diagdown & \diagup \\ \text{HO}-\text{C}-(\text{CH}_2)_y-\text{C}-\text{OH} \end{matrix}$	$\left[ \text{NH}-(\text{CH}_2)_x-\text{NH}-\overset{\text{O}}{\underset{\text{O-H}}{\text{C}}}-(\text{CH}_2)_y-\overset{\text{O}}{\underset{\text{O-H}}{\text{C}}} \right]_n$
<u>Phenol-formaldehyde plastics</u>	$\text{C}_6\text{H}_5\text{OH}$ $\text{CH}_2\text{O}$	$\text{C}_6\text{H}_5\text{O}-\text{CH}_2-\left[ \text{C}_6\text{H}_5\text{O}-\text{CH}_2 \right]_n$
<u>Polyurethanes</u>	$\text{HO}-\text{R}^1-\text{OH}$ $\text{O}=\text{C}=\text{N}-\text{R}^2-\text{N}=\text{C}=\text{O}$	$\left[ \text{R}^1-\text{O}-\overset{\text{O}}{\underset{\text{O-H}}{\text{C}}}-\text{NH}-\text{R}^2-\text{NH}-\overset{\text{O}}{\underset{\text{O-H}}{\text{C}}}-\text{O} \right]_n$

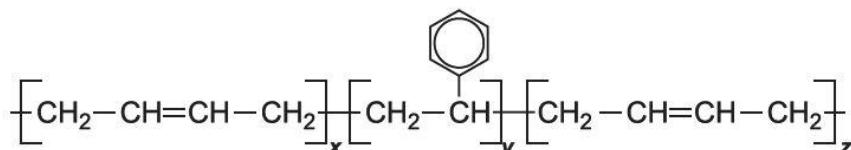
*(b) Homopolymers and heteropolymers (co-polymers)*

Another way of characterising polymers is to divide them into *homopolymers* and *heteropolymers*. Many of the well known polymers such as poly(vinylchloride) are produced from a single monomer and so are referred to as homopolymers (Table 1):

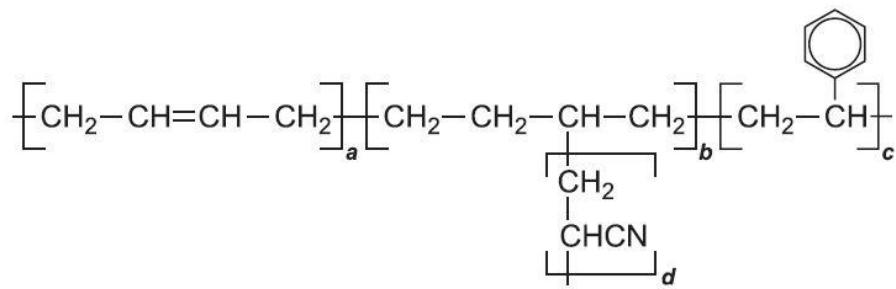


A heteropolymer, or as they are more commonly known, a *co-polymer*, is produced from two or more monomers. There are several types of co-polymer. One type is produced when two or more monomers are mixed and polymerized together. Depending on the reactivities of the monomers, they may form polymers with different arrangements of the monomer units (Figure 2).

SBS is an example of a *block co-polymer*. SBS is so named with S referring to Styrene (phenylethene) and B for Buta-1,3-diene. First, styrene is polymerized. Buta-1,3-diene is then added and it adds on to both the reactive ends of the polystyrene molecules to form SBS:



Another type of co-polymer is known as a *graft co-polymer*. An example is ABS. A is Acrylonitrile, the trivial name for propenonitrile. The backbone of the polymer is formed from phenylethene (styrene) and buta-1,3-diene. Propenonitrile (acrylonitrile) is added to the system and forms a grafted side chain onto the backbone. The nitrile adds to the double bond on the butadiene unit:



Co-polymers are very useful as they have the properties of the constituent polymers and thus can be produced for specific purposes. For example, polystyrene is brittle but when it is co-polymerized with buta-1,3-diene, the latter gives the polymer resilience and strength. Known as [High Impact Polystyrene \(HIPS\)](#), it can now receive impacts without damage.

### (c) Thermoplastics, thermosets, elastomers and fibres

Polymers can also be characterised into four classes:

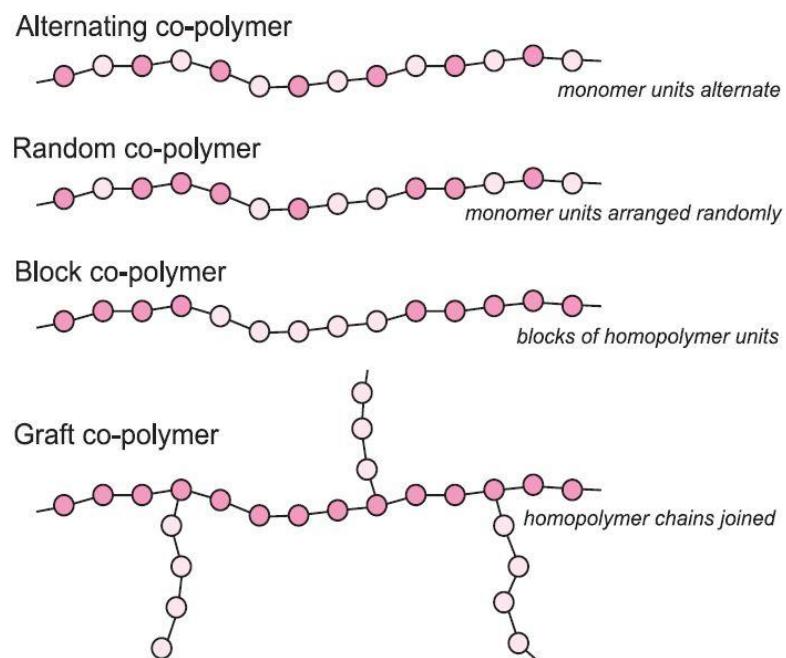
- thermoplastics
- thermosets (thermosetting resins)
- elastomers
- fibres

**Thermoplastics** consist of individual molecules with no covalent bonding between them but held together by intermolecular bonding. The polymers become soft on warming and can be moulded. They can be repeatedly warmed, softened and remoulded. A list of examples is given in Table 1.

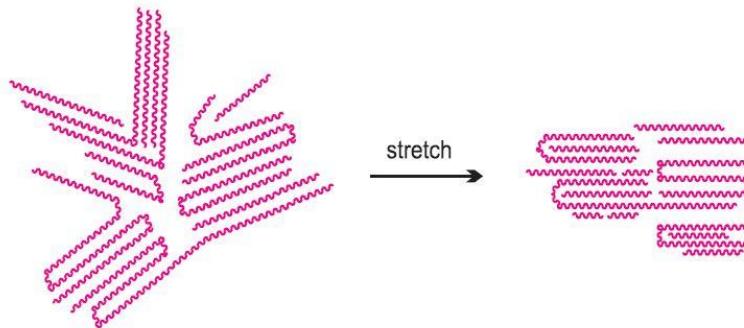
**Thermosets**, on the other hand, have many covalent bonds between the chains, leading to a three-dimensional structure, which can be regarded as a single molecule. They can be moulded by heat and pressure, but once moulded they cannot be remoulded. The most important examples include the plastics made from formaldehyde.

**Elastomers** are amorphous solids which, as the name suggests, are elastic (Table 3). They have coiled chains which can be stretched out but spring back to their original shape when the stretching force is released.

**Fibres** are thin threads which are produced by extruding a molten polymer through a die in which there are small holes. Fibres produced in this way include the polyamides (such as nylon), the polyesters (such as terylene) and poly(propene) (Table 4).



**Figure 2: Structures of different types of co-polymer**



**Figure 3:** After stretching to make a fibre, the crystallite regions are aligned along the axis of the fibre, and this adds strength to it

Having been extruded and stretched, the polymer molecules become aligned in the direction of the fibre. Any tendency to return to a random orientation is prevented by the strong intermolecular forces between the molecules (Figure 3). Fibres are twisted into threads and can then be woven into cloth or imbedded in a plastic to give it much greater strength (Table 4).

**Table 3: Some elastomers**

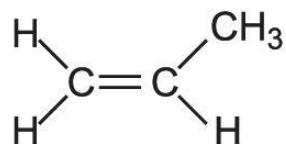
Polymer	Formula
<u>Poly(buta-1,3-diene)</u>	$\left[ \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \right]_n$
<u>Polyurethanes</u>	$\left[ \text{R}^1-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{NH}-\text{R}^2-\text{NH}-\overset{\text{O}}{\parallel}\text{C}-\text{O} \right]_n$
<u>ABS</u> (Acrylonitrile-butadiene-styrene)	$\left[ \text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2 \right]_a \left[ \text{CH}_2-\text{CH}_2-\underset{\substack{\text{CH}_2 \\   \\ \text{CHCN}}}{\text{CH}}-\text{CH}_2 \right]_b \left[ \text{CH}_2-\underset{\substack{\text{CH}_2 \\   \\ \text{CHCN}}}{\text{CH}} \right]_c$
<u>Silicones</u>	$\left[ \text{O}-\overset{\text{R}}{\underset{\text{R}}{\text{Si}}} \right]_n$

**Table 4: Some polymers used to make fibres**

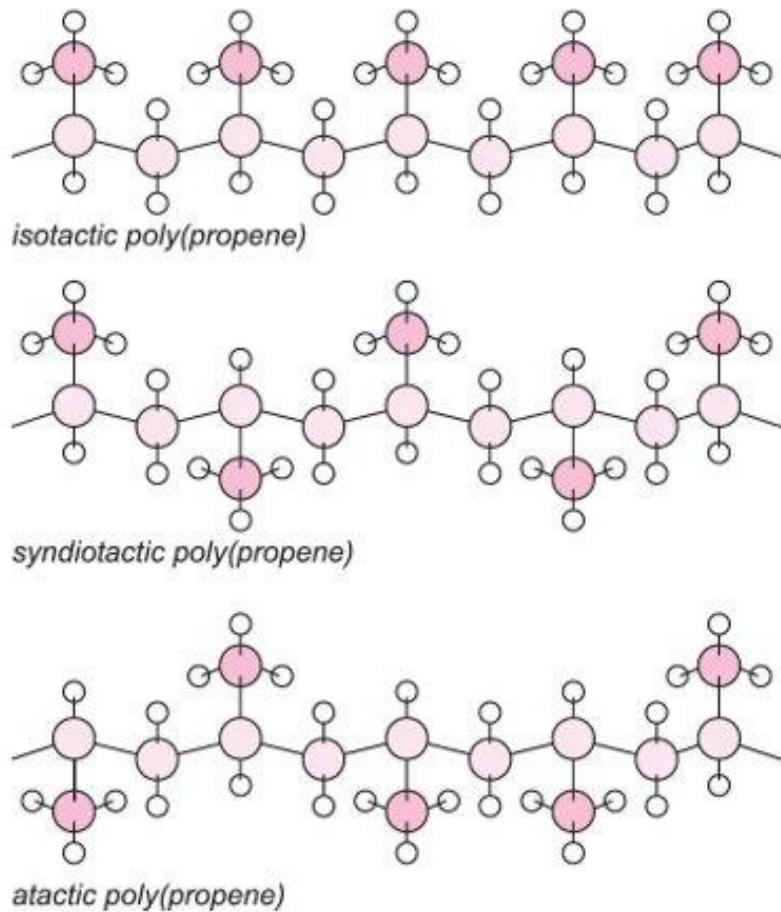
Polymer	Formula
<u>Polyamide 6</u>	$\left[ \text{NH}-(\text{CH}_2)_5-\overset{\text{O}}{\underset{\text{C}}{\text{  }}} \right]_n$
<u>Polyamide 6,6</u>	$\left[ \text{N}(\text{H})-(\text{CH}_2)_6-\text{N}(\text{H})-\overset{\text{O}}{\underset{\text{C}}{\text{  }}}-(\text{CH}_2)_4-\overset{\text{O}}{\underset{\text{C}}{\text{  }}} \right]_n$
The <u>polyester</u> ( <u>terylene</u> ) formed from the dimethyl ester of 1,4-benzenedicarboxylic acid and ethane-1,2-diol	$\left[ \text{O}-\overset{\text{O}}{\underset{\text{C}}{\text{  }}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\underset{\text{C}}{\text{  }}}-\text{O}-\text{CH}_2-\text{CH}_2 \right]_n$
<u>Poly(propenonitrile)</u>	$\left[ \text{CH}_2-\overset{\text{CH}}{\underset{\text{CN}}{\text{  }}} \right]_n$
<u>Poly(ethene)</u>	$\left[ \text{CH}_2-\text{CH}_2 \right]_n$
<u>Poly(propene)</u>	$\left[ \text{CH}_2-\overset{\text{CH}}{\underset{\text{CH}_3}{\text{  }}} \right]_n$
<u>Poly(chloroethene)</u>	$\left[ \text{CH}_2-\overset{\text{Cl}}{\underset{\text{CH}}{\text{  }}} \right]_n$
<u>Poly(tetrafluoroethene)</u>	$\left[ \text{CF}_2-\text{CF}_2 \right]_n$

#### (d) Steric structure

Another way of classifying polymers is by examining their steric structure. Polymers with side chains can be divided into two classes, one (stereoregular) which has a recurring pattern in terms of stereochemistry and one (atactic) with no regular structure. A simple example of a polymer with a side chain is poly(propene). Propene molecule is asymmetrical,



and, when polymerized, can form three basic chain structures dependent on the position of the methyl groups: two are stereoregular (isotactic and syndiotactic) and the third does not have a regular structure and is termed atactic as shown diagrammatically below:



**Figure 4: Molecular structures of poly(propene)**

The 'one handed' structure of isotactic poly(propene) causes the molecules to form helices. This regular form permits the molecules to crystallize to a hard, relatively rigid material, which, in its pure form, melts at 440 K.

The syndiotactic polymer, because of its regular structure, is also crystalline.

Atactic chains are completely random in structure and consequently they do not crystallize. High molecular mass atactic poly(propene) is a rubber-like material.

Commercial poly(propene) is a predominantly isotactic polymer containing 1-5% by mass of atactic material.

Stereoregular polymers are produced when using many Ziegler-Natta (see below) or [metallocene](#) catalysts.

## Manufacture of polymers

As discussed above, polymers can be characterised by the method of polymerization, [addition and condensation](#).

Many addition polymers are produced by using an organometallic compound, known as a Ziegler-Natta catalyst. They were first developed by Karl Ziegler and Giulio Natta which led to the two chemists being awarded the Nobel Prize in 1963 for this brilliant work.

Other addition polymers are produced by generating [free radicals](#) using a compound, known as an initiator, to catalyse the reaction.

Many condensation polymerization reactions, in which one or two monomers are the starting materials, also need catalysts. The catalysts are described in the unit devoted to each condensation polymer.

## Catalysts for polymerization reactions

### Ziegler-Natta catalysts

Ziegler-Natta catalysts are organometallic compounds, prepared from titanium compounds with an aluminium trialkyl which acts as a promoter:



The alkyl groups used include ethyl, hexyl and octyl.

The role of the titanium catalyst can be represented as shown in Figure 5.

The alkene monomer attaches itself to an empty coordination site on the titanium atom and this alkene molecule then inserts itself into the carbon-titanium bond to extend the alkyl chain. This process then continues, thereby forming a linear polymer, [poly\(ethene\)](#).

The polymer is precipitated when the catalyst is destroyed on addition of water. Because it is linear, the polymer molecules are able to pack together closely, giving the polymer a higher melting point and density than poly(ethene) produced by radical initiation.

Not only do Ziegler-Natta catalysts allow for linear polymers to be produced but they can also give stereochemical control. Propene, for example can polymerize in three ways, as shown below in Figure 5, to produce either atactic, isotactic or syndiotactic poly(propene). However, this catalyst only allows the propene to be inserted in one way and isotactic polypropene is produced. Even greater control of the polymerization is obtained using a new class of catalysts, the [metallocenes](#).

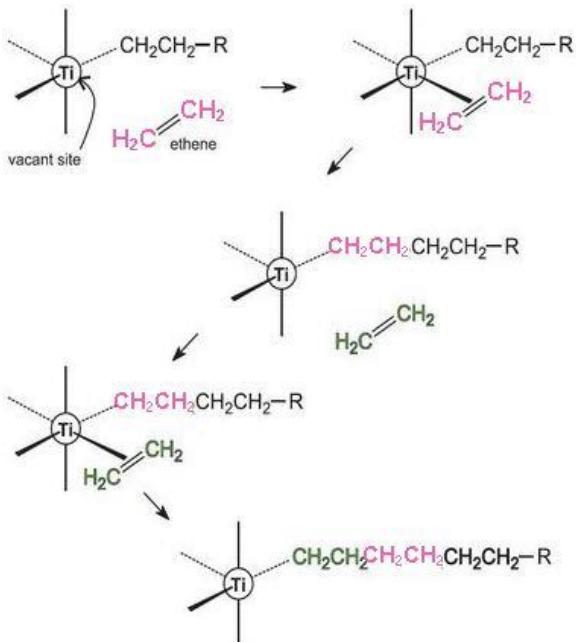
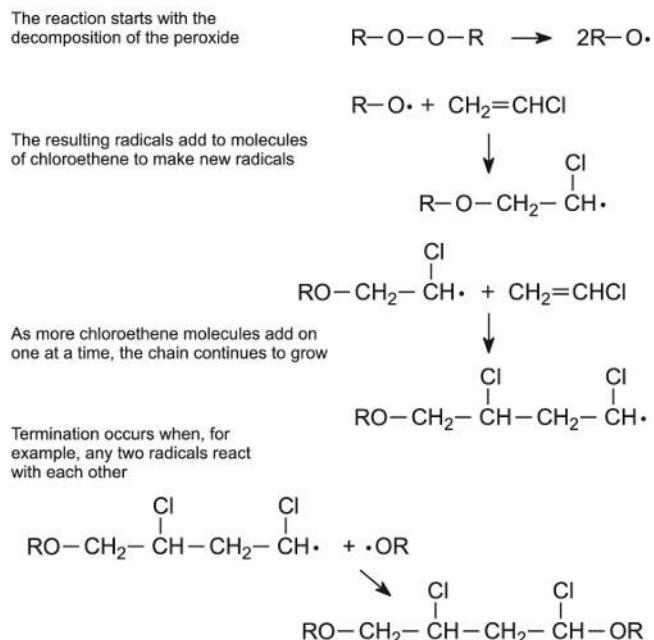


Figure 5: Illustrating the role of a Ziegler-Natta catalyst

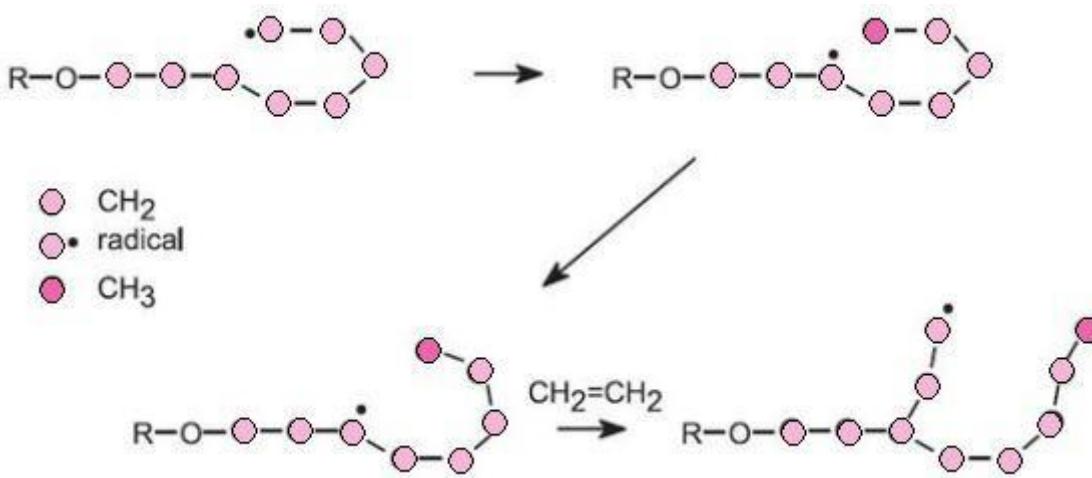
### Radical polymerization

Many polymers, including all of the addition polymers in Table 1, are produced using radical initiators, which act as catalysts. For example, the polymerization of chloroethene is started by warming it with a minute trace of a peroxide (R-O-O-R):



**Figure 6: A mechanism for the free radical polymerization of chloroethene to poly(chloroethene)**

In the case of ethene, by using the free radical process, the resulting polymer has a lower density and a lower softening point than the poly(ethene) produced using a Ziegler-Natta catalyst or a metallic oxide. The low density poly(ethene), LDPE, has side chains because the radicals react not only with molecules of ethene, by addition, but also with polymer molecules, by a process known as hydrogen abstraction. The polymer radical can also abstract a hydrogen atom from its own chain:



Both of these reactions lead to side chains so that the molecules of the polymer cannot pack together in a regular way. The polymer thus has a lower melting point and lower density.

## Plastics formulation

The properties of many plastics can be modified by varying their formulation. For example, one of the most versatile plastics is poly(chloroethene) (PVC). It can be made in either a flexible or a rigid form (and every combination between these extremes) by using various additives (Table 5).

**Table 5: Additives used to enhance the properties of plastics**

Additive	Examples	Function
Plasticiser	e.g. esters of benzene-1,2-dicarboxylic acid	Acts as a lubricant for polymer chains. Large amounts give a flexible product, low quantities produce a rigid one.
Stabiliser	e.g. lead carbonate (<1%), lead phosphate or, for non-toxic requirements, mixtures of metal octadecanoates and epoxidized oil	Prevents decomposition of polymer. Without a stabiliser, poly(chloroethene), for example, decomposes on heating to give a brittle product and hydrogen chloride. Some plastics become coloured (yellowing) when exposed to long periods of sunlight.
Extender	Chlorinated hydrocarbons	Extends the effect of the plasticiser, but generally cannot plasticise alone. They are cheaper than plasticisers, so help reduce costs.
Fillers	Chalk, glass fibre	Tailor the plastic for special requirements, or make it cheaper.
Miscellaneous	Flame retardants, UV stabilisers, antistatics, processing aids, pigments	Impart specially required properties to the plastic for the manufacturing process or for end-use.

### Processing plastics

Processing converts plastics into useful articles. Processing methods are given in Table 6.

**Table 6: Methods of processing plastics**

Process	Application
Compression moulding	Usually for thermosets - powder moulded under heat and pressure.
Injection moulding	Usually for thermoplastics - molten plastics injected into a mould under pressure. The mould surface detail can be accurately reproduced. Very widely used.
Rotational moulding	Usually for thermoplastics. The powder is heated in a closed mould which is rotated, fairly slowly, simultaneously about two axes. Surface detail is poor but this method can be used to make large hollow articles.
Reaction injection moulding	Usually for thermosets, polymerization takes place in the mould thereby producing the finished article directly from a resin.
Extrusion	Usually for thermoplastics - the molten plastics are fed by a screw through a die, which for sheet or film, for instance, is a slit. Various extensions to the process are possible - e.g. a tube may be inflated by air whilst still hot to produce a tubular film (for bags, etc.), or short lengths of hot extruded tube can be inflated in moulds to form bottles.
Calendering	Usually for thermoplastics - molten plastics squeezed between hot rollers to form foil and sheet.
Thermoforming	Heat-softened thermoplastic sheet is drawn into or over a mould. If a vacuum is used to 'suck' the sheet into a mould, the process is known as vacuum forming. This process is used for a variety of articles, ranging from chocolate box liners to acrylic baths.

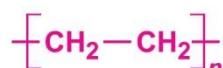
## Polymers: their manufacture and uses

While this unit is concerned with the general principles underlying the structure, formulation and processing of polymers produced today, the manufacture and properties of the polymers vary considerably. The following are discussed in other units:

- [Formaldehyde plastics](#)
- [Polyamides](#)
- [Polycarbonates](#)
- [Poly\(Vinyl chloride\)](#)
- [Polyesters](#)
- [Poly\(ethylene\)](#)
- [Poly\(methyl methacrylate\)](#)
- [Poly\(styrene\)](#)
- [Poly\(propylene\)](#)
- [Poly\(acrylic acid\)](#)
- [Poly\(acrylonitrile\)](#)
- [Poly\(tetrafluoroethylene\)](#)
- [Polyurethanes](#)
- [Silicones](#)

Important developments in recent years include [degradable plastics](#) and methods of [recycling polymers](#) which include reusing the polymer and degradation followed by repolymerization.

### Poly(ethene) (Polyethylene)



Well over 100 million tonnes of poly(ethene), often known as polyethylene and polythene, is manufactured each year making it the world's most important plastic. This accounts for over 60% of the ethene manufactured each year.

#### Uses of poly(ethene) (polyethylene)

Poly(ethene) is produced in three main forms: low density (LDPE) ( $< 0.930 \text{ g cm}^{-3}$ ) and linear low density (LLDPE) ( $ca\ 0.915\text{--}0.940 \text{ g cm}^{-3}$ ) and high density (HDPE) ( $ca\ 0.940\text{--}0.965 \text{ g cm}^{-3}$ ). The LDPE or LLDPE form is preferred for film packaging and for electrical insulation. HDPE is blow-moulded to make containers for household chemicals such as washing-up liquids and drums for industrial packaging. It is also extruded as piping.

