

# Electronic materials and components-Polymer basics

## Background

A polymer (from the Greek 'poly', meaning many, and 'meros', meaning part) is a long molecule consisting of many small units ('monomers') joined together. A typical polymer may include tens of thousands of monomers and, because of their large size, polymers are classified as 'macromolecules'. Typically formed by interlinked carbon atoms, polymers are commonly found in nature, in many forms of animal and plant life. One of the most common natural polymers is cellulose, a building material for all vegetation; a more specialist substance, but one which is more readily recognised as a polymer, is natural rubber.

For centuries people have used polymers in the form of oils, tars, resins, and gums. However, it was not until the industrial revolution that the modern polymer industry began to develop. In the 1830s, Charles Goodyear succeeded in producing a useful variant of natural rubber through a process known as 'vulcanisation', and some 40 years later, celluloid (a hard plastic formed from nitro-cellulose) was successfully commercialised.

The earliest artificial polymers were made by modifying natural polymers: the first totally synthetic polymer was Bakelite, produced in 1907 by combining phenol and formaldehyde. The two substances which the Belgian-born American chemist Baekeland united produced a third with properties far different from either of the originals. The giant Bakelite molecule is extremely complex; it consists of a network of benzene rings, each joined to another at one, two or three of its six corners by a chemical group of two atoms of hydrogen and one of carbon. The dark brown colours of much early electrical hardware and the 1930's radio were both Bakelite. As what is now called 'phenolic', this type of resin is still in use, for example, in making low-cost PCBs.

Progress in polymer science was slow until the 1930s, when materials such as vinyl, neoprene, polystyrene, and nylon were developed. The wide acceptance of these revolutionary materials began an explosion in polymer research that is still going on today. Modern polymers tend not to be natural compounds, but are manufactured mainly from oil-based raw materials in large scale chemical processing factories which are usually sited close to oil refineries in order to minimise the transport requirements, as large volumes of polymer materials are required for products such as paints, adhesives, elastomers, and fabrics.

## Polymer structure

The polymer molecule

The example shown in Figure 1 is polyethylene, the simplest hydrocarbon polymer, formed when ethylene gas is heated at high pressure in the presence of a suitable polymerisation initiator. The number of ethylene molecules which form the polymer molecule ('n' on the diagram) is usually of the order of 10,000, but may be as high as a million or as low as a thousand.

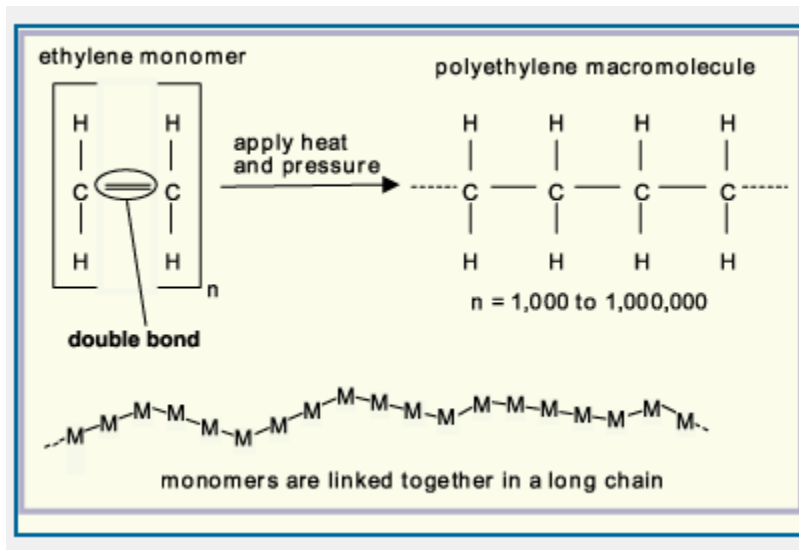


Figure 1: The polyethylene molecule

Different materials require different methods of preparation of the monomer, and slightly different techniques to induce polymerisation, but the starting point is the monomer, or small groupings of monomers, usually in a liquid state. The factor which initiates the polymerisation process can be different for different materials. Examples are heat, pressure, light, or a chemical additive. The chemical additive that starts this chain reaction is called an 'initiator' or 'promoter'. Since an initiator greatly speeds up the reaction rate, it is often referred to as a 'catalyst', though this is not strictly correct, because it is usually consumed in the reaction.

Different polymerisation conditions can be used to tailor the length of the molecule, which is proportional to the number 'n'. Figure 2 indicates how most physical properties of a polymer vary according to the molecular weight.

