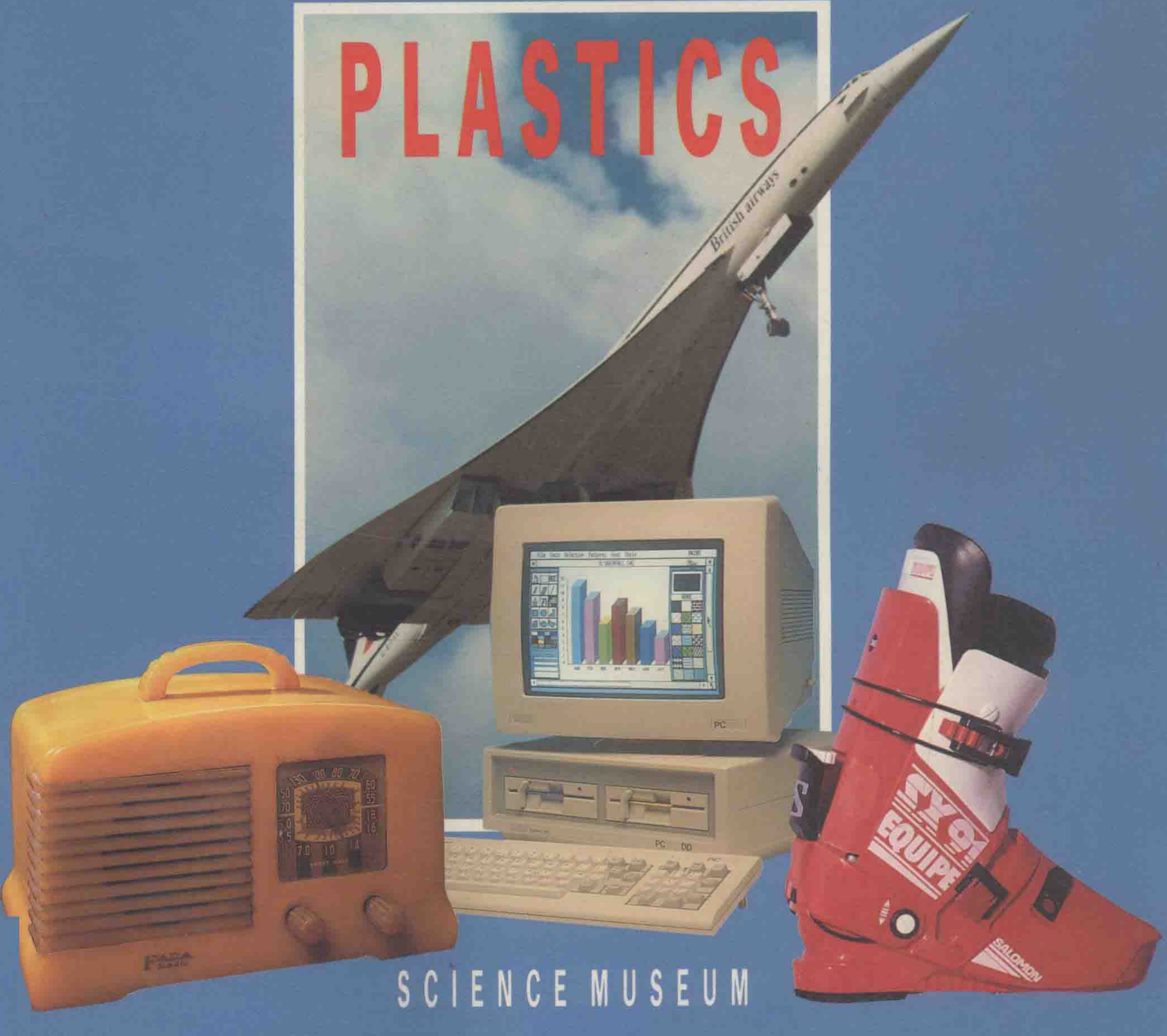
PLASTICS



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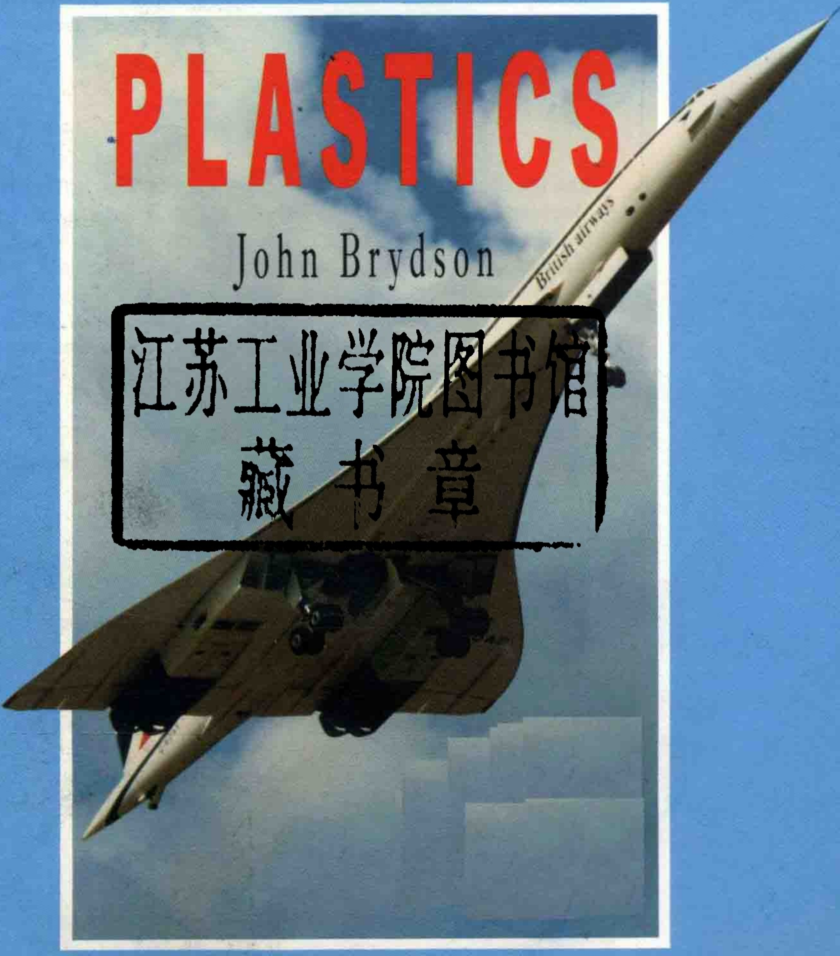

