Polymer Chemistry

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Polymer Science and Technology

By *Robert O. Ebewele*, CRC Press, 2000

1. Introduction

I. HISTORICAL DEVELOPMENT

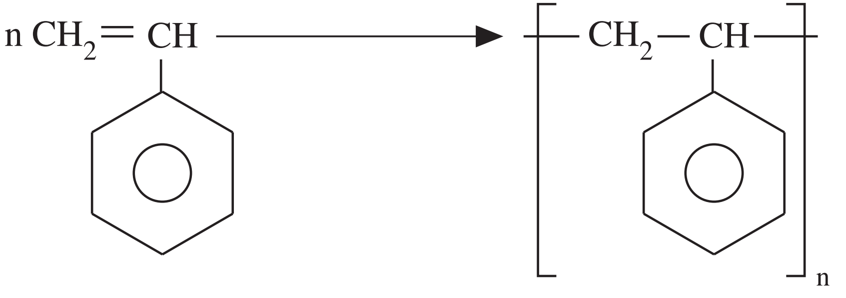
II. BASIC CONCEPTS AND DEFINITIONS

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.

Thousands of styrene molecules become linked together with opening this double bond.

The resulting structure, enclosed in square brackets, is the polymer polystyrene.



styrene (monomer)

polystyrene (polymer)

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****.* 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**.

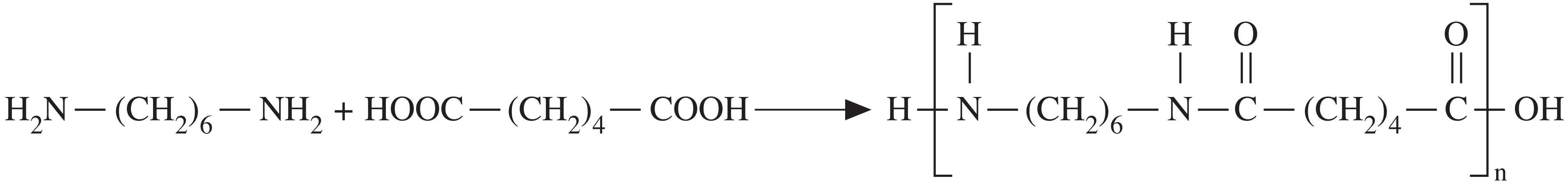
The residue from the monomer employed in the preparation of a polymer is referred to as the ***structural unit****.*

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 this type: polyethylene, polyacrylonitrile, and polypropylene.

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 is made from the reaction of hexamethylenediamine and adipic acid.



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

hexamethylenediamine adipic acid poly(hexamethylene adipamide)

The repeating unit in this case consists of two structural units: $–HN–(CH_2)_6–NH–$, the residue from hexamethylenediamine; and $–OC–(CH_2)_4–CO–$, the residue from adipic acid.

Other polymers that have repeating units with more than one structural unit include poly(ethylene terephthalate) and proteins.

The **subscript** designation, **n**, in the polymerization reaction indicates the number of repeating units strung together in the polymer chain (molecule). This is known as the ***degree of polymerization*** *(DP).*

DP specifies the **length of the polymer molecule**.

Polymerization occurs by the sequential reactions of monomers, which means that a successive series of reactions occurs as the repeating units are linked together. This can proceed by the reaction of monomers to form a *dimer,* which in turn reacts with another monomer to form a *trimer* and so on.

In either case, a series of linkages is built between the repeating units, and the resulting polymer molecule is often called a ***polymer chain****,* a description which emphasizes its physical similarity to the links in a chain.

Low-molecular-weight polymerization products such as dimers, trimers, tetramers, etc., are referred to as ***oligomers****.* No clear demarcation has been established between the sizes of oligomers and polymers.

Oliomers generally possess undesirable thermal and mechanical properties.

DP and properties: Polystyrene, with a DP of 7, is a viscous liquid, whereas commercial grade polystyrene is a solid (with DP of 1000).

The DP represents one way of quantifying the **molecular length** or **size** of a polymer.

This can also be done by use of the term ***molecular weight*** *(MW).*

By definition, MW(Polymer) = DP × MW(Repeat Unit).