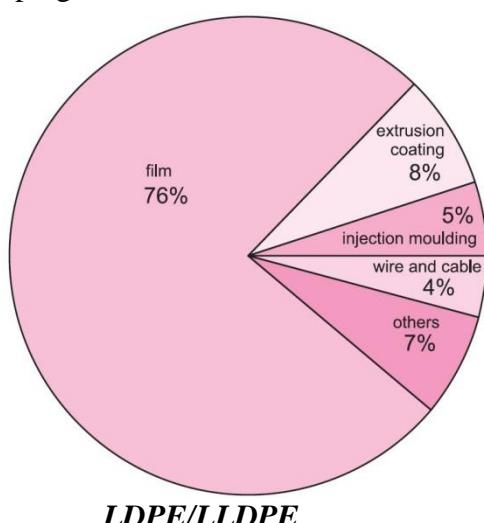
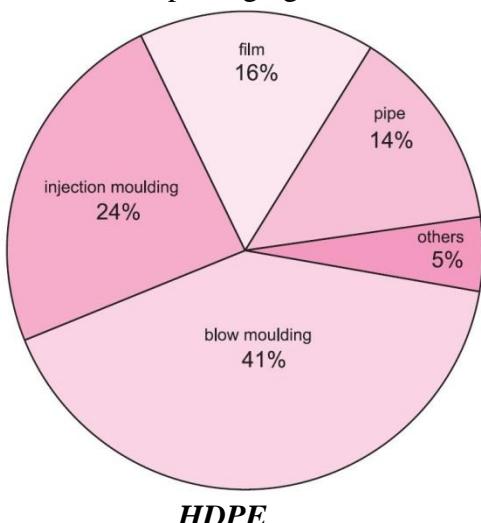


Figure 7: Uses of poly(ethene)

All forms can be used for injection-moulded products such as buckets, food boxes and washing-up bowls (Table 7).

**Table 7: Examples of uses of poly(ethene)**

<b>Process</b>	<b>HDPE</b>	<b>LDPE</b>	<b>LLDPE</b>
Making film	Food packaging Shopping bags	Cling film Milk carton lining	Stretch film
Injection moulding	Dustbins Crates	Buckets Bowls	Food boxes
Blow moulding	Detergent bottles Drums	Squeezable bottles	
Extrusion	Water pipes	Flexible water pipes Cable jacketing	Cable coating

Many plants can produce both forms of poly(ethene) and alter the amount that they produce of each type at short notice. Both use a Ziegler (or Phillips) catalyst. If pure ethene is used, HDPE is formed. LLDPE is produced when a small amount of another alkene, for example but-1-ene, is added to the ethene. Another form, discussed below, mLLDPE, is, at present, produced in much smaller quantities, but its demand is fast rising.

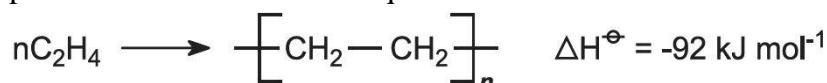
## Manufacture of poly(ethene) (polyethylene)

Poly(ethene) is made by several methods by addition polymerization of ethene, which is principally produced by the cracking of ethane and propane, naphtha and gas oil.

A new plant is being constructed in Brazil for the production of poly(ethene), from ethene, that is made from sugar cane via [bioethanol](#). This is sometimes termed [bio-based poly\(ethene\) \(bio-based polyethylene\)](#).

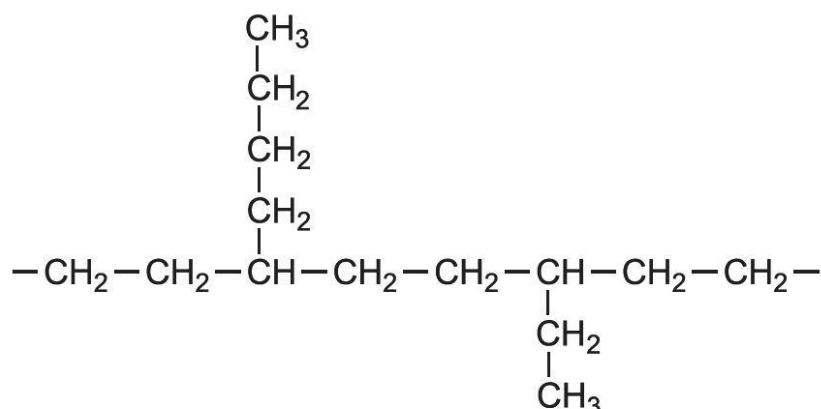
## *Low density poly(ethene) (LDPE)*

The process is operated under very high pressure (1000-3000 atm) at moderate temperatures (420-570 K) as may be predicted from the reaction equation:

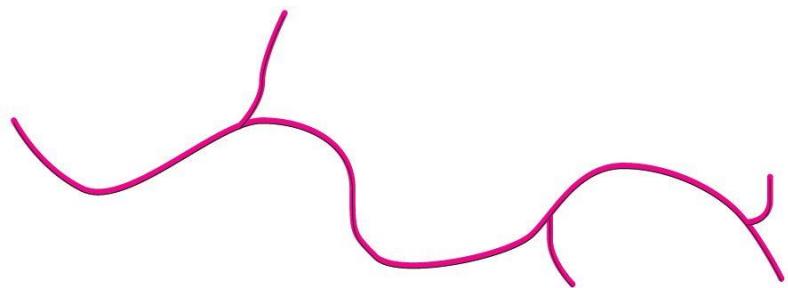


This is a radical polymerization process and an initiator, such as a small amount of oxygen, and/or an organic peroxide is used.

Ethene (purity in excess of 99.9%) is compressed and passed into a reactor together with the initiator. The molten poly(ethene) is removed, extruded and cut into granules. Unreacted ethene is recycled. The average polymer molecule contains 4000-40000 carbon atoms, with many short branches. For example,



It can be represented by:



There are about 20 branches per 1000 carbon atoms. The relative molecular mass, and the branching, influence the physical properties of LDPE. The branching affects the degree of crystallinity which in turn affects the density of the material. LDPE is generally amorphous and transparent with about 50% crystallinity. The branches prevent the molecules fitting closely together and so it has low density.

### **High density poly(ethene) (HDPE)**

Two types of catalyst are used principally in the manufacture of HDPE:

- a Ziegler-Natta organometallic catalyst (titanium compounds with an aluminium alkyl).
- an inorganic compound, known as a Phillips-type catalyst. A well-known example is chromium(VI) oxide on silica, which is prepared by roasting a chromium(III) compound at *ca* 1000 K in oxygen and then storing prior to use, under nitrogen.

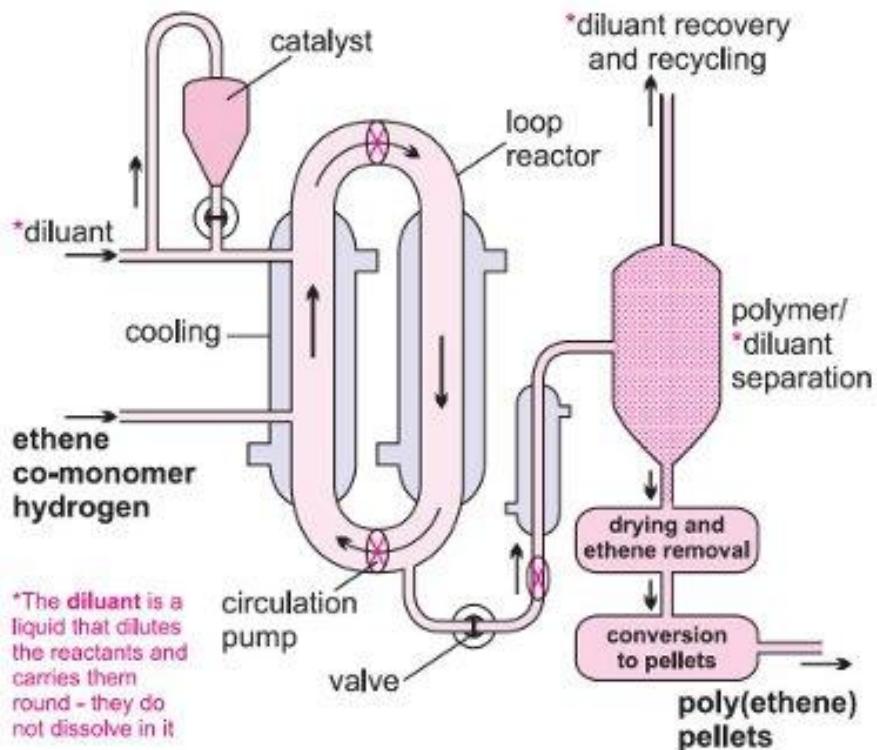
HDPE is produced by three types of process. All operate at relatively low pressures (10-80 atm) in the presence of a Ziegler-Natta or inorganic catalyst. Typical temperatures range between 350-420 K. In all three processes hydrogen is mixed with the ethene to control the chain length of the polymer.

#### **(i) Slurry process (using either CSTR (continuous stirred tank reactor) or a loop)**

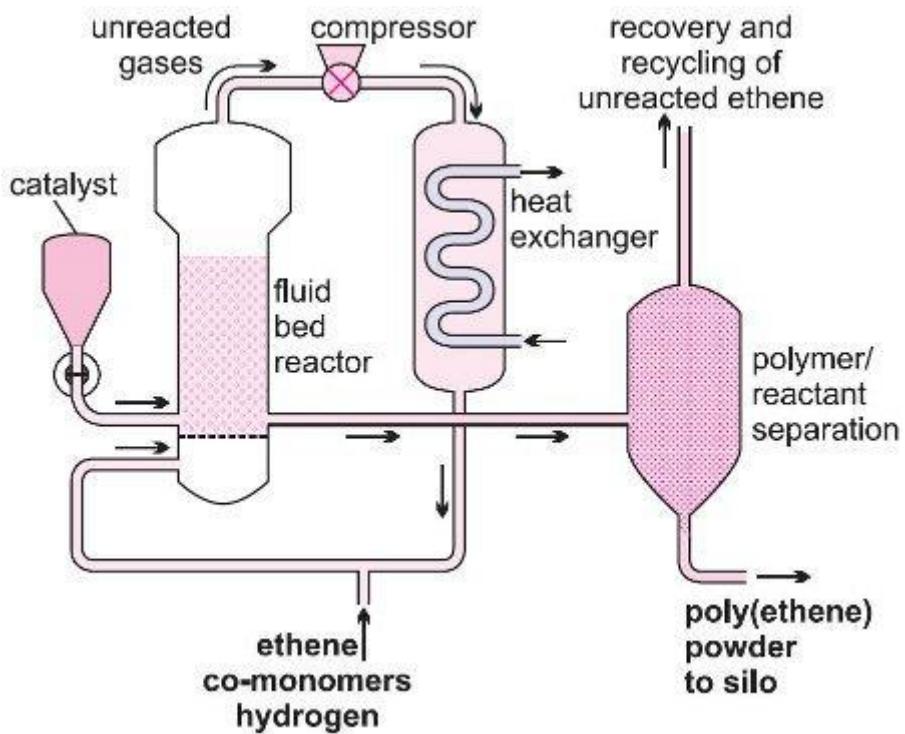
The Ziegler-Natta catalyst, as granules, is mixed with a liquid hydrocarbon (for example, 2-methylpropane (isobutane) or hexane), which simply acts as a diluent. A mixture of hydrogen and ethene is passed under pressure into the slurry and ethene is polymerized to HDPE. The reaction takes place in a large loop reactor with the mixture constantly stirred (Figure 4). On opening a valve, the product is released and the solvent is evaporated to leave the polymer, still containing the catalyst. Water vapour, on flowing with nitrogen through the polymer, reacts with the catalytic sites, destroying their activity. The residue of the catalyst, titanium(IV) and aluminium oxides, remains mixed, in minute amounts, in the polymer.

#### **(ii) Solution process**

The second method involves passing ethene and hydrogen under pressure into a solution of the Ziegler-Natta catalyst in a hydrocarbon (a C<sub>10</sub> or C<sub>12</sub> alkane). The polymer is obtained in a similar way to the slurry method.



**Figure 8:** The manufacture of poly(ethene) using the slurry process in a loop reactor



**Figure 9:** Low pressure gas-phase process

### (iii) Gas phase process

A mixture of ethene and hydrogen is passed over a Phillips catalyst in a fixed bed reactor (Figure 9). Ethylene polymerizes to form grains of HDPE, suspended in the flowing gas, which pass out of the reactor when the valve is released.

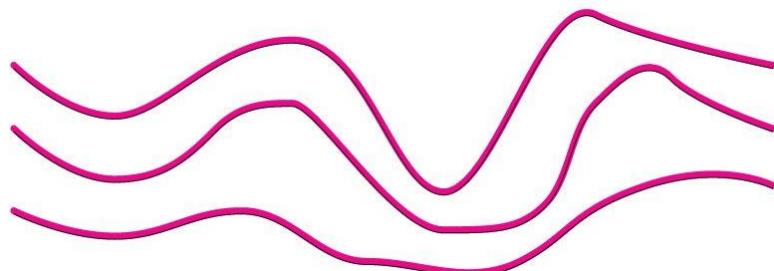
Modern plants sometimes use two or more of the individual reactors in series (for example two or more slurry reactors or two gas phase reactors) each of which are under slightly different

conditions, so that the properties of different products from the reactors are present in the resulting polymer mixture, leading to a broad or bimodal molecular mass distribution. This provides improved mechanical properties such as stiffness and toughness.



**Figure 10: Granules of poly(ethene) which are then used to make film, extruded into pipes or moulded**

The HDPE powder coming out of any of the reactors discussed above is separated from the diluent or solvent (if used) and is extruded and cut up into granules. This method gives linear polymer chains with few branches. The poly(ethene) molecules can fit closer together. The polymer chains can be represented thus:



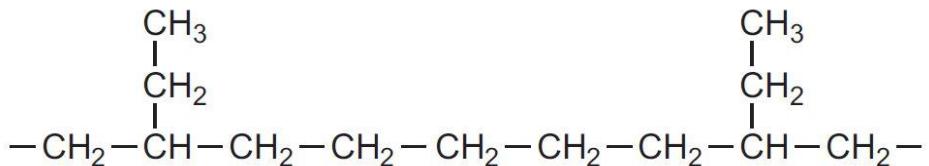
This leads to strong intermolecular bonds, making the material stronger, denser and more rigid than LDPE. The polymer is not transparent.

#### *Linear low density poly(ethene) (LLDPE)*

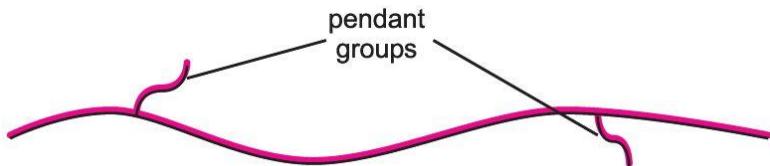
Low density poly(ethene) has many uses but the high pressure method of manufacture by which it is produced has high capital costs. However, an elegant technique has been developed, based on both [Ziegler-Natta](#) and inorganic catalysts to produce linear low density poly(ethene) LLDPE, which has even improved properties over LDPE. Any of the three processes, slurry, solution and gas phase, can be used when a Ziegler-Natta catalyst is chosen. The gas phase process is used when the inorganic catalyst is employed.

Small amounts of a co-monomer such as but-1-ene or hex-1-ene are added to the feedstock. The monomers are randomly polymerized and there are small branches made up of a few carbon atoms along the linear chains.

For example, with but-1-ene,  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ , the structure of the polymer is:



The side chains are known as pendant groups, or short chain branching. The molecule can be represented as:



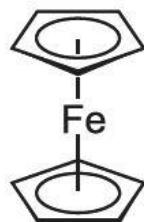
The structure is essentially linear but because of the short chain branching it has a low density. The structure gives the material much better resilience, tear strength and flexibility without the use of plasticisers. This makes linear low density poly(ethene) an ideal material for the manufacture of film products, such as those used in wrappings.

The properties of the polymer, and hence its uses, can be varied by varying the proportion of ethene and co-monomer and by using different co-monomers. All this can be done without shutting down the plant, an enormous advantage.

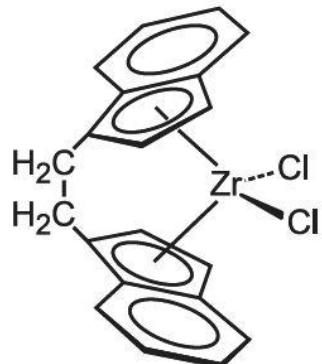
### *Metallocene linear low density poly(ethene) (mLLDPE)*

This poly(ethene), known as mLLDPE, is produced by a new family of catalysts, the metallocenes. Another name for this family is *single site catalyst*. The benefit is that the mLLDPE is much more homogenous in terms of molecular structure than classical LLDPE produced by Ziegler-Natta catalysts. Each catalyst is a single site catalyst which produces the same PE chain. Chemists have compared the structure of metallocenes to that of a sandwich. There is a transition metal (often zirconium or titanium) 'filling' a hole between layers of organic compounds.

Metallocenes are being increasingly used as catalysts for the production of poly(ethene) (mLLDPE) and poly(propene). Metallocenes are strictly defined as molecules which have a transition metal atom bonded between two cyclopentadienyl ligands which are in parallel planes. Ferrocene is a particularly well known example:



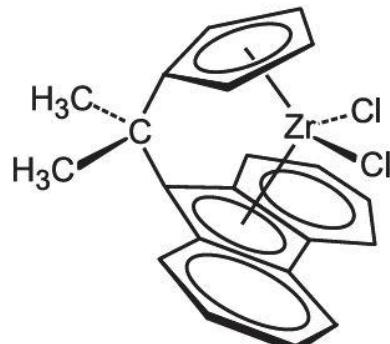
However, the term is now used more widely to include other ligands related to cyclopentadienyl. One such metallocene is based on zirconium:



Zirconium has an oxidation state of 4 and is bonded to two indenyl ligands (a cyclopentadienyl ligand fused to a benzene ring). They are joined by two CH<sub>2</sub> groups. In conjunction with an organoaluminium compound, it acts as a catalyst for the polymerization of alkenes such as ethene

and propene. The specific orientation of the zirconium compound means that each propene molecule, for example, as it adds on to the growing polymer chain is in the same orientation and an isotactic polymer is produced.

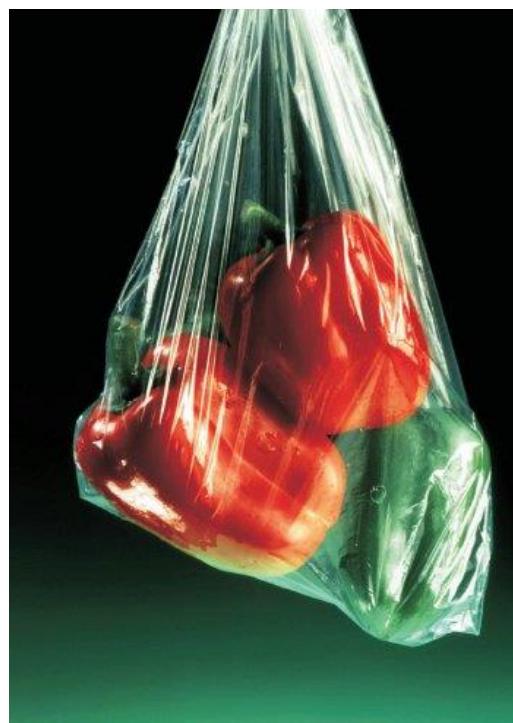
When a different zirconium compound is used,



the syndiotactic form of poly(propene) is produced. This is the only way of making syndiotactic poly(propylene) commercially. As with the Ziegler-Natta catalysts, the bulk or gas phase (described above) can be used. Alternatively, the [slurry process](#) is used. Poly(propylenes) made in this way, mPP, are used in particular to make non-woven fibres and heat-seal films. Metallocenes also catalyse the production of co-polymers of propene and ethene.

The catalysts are even more specific than the original [Ziegler-Natta](#) and it is possible to control the polymer's molecular mass as well as its configuration. Either the slurry or solution processes are usually used.

Poly(ethene) produced using a metallocene can be used as very thin film which has excellent optical properties and sealing performance, thus making them very effective for wrapping foods. The real plus for the metallocene catalysts are the enhanced mechanical properties of the films made out of mLLDPE.

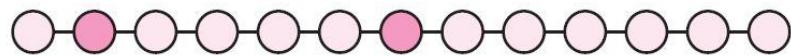


*Figure 11: Poly(ethene) film is used extensively for wrapping foods*

## Co-polymers

Ethene forms [co-polymers](#) with propene which have very useful properties.

There are two main types of co-polymer. The simplest are the [random co-polymers](#), produced by polymerizing together ethene and propene. Ethene units, usually up to 6% by mass, are incorporated randomly in the poly(propene) chains (Figure 12).

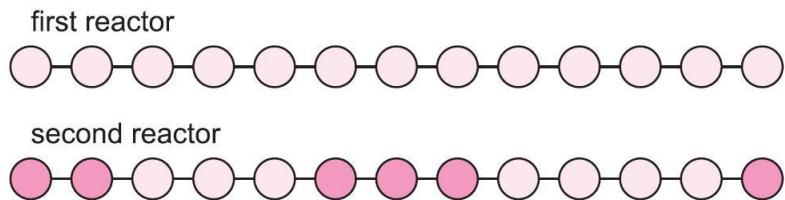


*Figure 12: Illustrating an alternating co-polymer formed from propene and a small amount of ethene.*

The crystallinity and melting point are reduced and the products are more flexible and are optically much clearer. Major uses for these random co-polymers are for medical products (pouches, vials and other containers) and packaging (for example, bottles, CD and video boxes).

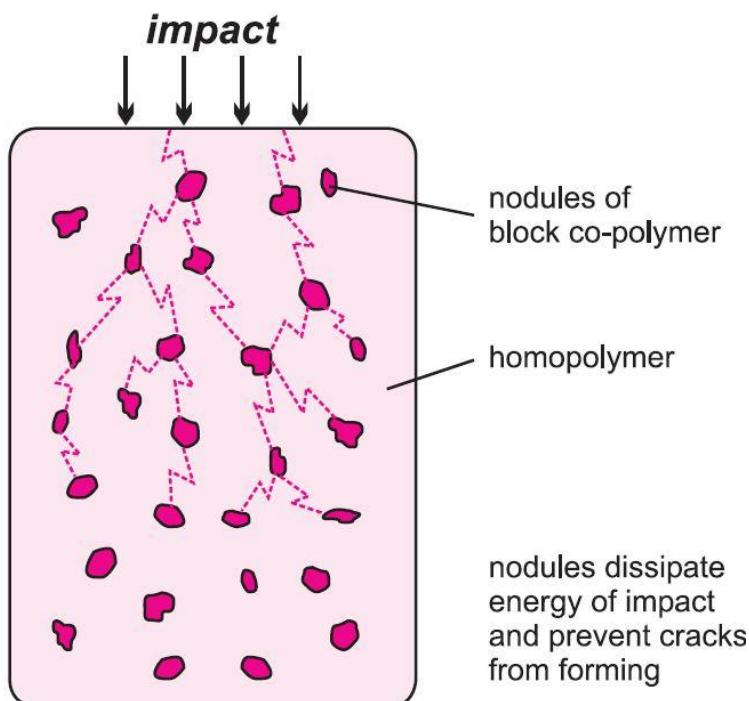
Many other co-polymers of ethene and propene, with higher alkenes such as hexene, are being developed which will produce polymers similar to [LLDPE](#) but which have better mechanical and optical properties.

The second type of co-polymers is the so-called 'block' co-polymers. These are made by following the poly(propene) homopolymerization with a further, separate stage, in which ethene and propene are co-polymerized in the gas phase. Thus these two processes are in series (Figure 13).



*Figure 13: Illustrating the homopolymer and the block co-polymer formed from propene and ethene.*

The products of these two processes form a [composite](#) in which nodules of the block co-polymer are distributed with the homopolymer (Figure 14).



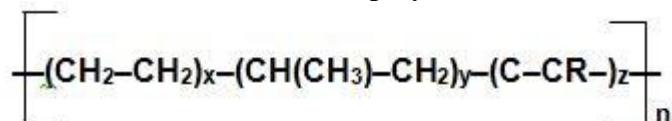
*Figure 14: The propene-ethene block co-polymer nodules dissipate impact energy and prevent cracking.*

The ethene content of the block co-polymer is larger (between 5 and 15%) than used in randomly alternating co-polymers. It has rubber-like properties and is tougher and less brittle than the

random co-polymer. Consequently, the composite is particularly useful in making crates, pipes, furniture and toys, where toughness is required.

When ethene, propene and a third monomer, a diene, are polymerized, a rubber is formed, known as EPDM (Ethene, Propene, Diene, polyMethylene). The ethene and propene molecules polymerize to form very long molecular chains, with several thousand monomer molecules in a chain.

The polymerization is usually effected in solution using a [Zeigler-Natta catalyst](#) but more recently, [metallocenes](#) have been used very successfully. Usually the ethene content is about 60% and that of the diene varies between 2 and 7%. The polymer chain has the structure,

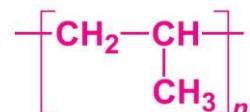


where R contains one carbon-carbon double bond.

As can be seen from the formula, it is a [block co-polymer](#).

As the diene (usually ENB ethylidene norbornene) has two double bonds, one is used in the chain and the other is used to form a three dimensional structure. The reactive sites are pendant (not part of the backbone of the chain) and are joined together in the next part of the process when the polymer is heated with sulfur, the process used to vulcanize rubber. The two dimensional structure shown above becomes three dimensional.

