STRUCTURE AND PROPERTIES OF POLYMERS

In terms of the classification systems, it is found that the polymers of major commercial importance tend to be the thermoplastics or addition polymers rather than the thermosets, and these will be dealt with first.

Poly (ethylene)

This polymer has one of the simplest molecular structures ($-CH_2CH_2-$) and is at present the largest tonnage plastic material, having first been produced commercially in 1939 for use in electrical insulation. There are four different industrial routes to the preparation of poly(ethylene), and they yield products having slightly different properties. The four routes are:

(i) High Pressure Processes, **(ii)** Ziegler Processes, (iii) The Phillips Process, (iv) The Standard Oil (Indiana) Process.

High Pressure Processes: use pressures of 1000-3000 atm and temperatures of 80-500 "C. Free-radical initiators, such as benzoyl peroxide or oxygen, are generally used, and conditions need to be carefully controlled to prevent a runaway reaction, which would generate hydrogen, methane, and graphite rather than polymer. In general, high-pressure processes tend to yield lower density poly(ethylenes), typically in the range 0.915-0.945 g cm-", which also have relatively low molar masses.

Ziegler processes are based on co-ordination reactions catalyzed by metal alkyl systems. Such reactions were discovered by Karl Ziegler in Germany and developed by G. Natta at Milan in the early 1950s. A typical Ziegler-Natta catalyst is the complex prepared from titanium tetrachloride and triethylaluminium. It is fed into the reaction vessel first, after which ethylene is added. Reaction is carried out at low pressures and low temperatures, typically no more than **70°C,** with rigorous exclusion of air and moisture, which would destroy the catalyst. The poly(ethylenes) produced by such processes are of intermediate density, giving values of about 0.945 gcm-". A range of relative molar masses may be obtained for such polymers by varying the ratio of the catalyst components or by introducing a small amount of hydrogen into the reaction vessel.

Phillips and the Standard Oil (Indiana) Processes: both yield high density poly(ethylenes), using relatively low pressures and temperatures.

Poly (propylene)

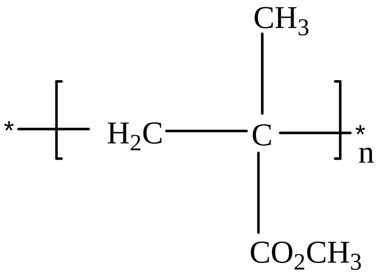
This polymer, which has the structure [-$CH_2CH(CH_3)$-], arose as a commercial material following the work of Natta on catalysts for the preparation of high relative molar mass polymers from alkenes. Following his work on the polymerisation of ethylene, Natta showed in 1954 that it was possible to prepare analogous polymers of propylene. Commercial exploitation followed rapidly, and poly(propy1ene) was first marketed in 1957. When poly(propy1ene) was first made, it was found to exist in two possible forms. One was similar to poly(ethylene), but had greater rigidity and hardness; the other was found to be amorphous and of little strength. The first of these is now known to be isotactic, that is with a regular stereochemistry at each alternating carbon atom. The other is now known to be atactic, that is with a random distribution of different stereochemical arrangements at each methyl-bearing carbon atom.

Commercial poly(propylene) is usually about 90-95% isotactic and is very similar to poly(ethy1ene) with the following exceptions: (i) It has a lower density (0.90 gcm-'). (ii) It has a higher softening point and hence can be used at higher temperatures. For example, it is used to make kettles, generally of the jug-type of design, and it is found to be well able to withstand the effects of exposure to boiling water. (iii) It is not susceptible to environmental stress cracking. (iv) It is more readily oxidised. This is a consequence of the relatively readily fragmented tertiary C&H bond within the molecule. Another interesting property of isotactic poly(propylene) is that it can be repeatedly flexed without causing weakness. Hence it is used for one-piece mouldings, such as boxes for card indexes, which can be used over many years without damage.

Poly (methyl methacrylate) - PMMA

This polymer, whose name is often abbreviated to PMMA, is the most important of the commercial ***acrylic*** polymers. These polymers are formally derived from poly (acrylic acid), [-$CH_2CH(CO_2H)$-]. In the case of PMMA, this derivation can be thought of as coming about by replacement of the tertiary hydrogen atom by a methyl group, CH_3, and by esterification of the carboxylic acid group with methanol, CH_2OH.