For polystyrene: 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).

With a DP of 1000, the molecular weight of this type of polystyrene is 104,000.

Molecular weight has a profound effect on the properties of a polymer.

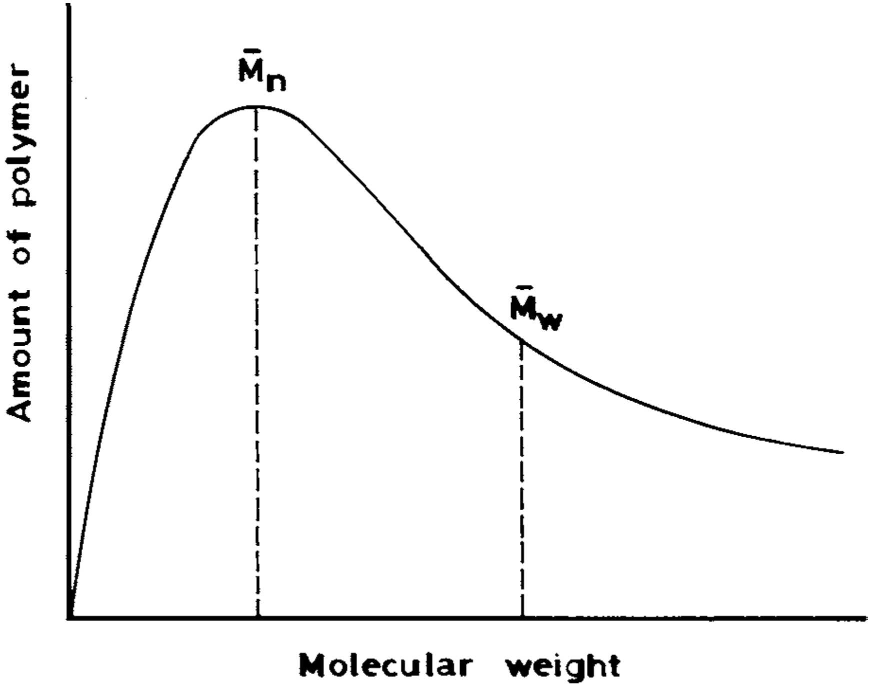
So far, we have been discussing a single polymer molecule. However, a given polymer sample (like a piece of polystyrene from your kitchenware) is actually composed of millions of polymer molecules.

For almost all synthetic polymers irrespective of the method of polymerization (formation), the **length of a polymer chain** is determined by **purely random events**.

Consequently, any given polymeric sample contains a mixture of molecules having different chain lengths (except for some biological polymers like proteins, which have a single, well-defined molecular weight [monodisperse]).

This means that a distribution of molecular weight exists for synthetic polymers.

A typical molecular weight distribution curve for a polymer:



Two types of molecular weight averages are most commonly considered:

number-average molecular weight (**M_n**) and **weight-average molecular weight (**M_w)

The number-average molecular weight is based on methods in which the contribution of each molecule to the observed effect depends on its size.

The ratio **M_w/M_n** is an indication of just how broad the differences in the chain lengths of the constituent polymer molecules.

The 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 ($M_w = M_n$ or $M_w/M_n = 1$).

This is not true for synthetic polymers – the **numerical value of Mw is always greater than that of M_n**. Thus as the ratio M_w/M_n increases, the molecular weight distribution is broader.

III. CLASSIFICATION OF POLYMERS

A. Natural *vs.* Synthetic

B. Polymer Structure

    1. Linear, Branched, or Cross-Linked Ladder vs. Functionality
    2. Amorphous or Crystalline
    3. Homopolymer or Copolymer
    4. Fibers, Plastics, or Elastomers

C. Polymerization Mechanism

D. Thermal Behavior

E. Preparative Technique

F. End Use

A. NATURAL *vs.* SYNTHETIC

Polymers may either be naturally occurring or purely synthetic.

All the conversion processes occurring in our body (e.g., generation of energy from our food intake) are due to the presence of enzymes. Life itself may cease if there is a deficiency of these enzymes.