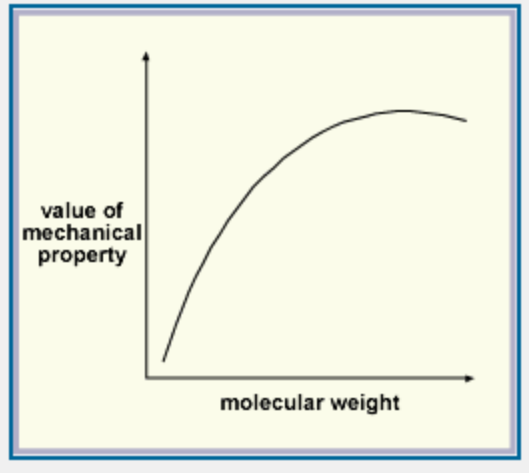


Figure 2: Dependence of physical properties on molecular weight

It is important to realise that when we talk about the number of monomers per polymer molecule, that this is an average, about which there is substantial variation. And, as Figure 3 illustrates with its analogy of piles of stones of the same average weight, we need to know whether some molecules are significantly different from the norm.

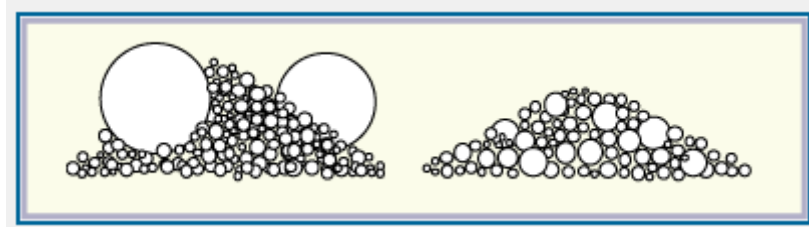


Figure 3: Two piles of stones with the same average weight after

Alvino 1994

Branching

The mechanical properties of a polymer are governed not only by the length of the molecule but by its shape. The first polymerisation of polyethylene (in 1935) produced a molecule with many side branches containing only a few carbon atoms, most often two or four (Figure 4).

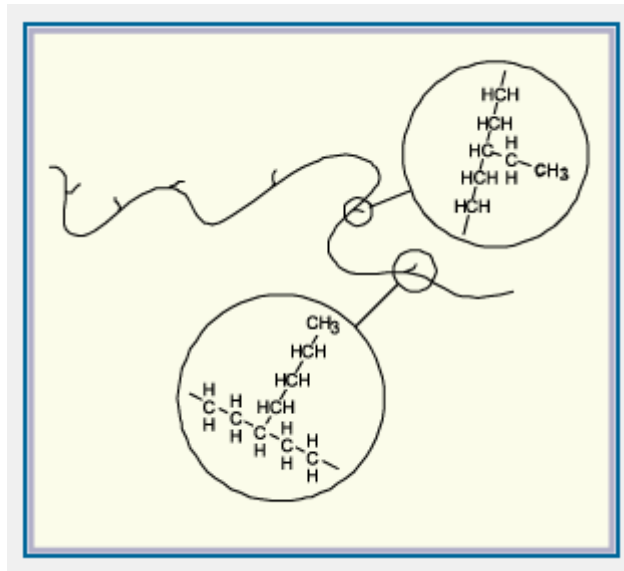


Figure 4: Side-branched polyethylene

However, the number of side branches may be varied by changing the temperature and pressure under which polymerisation is carried out. Even small variations in the number of side branches can cause appreciable changes in mechanical properties such as elastic modulus, creep resistance, and toughness.

Polymers with a high degree of branching are called dendrimers. Often in these molecules, branches themselves have branches, which tends to give the molecule an overall spherical shape in three dimensions.

Both linear and side-branched polyethylene behave similarly when heated: they melt and flow like a liquid, and when cooled will crystallise. This liquid-solid transition is 'reversible', and may be repeated time and time again. Such polymers are referred to as 'thermoplastic' (or thermal-flow) polymers.

#### Cross-linking

As well as the bonds which hold monomers together in a polymer chain, many polymers form bonds between neighbouring chains. These bonds can be formed directly between the neighbouring chains, or two chains may bond to a third common molecule. For polyethylene, cross-linking can be induced by treating the polymer with ionising radiation, but in other materials cross-linked networks are more frequently produced by chemical reactions triggered by heating in the presence of a catalyst.

Though not as strong or rigid as the bonds within the chain, these cross-links have an important effect on the polymer. Extensive cross-linking effectively turns the

entire specimen into one giant molecular network (Figure 5), in which the cross-links inhibit movement: the network (and consequently the shape of the specimen) are 'set'. This is the origin of the term 'thermoset', which is explained in more detail in Polymer types.