PLASTICS

John Brydson

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Contents

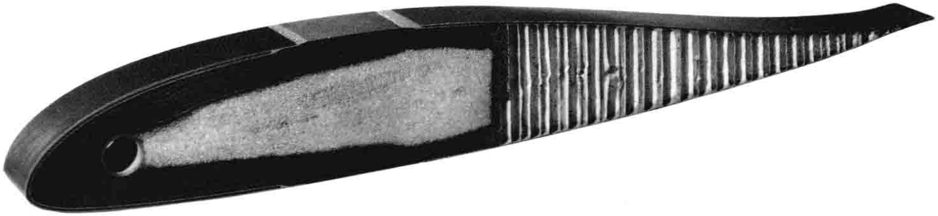
1 Plastics Today

It is difficult to think of the world as we know it today without plastics. If we had been born two hundred years ago, no matter how wealthy, our knowledge of the world would have been very limited. Communications were very slow for there were no telephone, radio or television. There were no photographs, and knowledge of what people and places looked like was limited either to personal contact or to paintings and drawings. There were no gramophone records or magnetic tapes, and outside the big cities there were few opportunities to hear a wide range of music. All of these objects which we take for granted today have one thing in common – they are now made in whole or in part from plastics.

Without doubt plastics have also made travel much easier. Cars produced early this century had few plastics parts, but today would be prohibitively costly to buy and to run and also lack the performance and comfort of modern vehicles. In a modern car we find a variety of plastics: under the bonnet in the form of carburettor floats, cooling fans, distributor caps; in the interior for upholstery, fascia panels, door armrests and roof linings; and externally for the radiator grilles and front- and rear-end bumpers. As I type these sentences on a word-processor, itself largely made of plastics, I am looking at a photograph of a small car. The caption underneath the photograph tells me that out of the 2,730 parts from which the car is assembled, 771 are of plastics. The use of plastics is of course not confined to land-based means of transport. Glass-reinforced plastics are used not only for pleasure craft but also for warships such as minesweepers. Owing to their high strength–weight ratio, reinforced plastics are also widely used in aircraft, for example, in tailplanes and main rotor blades for helicopters. A modern airliner may have about two tonnes of carbon fibre-epoxy resin composites alone.

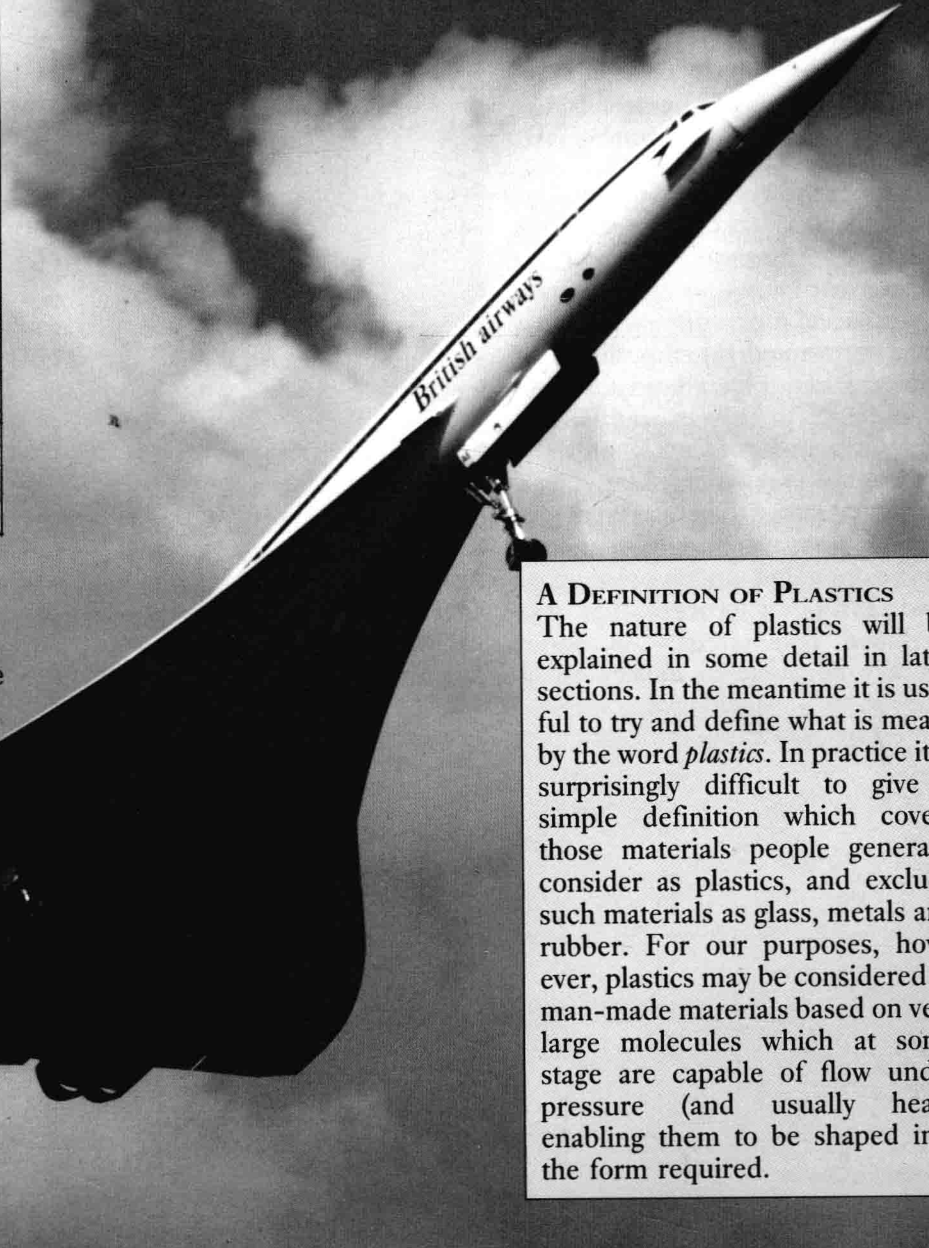
Sterilised, tough plastics are used in medicine for tubing, drip feeds, blood bags and components for kidney dialysis machines. Plastics are used in replacement surgery, taking the place of heart valves, hip joints and, of course, false teeth.

