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Polymer Science




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Learning Objective

- A brief history of the polymers and their evolution

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HISTORICAL BACKGROUND

Early evidence of the use of polymers in the form of rubber has been found in the excavations of the ancient Mayan civilization in Central America where children played with balls made from the rubber obtained from the rubber tree.

The synthetic polymers initially used were just modified forms of naturally occurring ones, such as cellulose. The polymers of styrene were first reported in 1839 and poly(ethylene glycol) and poly(ethylene succinate) were synthesized in 1860. Despite these advances, chemists believed that these large molecular weight substances were just aggregates of smaller molecules and had no idea regarding the structure of these materials.

In 1839, Charles Goodyear discovered vulcanization by combining natural rubber with sulfur and heating it to 270°F to form a vulcanized rubber, which is also a polymeric substance. The first synthetic polymer commercially used was *Bakelite*, a phenol-formaldehyde resin, developed in 1907 by Leo Baekeland. Other polymers such as polyester paints and polybutadiene rubber were also introduced around the same time. Yet, polymers were still considered to be aggregated small molecules held together by a certain unknown force.

Hermann Staudinger, a German chemist, presented to the world the modern polymer theory. He demonstrated that polymers are long-chain molecules and not just aggregates of smaller molecules. A polymeric structure for rubber was formulated, which was based on repeating isoprene units. In the 1930s, the American chemist Wallace Hume Carothers experimented on Staudinger's theory and subsequently developed neoprene rubber and polyamide (nylon) fibers. Hermann Staudinger was awarded the Nobel Prize in 1953 for his contributions to chemistry.

The term polymer was coined by Jons Jacob Berzelius in 1883 and is derived from the Greek words *polus*, meaning many and *meros*, meaning parts. A polymer is a high molecular weight chemical

compound containing a large number of repeating units called monomers. The monomers are linked together by covalent chemical bonds by the process called polymerization.

Since the twentieth century, polymers have permeated our lives in every way. Polymers find a variety of applications in our routine life from milk bottles, adhesives and toys to artificial hip joints and reabsorbable sutures. Since decades polymers have been used as tablet excipients, moving progressively into the parenteral division as blood circulation time enhancers. Presently, they are capable of sophisticated functions such as drug targeting.

CLASSIFICATION OF POLYMERS

Learning Objectives

- Different parameters used in polymer classification
 - Different classes of polymers with examples
1. Based on the nature of monomers
 - (a) Homopolymers
 - (b) Copolymers
 2. Based on the arrangement of monomers
 - (a) Random copolymers
 - (b) Graft copolymers
 - (c) Block copolymers
 3. Based on the structure of the polymers
 - (a) Linear
 - (b) Branched
 - (c) Cross-linked
 4. Based on the thermal response and polymer property
 - (a) Thermoplastics
 - (b) Thermosets
 - (c) Elastomers
 5. Based on the source
 - (a) Natural polymers
 - (b) Semisynthetic polymers
 - (c) Synthetic polymers
 6. Based on the form and use
 - (a) Plastics
 - (b) Elastomers
 - (c) Fibers
 - (d) Liquid resins

Homopolymers and Copolymers

Polymers are large molecules formed by repeated linking of monomers. A polymer is a macromolecule formed by sequential addition of smaller molecules called monomers to each other. For example, polyethylene is formed by repeated linkage of ethylene molecules (monomers).

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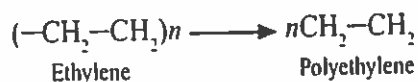
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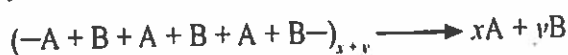
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Polyethylene is an example of a *homopolymer* since the fundamental unit (monomer) is only of one kind, that is, ethylene.

In certain other polymers, the fundamental units may be two or more similar molecules. Such polymers are called copolymers.



Examples of copolymers include ethylene vinyl acetate, poly(ethylene-co-propylene), poly(styrene-co-butadiene) and poly(vinylidene chloride-co-vinyl chloride).