## Poly(propene) (Polypropylene)



Propene undergoes addition polymerization to produce poly(propene), often known as polypropylene, which is one of the most versatile thermoplastic polymers available commercially. Mixtures of propene and other monomers form a wide range of important co-polymers.

### Uses of poly(propene) (polypropylene)

Poly(propene) is processed into film, for packaging and into fibres for carpets and clothing. It is also used for injection moulded articles ranging from car bumpers to washing up bowls, and can be extruded into pipe (Figure 15).

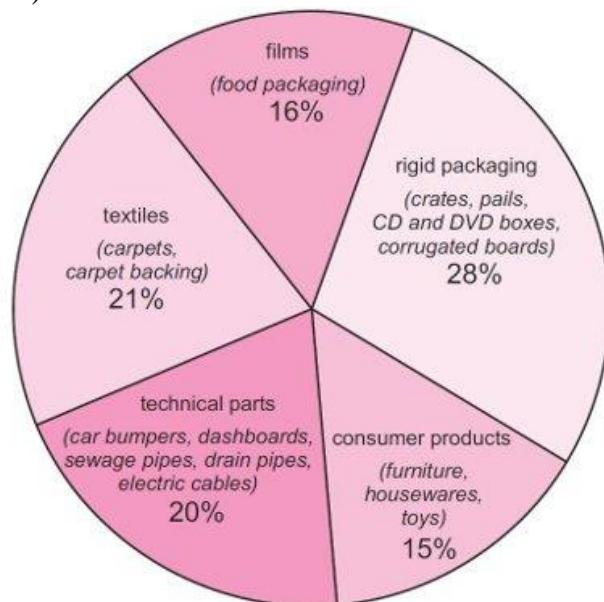


Figure 15: Uses of poly(propene)

Materials suitable for a much wider range of applications can be made by compounding poly(propene) with, for example, [fillers and pigments](#), and elastomers. Poly(propene) has remarkable properties, making it suitable to replace glass, metals, cartons and other polymers.

These properties include:

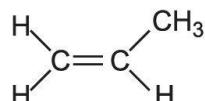
- low density (weight saving)
- high stiffness
- heat resistance
- chemical inertness
- steam barrier properties (food protection)
- good transparency
- good impact/rigidity balance
- stretchability (film and fibre applications)
- good hinge property (for example where a lid and box are made together, for DVD boxes)
- high gloss (appearance)
- easy to weld (design)
- recyclability

The majority (*ca* 60% of the total produced) of poly(propene) is produced as a homopolymer. Co-polymers are discussed below.

Poly(propene) is one of the lightest thermoplastics (density 0.905 g cm<sup>-3</sup>). It has a melting point of 440 K and a crystallinity of *ca* 50-60%. The polymer, unlike poly(ethene), is transparent.

### Structure of the polymer

The propene molecule is asymmetrical,



and, when polymerized, can form three basic chain structures dependent on the position of the methyl groups: two are stereoregular (isotactic and syndiotactic) and the third does not have a regular structure and is termed [atactic](#) as shown diagrammatically below:

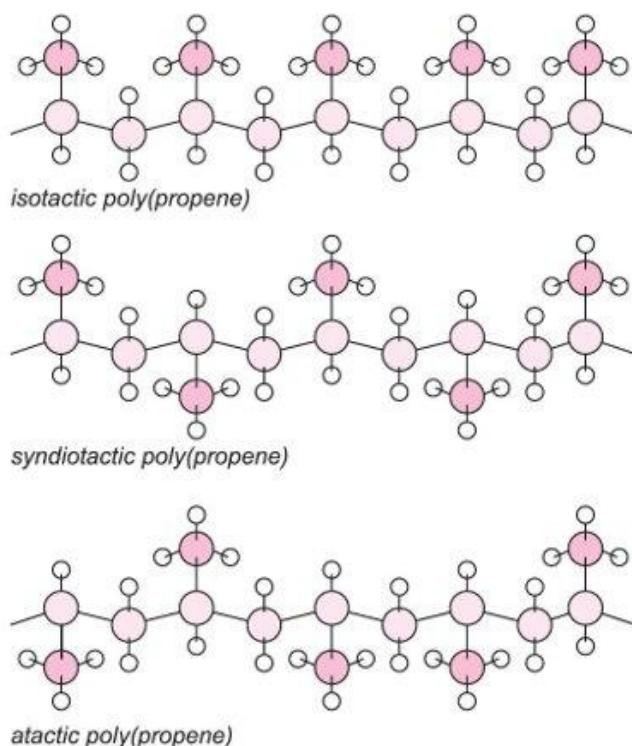


Figure 16: Molecular structures of poly(propene)

The 'one handed' structure of isotactic poly(propene) causes the molecules to form helices. This regular form permits the molecules to crystallize to a hard, relatively rigid material, which, in its pure form, melts at 440 K.

The syndiotactic polymer, because of its regular structure, is also crystalline.

Atactic chains are completely random in structure and consequently they do not crystallize. High molecular mass atactic poly(propene) is a rubber-like material. Commercial poly(propene) is a predominantly isotactic polymer containing 1-5% by mass of atactic material.

### Manufacture of poly(propene) (polypropylene)

Poly(propene) is produced from propene. Propene is produced in large quantities from gas oil, naphtha, ethane and propane. Parallel to this, there are several methods being developed to produce bio-based poly(propene) (bio-based polypropylene) via bio-based-propene.

#### (a) Using a Ziegler-Natta catalyst

Ziegler-Natta catalysts are used in the polymerization process. These are produced by interaction of titanium (IV) chloride and an aluminium alkyl, such as triethyl aluminium. Two main processes are used for making the polymer with these catalysts, although the slurry method is used as well.

#### (i) The bulk process

Polymerization takes place in liquid propene, in the absence of a solvent at a temperature of 340-360 K and pressures of 30-40 atm (to keep the propene as a liquid). After polymerization, solid polymer particles are separated from liquid propene, which is then recycled.

The use of liquid propene as a solvent for the polymer as it is formed means that there is no need to use hydrocarbons such as the C<sub>4</sub>-C<sub>8</sub> alkanes which are used in the parallel manufacture of poly(ethene).

#### (ii) The gas phase process

A mixture of propene and hydrogen is passed over a bed containing the Ziegler-Natta catalyst at temperatures of 320-360 K and a pressure of 8-35 atm.

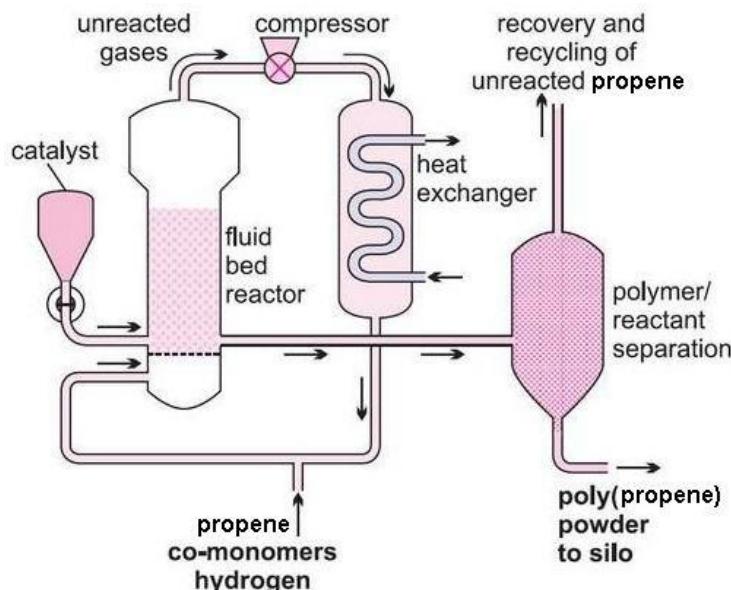


Figure 17: Low pressure gas-phase process

The polymer is separated from the gaseous propene and hydrogen using cyclones and the unreacted gas is recycled.

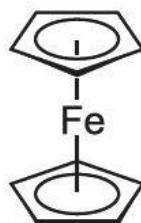
Both processes can be operated continuously and use 'stereospecific' Ziegler-Natta catalysts to effect the polymerization. The catalyst remains in the product and needs to be destroyed using water or alcohols, before the polymer is converted into pellets.

Both bulk and gas phase processes have virtually eliminated gaseous and aqueous effluents by the use of high activity catalysts, resulting in low residues in the final polymer.

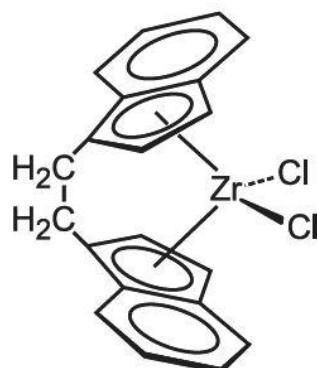
**(b) Using a metallocene as catalyst**

Metallocenes are being increasingly used as catalysts for the production of [poly\(ethene\)](#) ([mLLDPE](#)) and poly(propene).

Metallocenes are strictly defined as molecules which have a transition metal atom bonded between two cyclopentadienyl ligands which are in parallel planes. Ferrocene is a particularly well known example:

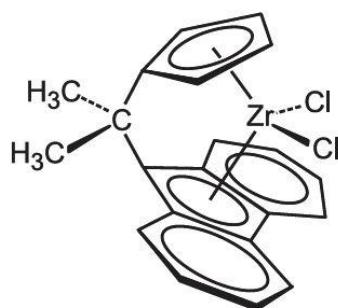


However, the term is now used more widely to include other ligands related to cyclopentadienyl. One such metallocene is based on zirconium:



Zirconium has an oxidation state of 4 and is bonded to two indenyl ligands (a cyclopentadienyl ligand fused to a benzene ring). They are joined by two  $\text{CH}_2$  groups. In conjunction with an organoaluminium compound, it acts as a catalyst for the polymerization of alkenes such as ethene and propene. The specific orientation of the zirconium compound means that each propene molecule, for example, as it adds on to the growing polymer chain is in the same orientation and an isotactic polymer is produced.

When a different zirconium compound is used,



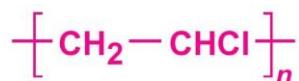
the syndiotactic form of poly(propene) is produced. This is the only way of making syndiotactic poly(propene) commercially.

As with the Ziegler-Natta catalysts, the bulk or gas phase (described above) can be used. Alternatively the [slurry process](#) is used.

Poly(propenes) made in this way, mPP, are used in particular to make non-woven fibres and heat-seal films.

Metallocenes also catalyse the production of co-polymers of propene and ethene.

## Poly(chloroethene) (Polyvinyl chloride)



Poly(chloroethene), usually known as polyvinyl chloride or just PVC, is the most versatile plastic and, after poly(ethene), the most widely used. The variety of uses comes from its ability to be formulated with different additives and with different molecular masses, giving plastics that range from rigid to pliable.

### Uses of poly(chloroethene) (polyvinyl chloride)

Poly(chloroethene) is used in *building and construction*, for example in making window and door profiles and in making pipes (from guttering to sewers, and ducting for cables).

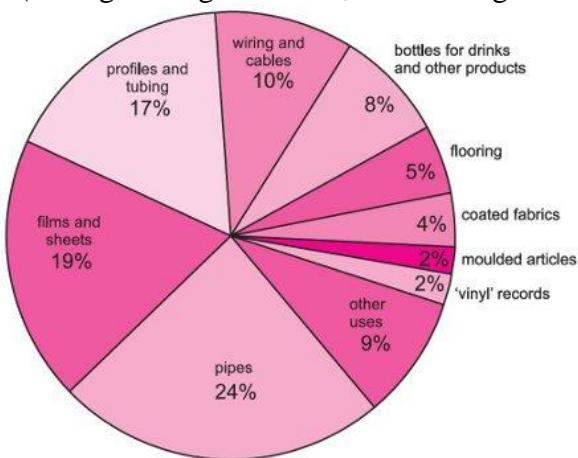


Figure 18: Uses of poly(chloroethene)

It is also much used for *packaging*, including film for food and bottles. *Wire and cable* insulation and sheathing, for example in telephones, computers as well as for power transmission cables, is another main outlet for the polymer.

Chloroethene (vinyl chloride) is also used to produce co-polymers, for example with ethenyl ethanoate (vinyl acetate). The co-polymer can be processed at much lower temperatures than poly(chloroethene) homopolymers of the same relative molecular mass. It is used for coating metals and wood. The film is flexible, hard wearing, resistant to chemical attack and can be pigmented so that it is particularly suitable, for example, for ships. The co-polymer is also used in adhesives and in inks.

### Manufacture of poly(chloroethene) (polyvinyl chloride)

The production of PVC involves several stages:

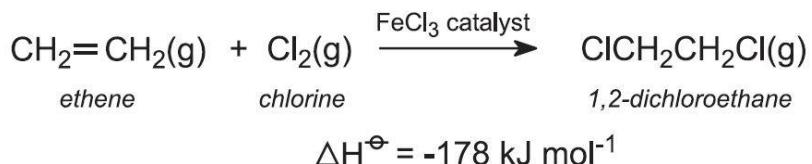
- ethene is converted into 1,2-dichloroethane
- 1,2-dichloroethane is cracked to chloroethene (vinyl chloride)
- Polymerization of chloroethene (vinyl chloride)

#### (a) Production of 1,2-dichloroethane

Ethene is obtained from the cracking of ethane, propane, naphtha and gas oil. In practice, two processes for the overall conversion of ethene to chloroethene are used in parallel.

##### (i) Direct chlorination

Ethene is reacted with chlorine in the liquid phase, using excess chloroethene as solvent. The catalyst, iron(III) chloride, is soluble in chloroethene. The reaction is exothermic, and no external heat is needed.

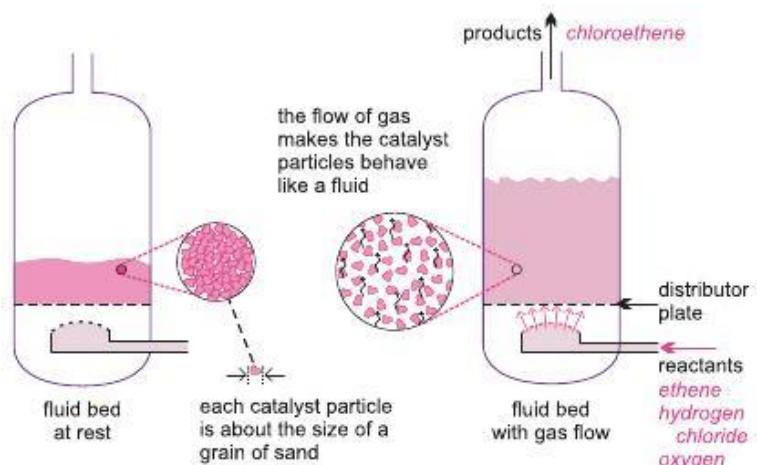


The reaction temperature is maintained at 320-350 K and with a pressure of ca 4 atm. Higher temperatures give unwanted polychlorinated compounds.

## (ii) Oxychlorination route

The cracking of 1,2-dichloroethane during stage (b) of the overall process forms hydrogen chloride as a by-product. It is unwanted as hydrogen chloride and is very detrimental to the environment. However, it can be used in this second method of making 1,2-dichloroethane.

Ethene is mixed with hydrogen chloride and air (enriched with oxygen). The gases are passed over a heated solid catalyst in metal tubes, in a **fluid bed reactor**, maintained at *ca* 500 K and 5 atm.



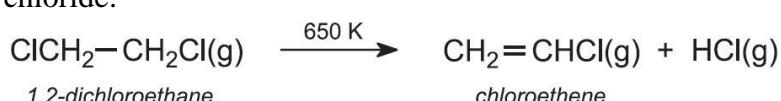
**Figure 19:** A diagram to illustrate the use of a fluid bed reactor for the oxychlorination of ethene to chloroethene. On the left hand side, the catalyst particles are at rest. On the right hand side, the particles are now acting as a fluid, as the gaseous reactants pass through the solid.

The catalyst generally used is a mixture of copper(II) and potassium chlorides, deposited on alumina. As the reaction is highly exothermic, the reactor vessel is cooled to give the optimum reaction temperature and to reduce unwanted by-product formation of, for example, chloroethane and 1,1,1,2-tetrachloroethane. 95% conversion of ethene to 1,2-dichloroethane is obtained.

Unreacted hydrogen chloride is removed by scrubbing the gases with aqueous sodium hydroxide solution. Impurities, such as unreacted ethene and unwanted chlorinated hydrocarbons, are removed by distillation. Ethene is recycled.

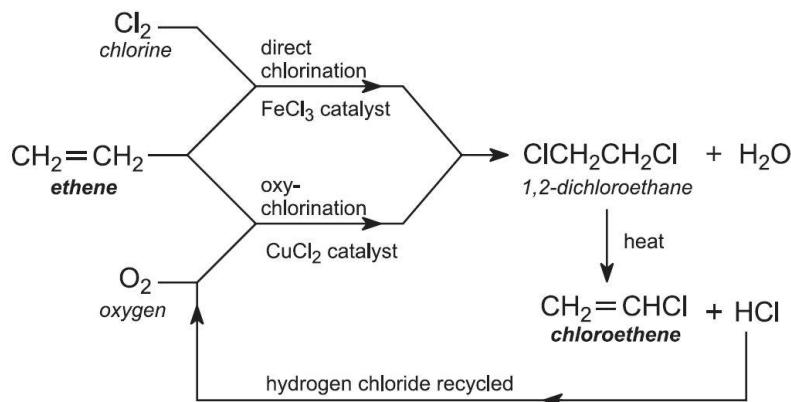
(b) Production of chloroethene (vinyl chloride)

1,2-dichloroethane is then passed rapidly through metal tubes heated to ca 650 K. It is cracked to eliminate hydrogen chloride:



Thus, the above two processes are normally operated in parallel, with the purified 1,2-dichloroethane from both routes cracked to give chloroethene (Figure 20). Chloroethene is separated from hydrogen chloride and unconverted 1,2-dichloroethane in a two-stage distillation process. Hydrogen chloride is removed in the first stage and recycled to the oxychlorination

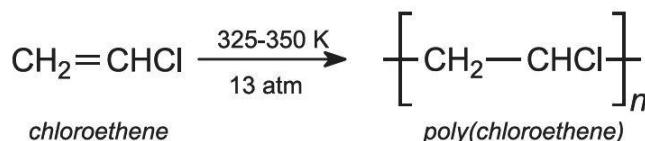
process. The second stage separates chloroethene from unreacted 1,2-dichloroethane, which is recycled to the cracker. The cracking process has been modified by increasing the volume of the reactor. This increase in volume increases the conversion and reduces the energy required to produce chloroethene.



**Figure 20: The manufacture of chloroethene**

### (c) Polymerization of chloroethene (vinyl chloride)

This is an example of addition polymerization. PVC is made by free-radical polymerization in suspension. The monomer (bp 259 K) is polymerized in aqueous dispersion at 325–350 K. Pressure (13 atm) is used to keep the monomer in a liquid phase. For polymerization to be controlled, an initiator is needed.



In suspension polymerization an initiator, an organic peroxide is used, which is soluble in chloroethene. After the reaction, excess monomer is removed and the polymer is separated, by centrifuging and drying.

During polymerization, the polymer precipitates out as it is formed, since it is insoluble in the monomer. It is used for the extrusion, injection moulding and film-making processes.

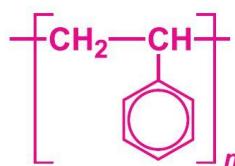
It is estimated that nearly 80% of the polymer is produced by suspension polymerization.

Alternatively, chloroethene is polymerized as an emulsion in water. Ammonium peroxodisulfate is often used as the catalyst as it is soluble in water. The monomer is in the form of very fine droplets rather similar to paint. On evaporation after the polymerization, a very fine powder is formed. This is used as a coating on, for example, flooring and wallpaper.

### The Future

Ethane is a much cheaper feedstock than ethene. Much work, over many years, has been devoted to developing a process to produce chloroethene directly from ethane, rather than first converting feedstocks, such as ethane to ethene. The first such plant has come on stream in Germany. Ethane, hydrogen chloride and oxygen (separated from air in a nearby unit are heated to *ca* 750 K over a catalyst. At present only a small plant has been built but if successful large plants will follow.

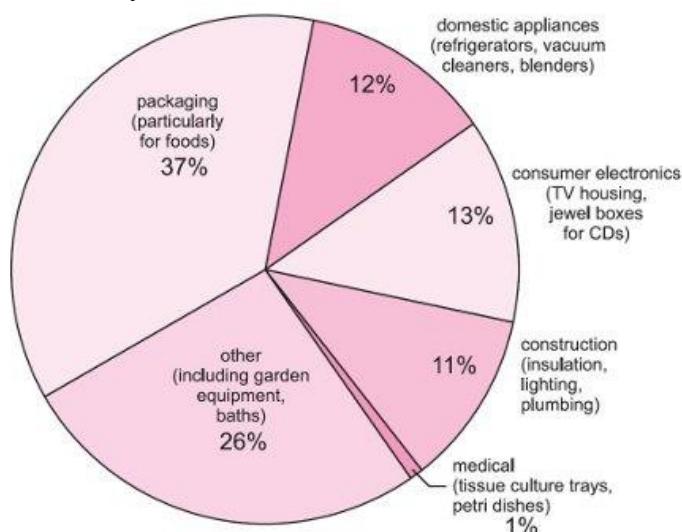
## Poly(phenylethene) (Polystyrene)



Poly(phenylethene), commonly known as polystyrene, is the third most important polymer, in terms of amount made from ethene. Its physical properties can be adjusted to suit a range of everyday uses. Techniques have been developed which increase its mechanical strength, its ability to absorb shock and its thermal insulating properties.

### Uses of poly(phenylethene) (polystyrene)

The largest use for poly(phenylethene) is for packaging, particularly for foods such as poultry and eggs, for cold drinks and take-away meals.



**Figure 21: Uses of poly(phenylethene)**

It is also used in making appliances, including refrigerators, microwaves and blenders. It is the leading choice for jewel boxes (cases for CDs and DVDs) and is also widely used for its insulating properties.

It is not only used to make poly(phenylethene) (polystyrene) itself but also for these important copolymers:

- phenylethene (styrene) with buta-1,3-diene, known as SBS
- phenylethene (styrene) with propenonitrile (acrylonitrile) and buta-1,3-diene, known as ABS (acrylonitrile-butadiene-styrene)
- phenylethene (styrene) with propenonitrile (acrylonitrile), known as SAN (styrene-acrylonitrile)

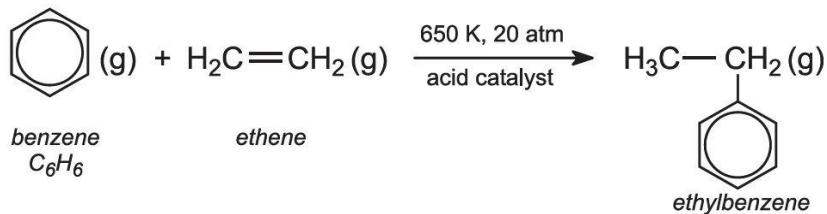
### Manufacture of poly(phenylethene) (polystyrene)

Poly(phenylethene) is manufactured from its monomer, phenylethene. Phenylethene, in turn, is produced from benzene and ethene via ethylbenzene. There are thus three stages:

- a) the manufacture of ethylbenzene from benzene
- b) the manufacture of phenylethene (styrene)
- c) the polymerization of phenylethene (styrene)

#### (a) The manufacture of ethylbenzene from benzene

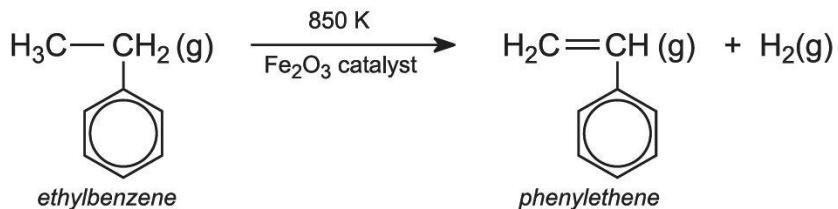
Benzene vapour and ethene are mixed and passed over an acid catalyst, at 650 K and 20 atm pressure:



This is an example of a Friedel-Crafts reaction. The acid catalyst now used is a [zeolite](#), ZSM-5, an aluminosilicate.

*(b) The manufacture of phenylethene (styrene)*

Ethylbenzene vapour is mixed with excess steam and passed over heated iron(III) oxide. Other metal oxides used as the catalyst including those of magnesium, chromium(III) and zinc, usually coated on carbon or alumina. It is dehydrogenated:



A small amount of potassium oxide is mixed with the iron(III) oxide (which keeps the catalyst in the iron(III) state). The steam reduces 'coking' (the formation of soot on the catalyst from the decomposition of ethylbenzene at the high temperatures used).

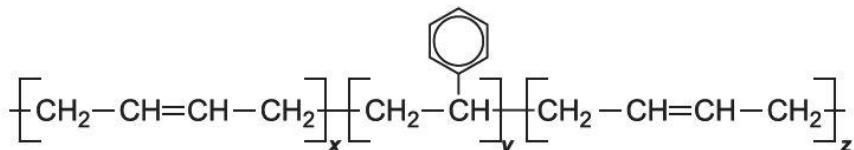
*(c) The polymerization of phenylethene (styrene)*

Radical polymerization is used to produce poly(phenylethene) (polystyrene). The process is an example of [addition polymerization](#). The predominant polymerization technique is continual thermal mass polymerization which is initiated by heat alone. Suspension polymerization is also used. This technique requires the use of an initiator such as dibenzoyl peroxide.