There are indeed few facets of modern life where plastics are not used. In many cases they have made possible products that could not have existed without them. In other cases the ability to make things cheaper has enabled many more of us to enjoy a standard of life undreamt of by our forebears. They are such a significant part of life today that it is important that we should try to understand what they are and what they can do. It is hoped that this booklet will help in this task.



Because of their high strength–weight ratio fibre-reinforced plastics are widely used in the aircraft industry. For example, up to 1800 kg of carbon fibre-epoxy resin composites are used in a modern airliner whilst some modern aircraft consist of about 20 per cent, by weight, of such materials. Helicopter rotor blades, such as the sectioned blade illustrated on the left, are made from composite materials based on glass and carbon fibres with thermosetting plastics. Such blades have better fatigue resistance than metal blades.

A ski boot.



The nose cone of Concorde is made from fibre-reinforced plastics.

A Definition of Plastics

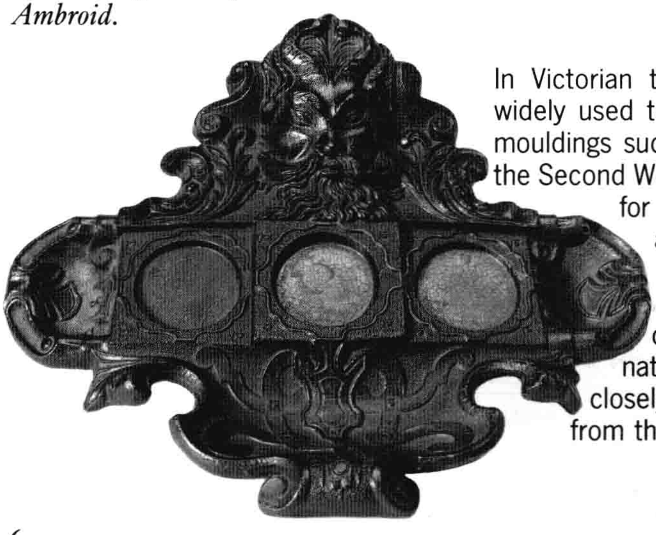
The nature of plastics will be explained in some detail in later sections. In the meantime it is useful to try and define what is meant by the word *plastics*. In practice it is surprisingly difficult to give a simple definition which covers those materials people generally consider as plastics, and exclude such materials as glass, metals and rubber. For our purposes, however, plastics may be considered as man-made materials based on very large molecules which at some stage are capable of flow under pressure (and usually heat), enabling them to be shaped into the form required.

2 The First Plastics

Articles made from Parkesine between 1860 and 1868. Developed by Alexander Parkes in North London it was the forerunner of Celluloid and Xylonite.

Plastics in the ancient world

While plastics are regarded as a product of the twentieth century their origins may be found in antiquity. The fossilised resin amber has been a prized gemstone for thousands of years: specimens have been found at Stonehenge, in Mycenaean tombs and in ancient European lake dwellings. Amber may be considered as a plastics material since fragments resulting from machining operations may be moulded under pressure at about 170°C, a process that was developed commercially in about 1880 to give a product known as *Ambroid*.



In Victorian times gutta percha was widely used to produce highly ornate mouldings such as this inkstand. Until the Second World War it was also used for undersea cable insulation and for bottles used to store hydrofluoric acid until replaced in each case by polyethylene. Like natural rubber, to which it is closely related, it is obtained from the latex of trees.

A number of other naturally occurring materials were also known to the ancient world, including shellac. This was used widely in the first half of this century to make gramophone records, whilst another natural material, *bitumen*, has only recently been replaced with a synthetic plastic in the casings of low-cost battery boxes. Gutta percha, closely related to natural rubber, was widely used in Victorian times.

Ebonite, celluloid and related materials

These naturally occurring materials were originally used without any deliberate modification although some change in the chemical structure may have occurred in some cases on exposure to light. Ebonite was the first plastics material which resulted from deliberate modification. This rigid, black, ebony-like material is obtained by heating natural rubber with about half its weight of sulphur. Although the first patent was taken out by Nelson Goodyear in 1851, both Charles Goodyear in the United States and Thomas Hancock in England had produced similar materials during the previous decade.

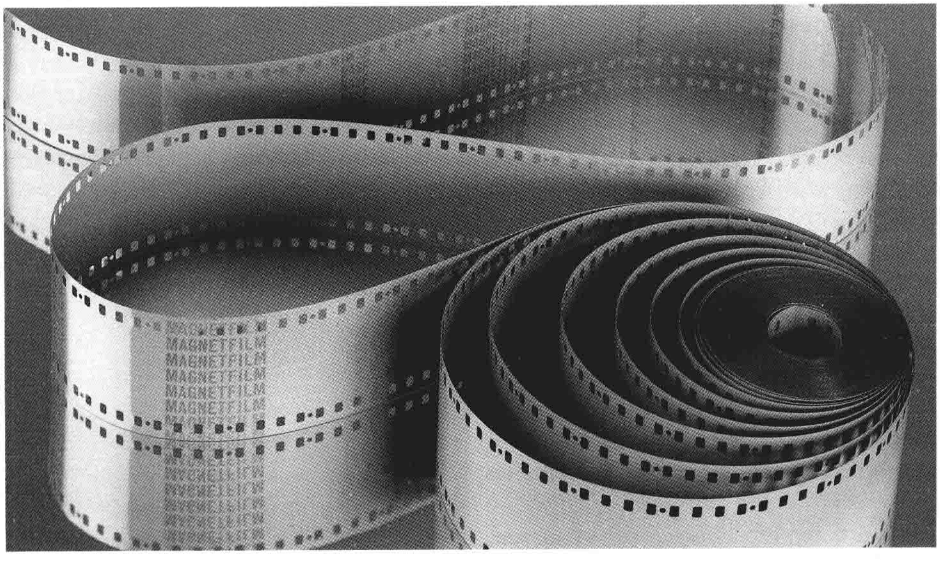
In 1862 another British inventor, Alexander Parkes, was awarded a bronze medal for his exhibit Parkesine which was displayed at the Great International Exhibition held in London. This material was made by reacting the natural material, cellulose, with nitric acid and blending the resultant cellulose nitrate with certain solvents and with vegetable oil. Parkesine was used to make articles such as combs, umbrella handles, knife-handles and chessmen. Some examples of these early plastics products still exist today. Unfortunately for Parkes, his Parkesine company went into liquidation in 1868, but his work paved the way for the development of the closely related material, Celluloid, by the Hyatt brothers in the United States, and of Xylonite by Daniel Spill in England. In essence these materials were blends of cellulose nitrate and camphor, the latter imparting the characteristic odour of these materials (which in recent years have been most commonly used to make table tennis balls).