Random Copolymers, Graft Copolymers and Block Copolymers

Based on the manner in which the monomers are arranged, copolymers can be classified as *random copolymers*, *graft copolymers* and *block copolymers*. In random copolymers, there is a random arrangement of monomers. In graft copolymers, the main polymer chain is made up of one monomer and the branches are made up of a different monomer. Block copolymers contain blocks of monomers of the same type.

The three types are illustrated in the Fig. 2.1.

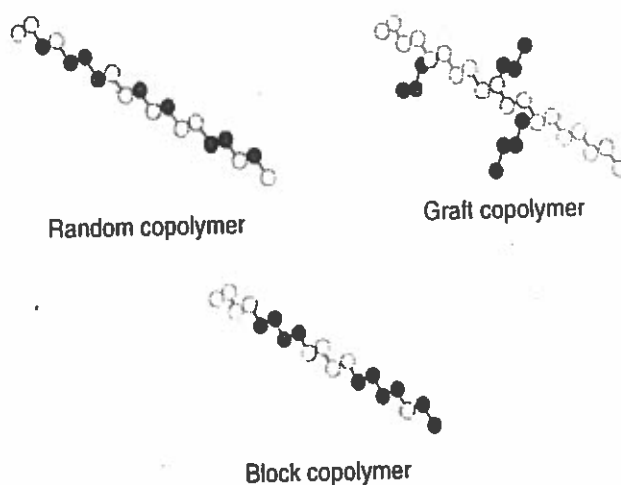


Figure 2.1 Diagrammatic Illustration of a Random, Graft and Block Polymer

Another example of a common copolymer is nylon, which is an alternating copolymer with two monomers, a 6 carbon diacid and a 6 carbon diamine.

Linear, Branched and Cross-linked Polymers

Based on their structure, polymers are classified as linear, branched and cross-linked. Polymers made of only long sequential strands are called *linear polymers*. They are characterized by high densities, high tensile strengths and high melting points. Examples of linear polymers are polyethylene, nylon and polyester.

A *branched polymer* molecule is composed of a main chain with one or more substituent side chains or branches. Depending on the nature of the branches they can be of different types as illustrated in

the Fig. 2.2. They are characterized by low densities, lower tensile strengths and low melting points. Examples of branched polymers are amylopectin and glycogen.

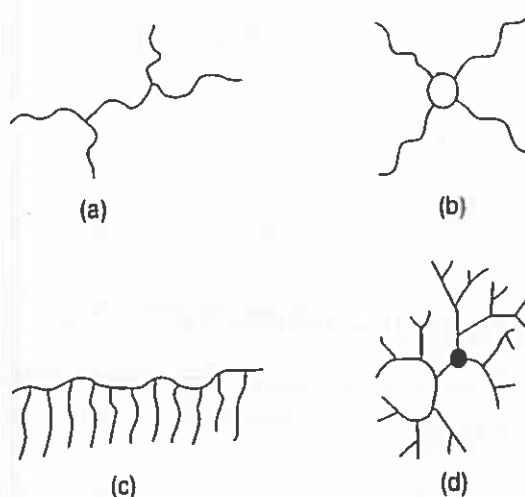


Figure 2.2 Pictorial Representation of Branched Polymers: (a) Branched Polymer, (b) Star Polymer, (c) Comb Polymer, (d) Dendritic Polymer

In *cross-linked* polymers monomeric units are linked together to constitute a three-dimensional network. They are hard, rigid and brittle. Examples of cross-linked polymers are Bakelite and melamine formaldehyde resin.

Thermoplastics, Thermosets and Elastomers

Based on the thermal response and polymer property, the polymers can be classified as thermoplastics, thermosets and elastomers.