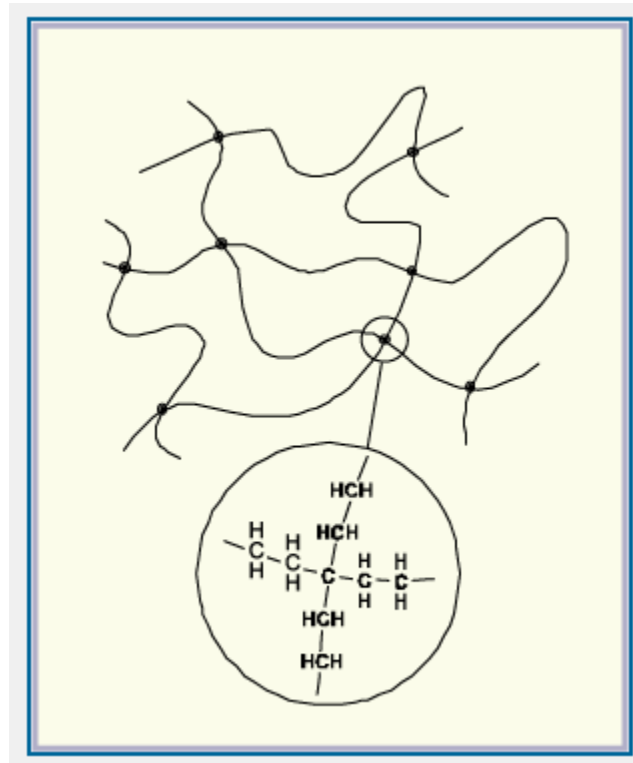


Figure 5: Molecular structure of cross linked

### **Addition and condensation polymers**

A very large number of monomers may be polymerised. The resulting polymers fall broadly into two categories, depending on the chemical mechanism by which polymerisation takes place. These are illustrated in Figure 6 & Figure 7: 'addition polymers' grow by adding 'unsaturated' monomers to the growing chain; in 'condensation polymers', the bonding is accompanied by the elimination of small molecules such as water.