One of the most serious disadvantages of Celluloid and related materials is its high flammability. There is an interesting story recalled by John Wesley Hyatt concerning one of their products, billiard balls: ‘In order to secure strength and beauty only colouring pigments were added, in the least quantity. In effect this meant that the billiard balls were coated with a film of almost uncontaminated guncotton. Consequently a lighted cigar applied would at once result in a serious flame and occasionally the violent contact of the balls would produce a mild explosion like a percussion guncap. We had a letter from a billiard saloon proprietor in Colorado, mentioning this fact and saying that he did not care so much about it but that instantly every man in the room pulled a gun.’

The first synthetic plastics

It was not until the first decade of the twentieth century that the first truly synthetic plastics material was successfully developed. Building on earlier work carried out in Russia, Germany and England, Leo Hendrik Baekeland, (a Belgian-American) reacted phenol and formaldehyde (methanal) under carefully controlled conditions to obtain a hard heat-resisting material which he marketed as Bakelite. Within a few years this trade name had become a household

Both still and cine photography today are based on the use of plastics films as the carrier for the photographic emulsion or magnetic material as in this slide. Cellulose nitrate products such as Celluloid are no longer used for this purpose because of their flammability.



Phenol-formaldehyde plastics (phenolics) were rapidly accepted by the new radio industry. The photograph shows a phenolic radio housing of the 1930s. The unusually light colour (for a phenolic) is the result of a special manufacturing technique.

A coffin (with a cut-away lid) made from phenolic plastics in the 1930s.

word and the material became widely used in the infant electronic and car industries. Very similar materials were used for laminated plastics and in plywood manufacture. Even coffins were moulded from this material.

One disadvantage of Bakelite-type materials (known generically as phenolic resins) is that they are normally dark in colour. No such colour restrictions occurred, when materials were made by reacting urea and formaldehyde. These urea-formaldehyde plastics were introduced commercially in 1928. They were available in a wide range of colours, superior to the phenolic materials in many of their electrical insulation properties, but inferior in heat and water resistance. Today they are widely used for electrical plugs and sockets, toilet seats and screw tops for jars, as well as wood adhesives, which are particularly useful in the manufacture of chipboard.

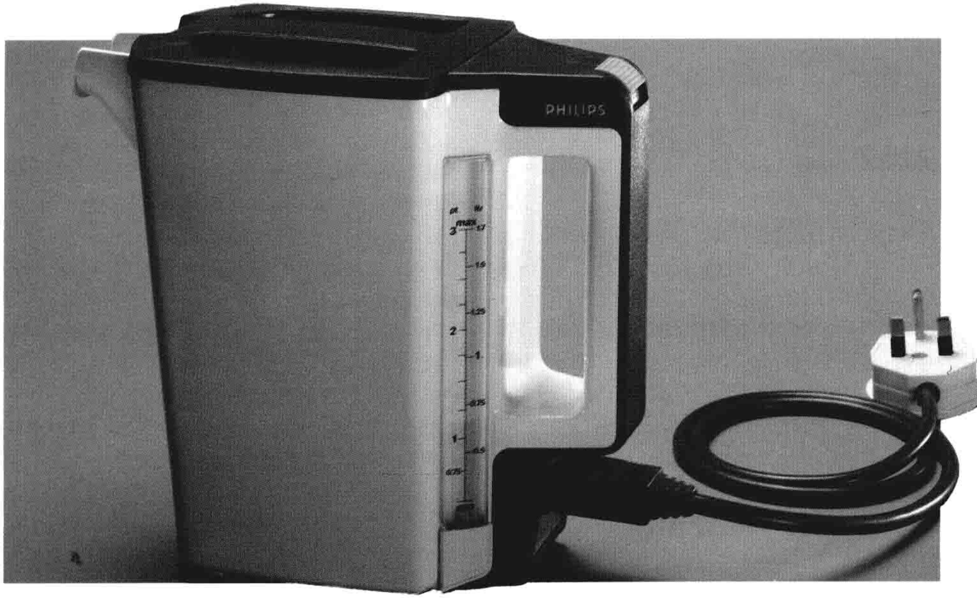
The discovery of polyethylene

The 1930s saw the emergence of many new plastics materials including polyethylene (known originally as polythene), polyvinyl chloride (PVC), polystyrene and polymethyl methacrylate. Their development came about not simply as a result of much careful laboratory experimentation but also because research chemists were careful to record and, later, to consider and exploit unexpected results. The discovery of polyethylene is a good example.

During the early 1930s workers at ICI were carrying out experiments at very high pressure (3,000 atmospheres) trying to bring about reactions which did not occur at normal atmospheric pressure. The results seemed to be generally disappointing. However, the two chemists carrying out the research programme, E.W.

Fawcett and R.O. Gibson, noted that in some attempted reactions which involved the gas ethylene, tiny white particles were to be seen floating about in the unreacted liquid. In a later experiment, on 27 March 1933, they attempted to react ethylene and benzene at 170°C and 1,400 atmospheres pressure. After the experiment, seemingly without reaction, they noticed a white waxy solid coating the walls of the reaction vessel.

Subsequent analysis showed this to be polyethylene. This was an unexpected result.* The ICI chemists repeated the experiment using ethylene alone and once again a small amount of polyethylene was produced. Subsequent attempts to make larger quantities by reacting at higher pressure led to an explosion which destroyed parts of the laboratory. When, in December 1935, an experiment led to the production of eight grammes of polyethylene it was felt that considerable progress had been made. It was subsequently found that this experiment had only been 'successful' because there had been a small leak in the apparatus which had resulted in exactly the right concentration of oxygen in the apparatus necessary to catalyse the reaction. Slowly the reaction became better understood and on 1 September 1939 – the day Germany invaded Poland and the Second World War broke out – ICI started operation of a pilot plant for the production of polyethylene.



Electric kettle jugs have enjoyed rapid acceptance because of their space saving shape, their capacity to boil only small amounts of water if required, and their design flexibility.