Thermoplastic polymers can be softened by heating and they return to their original state when cooled. This softening and solidifying can be carried out repeatedly. This behavior is possible because their molecules are held together by relatively weak intermolecular forces. Fabrication with these polymers requires simultaneous application of heat and pressure. Most linear and branched polymers with flexible chains are thermoplastic in nature. The major thermoplastics are produced by chain polymerization. They are very soft and ductile. Commercially available thermoplastics include polyvinyl chloride (PVC), polystyrene and poly(methyl methacrylate) (PMMA).

A *thermoset* or thermosetting plastic melts when heated for the first time but sets irreversibly. It does not soften on subsequent heating and hence cannot be remolded or reshaped. During heating of thermosets, strong covalent bonds are formed between the adjacent molecular chains. These bonds can be severed only by heating to excessive temperature but is accompanied by polymer degradation. Thermosets are polymers with a high degree of cross-linking, usually forming a three-dimensional networked structure. The result is a rigid structure with restricted movement of the polymer chains. Examples include cross-linked and network polymers such as vulcanized rubbers, epoxies and polyester resins.

Elastomers are rubbery polymers that can be stretched easily, without the necessity of heating. They can be stretched to several times their length. On releasing the applied stress, they rapidly return to their original dimensions. Elastomers have low density of cross-linking. The polymer chains have limited freedom to move, but they are prevented from permanently moving in relation to each other.

Natural, Semisynthetic and Synthetic Polymers

According to the source, polymers are classified as natural, semisynthetic and synthetic polymers.

Natural polymers are those obtained in nature. Examples include cellulose, starch, proteins and natural rubber. Polysaccharides such as cellulose, starch and proteins, which control various vital life processes, are also called as biopolymers.

Semisynthetic polymers are chemically modified natural polymers. For example, cellulose, a natural polymer, can be chemically modified into semisynthetic polymers such as cellulose acetate and cellophane. Vulcanized rubber is another example of a semisynthetic polymer.

Synthetic polymers are man-made polymers, artificially prepared in the laboratory. Examples are polythene, PVC, nylon, polyethylene terephthalate and Bakelite.

Plastics, Elastomers, Fibers and Liquid Resins

Based on the form and use, polymers are classified as plastics, elastomers, fibers and liquid resins.

Plastic is a polymer that is shaped into hard and tough utility material by the application of heat and pressure. Examples are PVC, polystyrene and PMMA [Poly(methyl methacrylate)].

When a polymer is vulcanized into a rubbery product exhibiting good strength and elongation, it is called an *elastomer*. Examples are rubber, synthetic rubber and silicon rubber.

When a polymer is drawn into a long filament-like material whose length extends to at least 100 times its diameter, it is known as a *fiber*. Examples are nylon and terylene.

When a polymer is used in the liquid form as an adhesive, potting compound or sealant, it is called a *liquid resin*. Examples are polysulfide sealants and epoxy adhesives.

Biodegradable and Nonbiodegradable Polymers

Based on the ability of the polymers to undergo degradation in natural environment and in biological systems, they can be classified as degradable and nondegradable polymers.

Biodegradable polymers slowly disappear from the site of administration. Examples are poly(lactic acid) (PLA), poly(glycolic acid) (PGA), polyanhydrides and poly(ortho esters). Nonbiodegradable polymers are inert in the environment of use. These are eliminated or excreted intact from the site of administration and serve essentially as rate-limiting barriers to the release of drug from the device. Examples are poly(ethylene vinyl acetate), poly(dimethylsiloxane) (PDS), polyurethane, ethyl cellulose and PVC.

POLYMER SYNTHESIS

Learning Objectives

- Addition polymerization and its types
- Condensation polymerization and its types
- Differences between addition and condensation polymerizations

Polymers can be synthesized by addition reactions and condensations and accordingly are called as addition polymers and condensation polymers.

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Addition Polymerization

Addition polymerization is a method wherein the monomers are added one after another to the active site on the growing chain. An *addition polymer* is formed when many monomers bond together via rearrangement of bonds without the loss of any atom or molecule. Addition polymers have $\{-C-C-\}$ linkage along the main chain and no other atom appears in the main chain.

