B.Sc. Semester-VI Organic Chemistry Paper-XIV



2. Synthetic Polymers

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1. Polymer Chemistry

The first **plastic**—a polymer capable of being molded—was celluloid. Invented in 1856 by Alexander Parke, it was a mixture of nitrocellulose and camphor. Celluloid was used in the manufacture of billiard balls and piano keys, replacing scarce ivory. The invention of celluloid provided a reprieve for many elephants, but caused some moments of consternation in billiard parlors because nitrocellulose is flammable and explosive. Celluloid was used for motion picture film until it was replaced by cellulose acetate, a less dangerous polymer.

The first synthetic fiber was rayon. In 1865, the French silk industry was threatened by an epidemic that killed many silkworms, highlighting the need for an artificial silk substitute. Louis Chardonnet accidentally discovered the starting material for a synthetic fiber when, while wiping up some spilled nitrocellulose from a table, he noticed long silklike strands adhering to both the cloth and the table. "Chardonnet silk" was introduced at the Paris Exposition in 1891. It was called *rayon* because it was so shiny that it appeared to give off rays of light.

The first synthetic rubber was synthesized by German chemists in 1917. Their efforts were in response to a severe shortage of raw materials as a result of blockading during World War I.

Hermann Staudinger was the first to recognize that the various polymers being produced were not disorderly conglomerates of monomers, but were made up of chains of monomers joined together. Today, the synthesis of polymers has grown from a process carried out with little chemical understanding to a sophisticated science in which molecules are engineered with predetermined specifications in order to produce new materials tailored to fit human needs. Recent examples of the many new polymers that are constantly being designed include Lycra[®], a fabric with elastic properties, and Dyneema[®], the strongest fabric commercially available.

Polymer chemistry is part of the larger discipline of **materials science**, which involves the creation of new materials to replace metals, glass, ceramics, fabrics, wood, cardboard, and paper. Polymer chemistry has evolved into a multibillion-dollar industry. Currently, there are approximately 30,000 patented polymers in the United States. More than 2.5×10^{13} kilograms of synthetic polymers are produced in the United States each year, and we can expect many more new materials to be developed by scientists in the years to come.

2. General Classes of Synthetic Polymers

Synthetic polymers can be divided into two major classes, depending on their method of preparation. Chain-growth polymers, also known as addition polymers, are made by chain reactions—the addition of monomers to the end of a growing chain. The end of the chain is reactive because it is a radical, a cation, or an anion. Polystyrene—used for disposable food containers, insulation, and toothbrush handles, among other things—is an example of a chain-growth polymer. Polystyrene is pumped full of air to produce the material known as Styrofoam.

Step-growth polymers, also called condensation polymers, are made by combining two molecules while, in most cases, removing a small molecule, generally water or an alcohol. The reacting molecules have reactive functional groups at each end. Unlike chain-growth polymerization, which requires the individual molecules to add to the end of a growing chain, step-growth polymerization allows any two reactive molecules to combine. Dacron[®] is an example of a step-growth polymer.

$$CH_{3}O-C-OCH_{3} + HOCH_{2}CH_{2}OH \xrightarrow{\Delta} - OCH_{2}CH_{2}O-C-OCH_{2}CH_{2}O-C \xrightarrow{Dacron^{\circ}} - CH_{3}OH$$

$$Dacron^{\circ}$$
a step-growth polymer

Dacron® is the most common of the group of polymers known as **polyesters**—polymers with many ester groups. Polyesters are used for clothing and are responsible for the wrinkle-resistant behavior of many fabrics. Polyester is also used to make the plastic film called Mylar®, needed in the manufacture of magnetic recording tape. This film is tear-resistant and, when processed, has a tensile strength nearly as great as that of steel. Aluminized Mylar® was used to make the Echo satellite that was put into orbit around the Earth as a giant reflector. The polymer used to make soft drink bottles is also a polyester.

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Table 1: Some Important Polymers and Their Uses

Monomer	Repeating unit	Polymer name	Uses
$CH_2 = CH_2$	$-CH_2-CH_2-$	polyethylene	film, toys, bottles, plastic bags
CH ₂ =CH	−СН ₂ −СН− Cl	poly(vinyl chloride)	"squeeze" bottles, pipe, siding, flooring
СН ₂ =СН-СН ₃	-СН ₂ -СН-	polypropylene	molded caps, margarine tubs, indoor/outdoor carpeting, upholstery
CH ₂ =CH	-CH ₂ -CH-	polystyrene	packaging, toys, clear cups, egg cartons, hot drink cups
CF ₂ =CF ₂	-CF ₂ -CF ₂ -	poly(tetrafluoroethylene) Teflon®	nonsticking surfaces, liners, cable insulation
CH ₂ =CH C≡N	$-CH_2$ $-CH$ $C \equiv N$	poly(acrylonitrile) Orlon [®] , Acrilan [®]	rugs, blankets, yarn, apparel, simulated fur
CH ₂ =C-CH ₃ COCH ₃	$-CH_2-C- \\ -CCH_3 \\ -COCH_3 \\ 0$	poly(methyl methacrylate) Plexiglas [®] , Lucite [®]	lighting fixtures, signs, solar panels, skylights
CH ₂ =CH OCCH ₃	$\begin{array}{c} -\text{CH}_2 - \text{CH} - \\ \text{OCCH}_3 \\ \parallel \\ \text{O} \end{array}$	poly(vinyl acetate)	latex paints, adhesives