Polymer Chemistry

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Part-I

(History and classification of polymers)

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Lecture Note-1 A

History of development

Polymers have been with us from the beginning of time, and form the building blocks of life. Animals, plants- all classes of living organisms - are composed of polymers. However in the middle of the 20th century 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. Subsequently polymers have changed our lives. It is hard to visualize today’s world with all its luxury and comfort without man-made polymeric materials.

The word *polymer* is derived from the greek words; *poly* and *meros*, meaning many and parts, respectively. Some scientists prefer to use the word *macromolecule,* or large molecule, instead of polymer.

Cellulose nitrate was the first plastic synthesised in 1862 to overcome the shortage of ivory from which billiard balls were made. Cellulose nitrate was 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.

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.

Introduction of Plastics Materials

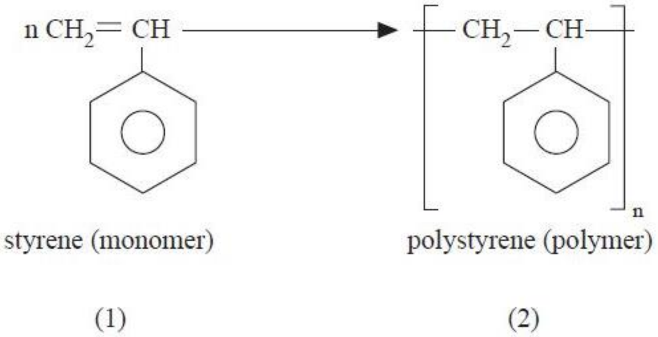
Date	**Material**	**Typical Use**
1868	Cellulose nitrate	Eyeglass frames
1909	Phenol–formaldehyde	Telephone handsets, knobs, handles
1919	Casein	Knitting needles
1926	Alkyds	Electrical insulators
1927	Cellulose acetate	Toothbrushes, packaging
1927	Poly(vinyl chloride)	Raincoats, flooring
1929	Urea–formaldehyde	Lighting fixtures, electrical switches
1935	Ethyl cellulose	Flashlight cases
1936	Polyacrylonitrile	Brush backs, displays
1936	Poly(vinyl acetate)	Flash bulb 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
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

BASIC CONCEPTS AND DEFINITIONS

Thus a polymer is a large molecule (macromolecule) built up by the repetition of small chemical units.

To illustrate this, following equation shows the formation of the polymer polystyrene.

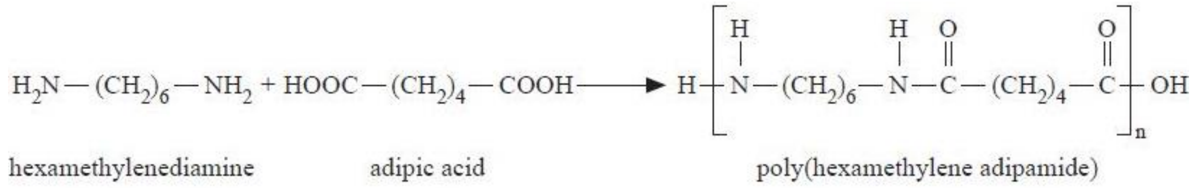


Equation 1

The styrene molecule (1) contains a double bond. The resulting structure, enclosed in square brackets, is the polymer polystyrene (2). Styrene is 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 polymer is referred to as the *structural unit*. In the case of polystyrene, the polymer is derived from a single monomer (styrene) and, consequently, the structural unit of the polystyrene chain is the same as its repeating unit. Other examples of polymers of this type are polyethylene, polyacrylonitrile, and polypropylene. Some polymers are formed

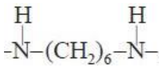
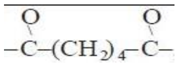
However, some polymers are derived from the mutual reaction of two or more monomers that are chemically similar but not identical. For example, poly (hexamethylene adipamide) or nylon 6,6 (5) is made from the reaction of hexamethylenediamine (3) and adipic acid (4).



$$H_2N-(CH_2)_6-NH_2 + HOOC-(CH_2)_4-COOH \longrightarrow H\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH$$