Enzymes, **nucleic acids**, and **proteins** are polymers of biological origin.

Starch, **cellulose**, and **natural rubber** are polymers of plant origin, and have relatively simpler structures than those of enzymes or proteins.

There are a large number of synthetic (**man-made**) polymers consisting of various families: fibers, elastomers, plastics, adhesives, etc. Each family itself has subgroups.

B. POLYMER STRUCTURE

1. Linear, Branched or Cross-linked, Ladder vs. Functionality

Functionality: The functionality of a molecule is simply its **interlinking capacity**, or the **number of sites** it has **available for bonding** with other molecules under the specific polymerization conditions.

A molecule may be classified as monofunctional, bifunctional, or polyfunctional depending on one, two, or greater than two sites available for linking with other molecules.

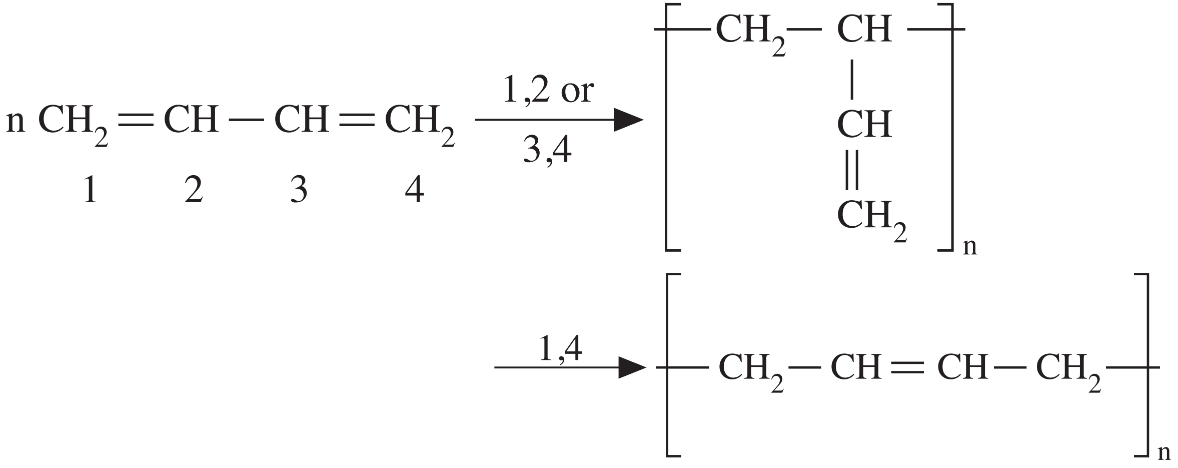
In styrene, the electrons pair in the double bond endows the ability to enter into the formation of two bonds. Styrene is therefore bifunctional.

The presence of two condensable groups in both hexamethylenediamine ($-NH_2$) and adipic acid ($-COOH$) makes each of these monomers bifunctional.

The interlinking capacity of a monomer is ordinarily apparent from its structure.

In butadiene, the presence of two double bonds on the structure would be expected to have a functionality of 4.

Butadiene can also have a functionality of 2 depending on the reaction conditions.



$$n\,\underset{1}{CH_2}=\underset{2}{CH}-\underset{3}{CH}=\underset{4}{CH_2} \xrightarrow[3,4]{1,2\text{ or}} \left[-CH_2-\underset{\underset{\underset{CH_2}{\|}}{CH}}{\underset{|}{CH}}-\right]_n$$

$$\xrightarrow{1,4} \left[-CH_2-CH=CH-CH_2-\right]_n$$

In 1,2-polymerization, one double bonds is involved in the polymerization reaction and the residual or unreacted double bond (***pendant group***) is attached to the main chain.

In 1,4-polymerization, the residual double bond shifts to the 2,3 position along the main chain.

In either case, the residual double bond is **inert** and is generally **incapable** of additional polymerization under the conditions leading to the formation of the polymer. In this case, butadiene has a functionality of 2.

However, under appropriate reaction conditions such as high temperature or crosslinking reactions, the residual unsaturation either on the pendant group or on the backbone can undergo additional reaction. In that case, butadiene has a total functionality of 4.