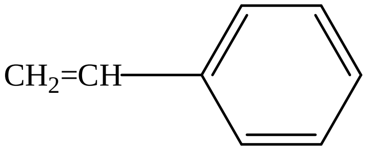
Commercially PMMA is becoming relatively less important as time passes. PMMA does, though, retain certain uses, including interestingly as the material from which plastic dentures are manufactured. PMMA is a transparent, glassy material, which is known from X-ray studies to be



amorphous at the molecular level. It is clearly polar, as is shown by its poor insulating properties relative to poly(ethy1ene) and its solubility in solvents such as ethyl propanoate and trichloroethane. The main applications for PMMA arise from the combination of its transparency and its good outdoor weathering properties. These are coupled with reasonable toughness and rigidity, *so* that PMMA is a useful material in a range of glazing applications. For example, it is used for display signs, street lamp fittings, and ceiling lights in factories and offices. It is also the standard material for automobile rear lamp housings.

Poly (styrene)

Poly(styrene) is a polymer which finds widespread use in the developed world on account of its desirable properties, combined with its relative cheapness. Among its features are excellent colour range, transparency, rigidity, and low water absorption. The monomer, styrene, is a derivative of benzene, vinyl benzene .



It is a colourless, mobile liquid that polymerises readily. The first report of the polymerisation reaction came in 1839, when E. Simon described the transformation of what was then called ‘styrol’. He believed he had oxidised the material and called the product styrol oxide. Later, when it was realised that it contained no oxygen, the product became known as metastyrene. The polymer is based on a simple head-to-tail arrangement of monomer units and is amorphous, since the specific position of the benzene ring is somewhat variable and hence inhibits crystallisation.

Despite its generally desirable properties, for many applications it is considered too brittle. Because of this, a number of approaches have been made to modify the mechanical properties of poly(styrene). The most successful of these have been (i) copolymerisation and (ii) the addition of rubbery fillers. A very large number of different copolymers of styrene have been produced and sold commercially. Among the most successful have been those polymers also containing butadiene. At the appropriate ratio of monomers, these copolymers behave as synthetic elastomers, known as styrene- butadiene rubber, SBR. Another important group of materials are the terpolymers of acrylonitrile, butadiene, and styrene, ABS. A large range of ABS materials can be made by varying not only the ratios of the three monomers but also the precise conditions of manufacture. ABS materials generally have high impact strength and can be readily moulded to give articles of good surface finish.

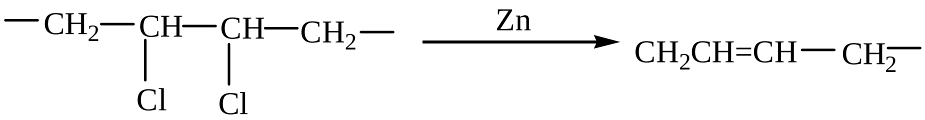
The alternative approach to producing strengthened styrene polymers is to use rubbery fillers. Such materials are known as high-impact poly(styrenes) , a name which reflects their improved mechanical properties. They are typically prepared by dissolving the rubber in the styrene monomer, followed by polymerization of the styrene in the usual way. The process gives a blend containing not only rubber and poly(styrene), but also small amounts of graft copolymer, comprising short poly (styrene) side chains attached to the molecules of the rubber. The overall effect of using this approach is to give materials with much better impact strengths than pure poly(styrene).

Lastly, the polymerisation of styrene is used for crosslinking unsaturated polyesters. Typically a polyester is produced which contains double bonds. Such a resin, known as a pre-polymer, is then mixed with styrene to give a viscous solution, and this solution is then worked into a glass fibre mat. The resulting composite material develops its final properties by polymerization of the styrene, which essentially undergoes homopolymerisation, but also incorporates the occasional double bond from the prepolymer molecule. This gives a large, three-dimensional network, intertwined with the glass reinforcement. The composite material has excellent properties and is widely used for boat hulls, shower units, and baths.

Poly(viny1 chloride), PVC

Poly(viny1 chloride) is the widely accepted trivial name for poly(l-chloroethene) and, in terms of worldwide production, is one of the three most important polymers in current use, the other two being poly(ethy1ene) and poly(styrene). PVC: has numerous uses, including cable insulation, packaging, and toys.