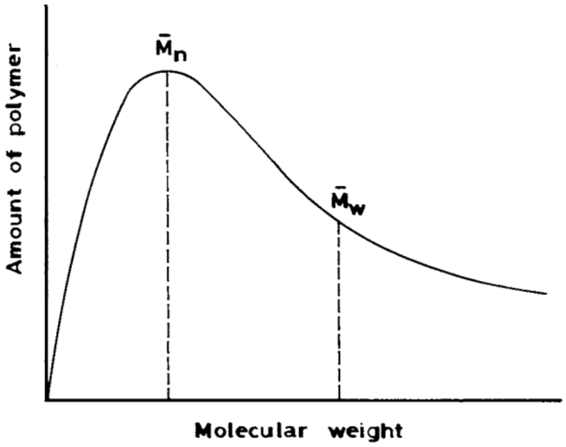
hexamethylenediamine (3) adipic acid (4) poly(hexamethylene adipamide) (5)

Equation 2

The repeating unit here consists of two structural units:  $-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-$ the residue from hexamethylenediamine; and  $-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$, the residue from adipic acid. Other polymers that have repeating units with more than one structural unit include poly (ethylene terephthalate) and proteins. The constitution of a polymer is usually described in terms of its structural units.

The subscript designation, n, in the equations indicates the number of repeating units present in the polymer chain (molecule). This is known as the ***degree of polymerization (DP)***. It specifies the length of the polymer molecule. Polymerization proceeds by the reaction of monomers to form a *dimer*, which in turn reacts with another monomer to form a *trimer* and so on. Reaction may also be between dimers, trimers, or any molecular species within the reaction mixture to form a progressively larger molecule. In either case, a series of linkages is built between the repeating units, and the resulting polymer molecule, often called a *polymer chain*. Low-molecular-weight polymerization products such as dimers, trimers, tetramers, etc., are referred to as *oligomers*. They generally possess undesirable thermal and mechanical properties. A high degree of polymerization is normally required for a material to develop useful properties so that it can be appropriately described as a polymer. Polystyrene, with a degree of polymerization of 7, is a viscous liquid (not of much use), whereas commercial grade polystyrene is a solid and the DP ›1000 . It must be emphasized, that no clear distinction has been established between the sizes of oligomers and polymers. The degree of polymerization can quantitatively estimate the molecular size of a polymer. This can also be done by use of the term *molecular weight (MW).* By definition, M W of the polymer = DP × Mol wt of repeating unit. To illustrate this let us go back to polystyrene (2). There are eight carbon atoms and eight hydrogen atoms in the repeating unit. Thus, the molecular weight of the repeating unit is 104 (8×12 + 1×8). For commercial grade polystyrene, DP ~1000. Consequently, the molecular weight of this type of polystyrene is 104,000. Molecular weight has a profound effect on the properties of a polymer.

A given polymer sample (like a piece of polystyrene from our kitchenware) is actually composed of millions of polymer molecules having different chain lengths (except for some biological polymers like proteins, which have a single, well-defined molecular weight [monodispersed]). This means that a distribution of molecular weight exists for synthetic polymers. A typical molecular weight distribution curve for a polymer is shown as:



The experimental measurement of molecular weight in the given sample gives only an average value. Two types of molecular weight averages are most commonly considered: ***the number-average molecular weight*** represented by ***Mn***, and the ***weight*-average molecular weight, Mw**. The number-average molecular weight is derived from measurements that count the number of molecules in the given sample. On the other hand, the weight-average molecular weight is based on its size.

Their ratio Mw/Mn indicates the differences in the chain lengths of the constituent polymer molecules in a given sample are. That is, this ratio is a measure of **polydispersity**, and consequently it is often referred to as the **heterogeneity index**. In an ideal polymer such as a protein, all the polymer molecules are of the same size (Mw= Mn or Mw/Mn= 1). This is not true for synthetic polymers – the numerical value of Mw is always greater than that of Mn. Thus as the ratio Mw/MN increases, the molecular weight distribution becomes broader.