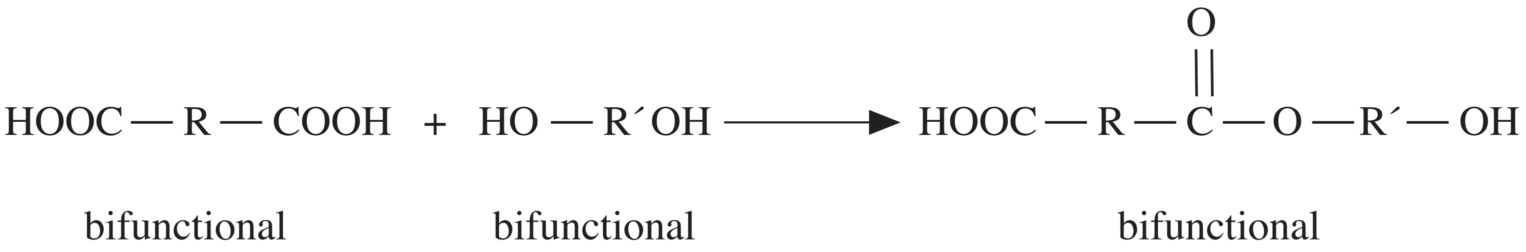
Monomers containing functional groups that react under different conditions are said to possess ***latent functionality***.

The reaction between two monofunctional monomers in an esterification reaction. The reactive groups on the acid and alcohol are used up completely and the ester is incapable of further esterification reaction.

$$R - COOH + R' - OH \longrightarrow R - \overset{\displaystyle O}{\overset{||}{C}} - O - R'$$

When two bifunctional molecules react: The ester resulting from this reaction is itself bifunctional, being terminated on either side by groups that are capable of further reaction.

This process can be repeated almost indefinitely.

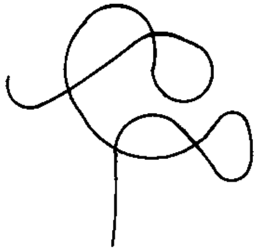


$$HOOC - R - COOH + HO - R'OH \longrightarrow HOOC - R - \overset{\displaystyle O}{\overset{||}{C}} - O - R' - OH$$

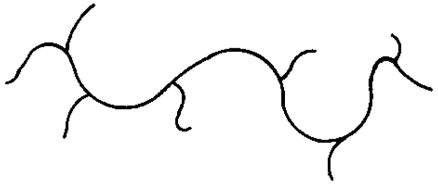
Bifunctional structural units can enter into two and only two linkages with other structural units. The sequence of linkages between bifunctional units is necessarily linear. The resulting polymer is said to be ***linear***.

The structural units (in polyfunctional molecules) may be linked to form nonlinear structures. In some cases the side growth of each polymer chain may be terminated before the chain has a chance to link up with another chain. The resulting polymer molecules are said to be ***branched***.

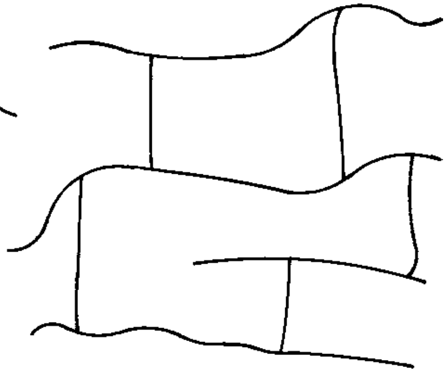
In other cases, growing polymer chains become chemically linked to each other, resulting in a ***cross-linked*** system.



Linear



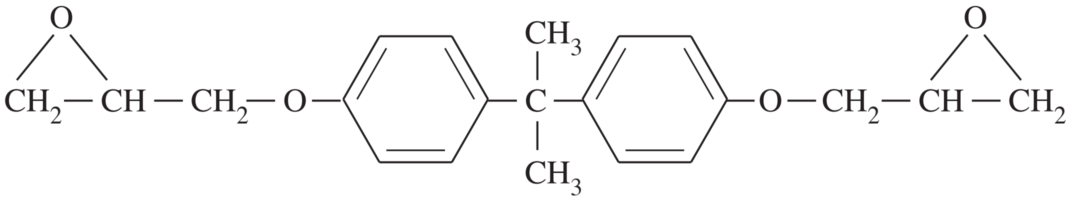
Branched



Crosslinked

The formation of a cross-linked polymer is exemplified by the reaction of **epoxy polymers**, which have been used traditionally as adhesives and coatings and, more recently, as the most common matrix in aerospace composite materials.