PVC has been shown to have a head-to-tail structure. Typical experimental evidence for this is that when dissolved in dioxin and treated with zinc dust, it undergoes a Wurtz-type reaction to yield a product containing a small amount of chlorine and no detectable unsaturation. The alternative possible structure, the head-to-head arrangement, would yield unsaturated sites where adjacent chlorine atoms had been removed.



$$-CH_2-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}-CH_2- \xrightarrow{Zn} CH_2CH{=}CH-CH_2-$$

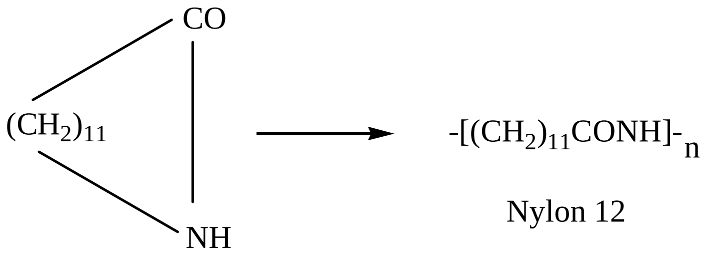
Uncompounded PVC is colourless and rigid, and possesses poor stability towards heat and light. Indeed, PVC is certainly the least stable of the high tonnage commercial polymers. Exposure to either light or heat at temperatures well below the softening point brings about a number of undesirable changes. Initially discoloration is apparent, as the polymer becomes yellow and passes progressively through deep amber to black on increasing time of exposure. At the same time the material becomes increasingly brittle. These changes are caused by the polymer undergoing dehydrochlorination, i.e loss of HCl from along the backbone. Such loss is autocatalytic, and may continue until there are only traces of chlorine left in the macromolecule. It has the effect of reducing molecular flexibility and of allowing absorption of light at the visible part of the electromagnetic spectrum. These alterations in the molecular features lead to the observed changes in the properties of the bulk polymer. In order to fabricate articles from PVC, and then use them in locations where they will be exposed to sunlight, it is necessary to add stabilisers at the compounding stage. A large number of chemicals have been used as stabilisers for PVC, including lead soaps, barium and cadmium laurates, and organotin compounds such as tin di-iso-octylthioglycollate. These latter compounds, the organosulfurtins, are relatively expensive but are used where good clarity and freedom from colour are important in the final compounded PVC. The mechanisms of degradation and the mode of action of the various PVC stabilisers have both been widely studied. Often at least one aspect of their operation is some sort of reaction with the first trace of hydrogen chloride evolved. This removes what would otherwise act as the catalyst for further dehydrochlorination, and hence significantly retards the degradation process. In addition, many stabilisers are themselves capable of reacting across any double bonds formed, thereby reversing the process that causes discoloration and embrittlement.

The Nylons

The name Nylon was given by the Du Pont company of America to their first synthetic condensation polymer formed by the reaction of difunctional acids with difunctional amines. It had been made as part of the fundamental programme of W. H. Carothers to investigate the whole topic of polymerisation. The term has gradually been extended to other related polymers. These materials are strictly polyamides, but this term includes that otherwise distinct class of natural macromolecules, the proteins. The term nylon is retained for its usefulness in distinguishing synthetic polyamides from the broader class of such polymers. As mentioned, nylons are condensation or step polymers and, because of this, they are different from all of the other commercially important polymers described *so* far. The nylons are distinguished from each other by a numbering system based on the number of carbon atoms in the starting materials. Thus, nylon **6,6,** which was first prepared in **1935** and is still the major commercial nylon, is prepared by reaction of hexamethylenediamine (six carbon atoms) with adipic acid (six carbon atoms).

$$nH_2N(CH_2)NH_2 \;+\; nHOOC\,(CH_4)COOH \longrightarrow HN_2[(CH_2)_6NHCO(CH_4)CO]n \;+\; (n\text{-}1)H_2O$$

Similarly nylon **6,10** is prepared from hexamethylenediamine and sebacic acid (ten carbon atoms). Certain nylons are designated not by two numbers, but by a single number; these are the nylons prepared from a single starting material. Such a starting material can be either a long-chain amino acid, such as u-aminodecanoic acid (eleven carbon atoms) which undergoes selfcondensation to yield nylon **11,** or a closed ring amide-type compound, known as a lactam, which will undergo a ring-opening reaction to yield a polymer. This is the method by which nylon 6 is prepared from caprolactam (six carbon atoms) and nylon 12 is prepared from dodecyl-lactam (twelve carbon atoms). The latter reaction may be represented by the equation shown below:

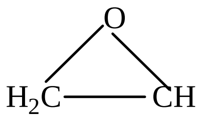


The various nylons tend to have similar physical properties. These include high impact strength, toughness, flexibility, and abrasion resistance. Also, because of the linear structure, they form excellent fibres. This was the basis of the early commercial success of nylon 6,6. Commercial production of fibres of nylon 6,6 began in 1938, and two years later nylon stockings became generally available in the USA. As is well known, they were a huge success, and became highly fashionable during the years of World War II.