Nylon and other thermoplastics

Whereas the development of polyethylene originated from the observation and following up of an unexpected experimental result, the development of nylon fibres and plastics was more deliberate. In 1928, W.H. Carothers joined the Du Pont company which wished to synthesise a material capable of replacing silk as a fabric in many applications. In his studies Carothers produced many new materials such as polyesters and polycarbonates but it was not until 1935 when he reacted hexamethylene diamine with adipic acid to produce a material now known as nylon 66 that he achieved his target. Commercial production of nylon 66 commenced in October 1938, after Du Pont had spent $27,000,000 (then an enormous sum of money) on its development.

In addition to the successful introduction of a material initially important as a filament and fibre and later as a plastics material, the work of Carothers had wider importance. This was because his work provided the theoretical basis of that branch of chemistry concerned with the synthesis of plastics, rubbers, fibres and related materials, known as polymer chemistry.

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*It was unexpected because up until that time it was believed that there were good theoretical reasons why polyethylene could not be made from ethylene.

Plastics as replacements for traditional materials

Before the Second World War most of the newer plastics were little more than curiosities. Polystyrene for example was a very expensive electrical insulator which cost about fifty dollars a pound, then about five times the weekly income of a skilled worker in Britain. War-time needs, in particular the problems arising from the unavailability of natural rubber to most of the combatants, led to considerable developments and by the 1950s polyethylene, PVC and polystyrene had become available as low-cost plastics, whilst polymethyl methacrylate, (probably best known as the sheet material Perspex), had become a familiar material.

Such a ready availability of materials at low cost soon led to serious problems. A lack of understanding of the properties of plastics, poor design and the use of inferior materials led to many bad applications, and plastics acquired a poor reputation. To counter this, the major suppliers of plastics materials initiated a large education exercise, set up huge technical service laboratories and published extensive technical literature. This resulted in a better appreciation of the capabilities and the limitations of the materials available and in consequence generally much improved product design.

Over the past 35 years there have been few new major tonnage plastics,[†] polypropylene being a well-known exception, but the overall market has grown enormously. In part this is because the cost of making plastics materials and shaping them into finished products has increased more slowly than for many more traditional materials in spite of the huge increase in the cost of oil (the main raw material for plastics) in the 1970s. Consequently it has frequently become cheaper to use plastics than to use metals, ceramics and other traditional materials.

The use of plastics as a replacement for metals may be economic for a number of reasons. Firstly, the cost of the raw material to make the product may be less. Secondly, most plastics materials are highly suitable for mass production techniques at temperatures much lower than those used to melt metals, and generate little scrap. Thirdly, it is often possible to make highly complex mouldings in one operation where previously the part had to be made by shaping and then assembling several pieces of metal.

Plastics for special purposes

In addition to the major tonnage materials, more specialised plastics have found important outlets. Due to their toughness, excellent abrasion resistance (superior to many metals) and resistance to hydrocarbon oils, the *nylons* have become well-established for gear wheels, bearings and many light engineering applications. One disadvantage of the nylons is their tendency to absorb water. In this respect the *polyacetals*, also first developed by Du Pont, are somewhat better and although their abrasion resistance is not quite so good they find many similar uses. Polytetrafluoroethylene (PTFE) has become well known in non-stick ovenware as well as being used in many hundreds of industrial applications.

Over the past 20 years several new plastics materials have appeared which show characteristics such as toughness and heat resistance. When properly used, the polycarbonates can be exceptionally tough. This was demonstrated when they were used as face shields by astronauts on their lunar space walks.

The many other uses of these materials include camera bodies, power tool bodies, food processor bowls and audio compact discs. In the past, they have also been used for safety helmets, but many grades are liable to crack in the presence of certain liquids, including some paints. Other plastics which are used in engineering applications include polysulphones, polyimides, polyphenylene oxides and polyphenylene sulphides.

As long ago as 1942 Whinfield and Dixon, when working in England for the Calico Printers Association, dis-

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[†] Any definition of a major tonnage material must be arbitrary but for this booklet we will take it to mean plastics which are produced in quantities in excess of 1,000,000 tonnes per year.

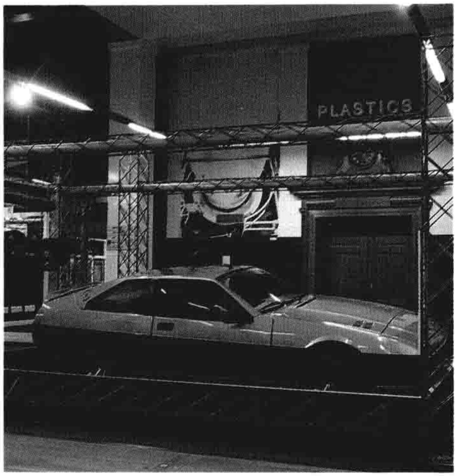
covered polyethylene terephthalate. This became very well known within a few years as the fibres Terylene and Dacron. It also became available in the form of film such as Mylar and Melinex. In more recent times, methods have been devised to make bottles and other containers out of this material. The bottles have been

Polycarbonates are widely used for compact discs.

Bottles of all shapes and sizes are now made from plastics. Plastics bottles are particularly valuable in the bathroom since unlike glass they are not liable to break on dropping onto hard surfaces. Polyethylene terephthalate bottles (made from the same polymer as Terylene and Dacron fibres) are widely used in the marketing of carbonated drinks and beers. They have adequately low gas permeability and are much lighter in weight than those made of glass, when empty.

particularly successful for marketing beers, colas and other carbonated drinks due to their low gas permeability and lightness compared with glass.

Polyethylene terephthalate is an example of a polyester of which there are many types. Some types show many of the characteristics of liquid crystals when molten. Known as liquid crystal polymers, the solidified materials have exceptional strength, toughness and stiffness, and have only appeared recently on the market.



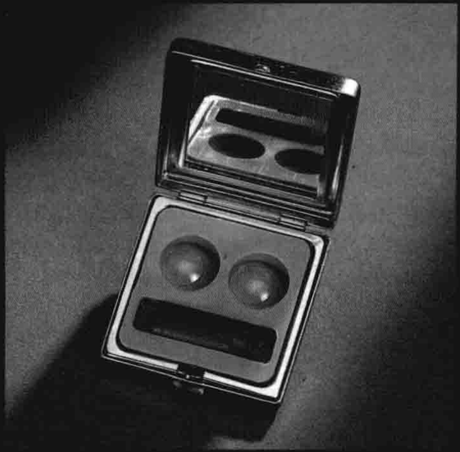
Polyester-glass fibre composites are widely used in sports car bodies. They are strong, light in weight and may be made with less expensive tooling than is used for mass-produced metal car bodies.