Poly(phenylethene) is a clear thermoplastic, with good moisture resistance, but is rather brittle. A tougher product is also manufactured by polymerizing phenylethene containing 5-10% dissolved [poly\(buta-1,3-diene\) rubber](#). This tougher product - generally known as High Impact Polystyrene (HIPS) - is made exclusively by continuous thermal mass polymerization, in which heat is required to initiate the polymerization reaction. This toughened polymer is translucent.

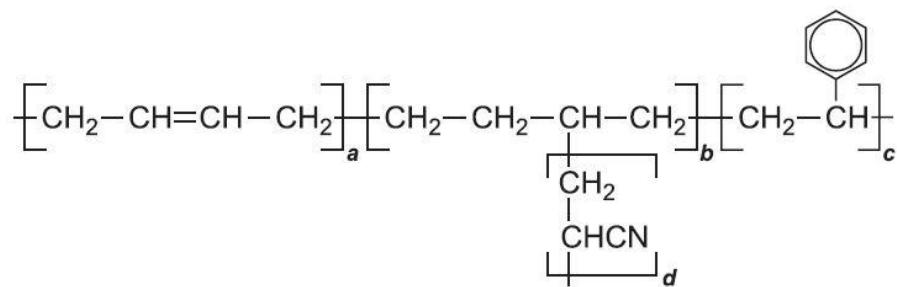
The structure of poly(phenylethene) made by these technologies is completely random in structure and is known as an [atactic](#) structure. By modification of the polymerization technique - principally by the use of metallocene catalysts - [stereoregular \(syndiotactic\)](#) structures can be obtained. This syndiotactic polymer (sPS) has improved properties - particularly thermal and mechanical.

A very important co-polymer is produced from phenylethene (styrene) with butadiene, [SBS](#), much used in car tyres. SBS is an example of a [block co-polymer](#). First, phenylethene is polymerized. Buta-1,3-diene is then added and adds on to both the reactive ends of the poly(phenylethene) molecules to form SBS:



A further modification involves the [co-polymerization](#) of styrene with acrylonitrile in the presence of poly(buta-1,3-diene) to make [ABS plastics](#). A, B, S represent acrylonitrile, butadiene and styrene, which give strength (A), flexibility (B), and hardness (S). Typically this plastic has a composition: 60% (w/w) styrene, 25% acrylonitrile, 15% butadiene. The initiator used is often potassium peroxydisulfate,  $\text{K}_2\text{S}_2\text{O}_8$ .

This is an example of a graft co-polymer. The backbone of the polymer is formed from styrene and butadiene. Acrylonitrile is added to the system and forms a grafted side chain onto the backbone. The nitrile adds to the double bond on the butadiene unit:



ABS is tougher, scratch proof and more chemically resistant than rubber-modified polystyrene and is used, for example, in casings for computers, cycle helmets, calculators, telephones, vacuum cleaners and toys.

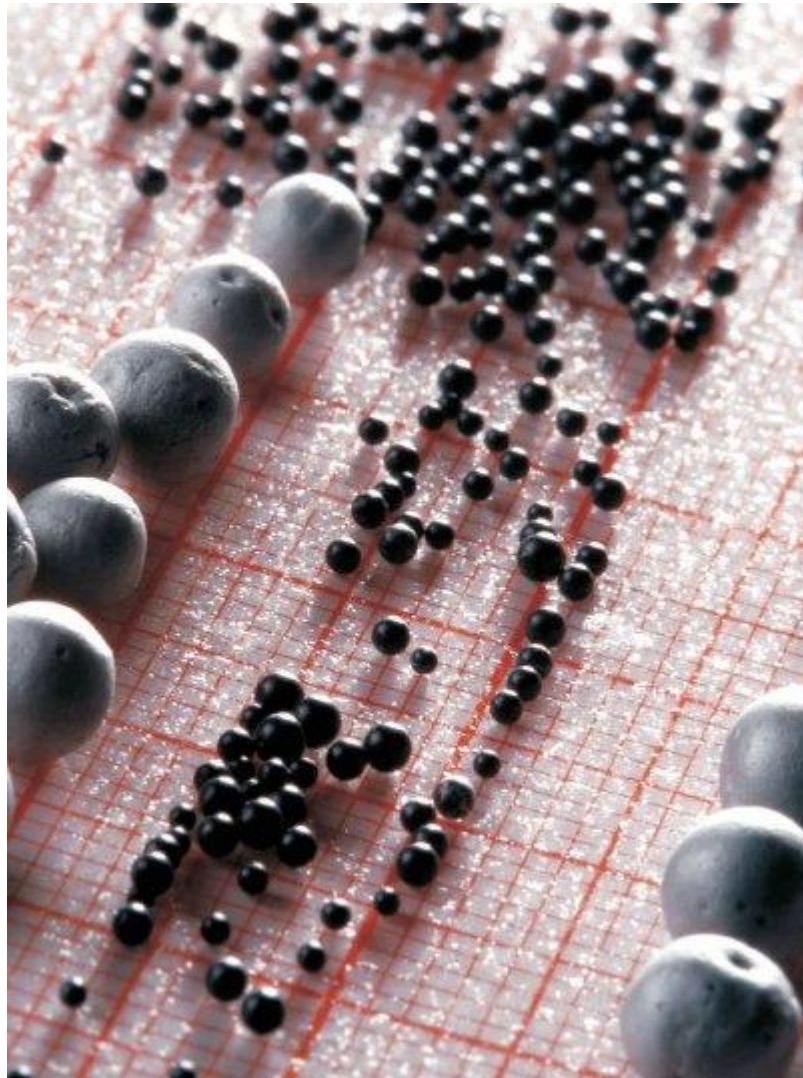
Another co-polymer is formed on polymerizing a mixture of phenylethene (styrene) and propenonitrile (acrylonitrile). It is known as SAN (styrene-acrylonitrile). It is less flexible, more transparent and has more resistance to heat and chemicals than poly(styrene). It is used in car headlamps, cassette covers, syringes and high quality kitchen appliances.

Often SAN is blended with ABS to make it an even more rigid polymer. Another variation is the [co-polymer](#) formed between ABS and [methyl 2-methylpropenoate](#), which has a high resistance to chemical attack, high transparency and is very tough.

Polystyrene accounts for 50% of the polymers produced from styrene and SBS, ABS and SAN, a further 27%, 11% and 1% respectively.

### **Expanded polystyrene**

Expanded polystyrene is manufactured as beads containing pentane (a liquid at room temperature). When they are heated in steam, the hydrocarbon volatilises and the beads expand (Figure 22). These are subsequently blown into moulds and fused by further steaming and then cooling. The expanded poly(phenylethene) has good thermal insulation and shock absorbing properties.



**Figure 22:** These polystyrene beads are shown prior to and after expansion. They were impregnated during manufacture with very fine particles of graphite to improve further their ability to absorb heat

## Polyesters

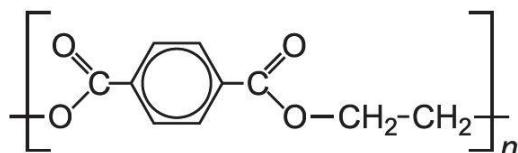


Polyesters are polymers formed from a dicarboxylic acid and a diol. They have many uses, depending on how they have been produced and the resulting orientation of the polymer chains.

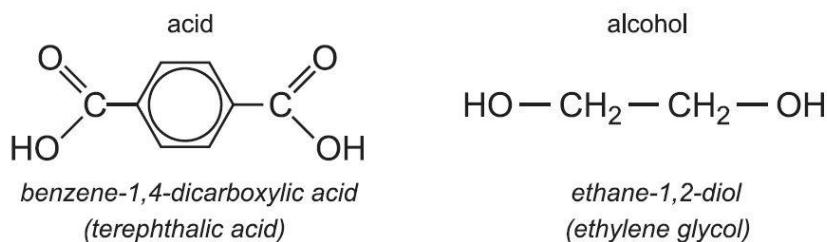
### Uses of polyesters

Polyesters are extremely important polymers. Their most familiar applications are in clothing, food packaging and plastic water and carbonated soft drinks bottles.

The most used of the polyesters has the formula:



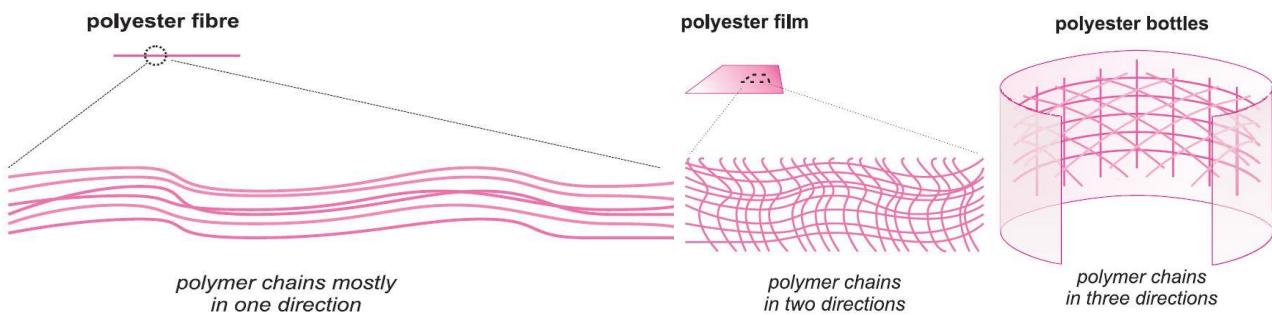
Being an ester, it is made from an acid, benzene-1,4-dicarboxylic acid (terephthalic acid), and an alcohol, [ethane-1,2-diol](#).



It is often known by its trivial name, polyethylene terephthalate (PET). The annual world wide production of PET is approximately 40 million tonnes and is growing at *ca* 7% per year. Of this, about 65% is used to make fibres, 5% for film and 30% for packaging.

Another useful polyester is produced from benzene-1,4-dicarboxylic acid and propane-1,3-diol (which replaces ethane-1,2-diol). It is known by its trivial name, [polytrimethylene terephthalate](#).

The different uses of polyesters depend on their structure. The benzene rings in the molecular chain give them a rigid structure, leading to high melting points (over 500 K) and great strength. They do not discolour in light. In PET *fibres*, the molecules are mainly arranged in one direction, in *film*, they are in two directions and for packaging, they are in three directions (Figure 23).



**Figure 23: Diagram to show the arrangement of PET molecules in PET fibres, films and packaging**

### As fibres

The polyester is produced as small granules. These are melted and squeezed through fine holes and the resulting filaments spun to form a fibre. This fibre, commonly known as Terylene or Dacron, is widely used in clothing (for example, in suits, shirts and skirts) either alone or in blends with other manufactured or natural fibres, principally cotton.

It is also used for filling anoraks and bedding duvets to give good heat insulation. Other uses include car tyre cords, conveyor belts and hoses, where its strength and resistance to wear are paramount.



**Figure 24: Polyesters are often used to make the suits and parachutes for sky divers**  
***As films***

The polyester can also be made into thin films which can be used in food packaging, audio and video tapes, electrical insulation, and X-ray films.

***As packaging***

A relatively newer use is for packaging, for example for bottles (see Figure 3). The small granules of the polyester are heated to about 500 K and further polymerization takes place. This heating is sometimes called solid-state polymerizing. The polymer is melted, moulded and then stretched. The molecules are now orientated in three directions giving the plastic great strength.

## **Manufacture of PET**

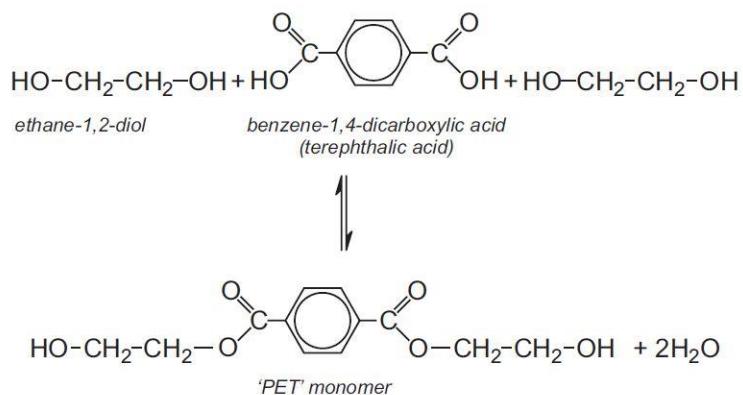
***(a) The production of the monomer***

Ethane-1,2-diol is reacted with benzene-1,4-dicarboxylic acid (sometimes known as terephthalic acid), or its dimethyl ester, in the presence of a catalyst, to produce initially the monomer and low molecular mass oligomers (containing up to about 5 monomer units). Using the acid provides a direct esterification reaction, while the dimethyl ester reaction involves ester interchange. The dimethyl ester route requires the use of an acid catalyst whereas direct esterification is self-catalysed by the carboxylic acid groups.

The dimethyl ester route was originally preferred because the ester could be purified more readily than the acid. Very pure acid is now available in large commercial quantities; the modern processes therefore start from the acid.

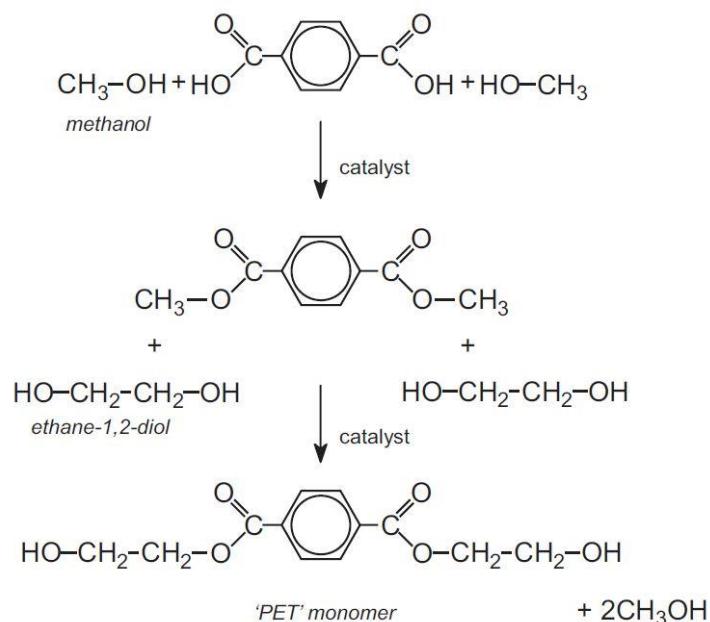
***(i) Starting from the acid: Direct Esterification Reaction***

The acid reacts directly with ethane-1,2-diol:



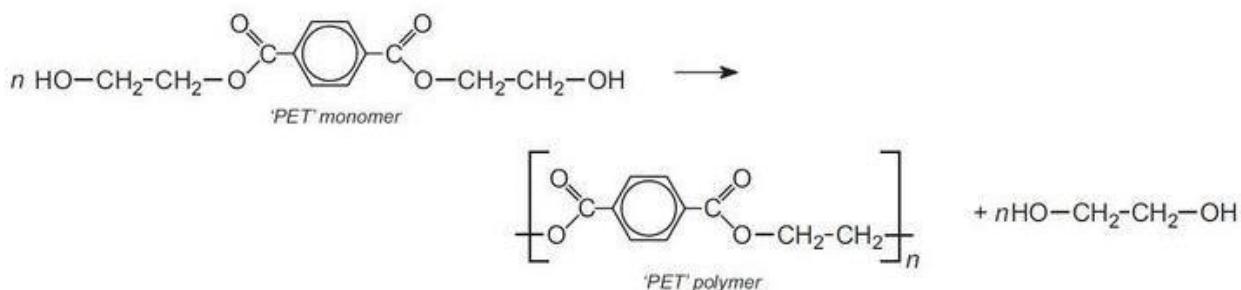
### (ii) Starting from the dimethyl ester: Ester Interchange Reaction

The acid reacts with methanol to form the dimethyl ester, with manganese(II) ethanoate being commonly used as the catalyst. The dimethyl ester is then reacted with ethane-1,2-diol, by a process known as transesterification, in which one alcohol (ethane-1,2-diol) exchanges for another (methanol):



### (b) Polymerization of the monomer

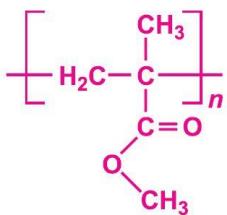
The monomer then undergoes polycondensation with the elimination of ethane-1,2-diol, a condensation reaction:



The polycondensation stage requires a catalyst, antimony(III) oxide, and is carried out at high temperatures (535–575 K) when the monomer and polymer are molten. Low pressures are used to favour product formation. Ethane-1,2-diol is recycled.

Polyester production can be carried out using both batch and continuous processes. In the production of polyester fibre, the products of a continuous process can be fed directly into melt-spinning heads. This removes the casting, chipping, blending and drying stages that are necessary with batch processing.

## Polymethyl methacrylate [Poly(methyl 2-methylpropenoate)]



Poly(methyl 2-methylpropenoate), often known as polymethyl methacrylate or PMMA, is one of the best known polymers, used widely under trade names such as Lucite, Perspex and Altuglas.

### Uses of poly(methyl 2-methylpropenoate) (polymethyl methacrylate)

Poly(methyl 2-methylpropenoate) is better known as Lucite, Perspex and Altuglas (when in sheet form) and as Diakon (when in powder form). The cast sheet is used in baths and other sanitary ware, which along with illuminated signs, is the largest use of the polymer. High molecular mass cast sheet (Perspex) is also used as a lightweight replacement for glass. Lower molecular mass products, made by suspension or solution polymerization (Diakon), are used in car lights and domestic lighting. Special grades are used in diverse applications such as false teeth and eyes and as a major component of bone cements. The monomer is used in adhesives, surface coatings and in [paints](#).

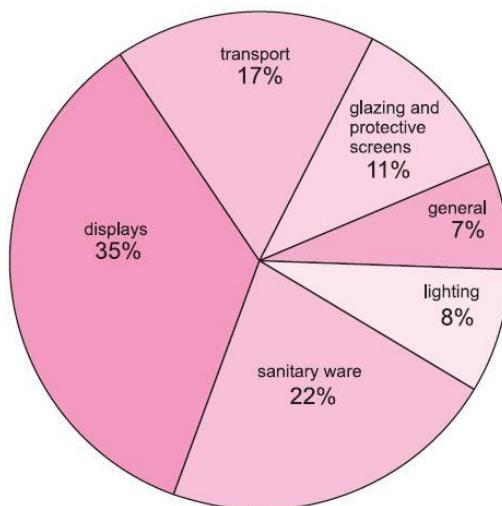
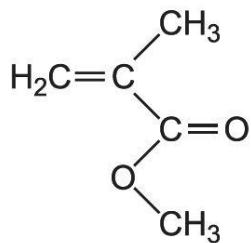


Figure 25: Uses of poly(methyl-2-methylpropenoate)

### Manufacture of poly(methyl 2-methylpropenoate) (polymethyl methacrylate)

#### (a) The monomer

The monomer is the methyl ester of 2-methylpropenoic acid, methyl 2-methylpropenoate (methyl methacrylate):

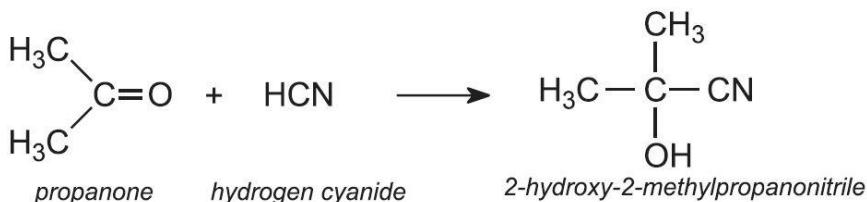


Currently, most of the monomer is made by two processes

#### (i) From acetone

Worldwide, over 80% of the monomer is made from propanone by a sequence of steps which begins by reacting propanone with hydrogen cyanide.

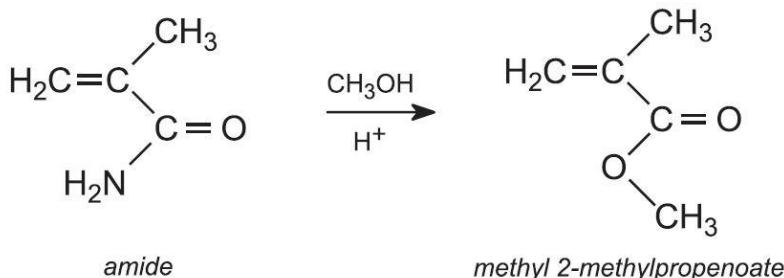
Propanone and hydrogen cyanide form 2-hydroxy-2-methylpropanonitrile:



This product, on reaction with concentrated sulfuric acid at about 430 K, is dehydrated and the nitrile group ( $\text{CN}$ ) hydrolyzed to the amide. This is a step-wise process involving both dehydration and hydrolysis. The reactions can be summarised as:



The temperature is decreased to 370 K and methanol is added. The amide group is hydrolyzed and esterified. The reactions can be summarised as:

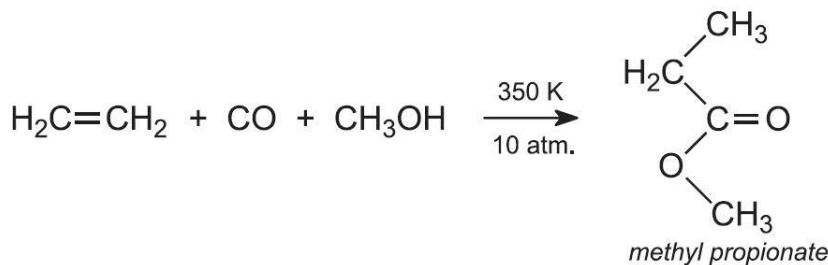


The product is continuously removed by steam distillation. A drawback to the process is the co-production of ammonium sulphate. Together with 'spent' sulfuric acid from the reactions above, the ammonium salt is heated strongly in oxygen in a furnace, in a process similar to that used for recycling [sulfuric acid](#). The products formed are nitrogen, carbon dioxide and sulfur dioxide. The latter is then converted to sulfuric acid using the [Contact Process](#). The use of pure oxygen reduces the size of the furnace which saves on both energy and equipment costs.

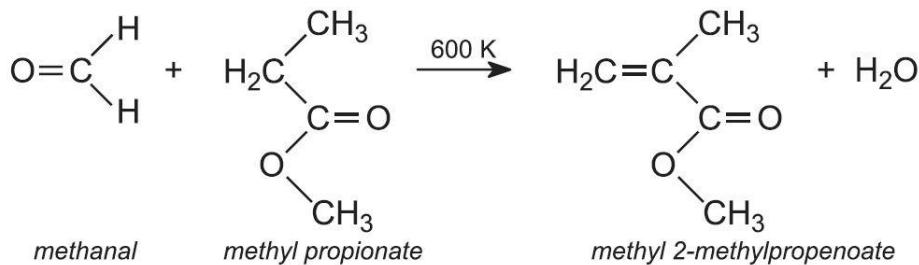
Research is being carried out to find efficient methods for the production of bio-based propanone from carbohydrates by the [ABE process](#).

## (ii) From ethene, carbon monoxide and methanol

Much work has been done to find alternative sources of the monomer and a promising route, which is now in use, uses a mixture of ethene, carbon monoxide and methanol in the liquid phase under pressure of about 10 atm at 350 K:



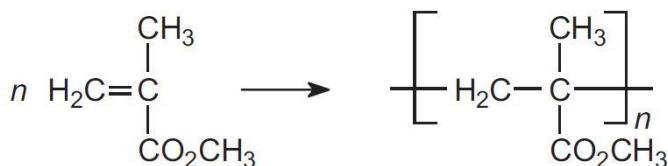
The resulting ester, methyl propionate, is reacted with methanol to form methyl 2-methylpropenoate. A [fixed bed reactor](#) is used and the reactor and catalyst (for example, caesium hydroxide on silica) are heated to 600 K:



Much work is being done to produce the monomer using bio-based reagents. The bio-based ethene, bio-based methanol and bio-based carbon monoxide can all be made from biomass.

### (b) The polymer

Polymerization of methyl 2-methylpropenoate is achieved by a free radical process using an initiator, such as an azo compound or a peroxide:



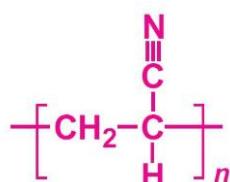
The amount of initiator employed affects both polymerization rate and resulting molecular mass of the polymer. Polymerization is carried out commercially in several ways, i.e., in bulk, solution, suspension and emulsion. The process is an example of addition polymerization.

### (c) Co-polymers

Co-monomers are often used together with the methyl 2-methylpropenoate. For example, most commercial grades of poly(methyl 2-methylpropenoate) used in injection moulding or extrusion applications contain a small amount (ca. 4%) of co-monomer, such as methyl propenoate (methyl acrylate) (when casting sheets of the polymer) and ethyl propenoate (ethyl acrylate) (when extruding sheets of the polymer). In these co-polymers, the monomers are randomly arranged. The resulting polymers have increased thermal stability compared to the homopolymer.

With butyl butyl acrylate, a co-polymer is produced which is used as a base for emulsion paints. It is also co-polymerized with ABS to produce a very tough polymer which is both rigid and has excellent clarity. It is used, for example, in medical applications and in cosmetic packaging.