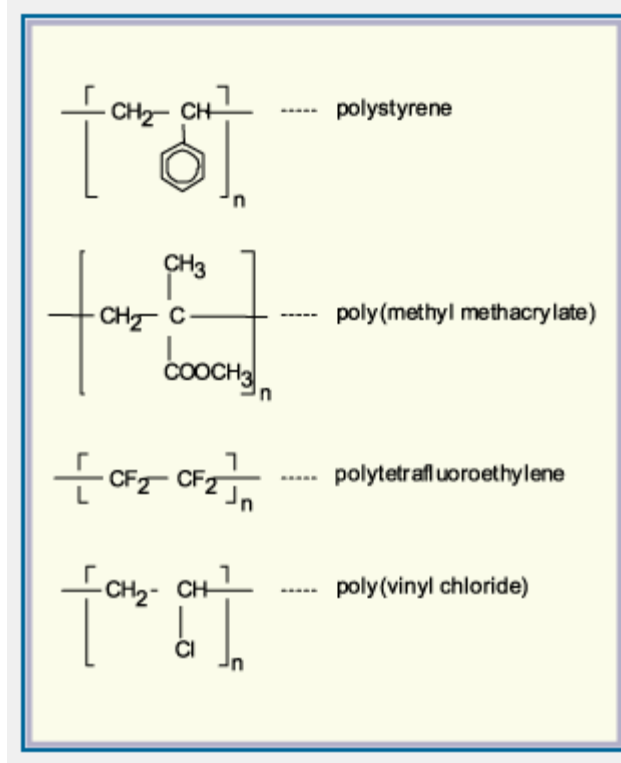


Figure 6: Some common addition polymers

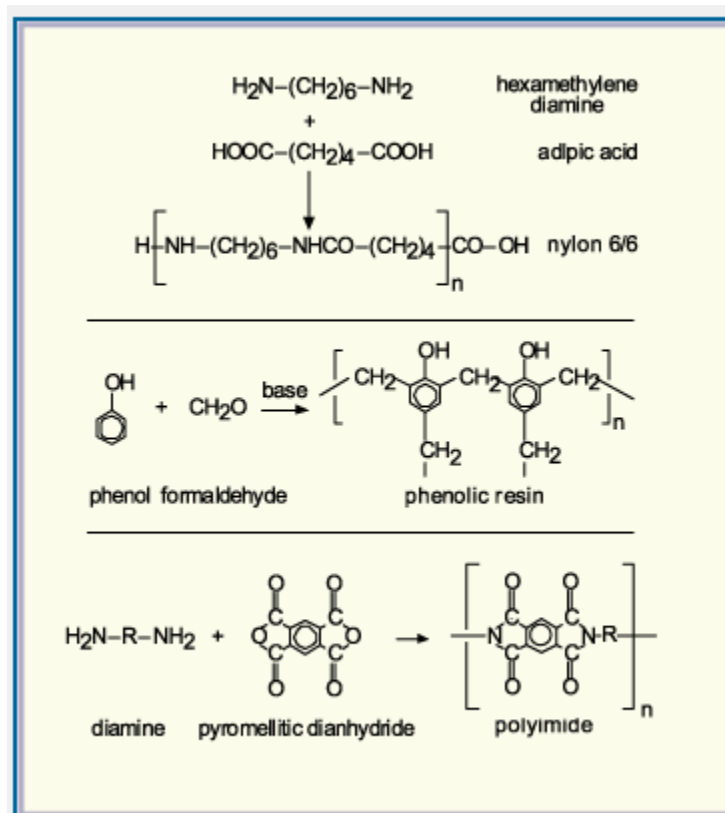


Figure 7: Some common condensation polymers

### Functionality

There is no relationship between the polymerisation mechanism and whether the resulting polymer is thermoplastic or thermosetting. The form of polymer produced depends instead on the capacity of the monomer to make external bonds, regardless of how these are made.

Mechanism for polymerisation	Form of polymer	Classification
Addition	Linear	Thermoplastic
Condensation	Linear, with side-branches	
	Some cross-linking	Elastomer
	Fully cross-linked	Thermoset

The number of bonds which each monomer molecule can make is referred to as the 'monomer functionality':

With a functionality of 2, a linear polymer is the only outcome – think of people holding hands! Branching can only be produced by extreme conditions, such as high pressure/temperature or chemical treatment, which induce side reactions

A functionality of 3 will allow branching

A functionality of 4 gives the ability to form cross links. The isoprene molecule which is the basis of natural rubber is an example where this functionality is provided by two double bonds.

Whatever the mechanism (or mechanisms) of bonding between monomer molecules, the higher the monomer functionality, the more cross-linked will be the network produced. For a given monomer functionality, the characteristics will also be affected by the size of the monomer molecule: the smaller the molecule, the shorter the distance between bonds, and the tighter the resulting network.

### Naming polymers

In general, a polymer with an unspecified number of monomers is named by adding the prefix 'poly' to the name of the 'constitutional repeating unit' (CRU), so the polymer formed by combining styrene monomers is called polystyrene. Where the monomer name is made of two or more words, these are separated from the prefix 'poly' with parentheses, as in poly(vinyl acetate), which is the common 'PVA'

adhesive used in building applications. There is a complete set of nomenclature rules which apply to monomers containing more than one sub-unit, but these become too complicated for this module!

## **Crystallinity**

As well as the shape of the molecules, the way they are arranged in a solid is an important factor in determining the properties of a thermoplastic polymer. One distinction made is between 'crystalline' and 'amorphous' materials:

Crystalline materials, such as table salt, ice and most metals, have a highly ordered and regular structure, with their molecules arranged in repeating patterns. Applying heat turns them from solid to liquid over a narrow range of temperature

Amorphous materials, such as glass, have molecules arranged randomly and in long chains which twist and curve around one-another, so that they have much less long-range internal structure. As the temperature is increased, these gradually turn from brittle solid-like materials to viscous liquids.

These differences can be seen when the materials are viewed between crossed polarizers, crystalline melting leading to striking changes in optical properties.

Crystalline polymeric material shows a high degree of order formed by folding and stacking of the polymer chains (Figure 8); the amorphous or glass-like structure shows no long range order, and the chains are tangled (Figure 9); most polymers are 'semi-crystalline', forming mixtures of small crystals and amorphous material. These structures have useful strength and stiffness properties, but melt over a range of temperature instead of at a single melting point.]