Epoxies exist at ordinary temperatures as **low-molecular-weight viscous liquids** or **prepolymers**, for example: diglycidyl ether of bisphenol A (DGEBA)



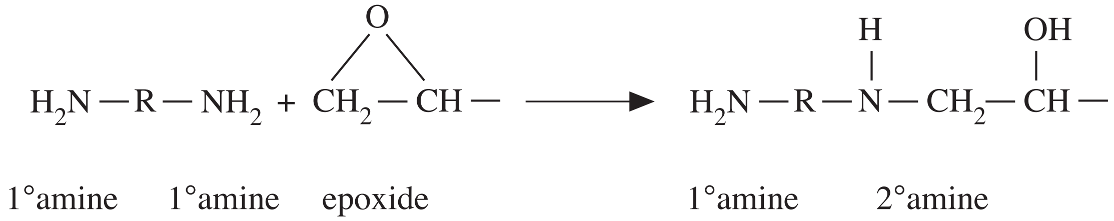
diglycidyl ether of bisphenol A (DGEBA)

The transformation of this viscous liquid into a hard, cross-linked three-dimensional molecular network involves the reaction of the prepolymer with reagents such as amines or Lewis acids.

This reaction is referred to as ***curing**.*

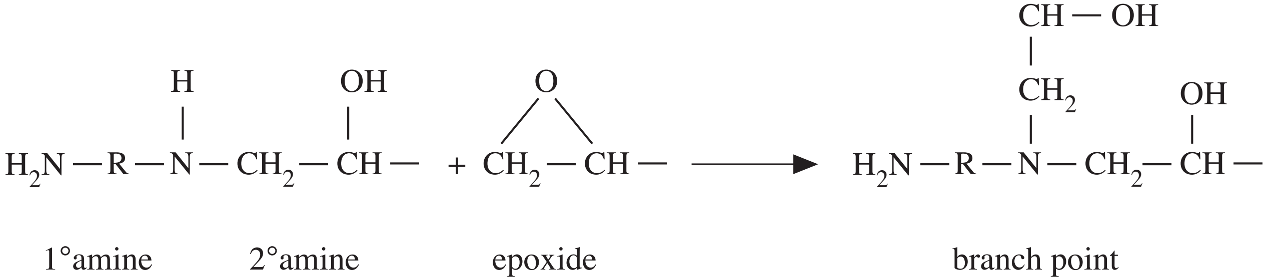
The curing of epoxies with a primary amine such as hexamethylenediamine:

1. The attack of an epoxide group by the primary amine



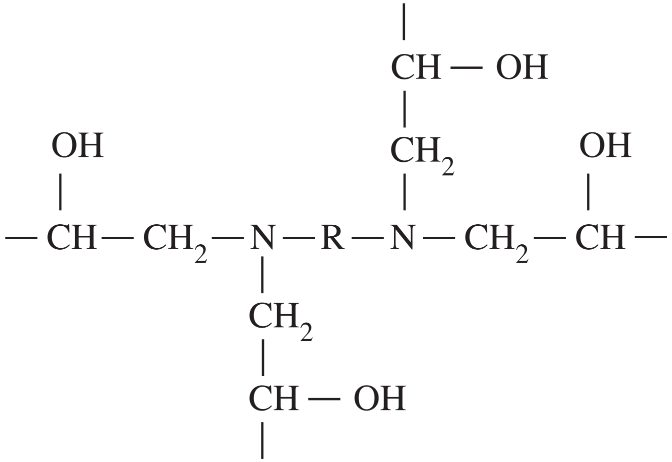
$$H_2N-R-NH_2 + \overset{O}{CH_2-CH}- \longrightarrow H_2N-R-\overset{\overset{H}{|}}{N}-CH_2-\overset{\overset{OH}{|}}{CH}-$$