## Poly(propenonitrile) (Polyacrylonitrile)

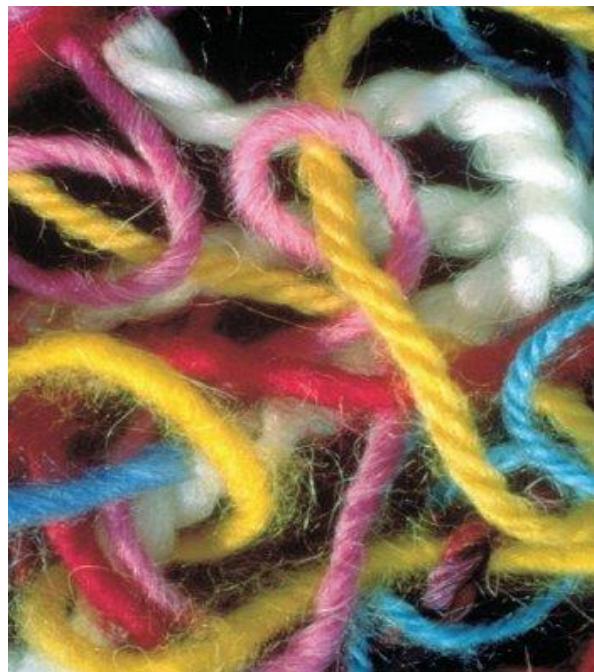


Poly(propenonitrile), usually known as polyacrylonitrile, is manufactured from propene via propenonitrile (acrylonitrile). It is very widely used in co-polymers, particularly in fabrics and when materials need to be made hard and shock proof.

### Uses of poly(propenonitrile) (polyacrylonitrile)

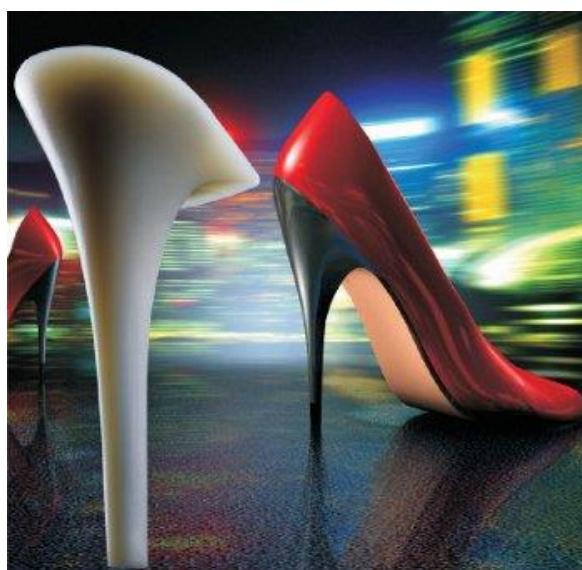
Poly(propenonitrile) itself is a very harsh fibre, rather like horse hair. An almost pure homopolymer is used when a very tough fabric is needed, for example for awnings, a soft top of a car or in brake linings. It is even used to reinforce concrete and in road construction. However, the vast majority of the polymer is co-polymerized. Although these co-polymers often contain more than 85% of propenonitrile units, they are much softer. The fibres formed from them are known as 'acrylic' fibres.

Two of the most used acrylic fibres are formed from the [co-polymerization](#) of propenonitrile with ethenyl ethanoate (vinyl acetate) and propenonitrile with methyl propenoate (methyl acrylate). The former is often mixed with cotton fibres to produce a light fabric, used in women's clothes. The latter is often used with wool (Figure 26).



**Figure 26: The co-polymer of propenonitrile and methyl propenoate is a wool substitute and is often mixed with wool itself for heavier fabrics, used in pullovers and jumpers and in suits**

The co-polymers with phenylethene (styrene) known as [SAN](#) and with butadiene and styrene, known as [ABS](#), are plastics which are very strong and able to withstand shocks.



**Figure 27: The high heels are made from a blend of ABS and a polyamide which is very strong**

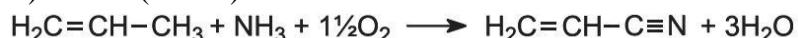
The co-polymers with phenylethene (styrene) known as [SAN](#) and with butadiene and styrene, known as [ABS](#), are plastics which are very strong and able to withstand shocks. Other co-polymers of propenonitrile include those when the co-monomer is methyl 2-methylpropenoate (methyl methacrylate) and with 1,1-dichloroethene. With 1,1-dichloroethene as the co-monomer, a [block co-polymer](#) is formed which is fire-resistant and is often used in children's clothing.

An increasing use of poly(propenonitrile) co-polymers is in producing [carbon fibres](#). If fibres of the polymer are heated under strictly controlled conditions the resulting fibres have remarkable strength.

### **Manufacture of poly(propenonitrile) (polyacrylonitrile)**

#### *(a) The monomer*

Propenonitrile (acrylonitrile), the monomer, is manufactured from propene. The alkene is mixed with ammonia and oxygen (from air) (1:1:2 volume ratio) and passed over a mixture of bismuth(III) and molybdenum(VI) oxides (Unit 2):



As it is a very exothermic reaction, and the temperature must be controlled at ca 600 K, a fluidized bed reactor (Unit 3) is used.

A small amount of hydrogen cyanide (3-6%) is also formed, which can be used in the manufacture of [methyl 2-methylpropenoate](#).

The process has been modified, in Japan, to use propane as the feedstock. It will become particularly important if propane becomes much cheaper than propene. The catalyst used is based on vanadium(V) and antimony(III) oxides.

#### *(b) The polymer*

The polymer is manufactured by [radical polymerization](#) initiated by either a peroxide or by a mixture of potassium peroxydisulfate,  $\text{K}_2\text{S}_2\text{O}_8$  and a reducing agent such as potassium hydrogensulfite,  $\text{KHSO}_3$ . About equal amounts of the stereoregular polymer, [isotactic](#) and [syndiotactic](#), are produced. The polymerization is either in solution or as a [slurry](#).

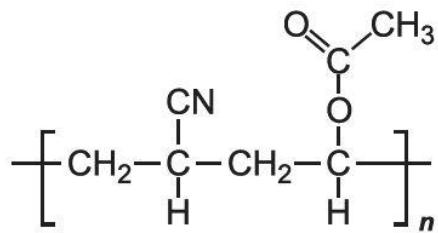


**Figure 28: The soft tops for high quality cars are produced from almost pure homopolymer**

#### *(c) Co-polymers*

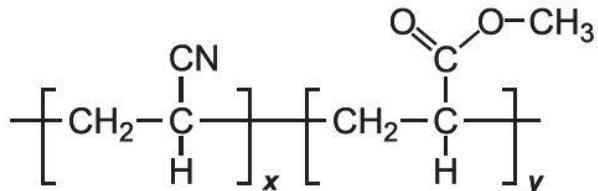
Polymerization takes place as for the homopolymer, a [radical polymerization](#). The two monomers are mixed prior to addition of the initiator. When, ethenyl ethanoate is used as the co-polymer, polymerization is initiated with small amounts of potassium hydrogensulfite and potassium peroxydisulfate which get incorporated into the co-polymer, giving it sites which can bind to colorants and make them fast. Alternatively, a small amount of a third monomer containing, for example a sulfonic acid group, serves the same purpose.

The co-polymer contains a more or less regular alternation of the individual monomers, an example of an [alternating co-polymer](#).

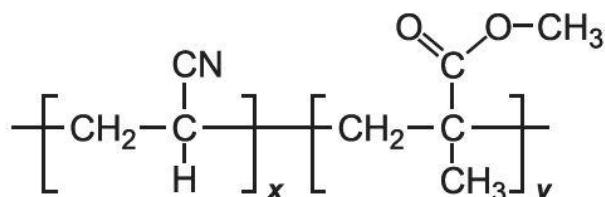


Similar procedures are used when other co-monomers are used.

With methyl propenoate and methyl 2-methylpropenoate, [block co-polymers](#) are produced:



*poly(propenonitrile-co-methyl propenoate)*

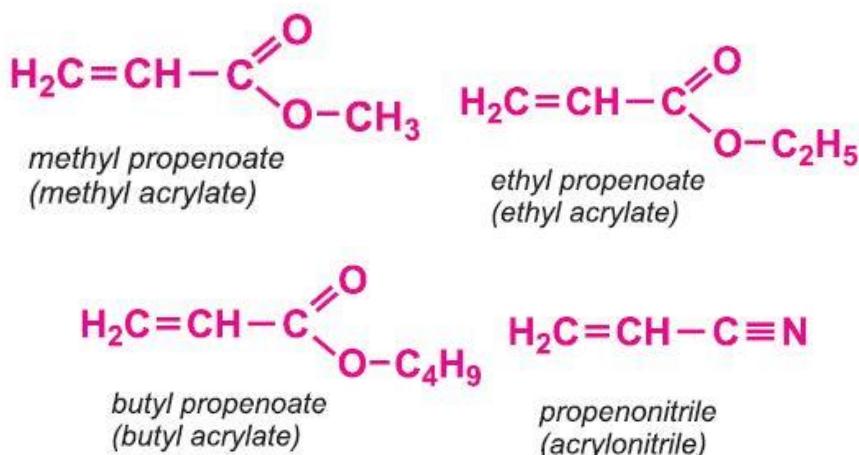


*poly(propenonitrile-co-methyl 2-methylpropenoate)*

An [alternating polymer](#) is produced with 1,1-dichloroethene as the co-monomer.

## Poly(propenoic acid) (Polyacrylic acid)

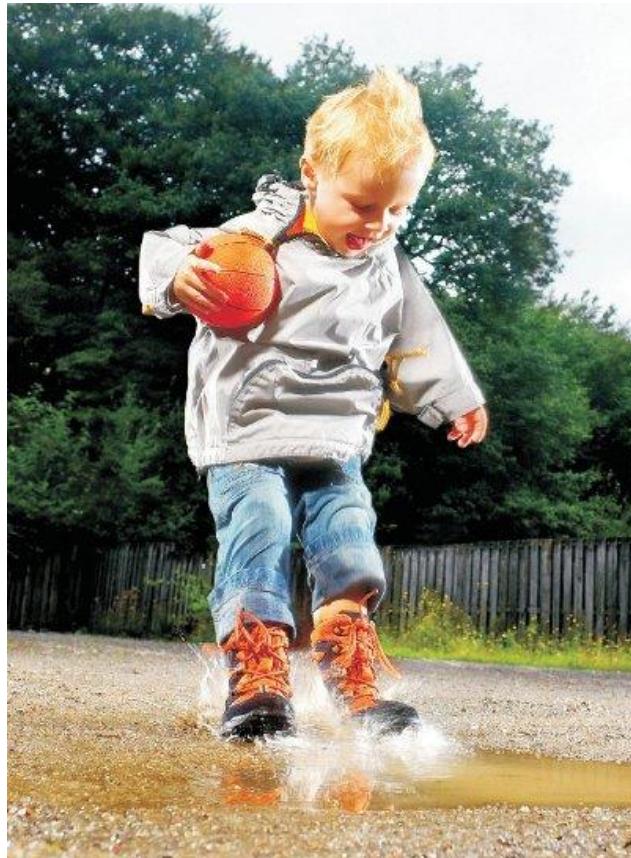
There is a group of polymers, the acrylics, which can be regarded as based on acrylic acid, more formally named propenoic acid. It also includes compounds derived from the acid, which include the methyl, ethyl and butyl esters and propenonitrile (acrylonitrile), all of which form widely used polymers.



This unit is concerned with propenoic acid (acrylic acid), its esters and the polymers produced from them.

### Uses of poly(propenoic acid) (polyacrylic acid)

Poly(propenoic acid) is used in detergents to remove calcium and magnesium ions from the water, thus softening it. This has meant that phosphates need not be used for this purpose thus producing a much more environmentally friendly detergent.



**Figure 29:** The child's shoes are made of a fabric with pores which allow air to circulate around the feet. They are lined with a fleece made of poly(propenoic acid). In the wet, the polymer soaks up the water and expands, sealing the shoe, making it watertight. When dry, the water evaporates and the polymer contracts allowing the fleece to become porous to air

A second use is the production of the so-called superabsorbents. These are polymers of mainly propenoic acid and sodium propenoate. Polymerization is initiated with, for example, potassium (or ammonium) peoxodisulfate,  $K_2S_2O_8$ , which decomposes to form radicals. Another compound is added at the same time to cross-link the chains *via* the carboxyl groups. One of these compounds is N,N'-methylenebis(2-propenamide). A gel is formed which absorbs water more than 1000-fold its mass (Figure 1), and is used as the basis of disposable nappies.

### Uses of polypropenoates (polyacrylates)

The polymers derived from the esters of propenoic acid are used as a base in many [paints](#) and varnishes. The polymers of ethyl and butyl propenoates are used in water-based emulsion paints, as is the co-polymer of butyl propenoate and methyl (2-methylpropenoate).

Methyl propenoate is used to produce a [co-polymer](#) with propenonitrile which is one of the most widely used 'acrylic' fibres. Methyl and ethyl propenoates are co-polymerized with methyl 2-methylpropenoate to assist in the fabrication of [poly\(methyl 2-methylpropenoate\)](#), the range of polymers such as Perspex.

### Uses of propenoic acid (acrylic acid)

About 50% is used to make esters, mainly methyl, ethyl and butyl propenoates. These are, in turn, polymerized (see below). About 30% is used to make poly(propenoic acid) and thus superabsorbents.

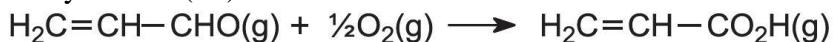
### Manufacture of propenoic acid (acrylic acid)

Propenoic acid is manufactured from propene in two steps.

The first stage is the oxidation of propene to propenal (acrolein). The alkene and air are mixed and passed over a heated catalyst, often a mixture of bismuth(III) and molybdenum(VI) oxides on silica, at *ca* 650 K (Unit 2):

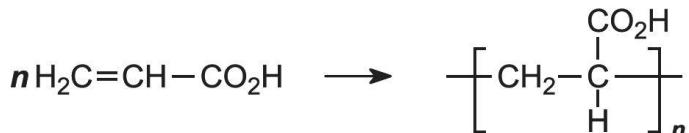


The second stage occurs when propenal and air are passed over another catalyst, a mixture of vanadium(V) and molybdenum(VI) oxides on silica at *ca* 550 K:



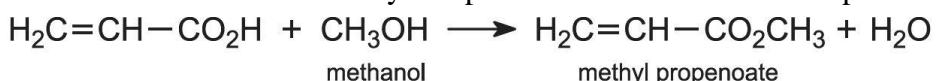
## Manufacture of poly(propenoic acid) (polyacrylic acid)

The polymerization of propenoic acid is a **free radical process**, using an organic peroxide as an initiator. It can be carried out with the pure monomer (known as bulk polymerization), but more often it is polymerized in an aqueous solution or as an emulsion, also in water:

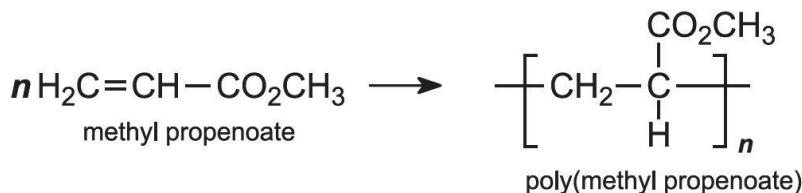


## Manufacture of the polypropenoates (polyacrylates)

Propenoic acid is reacted with an alcohol (for example, methanol, ethanol, butan-1-ol) in the liquid phase with a trace of sulfuric acid as a catalyst to produce the esters. For example:



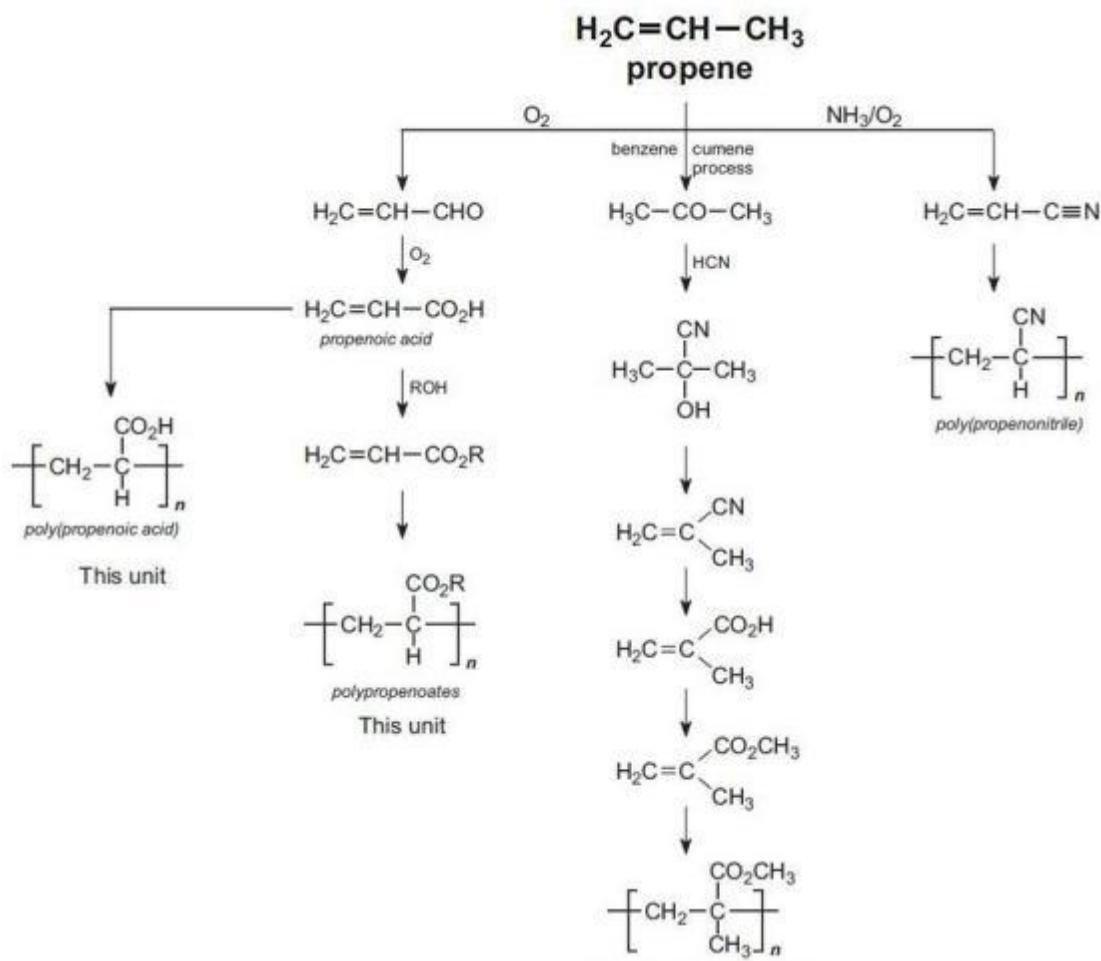
Subsequently the esters are polymerized, by a **free radical process**, using an organic peroxide as an initiator. The pure monomer may be used (known as bulk polymerization), but again more frequently the reaction is carried out in an aqueous solution or in an emulsion in water. For example:



If co-polymers of the esters are required, the two monomers are mixed prior to the polymerization reaction under similar conditions.

## A postscript on propene

All the propenoate (acrylic) polymers are derived from propene as the summary shows:



**Figure 30: Illustrating the manufacture of poly(propenoic acid), polypropenoates, poly(methyl 2-methylpropenoate) and poly(propenonitrile) from propene**

## Polyamides



Polyamides are polymers which contain repeating amide, -CO-NH-, linkages. Proteins are examples of naturally occurring polyamides. The best known manufactured polyamides are often called nylons (the trade name given by the manufacturer, DuPont) and these are aliphatic polyamides. However, other manufactured polyamides are also important and these include an aromatic polyamide, [Kevlar®](#) and plastics produced from carbamide (urea). The nomenclature for describing the linear, aliphatic polyamides (the nylons) is based on the number of carbon atoms in the repeating unit.

Polyamide (nylon)	Repeating unit
6	
6,6	
6,10	
11	
12	

### Uses of polyamides

The properties of the polyamides (nylons), which include high strength, abrasion resistance, and resilience, make them very important in the manufacture of clothing and carpets. Although these polyamides account for 95% of the material used in women's hosiery, this still only accounts for about 5% of the total fibres used to make clothing. Nevertheless this is more than either the [polypropenoates \(acrylics\)](#) or wool but it is substantially less than either cotton or [polyesters](#).



**Figure 31: The children's clothing is made of polyamide 6, impregnated with nanoparticles of titanium dioxide which gives protection against UV radiation, a very effective way of having a sunscreen**

The polyamides (nylons) are also used in engineering plastics, for example, in cars, and for making films for food packaging. They are used in films for their good balance between mechanical strength and barrier properties against oxygen, smells and oils.



**Figure 32: An important development is the use of polyamides to make safety airbags**

Polyamide 6,6 was first produced in the laboratory in 1935 by W H Carothers whilst working for DuPont in the US. Commercial production started in 1938, the same year as I G Farbenindustrie developed polyamide 6 in Germany. Polyamides 6 and 6,6 are the most widely used polyamides for fibres and for engineering materials. The remaining commercial polyamides, for example, polyamides 11 and 12, and 6,10, are most used as engineering plastics.

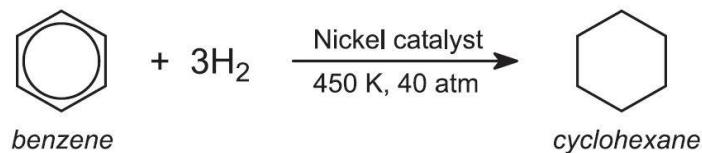


**Figure 33: Ropes made from polyamides are used by rock and ice climbers. They are not only very strong but they are also stretchy and thus reduce forces in the event of a fall, by spreading the duration of loading transmitted to anchors and to the body via the harness.**

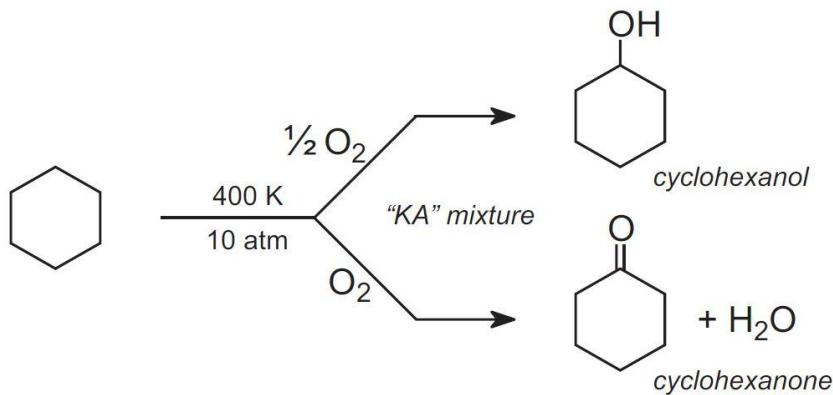
For use as an engineering plastic, polyamides are often compounded with fillers, pigments, glass fibre and toughening agents to give specific properties to the polymer. However, for either continuous filament or staple fibres, which are melt spun at very high speeds (*ca* 6 km every minute), there is great emphasis on controlling the polymer chemistry and the way the yarn is produced in order to ensure the production of the high quality material needed for particular purposes. For example, the thread for use in stockings needs to be strong, as well as very fine, so the molecular mass and hence tensile properties of the polymer must be carefully controlled.

### Manufacture of polyamide 6 and 6,6

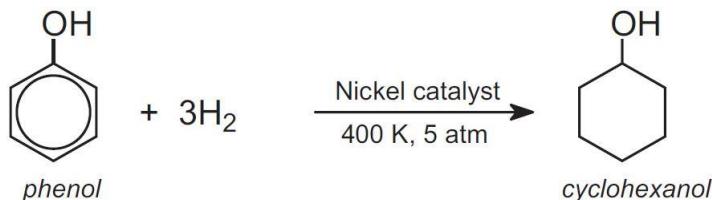
Both polyamides are manufactured from [benzene](#) via cyclohexane. Hydrogen is passed through liquid benzene in the presence of a nickel catalyst under pressure:



Cyclohexane is oxidized by passing air through the liquid under pressure in the presence of a catalyst (often a cobalt salt) to yield two products:

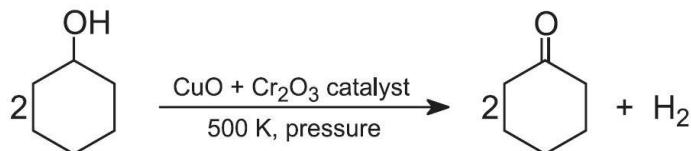


The mixture of cyclohexanol and cyclohexanone is known as "mixed oil" or KA (ketone/alcohol). An alternative route to cyclohexanol is via the hydrogenation of phenol using a nickel catalyst at ca 400 K and 5 atm:

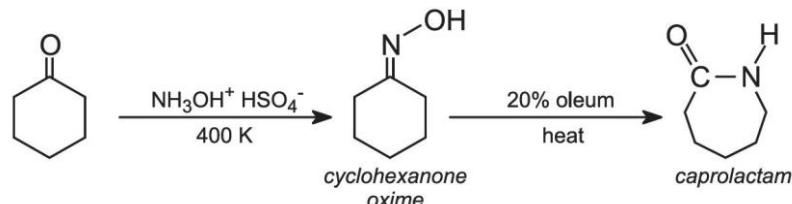


A more recent route to cyclohexanol is the Asahi process from benzene via its hydrogenation to cyclohexene and subsequent hydration to alcohol. This is more energy efficient than the other processes.

