

POLYMER SCIENCE and TECHNOLOGY

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Chapter 1

Introduction

I. HISTORICAL DEVELOPMENT

Before we go into details of the chemistry of polymers it is appropriate to briefly outline a few landmarks in the historical development of what we now know as polymers. Polymers have been with us from the beginning of time; they form the very basis (building blocks) of life. Animals, plants — all classes of living organisms — are composed of polymers. However, it was not until the middle of the 20th century that we began to understand the true nature of polymers. This understanding came with the development of plastics, which are true man-made materials that are the ultimate tribute to man's creativity and ingenuity. As we shall see in subsequent discussions, the use of polymeric materials has permeated every facet of our lives. It is hard to visualize today's world with all its luxury and comfort without man-made polymeric materials.

The plastics industry is recognized as having its beginnings in 1868 with the synthesis of cellulose nitrate. It all started with the shortage of ivory from which billiard balls were made. The manufacturer of these balls, seeking another production method, sponsored a competition. John Wesley Hyatt (in the U.S.) mixed pyroxin made from cotton (a natural polymer) and nitric acid with camphor. The result was cellulose nitrate, which he called celluloid. It is on record, however, that Alexander Parkes, seeking a better insulating material for the electrical industry, had in fact discovered that camphor was an efficient plasticizer for cellulose nitrate in 1862. Hyatt, whose independent discovery of celluloid came later, was the first to take out patents for this discovery.

Cellulose nitrate is derived from cellulose, a natural polymer. The first truly man-made plastic came 41 years later (in 1909) when Dr. Leo Hendrick Baekeland developed phenol-formaldehyde plastics (phenolics), the source of such diverse materials as electric iron and cookware handles, grinding wheels, and electrical plugs. Other polymers — cellulose acetate (toothbrushes, combs, cutlery handles, eyeglass frames); urea-formaldehyde (buttons, electrical accessories); poly(vinyl chloride) (flooring, upholstery, wire and cable insulation, shower curtains); and nylon (toothbrush bristles, stockings, surgical sutures) — followed in the 1920s.

Table 1.1 gives a list of some plastics, their year of introduction, and some of their applications. It is obvious that the pace of development of plastics, which was painfully slow up to the 1920s, picked up considerable momentum in the 1930s and the 1940s. The first generation of man-made polymers was the result of empirical activities; the main focus was on chemical composition with virtually no attention paid to structure. However, during the first half of the 20th century, extensive organic and physical developments led to the first understanding of the structural concept of polymers — long chains or a network of covalently bonded molecules. In this regard the classic work of the German chemist Hermann Staudinger on polyoxymethylene and rubber and of the American chemists W. T. Carothers on nylon stand out clearly. Staudinger first proposed the theory that polymers were composed of giant molecules, and he coined the word *macromolecule* to describe them. Carothers discovered nylon, and his fundamental research (through which nylon was actually discovered) contributed considerably to the elucidation of the nature of polymers. His classification of polymers as *condensation* or *addition* polymers persists today.

Following a better understanding of the nature of polymers, there was a phenomenal growth in the numbers of polymeric products that achieved commercial success in the period between 1925 and 1950. In the 1930s, acrylic resins (signs and glazing); polystyrene (toys, packaging and housewares industries); and melamine resins (dishware, kitchen countertops, paints) were introduced.

The search for materials to aid in the defense effort during World War II resulted in a profound impetus for research into new plastics. Polyethylene, now one of the most important plastics in the world, was developed because of the wartime need for better-quality insulating materials for such applications as radar cable. Thermosetting polyester resins (now used for boatbuilding) were developed for military use. The terpolymer acrylonitrile-butadiene-styrene (ABS), (telephone handsets, luggage,

Table 1.1 Introduction of Plastics Materials

Date	Material	Typical Use
1868	Cellulose nitrate	Eyeglass frames
1909	Phenol-formaldehyde	Telephone handsets, knobs, handles
1919	Casein	Knitting needles
1926	Alkyds	Electrical insulators
1927	Cellulose acetate	Toothbrushes, packaging
1927	Poly(vinyl chloride)	Raincoats, flooring
1929	Urea-formaldehyde	Lighting fixtures, electrical switches
1935	Ethyl cellulose	Flashlight cases
1936	Polyacrylonitrile	Brush backs, displays
1936	Poly(vinyl acetate)	Flashbulb lining, adhesives
1938	Cellulose acetate butyrate	Irrigation pipe
1938	Polystyrene	Kitchenwares, toys
1938	Nylon (polyamide)	Gears, fibers, films
1938	Poly(vinyl acetal)	Safety glass interlayer
1939	Poly(vinylidene chloride)	Auto seat covers, films, paper, coatings
1939	Melamine-formaldehyde	Tableware
1942	Polyester (cross-linkable)	Boat hulls
1942	Polyethylene (low density)	Squeezable bottles
1943	Fluoropolymers	Industrial gaskets, slip coatings
1943	Silicone	Rubber goods
1945	Cellulose propionate	Automatic pens and pencils
1947	Epoxies	Tools and jigs
1948	Acrylonitrile-butadiene-styrene copolymer	Luggage, radio and television cabinets
1949	Allylic	Electrical connectors
1954	Polyurethane	Foam cushions
1956	Acetal resin	Automotive parts
1957	Polypropylene	Safety helmets, carpet fiber
1957	Polycarbonate	Appliance parts
1959	Chlorinated polyether	Valves and fittings
1962	Phenoxy resin	Adhesives, coatings
1962	Polyallomer	Typewriter cases
1964	Ionomer resins	Skin packages, moldings
1964	Polyphenylene oxide	Battery cases, high temperature moldings
1964	Polyimide	Bearings, high temperature films and wire coatings
1964	Ethylene-vinyl acetate	Heavy gauge flexible sheeting
1965	Polybutene	Films
1965	Polysulfone	Electrical/electronic parts
1970	Thermoplastic polyester	Electrical/electronic parts
1971	Hydroxy acrylates	Contact lenses
1973	Polybutylene	Piping
1974	Aromatic polyamides	High-strength tire cord
1975	Nitrile barrier resins	Containers