2. The combination of the resulting secondary amine with a second epoxy group to form a branch point.



$$H_2N-R-\overset{\overset{H}{|}}{N}-CH_2-\overset{\overset{OH}{|}}{CH}- + \overset{O}{CH_2-CH}- \longrightarrow H_2N-R-\overset{\overset{\overset{CH-OH}{|}}{\overset{CH_2}{|}}}{N}-CH_2-\overset{\overset{OH}{|}}{CH}-$$

The presence of these branch points ultimately leads to a cross-linked infusible and insoluble polymer with structures such as:



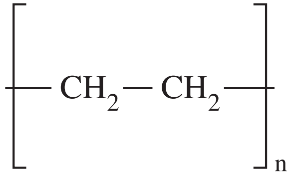
$$-\overset{\overset{OH}{|}}{CH}-CH_2-\underset{\underset{\underset{|}{\underset{CH-OH}{|}}}{\underset{CH_2}{|}}}{N}-R-\overset{\overset{\overset{|}{\overset{CH-OH}{|}}}{\overset{CH_2}{|}}}{N}-CH_2-\overset{\overset{OH}{|}}{CH}-$$

In this reaction, the stoichiometric ratio requires one epoxy group per amine hydrogen. Consequently, an amine such as hexamethylenediamine has a functionality of 4 (in the reaction of hexamethylenediamine with adipic acid, the amine has a functionality of 2).

In this reaction DGEBA is bifunctional since the hydroxyl groups generated in the reaction do not participate in the reaction.

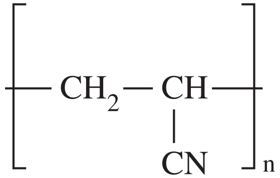
But when the curing of epoxies involves the use of a Lewis acid such as BF_3, the functionality of each epoxy group is 2 and the functionality of DGEBA is 4.

By **employing different reactants** or **varying the stoichiometry of reactants**, different structures can be produced, and the properties of the final polymer can also be varied.



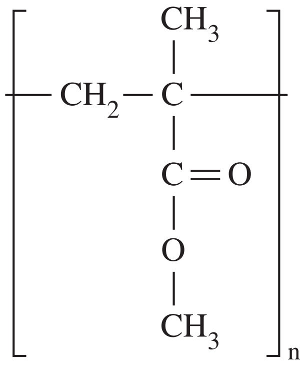
$$\left[-CH_2-CH_2-\right]_n$$

(21)



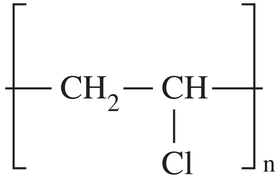
$$\left[-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-\right]_n$$

(22)



$$\left[-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle \underset{\displaystyle \underset{|}{O}-CH_3}{C=O}}{\underset{|}{C}}}}-\right]_n$$

(23)



$$\left[-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\right]_n$$

(24)

Linear polymers:

Polystyrene, polyethylene (21), polyacrylonitrile (22), poly(methyl methacrylate) (23), poly(vinyl chloride) (24)

Substituent groups such as –CH_3 , –O–C–CH_3, –Cl, and –CN that are attached to the main chain of skeletal atoms are known as ***pendant groups**.*

Their structure and chemical nature can confer unique properties on a polymer.

Linear and branched polymers are usually **soluble** in some solvent at normal temperatures. The presence of polar pendant groups can considerably reduce room temperature solubility.

Since cross-linked polymers are chemically tied together and solubility essentially involves the separation of solute molecules by solvent molecules, cross-linked polymers do not dissolve, but can only be swelled by liquids.

The presence of **cross-linking confers stability** on polymers.

Highly cross-linked polymers are generally **rigid** and **high-melting**.