To make **polyamide 6**, pure cyclohexanone is required. When the mixed oil is heated under pressure with copper(II) and chromium(III) oxides, the cyclohexanol, which is a secondary alcohol, is dehydrogenated to the corresponding ketone, cyclohexanone:

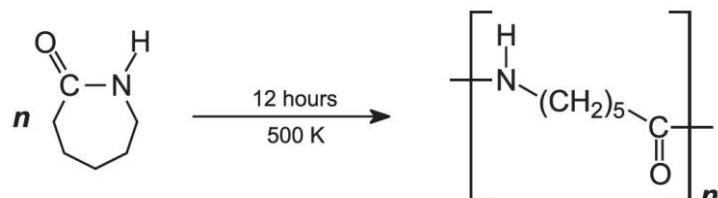


Cyclohexanone is then converted into caprolactam via the oxime (produced by the reaction of the ketone with hydroxylamine - in the form of the salt, hydroxylamine hydrogensulfate):



The isomerisation of the oxime to caprolactam by sulfuric acid is an example of the Beckmann rearrangement in which an oxime is transformed into an amide in the presence of acid. A zeolite, with acidic sites, is also being used to effect the rearrangement. The zeolite is regenerated and saves the use of sulfuric acid.

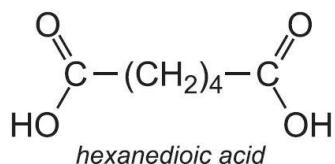
To produce the polymer, the caprolactam, water (acting as a catalyst) and a molecular mass regulator, e.g. ethanoic acid, are poured into a reaction vessel and heated under nitrogen at 500 K for about 12 hours:



This is an example of a batch process.

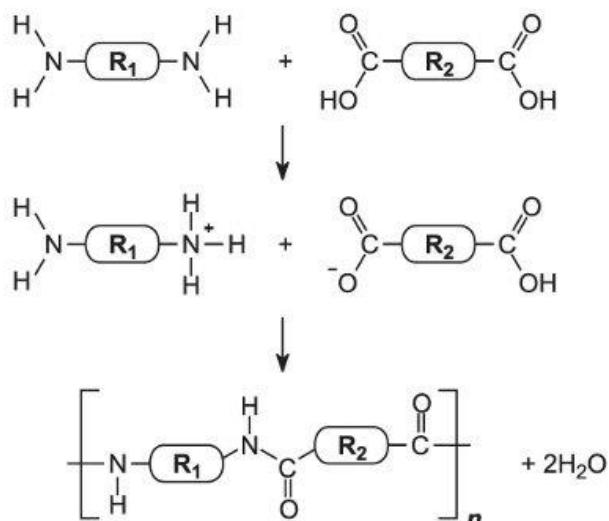
**Polyamide 6,6** is produced by reacting 1,6-diaminohexane (hexamethylenediamine) with hexanedioic acid (adipic acid) by [condensation polymerization](#).

One of the monomers, hexanedioic acid is also produced from KA mixed oil (cyclohexanol and cyclohexanone). The mixed oil is oxidized in the liquid phase using moderately concentrated (60%) nitric acid and a copper(II) nitrate and ammonium vanadate(V) catalyst, at 330 K to form hexanedioic acid:



This process has a considerable disadvantage. A side-product is nitrogen(I) oxide (nitrous oxide), N<sub>2</sub>O, a powerful greenhouse gas but it is carefully removed by thermal or catalytic treatment units. The second monomer, 1,6-diaminohexane, is produced from [buta-1,3-diene](#) and from [propenonitrile](#) (polyacrylonitrile).

To form the polymer, the acid and the diamine are then heated together to form a salt. The chemical reaction for aliphatic dicarboxylic acids and aliphatic diamines to yield an aliphatic polyamide via a condensation polymerization process can be represented, thus:

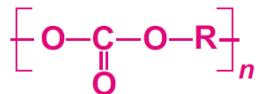


The chain length is regulated by controlling process conditions, such as reaction time, temperature and pressure. An aqueous solution of the salt is heated, in the absence of air, to *ca* 500 K. A pressure develops in the vessel. The temperature is then raised to 540 K, and the steam is bled off to keep the pressure constant. Eventually, the pressure is reduced and the polymer is extruded under nitrogen to yield a lace which is then granulated (Figure 34).



**Figure 34:** The granules are a polyamide from which the frames of the glasses have been moulded.

## Polycarbonates



The polycarbonates are polymers which have organic functional groups linked together by carbonate groups. The most used is a thermoplastic which has long molecular chains.

### Uses of polycarbonates

There are many polycarbonates which vary in properties depending on their molecular mass and structure. As the molecular mass increases, the polymer becomes more rigid. Further, the properties are changed by blending it with other polymers, for example, with [ABS](#) and polyesters such as [PET](#).

Because of their remarkable properties (they are flame and heat resistant, tough and transparent), the polymers are very widely used.



**Figure 35:** The properties of polycarbonates, their strength and remarkable transparency and their biocompatibility make them ideal materials for medical appliances. They are used in dialysis machines for kidney problems and, as shown here, for oxygenators which take over the work of the heart and lungs during serious operations on them, for example in by-pass surgery. The polycarbonate is readily sterilized with epoxyethane, radiation or heating in steam.

Among the uses of the polycarbonates and their blends are:

- medical (for example, for dialysis housing and spectacle lenses)
- electro-electronic (for example, sockets, lamp covers, fuse-boxes, computer and television housings)
- construction (for example, stadium roofs, signs, skylights)
- optical storage (CDs, DVD, HD-DVDs)
- cars (interior lighting and headlamps, sunroofs, side windows, radiators, grilles, bumpers)
- packaging (for example, large water bottles)



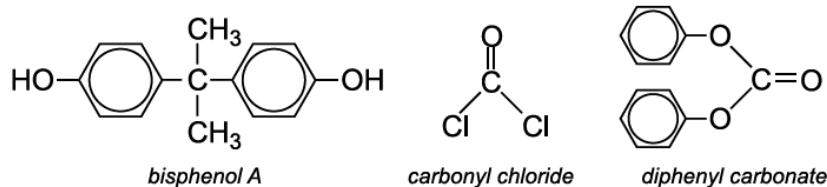
**Figure 36:** These DVDs are made from polycarbonate.



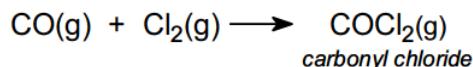
**Figure 37:** A polycarbonate is used to make the roof dome of this experimental car, named zaZan, created by the famous Swiss designer, Frank M Rinderknecht.

### Manufacture of polycarbonates

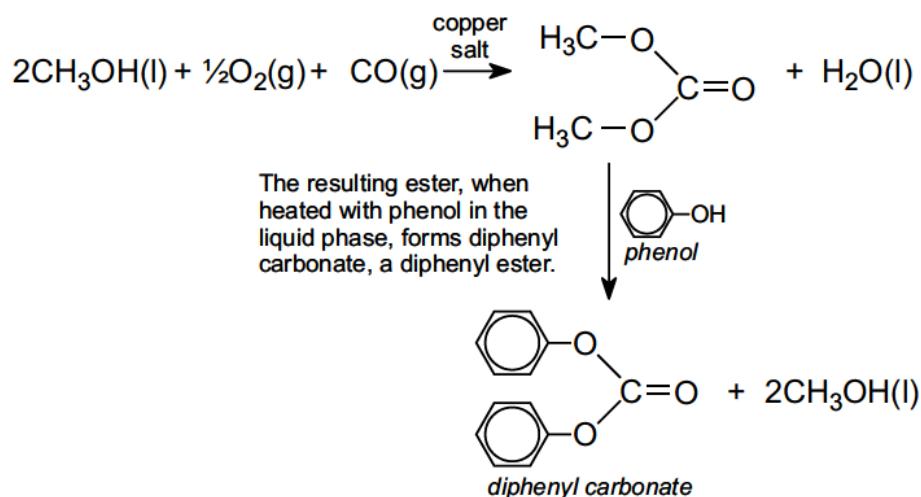
The polycarbonate most used is manufactured by [condensation polymerization](#) between bisphenol A and either carbonyl chloride or diphenyl carbonate.



Bisphenol A is produced by the condensation of phenol with acetone. Carbonyl chloride is produced from carbon monoxide and chlorine:

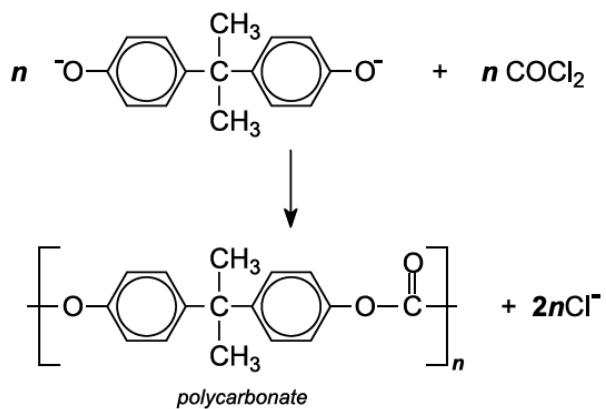


Diphenyl carbonate is produced from dimethyl carbonate, which is often made from methanol, oxygen and carbon monoxide in the liquid phase in the presence of a copper salt such as copper(II) chloride:



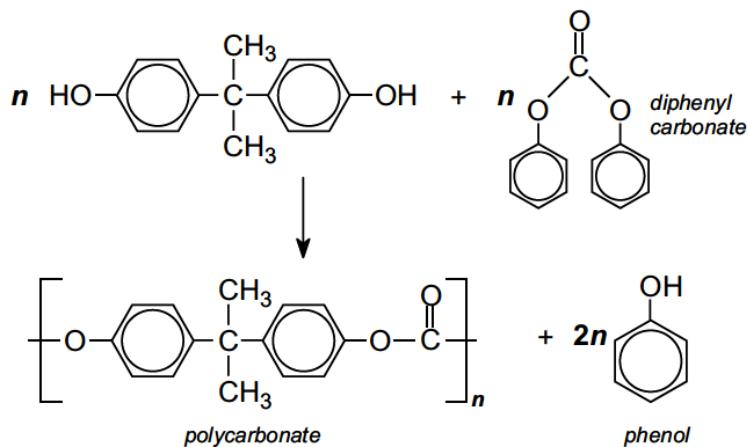
The polymer is usually formed by the reaction of bisphenol A and carbonyl chloride in a basic solution. A solution of bisphenol A in sodium hydroxide (i.e. a solution of the sodium salt of the

phenol) is prepared. It is mixed with a solution of carbonyl chloride in an organic solvent (dichloromethane). The polymerization takes place at the interface between the aqueous and organic layers with the help of a catalyst (an amine):



The polycarbonate is held in solution in the organic layer. This solution is then run off from the aqueous layer and is either evaporated to form granules of the polymer or ethanol is added to precipitate the solid polymer.

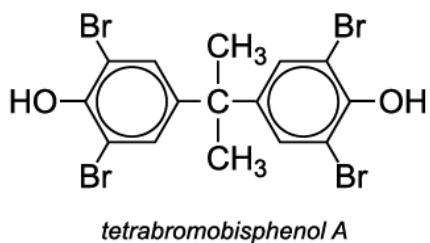
However, an increasing proportion of polycarbonates is made *via* diphenyl carbonate, in order to eliminate the use of carbonyl chloride, an extremely poisonous gas. Bisphenol A and the ester are heated together to form a molten mass of polymer:



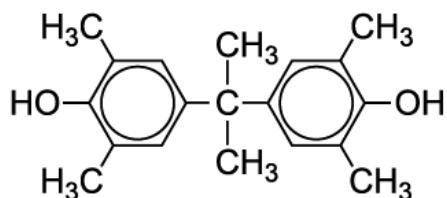
The phenol and excess reactants are removed by distillation under reduced pressure. The polycarbonate melt is then pressed through fine nozzles to form long 'spaghetti-like' threads, which are cooled down and granulated.

## Further developments

Although the polycarbonate derived from bisphenol A is easily the most widely used polycarbonate, co-polymers have been developed in which substituted bisphenols are added and reacted with diphenyl carbonate. For example, tetrabromobisphenol A is added, prior to polymerization. The resulting polymer has enhanced flame resistance.

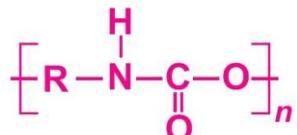


Another co-monomer used is tetramethyl bisphenol A, which improves the polycarbonate's resistance to heat.



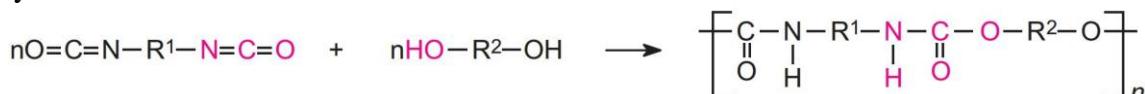
*tetramethylbisphenol A*

## Polyurethanes



The polymeric materials known as polyurethanes form a family of polymers which are essentially different from most other plastics in that there is no urethane monomer and the polymer is almost invariably created during the manufacture of a particular object.

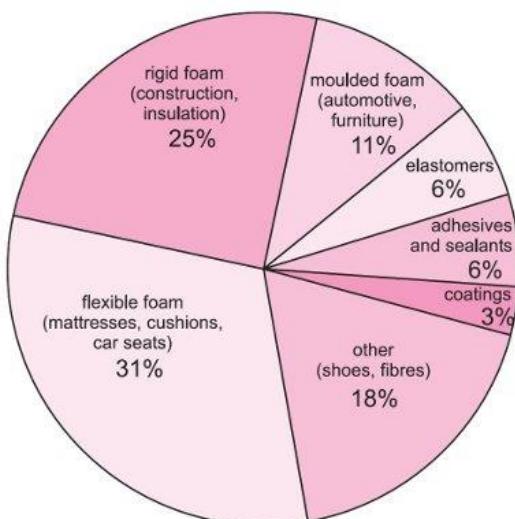
Polyurethanes are made by the exothermic reactions between alcohols with two or more reactive hydroxyl (-OH) groups per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group (-NCO) per molecule (diisocyanates, polyisocyanates). For example a diisocyanate reacts with a diol:



The group formed by the reaction between the two molecules is known as the 'urethane linkage'. It is the essential part of the polyurethane molecule.

### Uses of polyurethanes

The physical properties, as well as the chemical structure, of a polyurethane depend on the structure of the original reactants, in particular the  $\text{R}^1$  and the  $\text{R}^2$  groups. The characteristics of the polyols - relative molecular mass, the number of reactive functional groups per molecule, and the molecular structure - influence the properties of the final polymer, and hence how it is used.



**Figure 38: Uses of polyurethanes.**

There is a fundamental difference between the manufacture of most polyurethanes and the manufacture of many other plastics. Polymers such as poly(ethene) and poly(propene) are produced in chemical plants and sold as granules, powders or films. Products are subsequently made from them by heating the polymer, shaping it under pressure and cooling it. The properties of such end-products are almost completely dependent on those of the original polymer.

Polyurethanes, on the other hand are usually made directly into the final product. Much of the polyurethanes produced are in the form of large blocks of foam, which are cut up for use in cushions, or for thermal insulation. The chemical reaction can also take place in moulds, leading to, for example, a car bumper, a computer casing or a building panel. It may occur as the liquid reactants are sprayed onto a building surface or coated on a fabric.

The combined effects of controlling the polymer properties and the density lead to the existence of a very wide range of different materials so that polyurethanes are used in very many applications (Table 1).

Some examples of the main reasons for choosing polyurethanes are shown in Table 1.

**Table 8: Properties and uses of polyurethanes.**

Uses	Reasons
Cushioning	Low density, flexibility, resistance to fatigue
Shoe soles	Flexibility, resistance to abrasion, strength, durability
Building panels	Thermal insulation, strength, long life
Artificial heart valves	Flexibility and biostability
Electrical equipment	Electrical insulation, toughness, resistance to oils

Polyurethanes can be rigid or rubbery at any density between, say  $10 \text{ kg m}^{-3}$  and  $100 \text{ kg m}^{-3}$ . The overall range of properties available to the designer and the manufacturer is clearly very wide and this is reflected in the many, very different, uses to which polyurethanes are put.

### Manufacture of polyurethanes

As polyurethanes are made from the reaction between an isocyanate and a polyol, the section is divided into three parts:

- production of isocyanates
- production of polyols
- production of polyurethanes

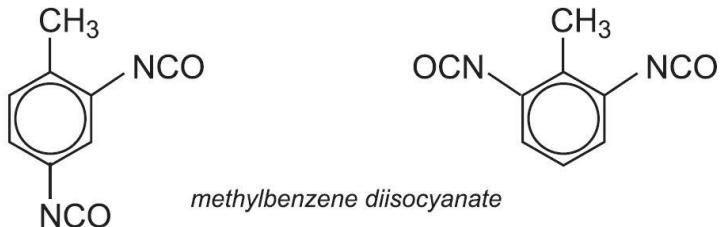
#### (a) Production of isocyanates

Although many aromatic and aliphatic polyisocyanates exist, two are of particular industrial importance. Each of them has variants and together they form the basis of about 95% of all the polyurethanes. They are:

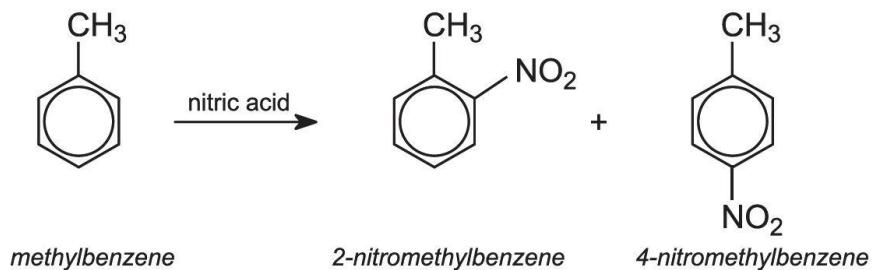
- **TDI** (toluene diisocyanate or methylbenzene diisocyanate)
- **MDI** (methylene diphenyl diisocyanate or diphenylmethane diisocyanate).

**TDI** was developed first but is now used mainly in the production of low density flexible foams for cushions.

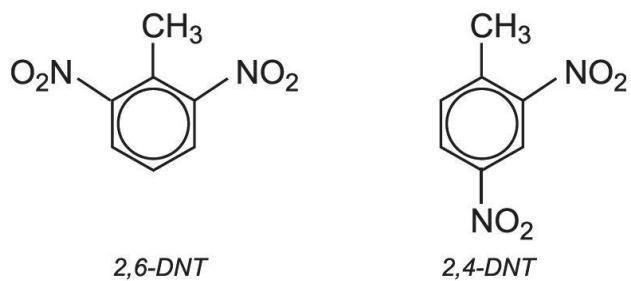
The mixture of diisocyanates known as TDI consists of two isomers:



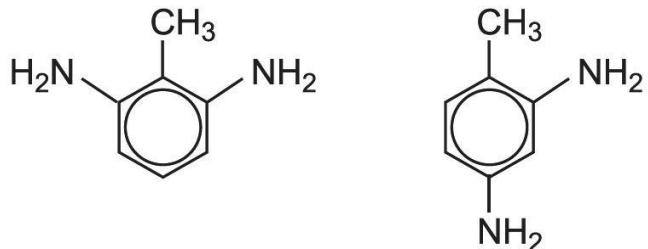
The starting material is methylbenzene (toluene). When it reacts with mixed acid (nitric and sulfuric), two isomers of nitromethylbenzene (NMB) are the main products.



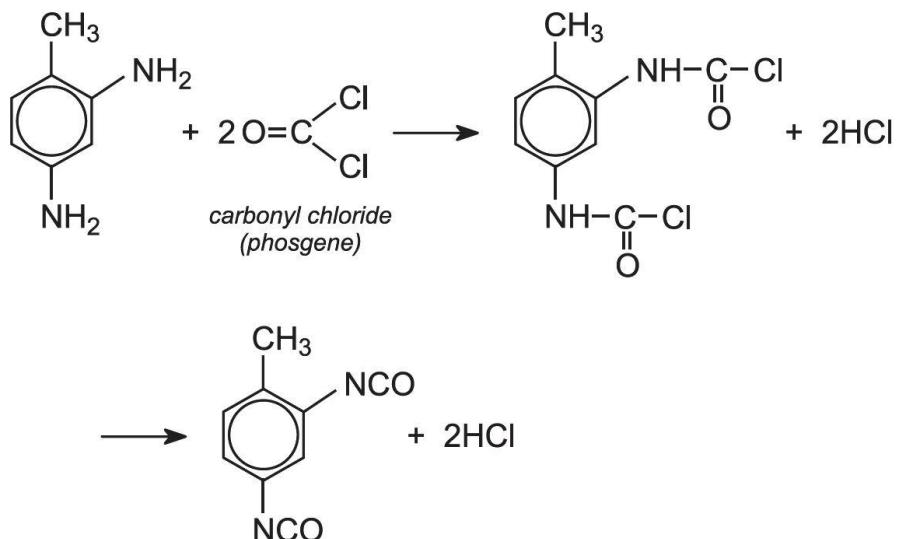
If this mixture is nitrated further, a mixture of dinitromethylbenzenes is produced. In industry they are known by their trivial names, 2,4-dinitrotoluene and 2,6-dinitrotoluene (DNT). 80% is 2,4-DNT and 20% is 2,6-DNT:



The mixture of dinitrobenzenes is then reduced to the corresponding amines:

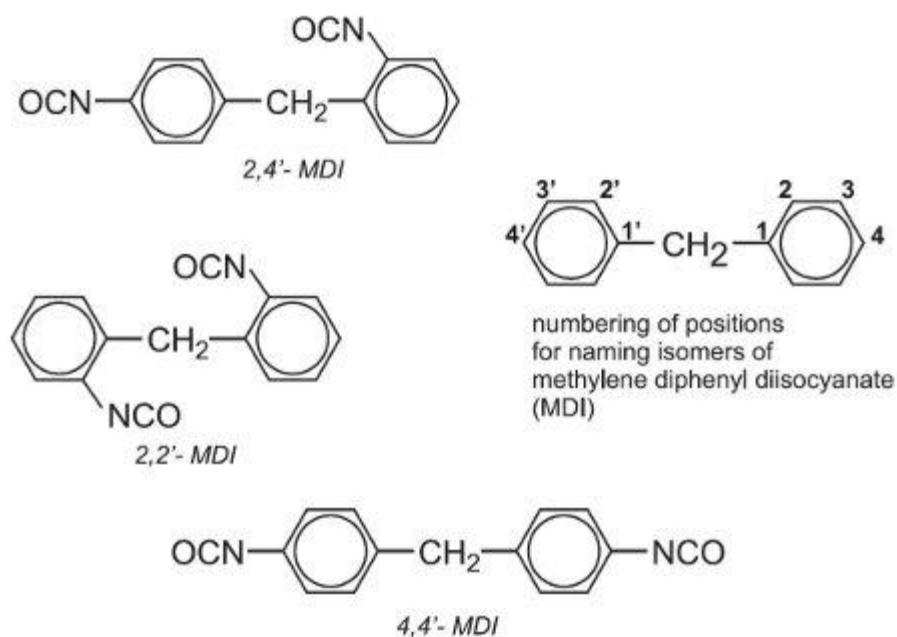


In turn, the amines, known commercially as Toluene Diamines or TDA, are heated with carbonyl chloride (phosgene) to produce the diisocyanates and this process can be carried out in the liquid phase with chlorobenzene as a solvent at about 350 K:



Alternatively, these reactions are carried out in the gas phase by vaporizing the diamines at *ca* 600 K and mixing them with carbonyl chloride. This is an environmental and economic improvement over the liquid phase process as no solvent is needed. In either process, the reagent is the isomeric mixture of the dinitrocompounds, 80% 2,4- and 20% 2,6-, so the product is a mixture of the diisocyanates in the same proportions. It is expensive to produce this mixture in different proportions. It means purifying the mixture of the nitromethylbenzenes, NMB, by very careful distillation. It is more fruitful to produce different properties in the polyurethanes by using different polyols which react with the 80:20 mixture of TDI to produce the polymers.