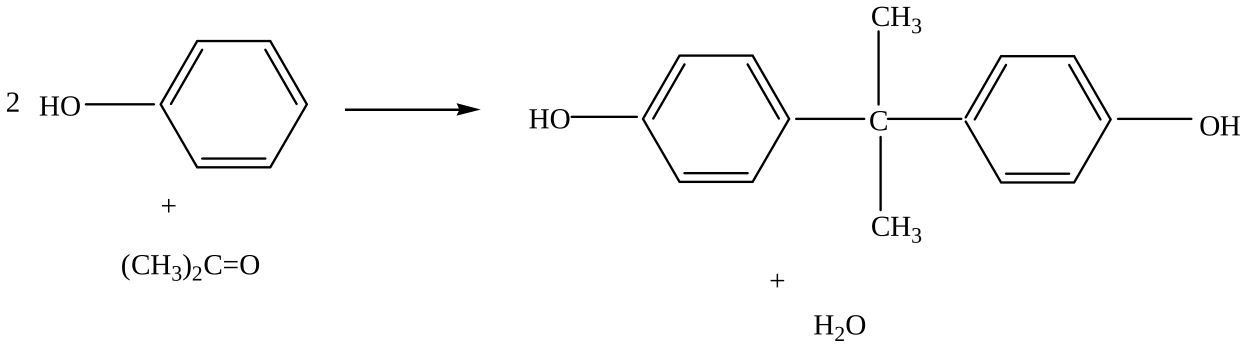
Nylons tend to show very good resistance to organic solvents, and also to fuels and oils. They are, however, readily attacked by concentrated mineral acids at room temperature and by alkalis at elevated temperatures. Nylons 6,6 and 6 are the ones usually employed as textile fibres. Where individual monofilaments are used, such as in brushes, sports equipment, or surgical sutures, nylons 6,lO and 11 tend to be used, because of their greater flexibility and water resistance. All nylons can be injection moulded and the resulting articles have found widespread use in engineering applications, such as bearings and gears.

Epoxy Resins

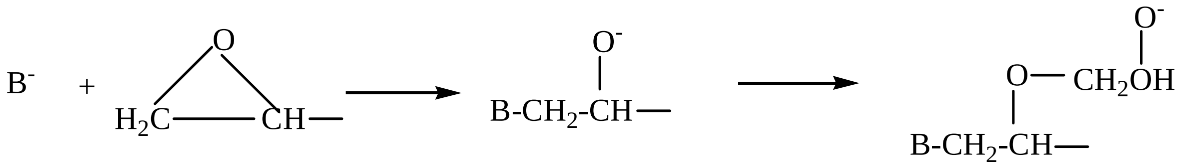
These polymers are based on the three-membered heterocyclic system either as the epoxy or oxirane ring.



For commercial application, diepoxides such as those derived from bisphenol A are employed, and they are cured via ringopening crosslinking reactions, into which the epoxy group enters readily. Bisphenol A is so-called because it is formed from two moles of phenol and acetone



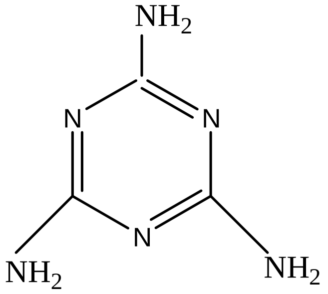
A variety of reagents can bring about these ring openings, including amines and anhydrides used in stoichiometric amounts,or Lewis acids such as SnCl, and Lewis bases such as tertiary amines, used in catalytic amounts. The crosslinking reactions are illustrated below, and they demonstrate that, in principle, only a trace of curing agent is necessary to bring about cure of epoxy resins. Selection of curing agent depends on various considerations, such as cost, ease of handling, pot life, cure rates, and the mechanical, electrical, or thermal properties required in the final resin.