Rather similar are certain polyamides, chemically related to the nylons. One of these was used to produce an extremely strong fibre, marketed by Du Pont as Kevlar, which is now widely used as a tyre cord fabric.

While most plastics have very good resistance to water some plastics swell or even dissolve in it. One particular type of plastics material, chemically similar to Perspex which swells extensively in water, is used to make soft contact lenses.

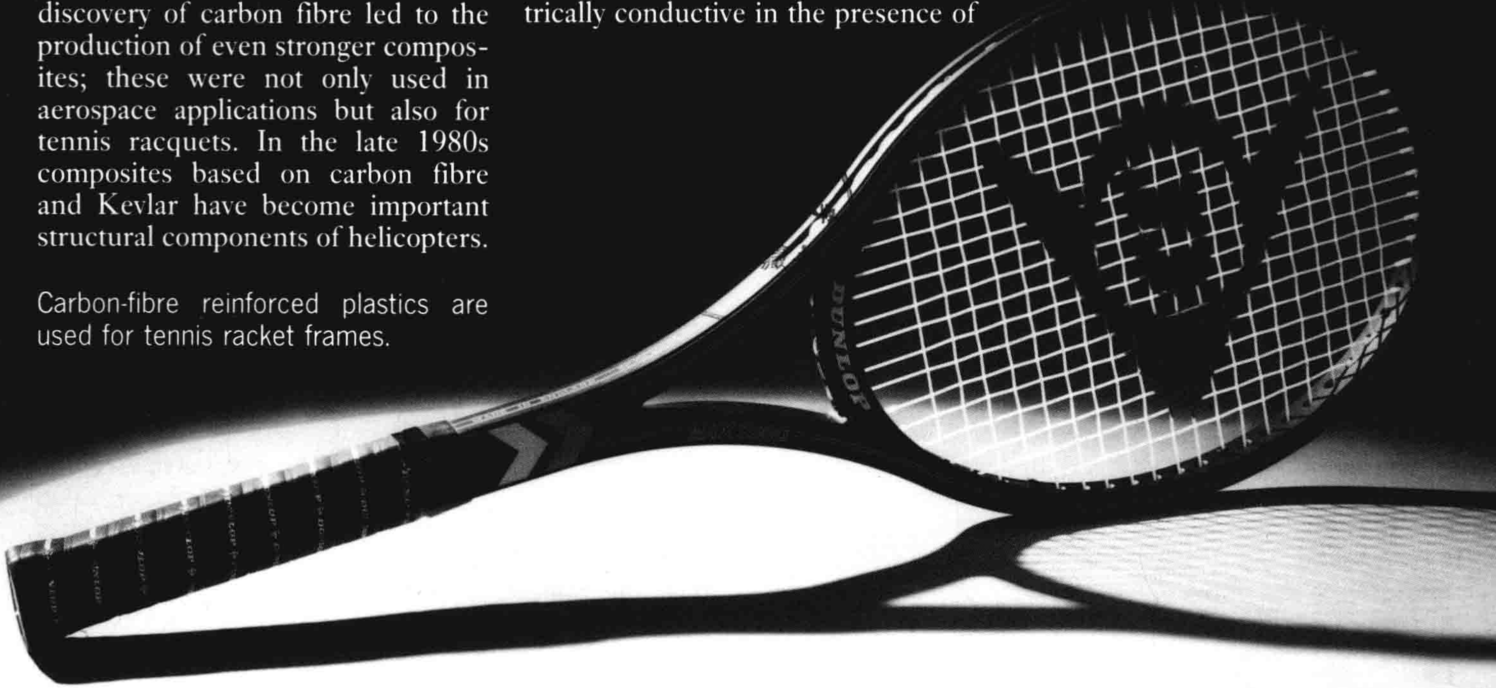
One disadvantage of plastics is that although they are lighter in weight, volume for volume, they are usually much less stiff and less strong than metals. It has long been recognised that the combination of the plastics material with a fibrous product could be beneficial. The resultant products have become known as composites. Paper-based laminates such as Formica have become well-known in the home. In the 1950s, glass-fibre rein-

Lorry cabins may also be made from polyester-glass fibre composites.



This pair of acrylic micro-corneal contact lenses dates from the 1960s.

forced plastics began to be used for sports car bodies, boat hulls and for a variety of industrial applications. The discovery of carbon fibre led to the production of even stronger composites; these were not only used in aerospace applications but also for tennis racquets. In the late 1980s composites based on carbon fibre and Kevlar have become important structural components of helicopters.



Carbon-fibre reinforced plastics are used for tennis racket frames.

Recently, highly specialised plastics such as polyether ether ketones and polyetherimides have been used with carbon fibres to make composites which possess exceptional strength and heat resistance.

Many newer plastics have unusual properties which still need to be exploited fully. Polyvinylidene fluoride exhibits piezoelectricity – that is, when a slab of the material is subjected to pressure, charges of positive and negative electricity are produced on opposite faces. This property has been of interest to telephone manufacturers and utilised in the making of earphones for personal stereo equipment. Polyvinyl carbazole may be made photoconductive, that is, it becomes electrically conductive in the presence of light. This has been made use of in electrostatic dry copying machines. A polydiacetylene derivative has magnetic characteristics and it is possible to make the needle of a compass from this material without any metal being present. Whilst many plastics have been recognised for many years to be excellent electrical insulators there are high hopes that some of the newer materials will become important as conductors. Each year the range of plastics properties continues to grow. This will lead to an ever widening number of applications which, if used properly, should help us to improve the quality of our lives.

3 Plastics and Polymers

Atoms and molecules

You will have noticed that many plastics materials have names which begin with the prefix *poly* such as polyethylene, polypropylene, polystyrene and polyvinyl chloride. This is because plastics belong to a class of chemicals known as *polymers*. Before we can understand what this means, we first need an explanation of 'atoms' and 'molecules' and related terms.