**MDI** is more complex and permits the polyurethane manufacturer more process and product versatility. The mixture of diisocyanates is generally used to make rigid foams. The starting materials are phenylamine (aniline) and methanal (formaldehyde) which react together to form a mixture of amines, known as MDA (methylenedianiline). This mixture reacts with carbonyl chloride (phosgene) to produce MDI in a similar way to the manufacture of TDI. MDI contains the following diisocyanates:

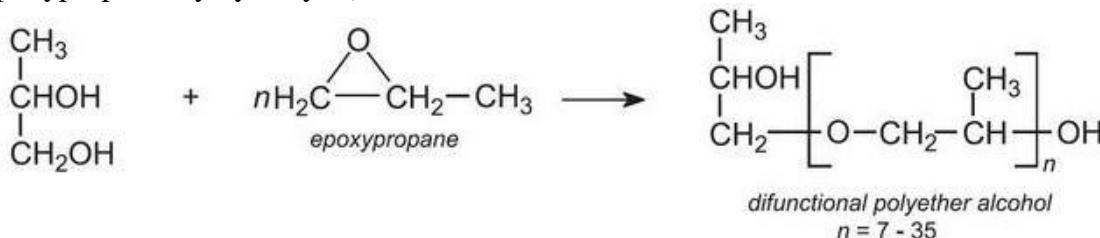


**Figure 39: Isomers of MDI.**

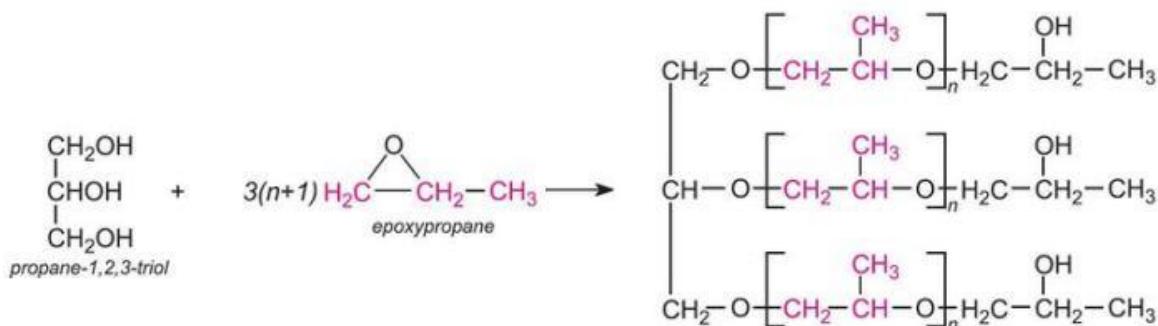
The term MDI refers to the mixture of the three isomers in Figure 3. They can be separated by distillation.

(b) Production of polyols

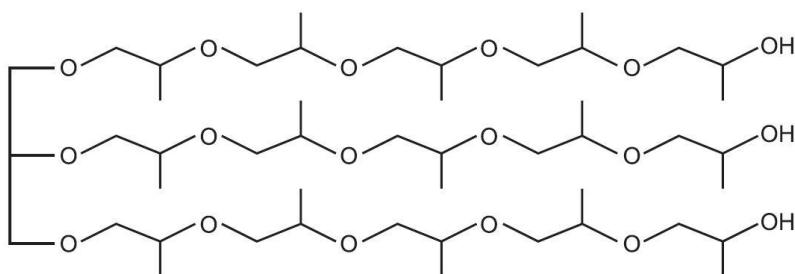
The polyols used are either hydroxyl-terminated polyethers (in about 90% of total polyurethane manufacture) or hydroxyl-terminated polyesters. They have been developed to have the necessary reactivity with the isocyanate that will be used and to produce polyurethanes with specific properties. The choice of polyol, especially the number of reactive hydroxyl groups per polyol molecule and the size and flexibility of its molecular structure, ultimately control the degree of cross-linking between molecules. This has an important effect on the mechanical properties of the polymer. An example of a polyol with two hydroxyl groups (ie a long chain diol) is one made from **epoxypropane** (propylene oxide), by interaction with propane-1,2-diol, (which itself is formed from epoxypropane, by hydrolysis):



An example of a polyol which contains three hydroxyl groups is produced from propane-1,2,3-triol (glycerol) and epoxypropane:



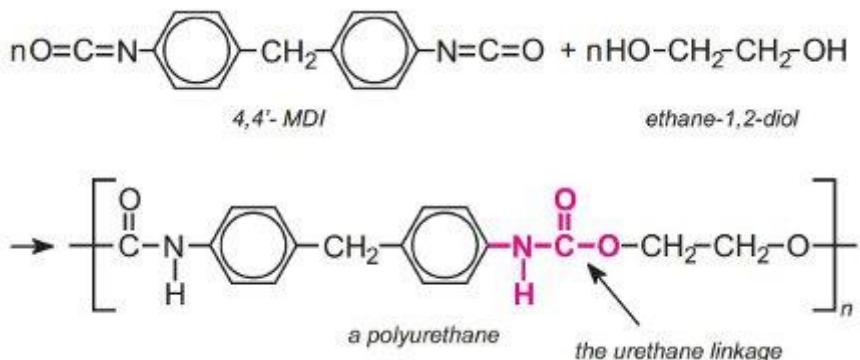
which may be represented as this idealised structure:



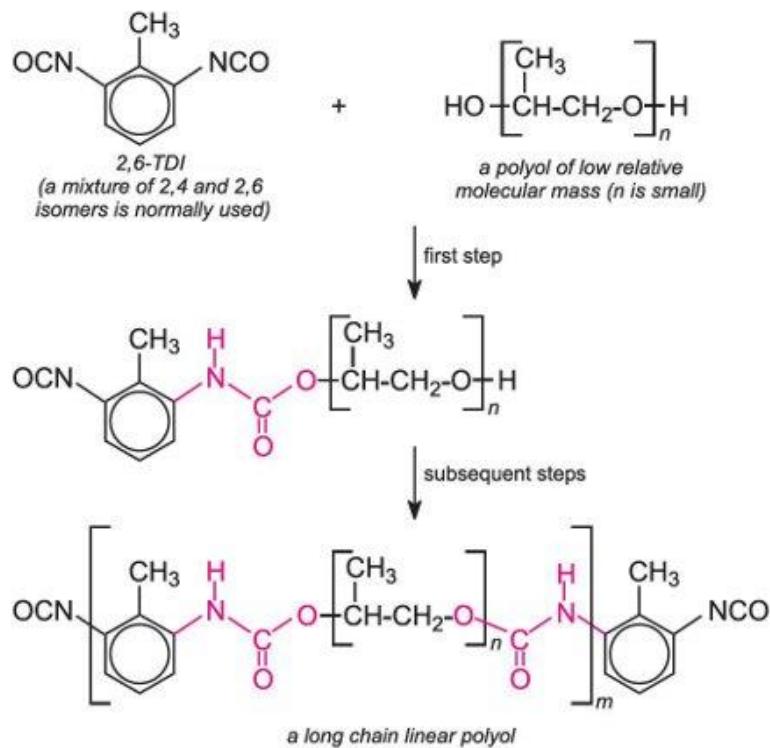
Soya bean oil contains triglycerides of long chain saturated and unsaturated carboxylic acids, which, after hydrogenation, can, on reaction with epoxypropane, form a mixture of polyols suitable for the manufacture of a wide range of polyurethanes. The use of these biopols means that at least part of the polymer is derived from renewable sources.

(c) Production of polyurethanes

If the polyol has two hydroxyl groups and is mixed with either TDI or MDI, a linear polymer is produced. For example, a linear polyurethane is produced by reaction with a diisocyanate and the simplest diol, ethane-1,2-diol, a **condensation polymerization** occurs:



A much used polyurethane is made from TDI and a polyol derived from epoxypropane:



If the polyol has more than two reactive hydroxyl groups, adjacent long-chain molecules become linked at intermediate points. These crosslinks create a stiffer polymer structure with improved mechanical characteristics which is exploited in the development of 'rigid' polyurethanes. Thus a diisocyanate, such as MDI or TDI which reacts with a polyol with three hydroxyl groups, such as one derived from propane-1,2,3-triol and epoxyethane, undergoes crosslinking and forms a rigid **thermosetting polymer**.

As well as polyisocyanates and polyols, the manufacture of polyurethanes needs a variety of other chemicals to control the polyurethane-forming reactions and to create exactly the right properties in the end-product. All practical polyurethane systems include some, but not necessarily all, of those described in Table 9.

**Table 9: Additives used in the manufacture of polyurethanes.**

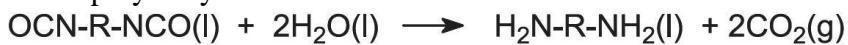
Additives	Reasons for use
catalysts	to speed up the reaction between polyol and polyisocyanate
cross-linking and chain-extending agents	to modify the structure of the polyurethane molecules and to provide mechanical reinforcement to improve physical properties (for example, adding a polyisocyanate or polyol with more functional groups)
blowing agents surfactants	to create polyurethane as a foam to control the bubble formation during the reaction and, hence, the cell structure of the foam
pigments	to create coloured polyurethanes for identification and aesthetic reasons
fillers	to improve properties such as stiffness and to reduce overall costs
flame retardants	to reduce flammability of the end product
smoke suppressants	to reduce the rate at which smoke is generated if the polyurethane is burnt
plasticisers	to reduce the hardness of the product

### Manufacturing process

As an example, consider the manufacture of a moulded item that might otherwise be made from a thermoplastic polymer by injection moulding. To make it of polyurethane, it is necessary to mix exactly the right masses of the two major components (polyisocyanate and polyol), which must be liquids. The reaction starts immediately and gives the solid polymer. Depending on the formulation, the catalysts used and the application, the reaction is typically completed in between a few seconds and some minutes. In this time, therefore, it is essential to dispense the reacting liquid mixture into the mould and also to clean the combined 'mixing and dispensing' equipment ready for the next operation. The exothermic chemical reaction is completed within the mould and the manufactured article can be taken from the mould immediately.

### Foamed polyurethanes

When the two liquids react, a solid polymer is formed. The polymer may be elastic or rigid. However, it may also contain bubbles of gas so that it is cellular - a foam. When producing a foamed polyurethane, there are two possible ways to generate a gas inside the reacting liquid mixture. The so called chemical blowing uses water that may have been added to the polyol which reacts with some of the polyisocyanate to create carbon dioxide:



Alternatively (physical blowing), a liquid with a low boiling point, for example pentane, is mixed into the polyol. The reaction is exothermic and so, as it proceeds, the mixture warms up and the pentane vaporizes. A tiny amount of air is dispersed through the mixture of polyisocyanate and polyol. This provides nucleation seeds for the multitude of gas bubbles that are produced throughout the polymer. Heat makes the bubbles expand until the chemical reaction changes the liquid to solid polymer, and the available gas pressure cannot create any further expansion.

A shoe sole, for example, may be 'blown' to double the volume of solid polymer. This process is so versatile that the expansion can be taken much further. In low-density foams for upholstery or thermal insulation less than 3% of the total volume is polyurethane. The gas has expanded the original volume occupied by the liquid by 30 to 40 times. In the case of cushions, only just enough solid polymer is needed to ensure that we can sit comfortably.

In thermal insulation, it is the gas trapped in the cells which insulates. The polymer that encloses the cells reduces the insulation efficiency, so it makes sense to have as little of it as possible.

### **Adhesion**

In the final stages of the polyurethane-forming reaction, the mixture becomes a gel with very effective surface adhesion. Hence polyurethanes can be used as adhesives. Equally important is the fact that polyurethanes, which are being created as, for example, cushioning or insulation materials, can be bonded to surface materials without the introduction of separate adhesives. Flexible foam and fabric can create a composite cushion or rigid foam and sheet building materials (e.g. plasterboard, steel sheet, plywood) can provide composite building insulation panels.

## **Methanal plastics (Formaldehyde plastics)**

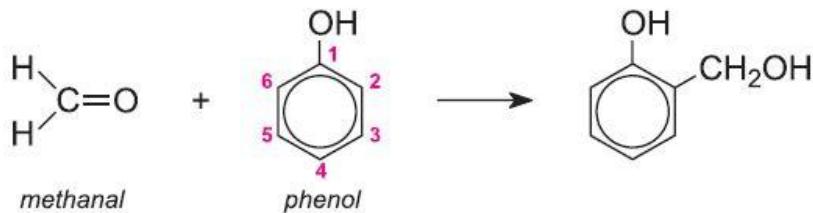
Methanal (formaldehyde) reacts with phenol, carbamide (urea) and melamine to form three of the most important thermosetting plastics (resins). Sometimes, the resins are called PF (phenol-formaldehyde), UF (urea-formaldehyde) and MF (melamine-formaldehyde). The processes are all examples of [condensation polymerization](#).

### **Phenol-methanal (phenol-formaldehyde) plastics**

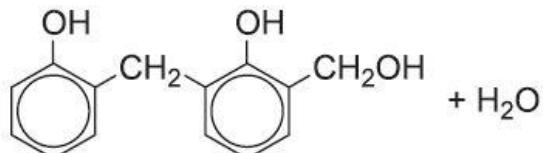
These are amongst the oldest plastics, Backland patenting the process in 1910. They are prepared from phenol and methanal on the addition of acid or alkali.

#### *Manufacture of phenol-methanal plastics*

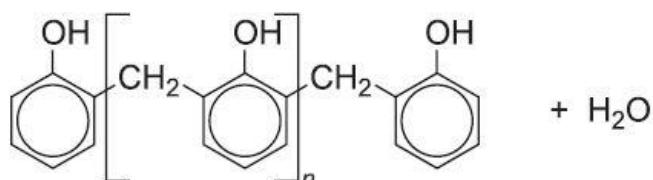
Phenol and methanal are heated in an acidic or alkaline solution. The first step in forming a polymer chain involves substitution of methanal in the phenol ring in the 2- or 4- position:



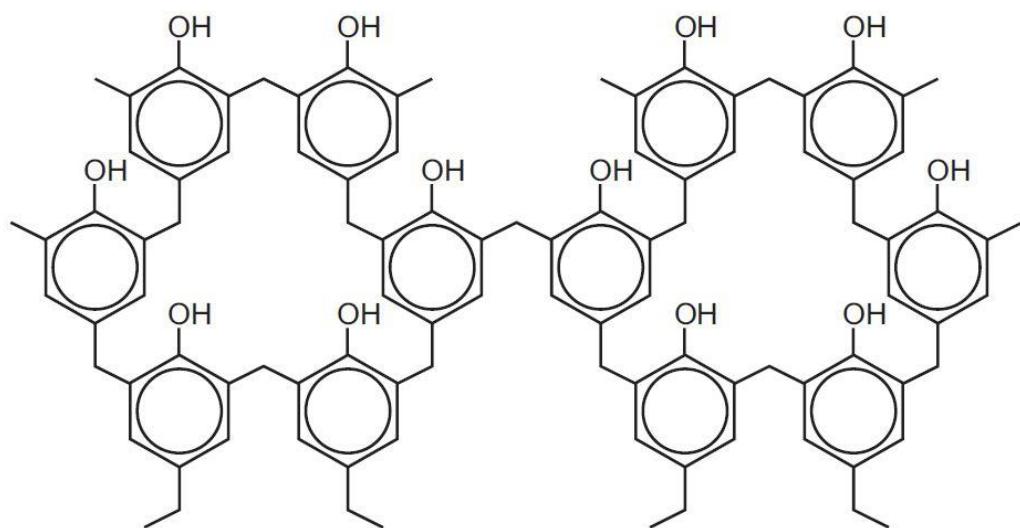
The product then undergoes a condensation reaction:



When methanal and phenol, in the proportion of 0.5:1, are reacted under acidic conditions, a resin (often known as a novalac resin) is produced, where  $n = 0$  to 6.



With higher proportions of methanal and with the 4-position vacant, branching is possible, the methanal providing additional  $-CH_2-$  links. On heating a resin is produced. Part of the 3-dimensional cross-linked structure is illustrated:



The properties of a resin can be altered by using other phenols. For example, if the phenol has an alkyl group with four or more carbon atoms (for example, a butyl group) in the 4-position, the resulting polymer is soluble in oils. Such polymers also have lighter colours.

#### *Uses of phenol-methanal plastics*

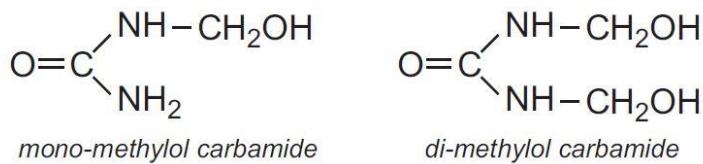
The polymers with giant three-dimensional, cross-linked structures form resins that cannot be melted and reshaped. On heating to high temperatures, they begin to decompose and char. They are also insoluble in a wide range of solvents and are unreactive. Their high electrical and heat resistance means that they are used as an electrical insulator and for the manufacture of brake and clutch linings for vehicles. When they are used with fillers such as wood flour (wood that has been pulverised roughly to the size of a rice grain) or mica, they have major applications in the construction of worktops and printed circuit board insulation. They are also widely used as adhesives, for example in producing plywood and hardboard.

#### **Carbamide (urea)-methanal (formaldehyde) plastics**

Of the three methanal plastics, the carbamide (urea) - methanal (formaldehyde) resins (UF) are the most used.

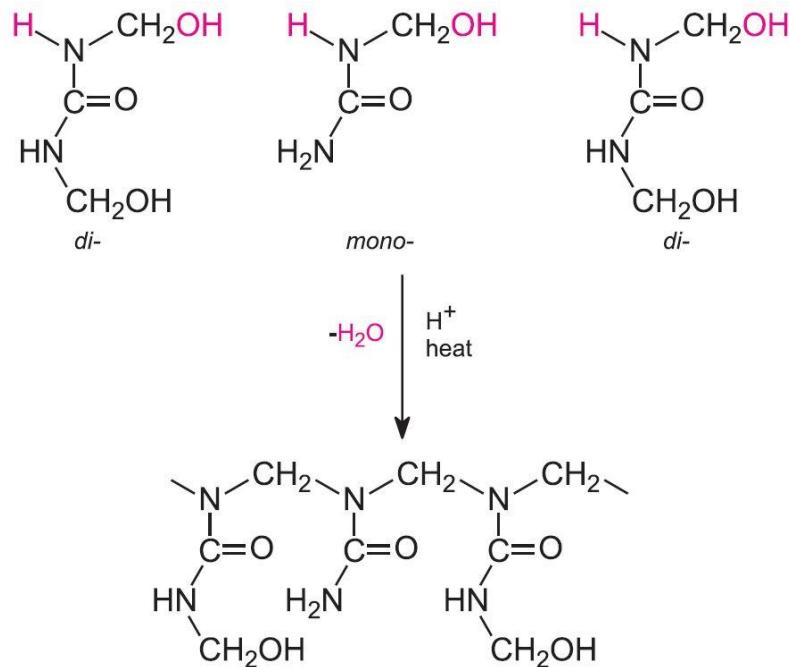
## *Manufacture of carbamide-methanal plastics*

Carbamide (urea) is manufactured by heating ammonia and carbon dioxide under pressure. Reaction between methanol and carbamide (urea) in alkaline solution gives mono- and di-methylol carbamides:



These products condense together in acidic conditions to give a linear polymer. Water is eliminated. Further heating (curing) causes further condensation, with the elimination of water between the OH and NH groups, resulting in a cross-linked 3-dimensional structure.

The plastic is produced either as a powder or as granules.



## *Uses of carbamide-methanal plastics*

These plastics are often used after incorporating fillers such as paper pulp and wood flour. They have the advantage over phenolic resins of being colourless, although they are less water resistant and less heat resistant.

Their greatest use is as wood adhesives, usually mixed at point of use with filler, extenders and acidic hardeners. They are used in particular as a binder in the production of chipboard. The resin powder or granules are moulded into electrical plugs and sockets, toilet seats and some table wear. Used in solution, the resins wet-strengthen paper and improve the shrink resistance of cotton, wool and rayon where a stiff finish is required.

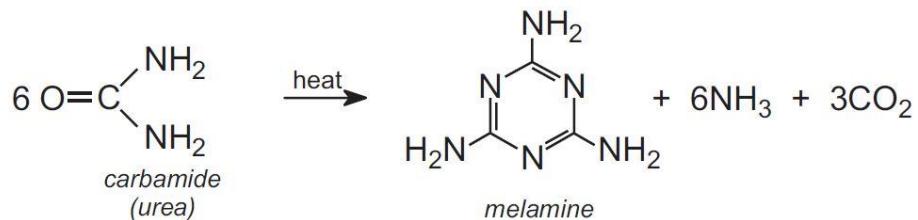
The key restraint is the emission of toxic emissions of methanal vapour which has been of concern in many countries. For example, the California Air Resources Board has strict limits on the amount of methanal emitted and this has restricted the use of the resin.

## Melamine-methanal (melamine-formaldehyde) plastics

Melamine resins combine the best of the properties of phenolic (PF) and carbamide (urea) (UF) resins. They are stable to heat, light and moisture and are colourless, and can absorb dyes easily.

## *Manufacture of melamine-methanal plastics*

Melamine is produced by heating carbamide (urea):



The production of melamine-methanal (MF) plastics is similar to that for carbamide (urea)-methanal polymers, and their structures are analogous.

The resin is usually produced as a powder.

## *Uses of melamine-methanal plastics*

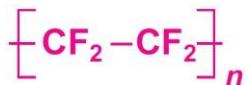
The powder can be moulded under pressure and most of the resin is used to make laminates for surfaces. Kitchen worktops can be made using a cheaper phenolic resin to form the base, which is then coated with a more expensive melamine surface. Light-weight picnicware and tableware (e.g. Melaware) can also be made from melamine.

Like the carbamide (urea) resins, melamine resins are also used, in solution, to wet-strengthen paper and to improve the shrink resistance of cotton, wool and rayon. Resins are also used as adhesives and as ion-exchange resins to demineralise water. If melamine, methanal and an alcohol (for example, butanol) are heated together, a resin is formed with both  $-\text{CH}_2\text{OH}$  and  $-\text{CH}_2\text{OR}$  groups. The resulting resins are then cross linked with other polymers to form paints for cars.



**Figure 40:** To absorb sound, and make commuting more comfortable, the roofs of 25 new subway stations built recently in Seoul, Republic of Korea are constructed of perforated steel behind which is a layer of melamine resin. The resin is produced as three-dimensional network structure consisting of slender and thus easily shaped webs.

## **Poly(tetrafluoroethene) (Polytetrafluoroethylene)**



The uses of poly(tetrafluoroethene) (PTFE) are a function of its resistance to chemical attack, unreactivity (even above 500 K), low friction, non-stick properties and high electrical resistance.

### **Uses of poly(tetrafluoroethene) (polytetrafluoroethylene)**

In many applications, tetrafluoroethene (TFE) is co-polymerized with other fluorinated monomers, such as hexafluoropropene and perfluoropropyl vinyl ether, and also with ethene.

Poly(tetrafluoroethene) (PTFE) and its co-polymers are used in:

- cable insulation
- reactor and plant equipment linings, when reactants or products are highly corrosive to ordinary materials such as steel
- semi-permeable membranes in chlor-alkali cells and fuel cells
- bearings and components in mechanical devices such as small electrical motors and pumps
- permeable membrane (e.g. Gore-Tex™), for clothing and shoes, which allows water vapour to diffuse away from the skin but prevents liquid water (rain) from soaking in
- non-stick domestic utensils, e.g. frying pans
- medical - catheter tubing
- hose and tubing
- solid lubricants
- combinations with magnesium and aluminium as an igniter for explosives



**Figure 41:** The retractable roof of the Centre Court at Wimbledon is made of poly(tetrafluoroethylene). In this photo, the roof is being closed.

### Manufacture of poly(tetrafluoroethylene) (polytetrafluoroethylene)

PTFE is made from methane in a series of reactions:

- a) production of trichloromethane (chloroform)
- b) production of chlorodifluoromethane
- c) production of tetrafluoroethylene (TFE)
- d) polymerization of tetrafluoroethylene

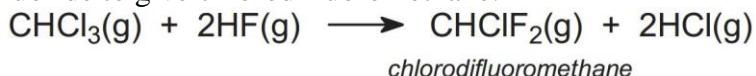
#### (a) Production of trichloromethane (chloroform)

Trichloromethane is one of the products formed by the reaction of methane and a mixture of chlorine and hydrogen chloride. This can be performed in the liquid phase at 370–420 K using a zinc chloride catalyst. Alternatively, the reaction is carried out in the vapour phase, using alumina gel or zinc oxide on silica as a catalyst at 620–720 K.



#### (b) Production of chlorodifluoromethane

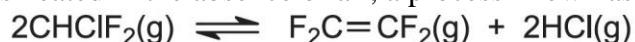
Trichloromethane is reacted with anhydrous hydrogen fluoride in the presence of antimony(III) and antimony(V) chlorofluoride to give chlorodifluoromethane:



#### (c) Production of tetrafluoroethylene (tetrafluoroethylene, TFE)

Since TFE is an explosive gas (bp 197 K), it is usually made when and where required for polymerization so that there is minimum storage time of the monomer between its production and its polymerization.

Chlorodifluoromethane is heated in the absence of air, a process known as *pyrolysis*:



$$\Delta H^\ominus = +127.6 \text{ kJ mol}^{-1}$$

Low pressures (atmospheric) and high temperatures (940–1070 K) favour the reaction.

Steam, preheated to 1220 K, and chlorodifluoromethane, at 670 K, are fed into a reactor. Steam is used to dilute the reaction mixture and hence reduce the reactant partial pressure, and thus the formation of carbon and toxic by-products. The steam also supplies all the heat required by this endothermic reaction. Very little hydrolysis of reactant and product occurs.

Once formed, the product must be rapidly cooled to 770 K to prevent the reverse reaction occurring and the explosive decomposition of TFE:



$$\Delta H^\ominus = -282 \text{ kJ mol}^{-1}$$

The cooling is done by passing the vapour through a water-cooled heat exchanger, made of graphite to resist chemical attack and thermal shock. Reactor residence time is 1 second.

#### (d) Polymerization of tetrafluoroethylene (tetrafluoroethylene)

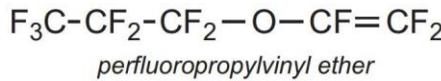
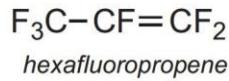
The monomer is transformed into the polymer, PTFE, by radical polymerization. The reaction is carried out by passing TFE into water containing a radical initiator, e.g. ammonium persulfate,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , at 310-350 K and a pressure of 10-20 atm.