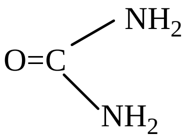
Epoxy resins are relatively expensive, but despite this, they are firmly established in a number of important applications. These include adhesives, protective coatings, laminates, and a variety of uses in building and construction.

Amino Resins

Amino resins are those polymers prepared by reaction of either urea or melamine with formaldehyde. In both cases the product that results from the reaction has a well crosslinked network structure, and hence is a thermoset polymer. The structures of the two parent amino compounds are shown below:



Melamine



Urea

The initial step of the polymerisation process is reaction of the amine groups with formaldehyde to generate methylol units.

$$-NH_2 + HCHO \longrightarrow -NHCH_2OH$$

Further heating of the polymer then leads to a variety of reactions. For example, the methylol groups can undergo self-condensation.

$$-NHCH_2OH \longrightarrow NH_2OCH_2NH^- + H_2O$$

Alternatively the methylol groups can react with further amino groups, also evolving a molecule of water in what is another condensation reaction.

$$-NHCH_2OH + H_2N^- \longrightarrow -NH_2OCH_2NH^- + H_2O$$

Unlike phenol-formaldehyde polymers, the amino resins are not themselves deeply coloured, but are of a naturally light appearance. They can be easily pigmented to give a variety of shades, which leads to application in uses where good appearance **is** highly valued, for example in decorative tableware, laminated resins for furniture, and modern white electrical plugs and sockets. When crosslinked, amino resins are very resistant to most organic solvents, though they tend to be attacked by both acids and alkalis. Urea-formaldehyde polymers are more susceptible to attack than those prepared from melamine and formaldehyde.

Poly(tetrafluoroethylene) , PTFE

This polymer is the completely fluorine-substituted analogue of poly(ethy1ene) ie. [$-CF_2CF_2-$] The amount of this polymer produced commercially is very small compared with the output of many other synthetic polymers, but it has a number of important specialised uses and so is worth considering briefly. PTFE is a white solid with a waxy appearance. It is very tough and flexible, with a good electrical insulation properties. The surface energy and coefficient of friction are both very low, the latter being the lowest of any solid. The combination of low surface energy and low coefficient of friction cause PTFE to have excellent non-stick characteristics, a feature which underlies many of the everyday uses of this polymer. In addition to its unique mechanical properties, PTFE has excellent chemical resistance to a very wide range of reagents, with the exception of molten alkali metals and fluorine. There is no known solvent for PTFE.

PTFE is a linear polymer of the addition type, formed by polymerisation of the unsaturated monomer tetrafluoroethylene, CFFCF~. Despite the fact that this structure ought to impart thermoplastic character to the polymer, PTFE does not show conventional melting behaviour. It does not apparently liquify on heating, nor does it give a melt that will flow. Instead it forms a high-viscosity translucent material which fractures rather than flows when an appropriate force is applied.

Because PTFE cannot be dissolved or melted, there are problems with fabricating articles out of the polymer. These are overcome by using a technique similar to powder metallurgy, in which granular particles are fused under high pressures and temperatures. The main domestic use for PTFE is on non-stick utensils such as frying pans. Industrially, the polymer is used for gaskets, pump parts, and laboratory equipment.

Polyurethanes

'Urethane' is the name given to the functional group formed from the reaction of an isocyanate group with a hydroxy-group

$$-N=C=O \quad + \quad HO^- \longrightarrow \quad NHCOO-$$

Polyurethanes are thermoset polymers formed from di-isocyanates and polyfunc tional compounds containing numerous hydroxy- groups. Typically the starting materials are themselves polymeric, but comprise relatively few monomer units in the molecule. Low relative molar mass species of this kind are known generally as *olzgows.* Typical oligomers for the preparation of polyurethanes are polyesters and polyethers. These are usually prepared to include a small proportion of monomeric trifunctiona1 hydroxy compounds, such as trimethylolpropane, in the backbone, so that they contain pendant hydroxyls which act as the sites of crosslinking. A number of different di-isocyanates are used commercially. The major use of polyurethanes is as rigid or flexible foams. The rigid polyurethanes have a variety of uses, including insulating material for filling cavity walls of houses. Flexible polyurethanes have been widely used in soft furnishing. They suffer from the considerable disadvantage that they burn easily with a very smokey and toxic flame, which has led to severe problems in accidental domestic fires. The use of these materials for this purpose is now declining.