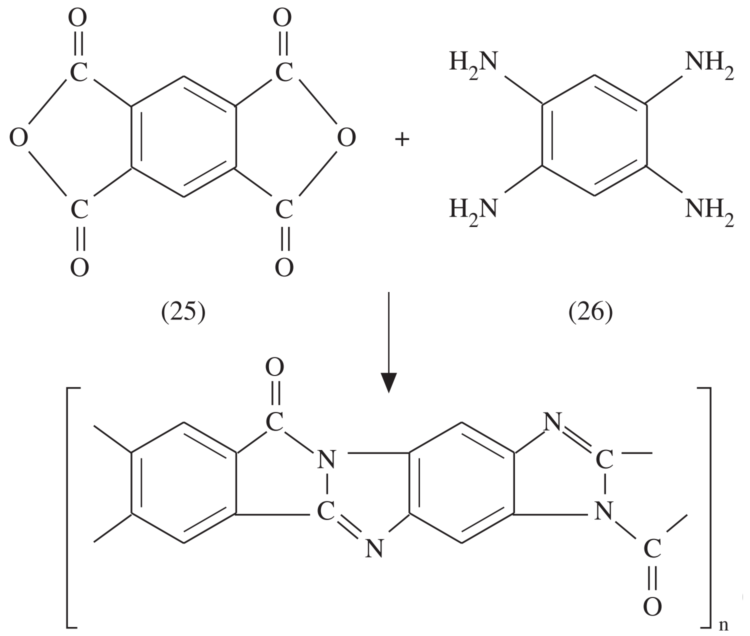
Cross-links occur randomly in a cross-linked polymer. Consequently, it can be broken down into smaller molecules by random chain scission.

Ladder polymers constitute a group of polymers with a regular sequence of cross-links.

A ladder polymer consists of two parallel linear strands of molecules with a regular sequence of crosslinks.

Ladder polymers have only condensed cyclic units in the chain; they are also commonly referred to as **double-chain** or **double-strand** polymers.

A typical example is poly(imidazopyrrolone), which is obtained by the polymerization of aromatic dianhydrides such as pyromellitic dianhydride or aromatic tetracarboxylic acids with 1,2,4,5-tetraaminobenzene:



The molecular structure of ladder polymers is more rigid than that of conventional linear polymers.

Numerous members of this family of polymers display exceptional thermal, mechanical, and electrical behavior.

2. Amorphous or Crystalline

Structurally, polymers in the solid state may be *amorphous* or *crystalline.*

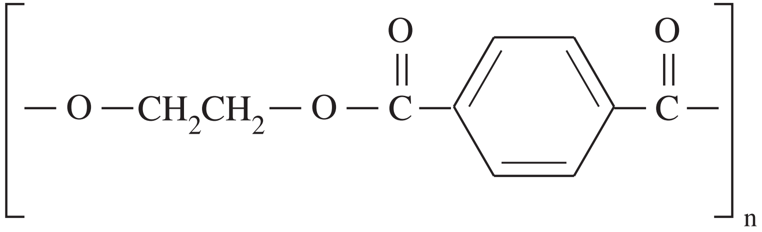
When polymers are cooled from the molten state or concentrated from the solution, molecules are often attracted to each other and tend to aggregate as closely as possible into a solid with the least possible potential energy.

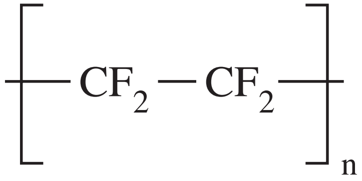
For some polymers, in the process of forming a solid, individual chains are folded and packed regularly in an orderly fashion. The resulting solid is a crystalline polymer with a long-range, three-dimensional, ordered arrangement.

Since the polymer chains are very long, it is impossible for the chains to fit into a perfect arrangement equivalent to that observed in low-molecular-weight materials.

A measure of imperfection always exists. The **degree of crystallinity**, i.e., the fraction of the total polymer in the crystalline regions, may vary from a few percentage points to about 90% depending on the crystallization conditions.

Examples of crystalline polymers include polyethylene, polyacrylonitrile, poly(ethylene terephthalate), and polytetrafluoroethylene.