safety helmets, etc.) owes its origins to research work emanating from the wartime crash program on large-scale production of synthetic rubber.

The years following World War II (1950s) witnessed great strides in the growth of established plastics and the development of new ones. The Nobel-prize-winning development of stereo-specific catalysts by Professors Karl Ziegler of Germany and Giulio Natta of Italy led to the ability of polymer chemists to "order" the molecular structure of polymers. As a consequence, a measure of control over polymer properties now exists; polymers can be tailor-made for specific purposes.

The 1950s also saw the development of two families of plastics — acetal and polycarbonates. Together with nylon, phenoxy, polyimide, poly(phenylene oxide), and polysulfone they belong to the group of plastics known as the engineering thermoplastics. They have outstanding impact strength and thermal and dimensional stability — properties that place them in direct competition with more conventional materials like metals.

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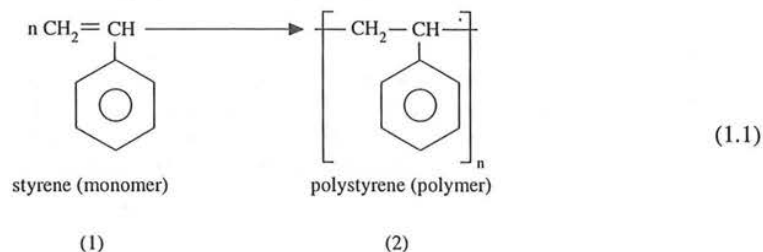
The 1960s and 1970s witnessed the introduction of new plastics: thermoplastic polyesters (exterior automotive parts, bottles); high-barrier nitrile resins; and the so-called high-temperature plastics, including such materials as polyphenylene sulfide, polyether sulfone, etc. The high-temperature plastics were initially developed to meet the demands of the aerospace and aircraft industries. Today, however, they have moved into commercial areas that require their ability to operate continuously at high temperatures.

In recent years, as a result of better understanding of polymer structure–property relationships, introduction of new polymerization techniques, and availability of new and low-cost monomers, the concept of a truly tailor-made polymer has become a reality. Today, it is possible to create polymers from different elements with almost any quality desired in an end product. Some polymers are similar to existing conventional materials but with greater economic values, some represent significant improvements over existing materials, and some can only be described as unique materials with characteristics unlike any previously known to man. Polymer materials can be produced in the form of solid plastics, fibers, elastomers, or foams. They may be hard or soft or may be films, coatings, or adhesives. They can be made porous or nonporous or can melt with heat or set with heat. The possibilities are almost endless and their applications fascinating. For example, *ablation* is the word customarily used by the astronomers and astrophysicists to describe the erosion and disintegration of meteors entering the atmosphere. In this sense, long-range missiles and space vehicles reentering the atmosphere may be considered man-made meteors. Although plastic materials are generally thermally unstable, ablation of some organic polymers occurs at extremely high temperatures. Consequently, selected plastics are used to shield reentry vehicles from the severe heat generated by air friction and to protect rocket motor parts from hot exhaust gases, based on the concept known as ablation plastics. Also, there is a “plastic armor” that can stop a bullet, even shell fragments. (These are known to be compulsory attire for top government and company officials in politically troubled countries.) In addition, there are flexible plastics films that are used to wrap your favorite bread, while others are sufficiently rigid and rugged to serve as supporting members in a building.

In the years ahead, polymers will continue to grow. The growth, from all indications, will be not only from the development of new polymers, but also from the chemical and physical modification of existing ones. Besides, improved fabrication techniques will result in low-cost products. Today the challenges of recycling posed by environmental problems have led to further developments involving alloying and blending of plastics to produce a diversity of usable materials from what have hitherto been considered wastes.

II. BASIC CONCEPTS AND DEFINITIONS

The word *polymer* is derived from classical Greek *poly* meaning “many” and *meres* meaning “parts.” Thus a polymer is a large molecule (macromolecule) built up by the repetition of small chemical units. To illustrate this, Equation 1.1 shows the formation of the polymer polystyrene.



The styrene molecule (1) contains a double bond. Chemists have devised methods of opening this double bond so that literally thousands of styrene molecules become linked together. The resulting structure, enclosed in square brackets, is the polymer polystyrene (2). Styrene itself is referred to as a *monomer*, which is defined as any molecule that can be converted to a polymer by combining with other molecules of the same or different type. The unit in square brackets is called the *repeating unit*. Notice that the structure of the repeating unit is not exactly the same as that of the monomer even though both possess identical atoms occupying similar relative positions. The conversion of the monomer to the polymer involves a rearrangement of electrons. The residue from the monomer employed in the preparation of a

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