If you were to take a glassful of water and drink half the contents, what is left in the glass would still be water. This division could be repeated many times although in practice you would soon be dealing with minute quantities of water, and it would be very difficult to drink exactly half each time. If however we assume that you have the perfect ability to drink just half each time, the point would eventually be reached where if you tried to subdivide the material it would no longer be water. At this stage we would have one *molecule* of water. If this molecule were divided up we would find that it consisted of three *atoms*, two of hydrogen and one of oxygen. About 90 types of atoms occur in nature and some others have been created in the laboratory. These different types are known as *elements*. Well-known elements include carbon, hydrogen, oxygen, nitrogen, sulphur, iron, copper, gold, sodium and phosphorus. The lightest is hydrogen, an atom of which weighs about 0.000 000 000 000 000 000 000 002 grammes (about a million million million millionth of a gramme). Some idea of just how small this is is obtained if we realise that the weight of a hydrogen atom compared to that of a large spoonful of sugar is in about the same ratio as the weight of that spoonful of sugar to the weight of the earth. When we wish to talk about the weight of the atoms of the other elements it is convenient to express them in terms relative to the hydrogen atom and we call this the *relative atomic mass*. For carbon this is about 12, for nitrogen 14 and oxygen 16. Since a molecule of water consists of two hydrogen and one oxygen atom its mass will be about 18 times that of hydrogen and we say that the *relative molecular mass* or *molecular weight* of water is 18.

Big molecules and polymers

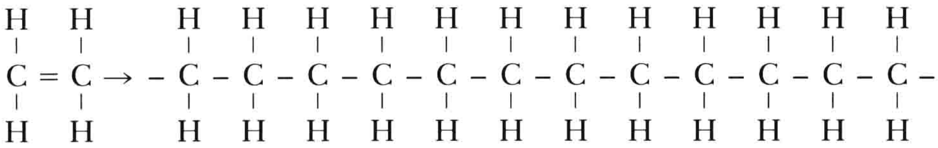
Most of the chemicals encountered in school science syllabuses have relative molecular masses of less than 300. For example common salt (sodium chloride) is about 58, carbon dioxide 44, ethyl alcohol 46 and benzene 78. In contrast the molecules from which plastics are made are very much bigger. For example the average relative molecular mass of commercial polystyrene is about 200,000 whilst that of an acrylic sheet material such as Perspex is of the order of 1,000,000. Whilst the molecule is still small (it will weigh only about a million million millionth of a gramme), it is a giant molecule compared with that of water and this will greatly influence its properties.

Giant molecules occur in nature. Examples include cellulose (present in all plants, for example, cotton is almost pure cellulose), starch, proteins (such as those of wool, silk and leather) and natural rubber. It is worth noting that such natural materials include fibres, rubbers and adhesives. The synthetic fibres, rubbers and adhesives and also surface coatings are also, like plastics, giant molecules of the type known as polymers.

The prefix *poly* means 'many' whilst a *mer* is a repeating unit so that 'polymer' means many repeating units. In practice synthetic polymers are made by joining together small molecules known as *monomers*, the process being known as *polymerisation*. Thus polystyrene is prepared by the polymerisation of styrene, and polyvinyl chloride by the polymerisation of vinyl chloride. The polymerisation process and the types of products that may be obtained from them are discussed in further detail in the rest of this section.

Double bond polymerisation: the polymerisation of ethylene

Ethylene (ethene) molecules consist of two carbon atoms linked together by a double bond and four hydrogen atoms, two of which are attached to each carbon atom. This satisfies the requirement that there should be four links, or valencies, to each carbon and one to each hydrogen. Appropriate treatment of the ethylene molecules causes one of the two links between the carbon atoms to break; this enables the resultant 'free arms' to link to similar molecules. If we represent the carbon atom by a letter C and a hydrogen atom by H the process may be schematically outlined as follows:



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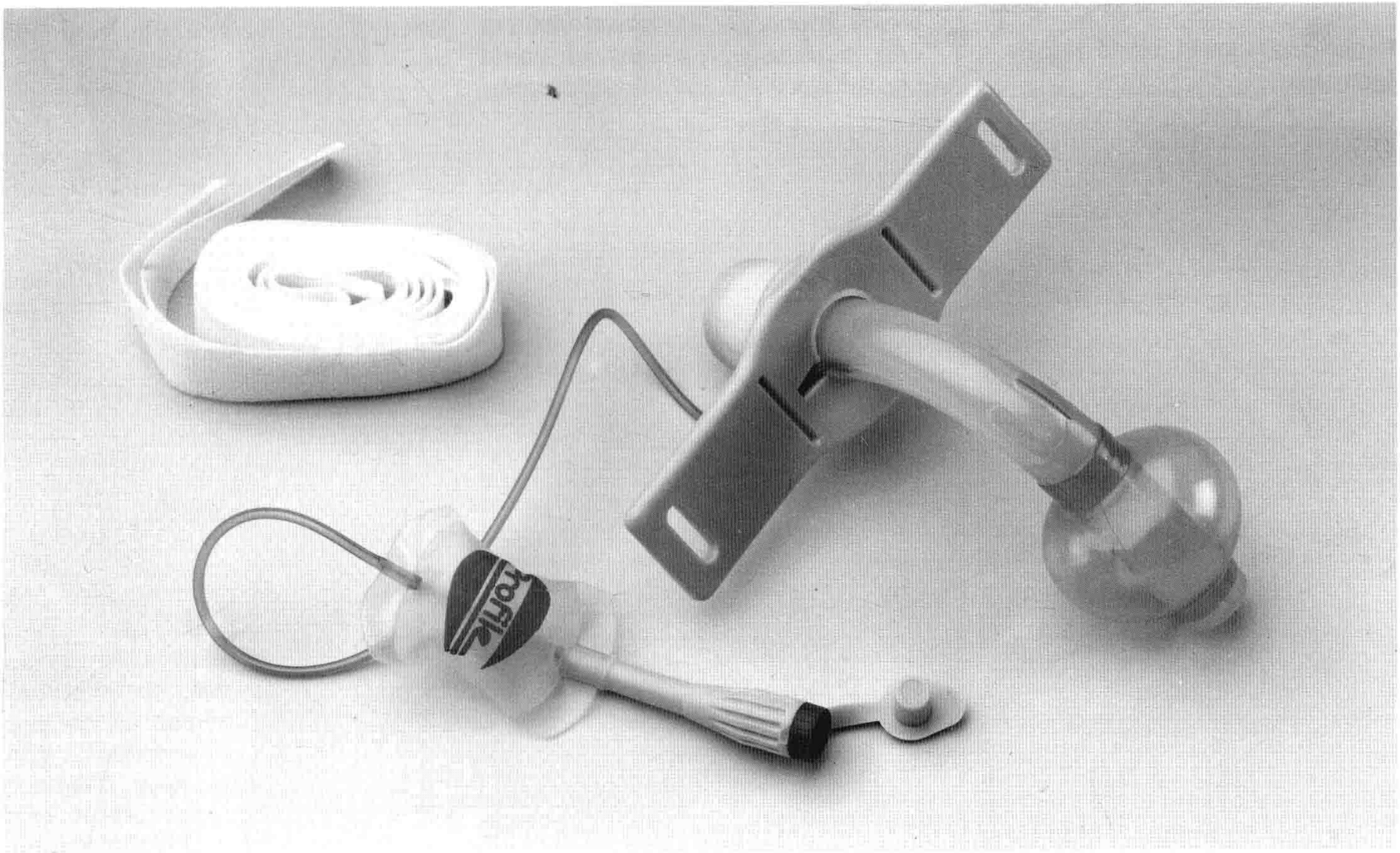
Ethylene **Polyethylene**