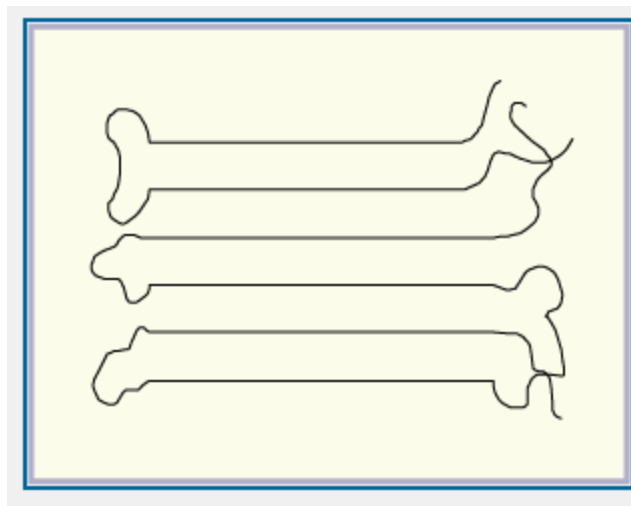


Figure 8: Crystalline polymer structure



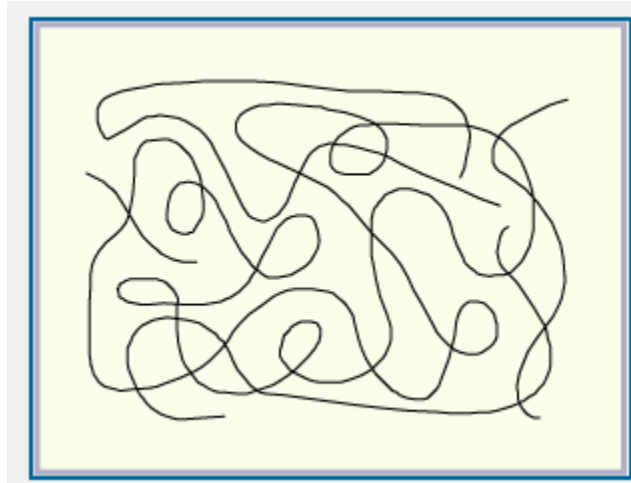


Figure 9 : Amorphous polymeric structure

The proportion of crystals in the polymer is influenced by:

the degree of polymerisation – short chains organise themselves into crystalline structures more readily than long molecules

the size and shape of the monomer groups – large and irregular monomers tend to make amorphous solids

the cooling rate – slow cooling provides more time for crystallisation to occur, whereas rapid quenches yield highly amorphous materials

any subsequent annealing (heating and holding at an appropriate temperature below the crystalline melting point, followed by slow cooling), which, as with metals, can significantly increase crystallinity, as well as relieving stresses

(for polymer fibres) stretching when in a semi-crystalline state, which increases chain alignment, crystallinity and strength.

### **Initiating cure**

The curing reaction, which is the final stage of polymerisation for cross-linked thermoset polymers, is usually induced by adding a catalyst or applying heat/pressure. Most reactions are however 'exothermic', that is they generate heat themselves. Whilst this may make process control difficult when large quantities of resin are being handled, in typical electronics applications the resin quantities are smaller, so an external source of energy is needed.

Oven heating is relatively inefficient, as both oven and air are heated, rather than just the workload, and the process relies on heat being conducted from the surface to the bulk of the material. Alternative curing methods used include infrared,

microwave, and high-frequency heating, which all rely on the material absorbing electromagnetic energy, yet allowing sufficient penetration for the internal parts to be cured.

Infra-red processing is used mostly to drive solvents from coatings, rather than cure coatings of 100% solids content.

Microwave processing has been used to cure inks, coatings and moulded parts, and fabricate foamed plastics as well as resin-impregnated fabric.

The electronics industry also uses ultraviolet (UV) and electron beam processing in the manufacture of PCBs, conformal coatings, adhesives, coil lead encapsulants, solder masks, and resists, and in ink processing.

Ultra-violet light involves exposing the material to radiation with wavelength from 200-400nm, generated by either medium-pressure mercury lamps or microwave-excited lamps. The cure efficiency is affected by the extent to which the resin transmits UV light, and thickness is usually limited to 0.25mm.

Electron beam processing uses electrons which are emitted from a heated filament in an evacuated chamber, are accelerated and deflected by electrostatic and magnetic fields, and directed toward their target through a thin foil window.

The motive behind its development and use has been the need to develop more environmentally compatible processes. Radiation processing requires less process time and less energy, is environmentally safe, and does not require elevated temperatures, so that it can be used with heat-sensitive parts or components. However, a limitation is that equipment capital costs are high.

Although many chemicals accelerate the polymerisation process, there are exceptions. For example, oxygen can inhibit both UV and electron beam processes.

Author: Martin Tarr

**Source: [http://www.ami.ac.uk/courses/topics/0209\\_pme/index.html](http://www.ami.ac.uk/courses/topics/0209_pme/index.html)**