Naturally Occurring Polymers

There are a number of naturally occurring polymers which find technical application, including cellulose and its derivatives, starch, and rubber. In addition, a number of important biological materials, most notably the proteins, are made up of macromolecules.

Cellulose

This is a very widely available polymer, since it is the main component of the cell walls of all plants. It is a carbohydrate of molecular formula $(C_6H_{10}O_5)_n$ where *n* runs to thousands. The cellulose 'monomer' is D-glucose, and the cellulose molecules are built up from this substance, effectively by condensation and removal of the elements of water. D-Glucose itself is highly soluble in water, but cellulose is not. This is essentially a kinetic phenomenon; the hydroxy-groups in cellulose would, in principle, readily form hydrogen bonds with water molecules, and hence the cellulose macromolecule would be carried off into aqueous solution. But these hydroxy-groups interact with neighbouring cellulose molecules, making it impossible for water molecules to penetrate, or solvate, the individual molecules. Cellulose will, however, dissolve in aqueous ammoniacal cupric hydroxide, $Cu(NH3)_4(OH)_2$

Cellulose is a linear polymer. Despite this, it is not thermoplastic, essentially because of its extensive intermolecular hydrogen bonding which never allows the molecules to move sufficiently for the polymer to melt. Cellulose may be solubilised by treatment with sodium hydroxide and carbon disulfide. It can be regenerated by acidification of the solution. This is the basis of the production of regenerated cellulose fibre, so-called 'viscose rayon', which is a major textile fibre. The technique is also used for the production of continuous cellulose-derived film, so-called 'cellophane' (from 'cellulose' and 'diaphane', the latter being French for transparent). Cellulose is also commercially modified by acetylation to produce a material suitable for X-ray and cine film. Commercially cellulose ethers are also prepared, such as methylcellulose. This material is water-soluble and gives a highly viscous solution at very low concentrations. Hence it is widely used as a thickener in latex paints and adhesives, in cosmetics and for coating pharmaceutical tablets.

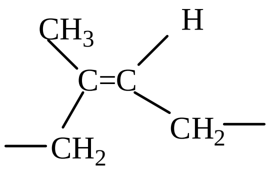
Starch

Starch is a widely distributed material which occurs in roots, seeds, and fruits of plants, For commercial use, corn is the principal source, though wheat and potatoes are also used. Starch is extracted by grinding with water, filtering, centrifuging, and drying, a process which yields starch in a granular form.

Starch consists of two components, amylose and amylopectin. The ratio of these varies with the source of the starch, with amylopectin usually predominating and representing some 70-85% of the total mass of the starch. Amylopectin is the polymeric component of starch and consists mainly of glucose units joined at the 1,4 positions. Relative molar mass tends to be very high, e.g. between 7 and 70 million. **A** variety of modified starches are used commercially which are produced by derivatisation to give materials such as ethanoates (acetates), phosphates, and hydroxyalkyl ethers. Modified and unmodified starches are used in approximately equal tonnages, mainly in paper-making, paper coatings, paper adhesives, textile sizes, and food thickeners.

Natural Rubber

Rubber is obtained from the juice of various tropical trees, mainly the tree ***Heuea brasiliensis.*** The juice is a latex consisting of a dispersion of polymer phase at a concentration of about ***35%*** by mass, together with traces of proteins, sterols, fats, and salts. The rubber is obtained either by coagulation of the latex with acid, either ethanoic or methanoic, or by evaporation in air or over a flame. The material that results from this process is a crumbly, cheese-like substance, sometimes called raw rubber or caoutchouc. In order to develop the mechanical properties that are considered characteristic of rubber, i.e. so-called rubberlike elasticity, this raw rubber needs further processing, and in particular lightly crosslinking. This is achieved in the process known as **vulcanization.** The polymer in natural rubber consists almost entirely of ***cis***poly(isoprene).



The molecules are linear, with relative molar mass typically lying between 300,000 and 500,000. The macromolecular nature of rubber was established mainly by Staudinger in **1922,** when he hydrogenated the material and obtained a product that retained its colloidal character, rather than yielding fragments of low relative molar mass.