Two different procedures are used:

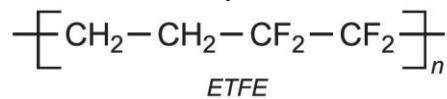
- granular polymerization gives a suspension of string-like PTFE particles up to 1 cm long in water. These are milled to produce fine powders (30 pm) used for moulding. The fine powders are also agglomerated to larger particles (500 pm) to give better flow. Unlike other thermoplastics, such as PVC, PTFE cannot be processed by melt extrusion. The powder is therefore moulded into rods for extrusion and heating at temperatures above 530 K to force the particles to stick together.
- dispersion polymerization can be used to obtain a colloidal dispersion of PTFE particles (0.25 pm) in water. The dispersion can be concentrated and used for dip coating or spraying articles. The dispersion can also be coagulated and dried to give a powder, which, in turn, is made into a paste and extruded on to wire.

### Co-polymers

There is a group of co-polymers which are formed by the co-polymerization of tetrafluoroethene and other unsaturated organic compounds such as ethene, hexafluoropropene and perfluoropropylvinyl ether. As described above, these co-polymers are used in many of the examples given for PTFE.



The co-polymer produced from ethene and tetrafluoroethene is an alternating co-polymer usually known by its trivial name, ethylene tetrafluoroethylene (ETFE):



It is used, in particular as a lining for containers as it is stable to attack by concentrated solutions of acids and alkalis, and because of its good electrical properties of insulation and its strength, it is used as a coating for wires and cables. Its most spectacular use is as a roofing material in buildings such as the O<sub>2</sub>Arena in London, the Eden Project in Cornwall and the Birds Nest Olympic Stadium in Beijing. The roofs are made up of 2 - 5 layers of large cushions of ETFE. It is also used as an outer skin of large buildings (Figure 42).



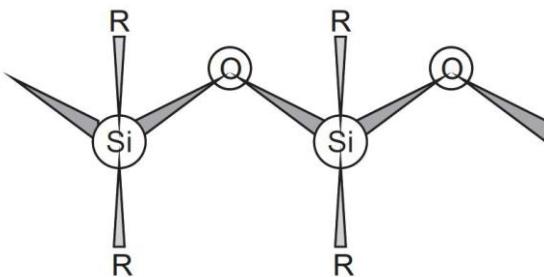
**Figure 42: The outer skin of the Allianz Arena in Munich is made of cushions of ETFE. There are lights inside the cushions which are changed depending on which team is playing: white when the German national team is playing, red for FC Bayern Munich and blue for TSV1860 Munich.**

## Silicones

Silicones have unique properties amongst polymers because of the simultaneous presence of organic groups attached to a chain of inorganic atoms. They are used in many industries including those devoted to electronics, paints, construction and food.

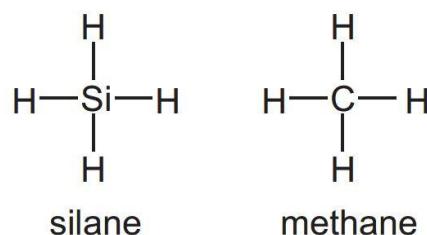
### Structures and properties of silicones

Silicones are synthetic polymers with a silicon-oxygen backbone similar to that in silicon dioxide (silica), but with organic groups attached to the silicon atoms by C-Si bonds. The silicone chain exposes organic groups to the outside.

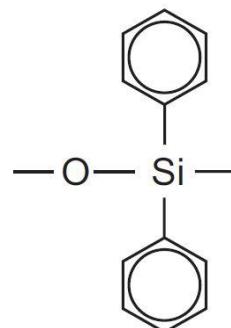


Thus, despite having a very polar chain, the physical properties of silicones are similar to those of an alkane. However, the -Si-O-framework of the silicone gives the polymers thermal stability, as in silica, and so they can be used where comparable organic materials would melt or decompose.

To distinguish between different silicones, systematic names are used, based on the monomer. The simplest silicon compound is silane,  $\text{SiH}_4$  which belongs to the homologous series of silanes. Silanes correspond to the alkanes whose simplest member is methane,  $\text{CH}_4$ .

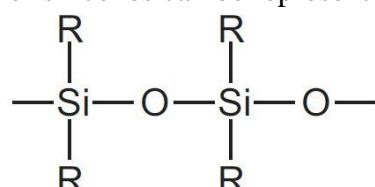


The presence of the oxygen atoms in the silicone chain is indicated by using the systematic name, siloxane, so termed as it contains a **silicon** atom, an **oxygen** atom and it is saturated as in an **alkane**. Thus if the groups attached to the siloxane chain are phenyl groups, the resulting silicone is called poly(diphenylsiloxane) and has repeating units along the chain.

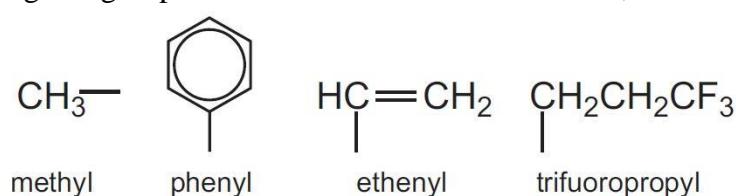


The most widely used silicones are those which have methyl groups along the backbone. Properties such as solubility in organic solvents, water-repellence and flexibility can be altered by substituting other organic groups for the methyls. For example, silicones with phenyl groups are more flexible polymers than those with methyl groups. They are also better lubricants and are superior solvents for organic compounds.

The structure of the repeating units of silicones can be represented as:



Where R represents organic groups attached to the silicone backbone, for example:



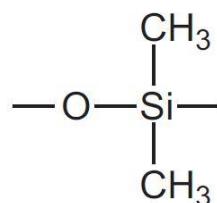
## Uses of silicones

Silicones can be sub-divided into four classes:

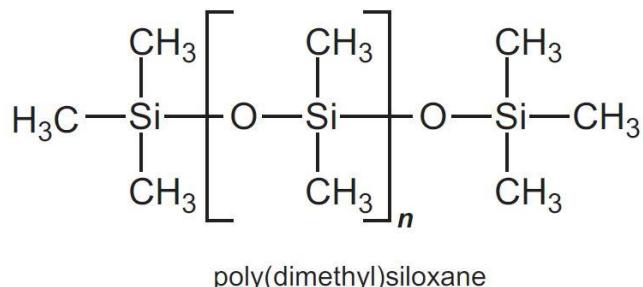
- a) Silicone fluids
- b) Silicone gels
- c) Silicone elastomers (rubbers)
- d) Silicone resins

Their physical form and uses depend on the structure of the polymer.

(a) **Silicone fluids** are typically straight chains of poly(dimethylsiloxane), with the repeating structure:



They usually have trimethylsilyl groups,  $\text{Si}(\text{CH}_3)_3$  at each end of the chain:



The silicones with short chains are *fluids* which, compared to hydrocarbons, have a more or less constant viscosity over a wide temperature range (200 to 450 K). They also have very low vapour pressures.

The low surface tension of silicone fluids gives them unique surface properties. They are, for example, used as lubricants in polishes (a mixture of wax and a silicone fluid dissolved in an organic solvent), in paints and for water-proofing fabrics, paper and leather. They also have anti-foaming properties and have been used, for example, to suppress the foaming of detergents in sewage disposal plants.

They have a low enthalpy of vaporization and a smooth, silky feel and thus are attractive as a basis for personal care products such as perspirants and skin care lotions.

A range of fluids is made by mixing polysiloxanes of low molecular masses with others with higher molecular masses. Some use the cyclic silicones which are formed during the preparation of the linear polysiloxanes.

(b) **Silicone gels** are based on the poly(dimethylsiloxane) chains but with a few cross-links between the chains, giving it a very open three-dimensional network. Often the cross-linking is done after a silicone fluid, together with a reactive group, is poured into a mould and then warmed or catalysed so that there is interaction to form cross-linking between the polymer chains. This is a very effective technique for protecting sensitive electronic equipment from damage from vibration and the polymer also acts as an electrical insulator. Pads containing a silicone gel are also used as shock absorbers in shoes, particularly in high-performance trainers and running shoes.

(c) **Silicone elastomers (rubbers)** are made by introducing even more cross-linking into the linear chain polymers. The structure is somewhat similar to natural rubber and they behave as elastomers. Their structure is determined by the amount of cross linking and the length of the chains.



**Figure 43:** These silicone elastomer particles are used in skin creams. Their small and perfectly spherical shape combined with a rubbery texture improves the feel of the cream as it is applied to the skin.

Although their strength at normal temperatures is inferior to that of natural rubber, silicone rubbers are more stable at both low temperatures (200 K) and high temperatures (450-600 K) and are generally more resistant to chemical attack. Silica is added as a filler (Unit 53) to make the elastomer stronger.

**(d) Silicone resins** have a three-dimensional structure with the atoms arranged tetrahedrally about the silicon atoms. The resins are usually applied as a solution in an organic solvent, and are used as an electrical insulating varnish or for paints where water repellence is desired, for example, to protect masonry. They are also used to give an 'anti-stick' surface to materials coming into contact with 'sticky' materials such as dough and other foodstuffs.

Hydroxyl groups on the resin react with hydroxyl groups that are on the surfaces of various inorganic surfaces such as silica and glass, thus making the surface water-repellent.

A large range of silanes, known as *coupling agents*, has been developed to enable chemists to bond an inorganic substrate (such as glass, minerals and metals) to organic materials (for example, organic polymers such as the acrylics, polyamides, urethanes and polyalkenes).

The resulting coatings confer the surface properties of a silicone to a very wide range of materials. Similar mechanisms enable some resins to be used as adhesives.

### Manufacture of silicones

Silicones are manufactured from pure silicon which has been obtained by the reduction of silicon dioxide (silica) in the form of sand with carbon at high temperatures:



The production of silicones from silicon takes place in three stages:

- synthesis of chlorosilanes
- hydrolysis of chlorosilanes
- condensation polymerization

#### (a) *Synthesis of chlorosilanes*

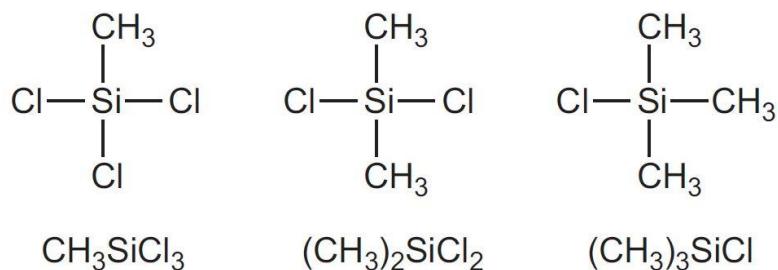
Silicon is first converted into chlorosilanes, e.g.  $\text{RSiCl}_3$ ,  $\text{R}_2\text{SiCl}_2$  and  $\text{R}_3\text{SiCl}$ , where R is an organic group.

When chloromethane is passed through heated silicon at about 550 K under slight pressure and in

the presence of a copper catalyst (often copper itself but other copper-containing materials can be used, for example, brass or copper(II) chloride), a volatile mixture of chlorosilanes distils over. For example:



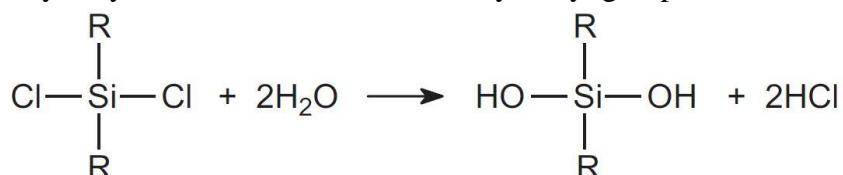
The mixture of liquids contains these three compounds:



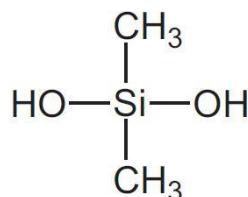
Careful distillation of the liquid mixture of chlorosilanes produces pure fractions of each chlorosilane. Dimethyldichlorosilane is the main product (ca 70-90%, the amount depending on the conditions used).

### (b) Hydrolysis of chlorosilanes

A dichlorosilane is hydrolyzed to a molecule with two hydroxyl groups:

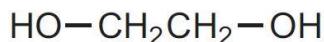


The product is a disilanol. The suffix *-ol* in a silanol is to show that the molecule contains at least one hydroxyl group attached to a silicon atom and the simplest example is dimethyldisilanol:



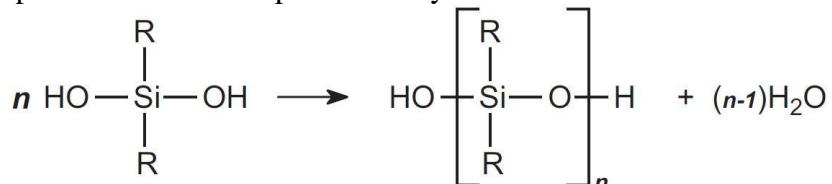
dimethyldisilanol

This nomenclature is similar to that of the alcohols, the simplest alcohol with two hydroxyl groups being ethane-1,2-diol:



ethane-1,2-diol

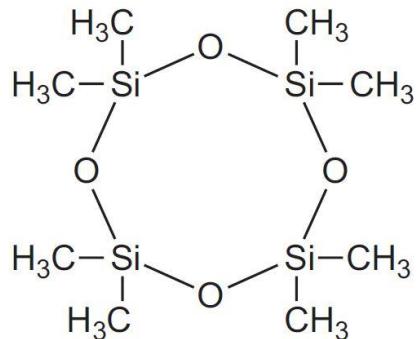
The hydroxyl groups of silanols react spontaneously to form a siloxane:



If R is a methyl group, the polymer is a poly(dimethylsiloxane).

Poly(dimethylsiloxanes) are produced with  $n = 20-50$ , which is not long enough to produce useful silicones.

These relatively short polymers are known as *oligomers*. Cyclic polymers, for example  $((\text{CH}_3)_2\text{SiO})_4$ , are also produced and then separated out.

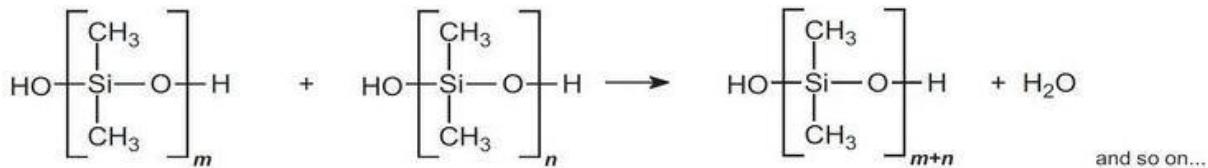


The oligomers are washed and dried. The hydrochloric acid is recycled and reacts with methanol to regenerate chloromethane:



### (c) Condensation polymerization

The oligomers condense rapidly in the presence of an acid catalyst to form long chain polymers:

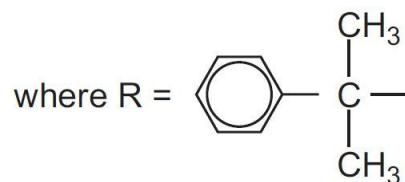


These materials are silicone fluids.

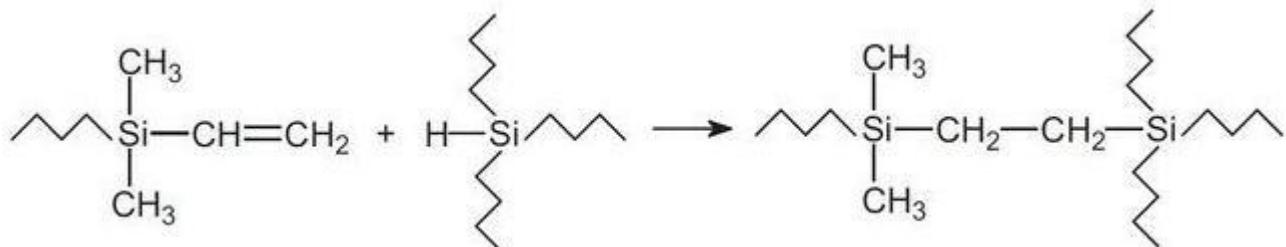
The value of (m+n) is usually between 2000 and 4000. The production of longer chains is favoured if the water is removed, for example by working under vacuum.

To form *silicone gels*, *elastomers* and *resins*, the long siloxane chains are induced to cross-link. There are four main ways of doing this:

(i) Cross-linking is often effected by first synthesizing silanes with a functional group, in place of a methyl group, that will react further. For example, a silane containing an ethenyl (vinyl) group such as ethenylmethyldichlorosilane, can be added to, for example, dimethyldichlorosilane. However with ethenyl groups in the chain, the chains are also able to undergo [free radical addition reactions](#), in a similar way to the free radical polymerization of chloroethene (vinyl chloride). This leads to cross-linking between the polymer chains. As with this polymerization, the addition reactions are initiated by radicals supplied on decomposition of an organic peroxide (for example, dicumyl peroxide):



(ii) Cross-linking can also be achieved by using siloxanes with ethenyl (vinyl) groups and other siloxanes containing Si-H groups, with a platinum compound as catalyst:





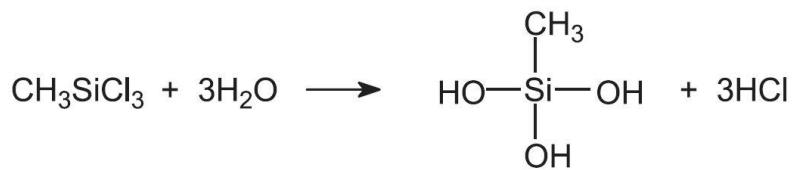
**Figures 44 and 45: Silicones played an important part in the construction of the London Eye, the largest observation wheel in the world.**

For example, the windows of the capsules are made of reinforced glass (using polyvinyl butyral, PVB as the laminate) which is anchored to the metal frame with a silicone resin. This resin is prepared *in situ* from two components one of which is a silicone with alkoxy groups which provide the cross-linking needed to form the resin.

The result is that the capsule can withstand winds of  $280 \text{ km h}^{-1}$ . These systems are also being used in buildings which are considered to be vulnerable to terrorist attacks, the glass, resistant to bomb blasts and bullets, will keep in place because of the very strong bonding to the metal frames.

(iii) A further way of producing cross-linking is to have an ethanoyl group in the silane. When these silicones are exposed to the air, the moisture reacts with the functional group, yielding a cross-linked silicone. An organometallic tin compound catalyses the reaction. These systems are often used as sealants and can be used in the home. The other product formed is ethanoic acid which can be recognized by its vinegary smell.

(iv) If some methyltrichlorosilane is added to the reactant, say dimethyldichlorosilane, the three chlorine atoms are hydrolyzed, thus producing a three dimensional network.



In all four methods, the physical properties of the silicone can be modified by varying the proportions of the reactants, which controls the extent of cross-linking and hence how *rubbery* is the product.

### Alkyd Resins

Alkyd resins are oligomers in which polyester functions have been inserted into natural “drying oils”. Before 1929, glass paints were based on drying oils themselves. These are triglycerides containing unsaturated fatty acids. Linseed oil, for example, is mainly linolenic acid triglyceride. Linolenic acid is

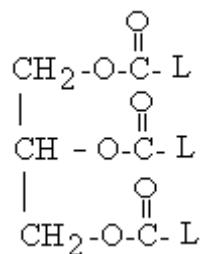


While linoleic acid, found in soybean oil, has one fewer double bond:

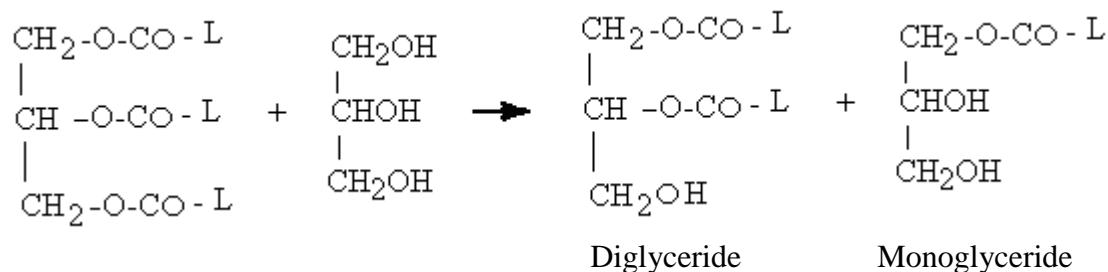


The drying oil was dissolved in a solvent and mixed with pigment. An oil soluble metal salt such as lead or cobalt naphthenate was added as an initiator. It introduced peroxide formation when the paint was spread as a thin film. The peroxide in turn catalyzed the polymerization of double bonds in the linseed oil to give a paint film. The drying oils used were primarily linseed oil and tung oil. Soybean oil could not be used because it does not contain enough unsaturation. It is valuable in alkyds because, whereas the oil has only 3 fatty acid residues, the alkyd has 6-10.

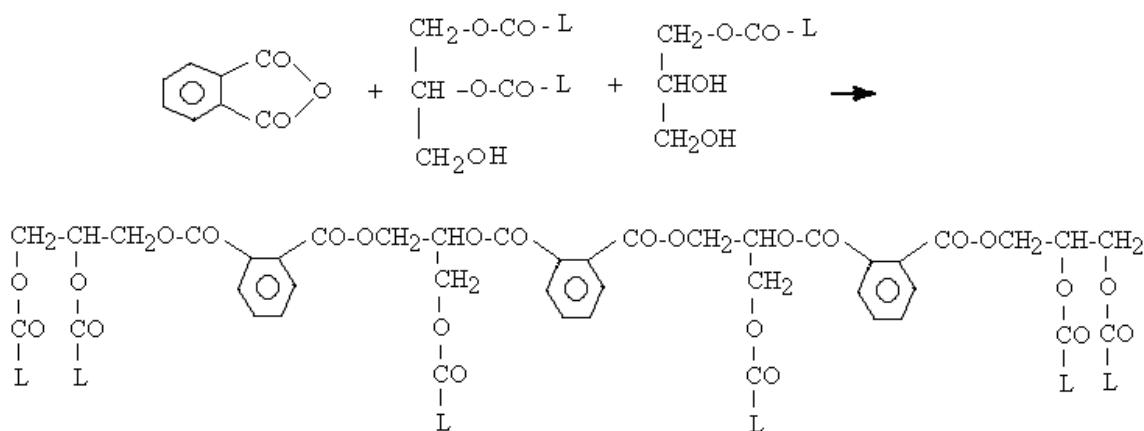
These paints based on natural drying oils had little resistance to solvents, chemicals or UV light. They were replaced by oil-modified alkyd resins, which are made by heating or interesterifying a drying oil with a polyol, such as glycerol, and esterifying the product with a dibasic acid or anhydride, such as phthalic anhydride. If linoleic or linolenic acid is written L-COOH, then glyceride is:



Interestering with glycerol gives a mixture of esters:



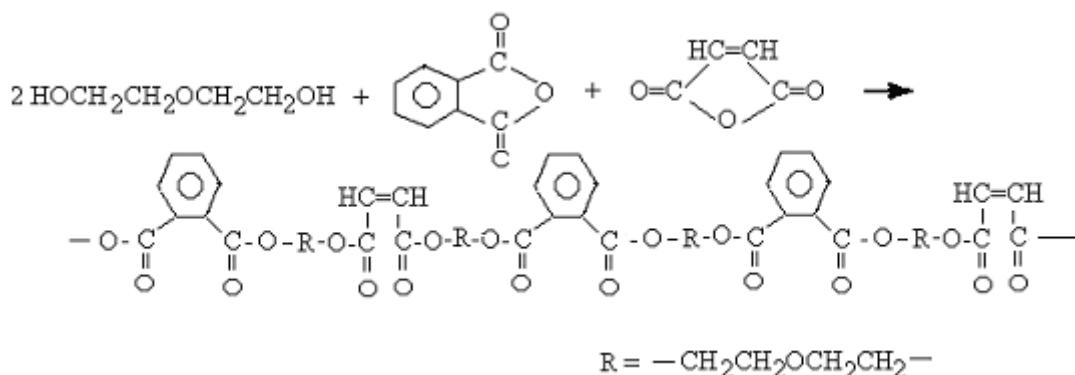
These react with phthalic anhydride to give a more or less linear polymer, the chain length of which is determined by the ratio of mono- or diglycerides in the mixture. This polymer is called an alkyd.



The incorporation of the polyester function gives the paint film greater solvent and ultraviolet resistance and also imparts somewhat greater corrosion-resistance.

### Unsaturated Polyester Resins

Unsaturated polyester resins are oligomers that result from the condensation of phthalic anhydride, maleic anhydride and a glycol such as diethylene glycol. The unsaturated oligomers are copolymerized with styrene or less frequently with methyl methacrylate in the presence of a peroxide initiator.



Unsaturated polyesters reinforced with glass cloth or fibers are used for the automobiles. They are used as a metal replacement for the fabrication of pipe and storage tanks, and in the manufacture of small boats and even large minesweepers, where the absence of metal is essential.

### Epoxy Resins

Epoxy resins are oligomers resulting from the condensation of bisphenol A and epichlorohydrin. When cross-linked, they are hard, chemically resistant, and dimensionally stable, and have excellent electrical properties. Their largest use is for protective coatings of metal containers, appliances and ships, as well as for general maintenance where resistance to severe

corrosion is required. They are used in the computer industry for “potting” electrical components. The second largest use is in fibre-reinforced composites for circuit boards, aerospace components, and sporting equipment. Other uses include adhesives, sealants, patching and flooring compounds, and castings.