Addition polymerization can be of the following types:

1. Free radical polymerization
2. Ionic polymerization
 - (a) Cationic polymerization
 - (b) Anionic polymerization

1. **Free Radical Polymerization:** This is the most common type of addition polymerization. Free radicals are mostly generated by the division of a molecule into fragments along a single bond. In free radical polymerization, the radical attacks one monomer and the electron migrates to another part of the molecule. The newly formed radical attacks another monomer and the process is repeated. Thus, the active center moves down the chain as polymerization occurs. There are three reactions that take place in addition polymerization, namely initiation, propagation and termination.
2. **Ionic Polymerization:** Active center is ionic charged instead of free radical. Only monomers that can sufficiently stabilize positive or negative charge will undergo ionic polymerization. Hence, ionic polymerization is more monomer specific. Most monomers cannot be polymerized by ionic polymerization. Ionic polymerization also occurs in three stages, namely initiation, propagation and termination.

Examples of polymers synthesized by addition polymerization are polyethylene, polypropylene, PVC and polystyrene.

Condensation Polymerization

In condensation polymerization or step growth polymerization, polymeric materials are synthesized from small molecules called monomers with more than two reactive sites on the monomer. Small molecules such as water or methanol are released as by-products. Condensation polymers are formed from intermolecular reactions between bifunctional or polyfunctional monomer molecules with the elimination of a small by-product molecule.

The condensation reactions are characterized by the following features:

1. Repeat unit often not same as monomer structure
2. Release of small molecules such as H_2O and HCl
3. Gradual growth of molecular weight
4. Relatively slow reaction

Examples of polymers synthesized by condensation method are polyamides, polyesters and polyethers.

CROSS-LINKING OF POLYMERS

Learning Objective

- Advantage of cross-linking of polymers

Improvement of the thermal, mechanical and physicochemical properties of polymers is a challenge in both synthesis of new polymers and in modification of the existing polymers.

Researchers prefer modification and improvement of known polymers rather than the synthesis of polymers from new monomers. Polymer materials in the lower molecular weight range can be cross-linked to obtain satisfactory mechanical properties. Polymers can be cross-linked in different ways:

1. Covalent cross-linking
2. Ionic bonds
3. Physical cross-linking (through Van der Waals, hydrogen bonds or other interactions)

Cross-linking of polymers can be achieved using radiations (ultraviolet rays, x-rays or γ -rays) or by chemical crosslinking.

POLYMER DEGRADATION — STEPS AND TYPES

Learning Objectives

- Different types of polymer degradation
- Biodegradable and nonbiodegradable polymers
- Mechanisms of biodegradation
- Surface erosion and bulk erosion
- Factors influencing biodegradation of polymers

Polymer degradation can be defined as a process that deteriorates polymer properties or their outward appearance, for example, discoloration, stiffening and changes in tensile strength and shape. Several factors such as heat, mechanical energy, radiation or ozone can cause this degradation. Such changes can be undesirable when they occur during the shelf life of the product. Moreover, the changes shall be desirable in case of biodegradation or deliberately lowering the molecular weight of a polymer. Studying the degradation process can be useful in understanding the structure of a polymer or recycling the polymer waste.

Types of Polymer Degradation

1. Photoinduced degradation or photolysis
2. Thermal degradation or thermolysis
3. Chemical degradation
 - (a) Solvolysis and hydrolysis
 - (b) Ozonolysis
 - (c) Oxidation
 - (d) Galvanic action
 - (e) Chlorine-induced cracking
4. Biological degradation or biodegradation

When polymers are used in drug delivery systems, the main concern is their ability to degrade in the biological system. Based on their biological degradation, polymers can be biodegradable or nonbiodegradable. The outstanding property of a biodegradable polymer is its degradation and erosion behavior. The cleavage of polymer chains results in the degradation of polymers, which is also accompanied by the reduction of molecular weight. The degradation can occur either enzymatically or by hydrolysis. On the other hand, erosion is the sum of all process leading to the loss of the polymer matrix.

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