Plastics tubing is widely used in surgery and post-operative care. Shown here are tracheotomy tubes.

In this way many hundreds or even thousands of ethylene molecules may be joined together in a single chain. This is the process known as polymerisation. The starting material, ethylene, is known as a monomer and the product, polyethylene, is known as a polymer. Since the polymer is obtained by adding the monomers together, this particular process may be referred to as *additional polymerisation* or since it involved the opening of a double bond, as *double bond polymerisation*.

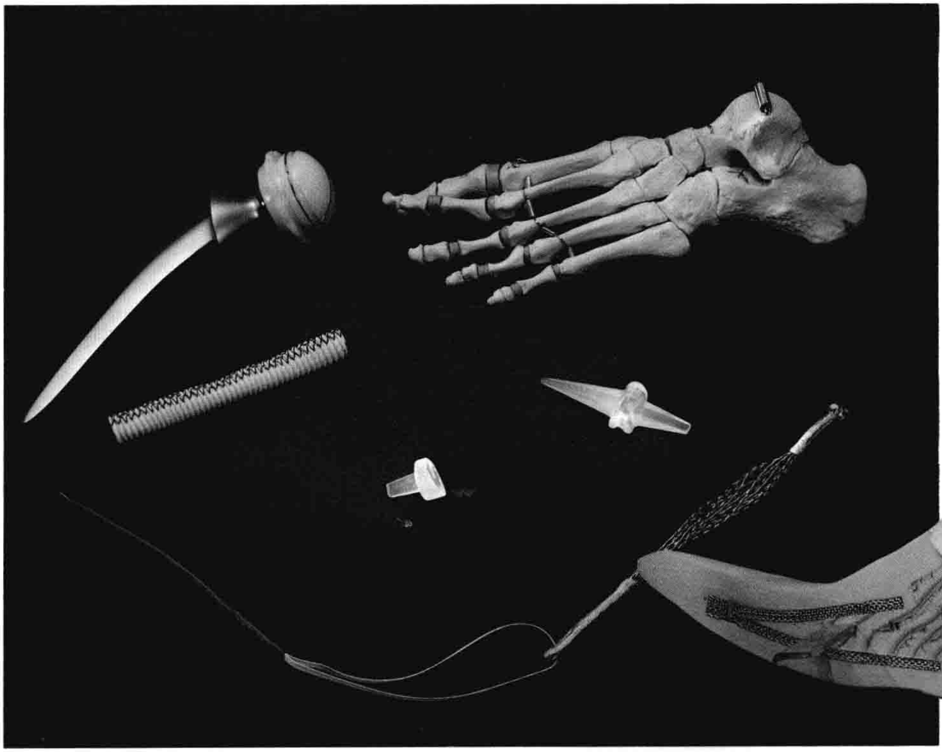
Copolymerisation

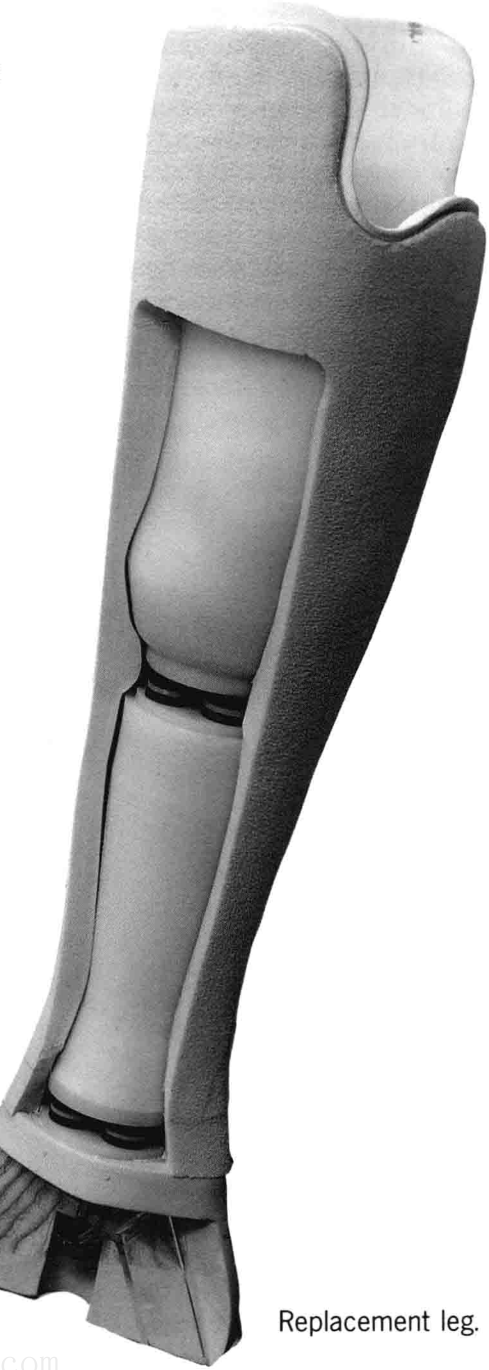
In many instances it is possible to put two monomers into the reacting vessel and obtain a molecule where both monomers are incorporated into the same chain. Thus if we represented two monomers as A and B the chain might have the following structure:

~AABABBBABAAABABBBAA-
BAABABBBABAABBBAABB-
BABABBBB~

Such a structure would be called a *random copolymer* (strictly a random binary copolymer as two monomers only were used) whereas we could use the word *homopolymer* to describe

Replacement joints, blood vessels and ligaments.





Replacement leg.