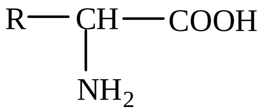
Vulcanisation is the term used for the process in which the rubber molecules are lightly crosslinked in order to reduce plasticity and develop elasticity. It was originally applied to the use of sulfur for this purpose, but is now used for any similar process of crosslinking. Sulfur, though, remains the substance most widely used for this purpose.

Sulfur reacts very slowly with rubber, and so is compounded with rubber in the presence of accelerators and activators. Typical accelerators are thiazoles and a typical activator is a mixture of zinc oxide and a fatty acid. The chemistry of the vulcanization reactions is complicated, but generates a three-dimensional network in which rubber molecules are connected by short chains of sulfur atoms, with an average of about five atoms in each chain.

A much more heavily crosslinked material can be obtained by increasing the amount of sulfur in the mixture, so that it represents about a third of the mass of the product. Heating such a mixture of raw rubber and sulfur at 150^{o}C until reaction is complete gives a hard, thermoset material that is not at all elastic. This material is called ebonite and is used to make car battery cases.

Proteins

The proteins are a group of macromolecular substances of great importance in biochemistry. Their very name provides testimony to this - it was coined by Mulder in 1838 from the Greek word ‘proteios’, meaning ‘of first importance’. They appear in all cells, both animal and plant, and are involved in all cell functions. Proteins are linear polyamides formed from a-amino acids. An aamino acid is one in which carboxylic acid and the amino group reside on the same carbon atom.



$$R-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$$

In nature, there are 20 amino acids available for incorporation into the protein chain. They are arranged in a specific and characteristic sequence along the molecule. This sequence is generally referred to as the ‘primary structure’ of the protein. Also part of the primary structure is the relative molar mass of the macromolecule. As a result of the particular amino acid sequence, the protein molecule adopts a characteristic arrangement, such as symmetrical coils or orderly foldings. This is known as the ‘secondary structure’. Such individual coils or folded structures bring about a longer range stable arrangement called the ‘tertiary structure’. Lastly, several protein molecules may join together to form a complex, this final grouping being known as the ‘quaternary structure’.

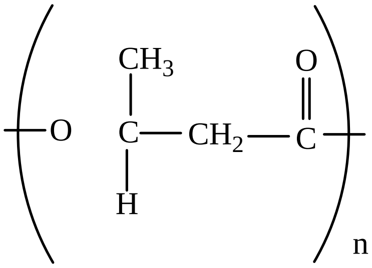
Proteins themselves consist of large molecules with several hundred amino acids in the primary structure. Smaller units, known as polypeptides, may be formed during physiological processes. There is no clear distinction between a protein and a polypeptide; about 200 amino acid units in the primary structure is usually taken to be the minimum for a substance to be considered a protein.

The diversity in primary, secondary, tertiary, and quaternary structures of proteins means that few generalisations can be made concerning their chemical properties. Some fulfill structural roles, such as the collagens (found in bone) and keratin (found in claws and beaks), and are insoluble in all solvents. Others, such as albumins or globulins of plasma, are very soluble in water. Still others, which form part of membranes of cells, are partly hydrophilic (‘water-loving’, hence water-soluble) and partly lipophilic (‘lipid-loving’, hence fat-soluble).

Because proteins are not composed of identical repeating units, but of different amino acids, they do not fall within the formal definition of polymers. They are nevertheless macromolecular and techniques developed for the study of true polymers have been applied to them with success.

Poly (3-hydroxybutyrate)

Poly(3-hydroxybutyrate) is a bacterial polyester that behaves as an acceptable thermoplastic, yet can be produced from renewable agricultural feedstocks and is biodegradable.



$$\left(-O-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}- \right)_n$$

poly(3-hydroxybutyrate)

It is typically produced not in the pure state, but formed alongside minor amounts of poly(3-hydroxyvalerate). The ratio of these two polymers in a given sample is determined by the ratio of glucose and propionic acid in the medium in which the bacteria live and carry out their metabolic processes. The carbon atom which carries the methyl group is chiral, but biosynthesis is stereoselective, and gives rise to a natural polymer with the *R* configuration. The polymer is a partially crystalline thermoplastic which melts at about 80^{o}C.

Poly(3-hydroxybutyrate) has attracted interest as an environmentally degradable thermoplastic that can be used in packaging, agriculture and medicine. It undergoes enzymic degradation quite readily, becoming less crystalline and rapidly decreasing in molar mass. The rate of degradation depends on a number of factors, such as moisture level, nutrient supply, temperature, and pH.