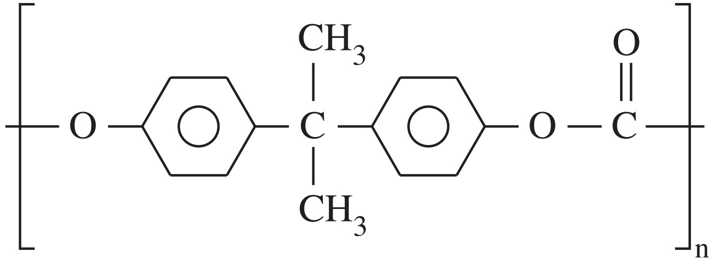




In contrast to crystallizable polymers, amorphous polymers possess chains that are incapable of ordered arrangement.

They are characterized in the solid state by a short-range order of repeating units. These polymers **vitrify**, forming an amorphous glassy solid in which the molecular chains are arranged at random and even entangled.

Poly(methyl methacrylate) and polycarbonate are amorphous polymers.



The solid states of crystalline and amorphous polymers are characterized by a **long-range order of molecular chains** and a **short-range order of repeating units**, respectively. On the other hand, the melting of either polymer marks the onset of disorder.

There are some polymers which deviate from this general scheme in that the structure of the ordered regions is more or less disturbed. These are known as ***liquid crystalline polymers**.*

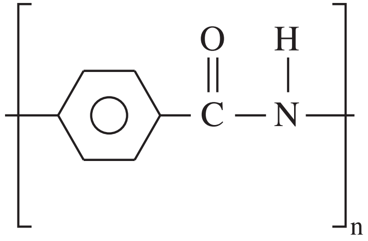
They have phases characterized by structures intermediate between the ordered crystalline structure and the disordered fluid state.

Solids of liquid crystalline polymers melt to form fluids in which much of the molecular order is retained within a certain range of temperature.

The ordering is sufficient to impart some solid-like properties on the fluid, but the forces of attraction between molecules are not strong enough to prevent flow.

An example of a liquid crystalline polymer is polybenzamide.

Liquid crystalline polymers are important in the fabrication of lightweight, ultra-high-strength, and temperature-resistant fibers and films such as Dupont's Kevlar and Monsanto's X-500.



3. Homopolymer or Copolymer

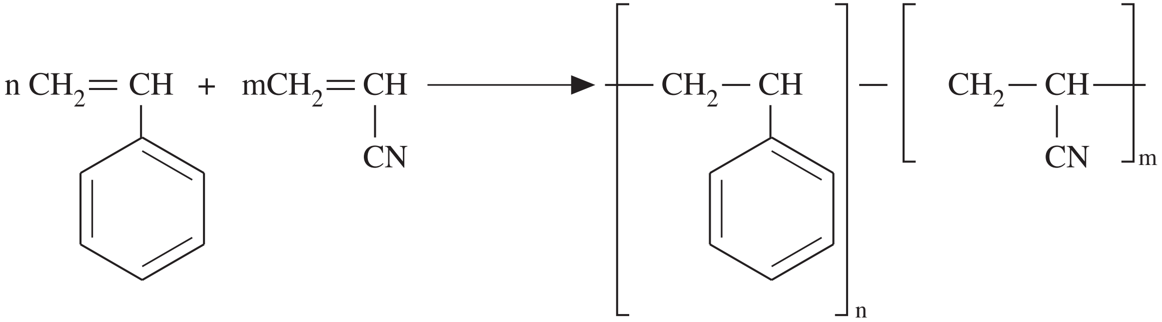
Polymers may be either homopolymers or copolymers **depending on the composition**.

Polymers composed of only one repeating unit in the polymer molecules are known as *homopolymers.*

Polymers composed of two different repeating units in the polymer molecule are defined as *copolymers.*

A styrene-acrylonitrile copolymer formed when styrene and acrylonitrile are polymerized in the same reactor.

The repeating unit and the structural unit of a polymer are not necessarily the same.



The repeating units on the copolymer chain may be arranged in various degrees of order along the backbone; it is even possible for one type of backbone to have branches of another type.

There are several types of copolymer systems:

- **Random copolymer** — The repeating units are arranged randomly on the chain molecule. It we represent the repeating units by A and B, then the random copolymer might have the structure shown below:

—AABBABABBAAABAABBA—

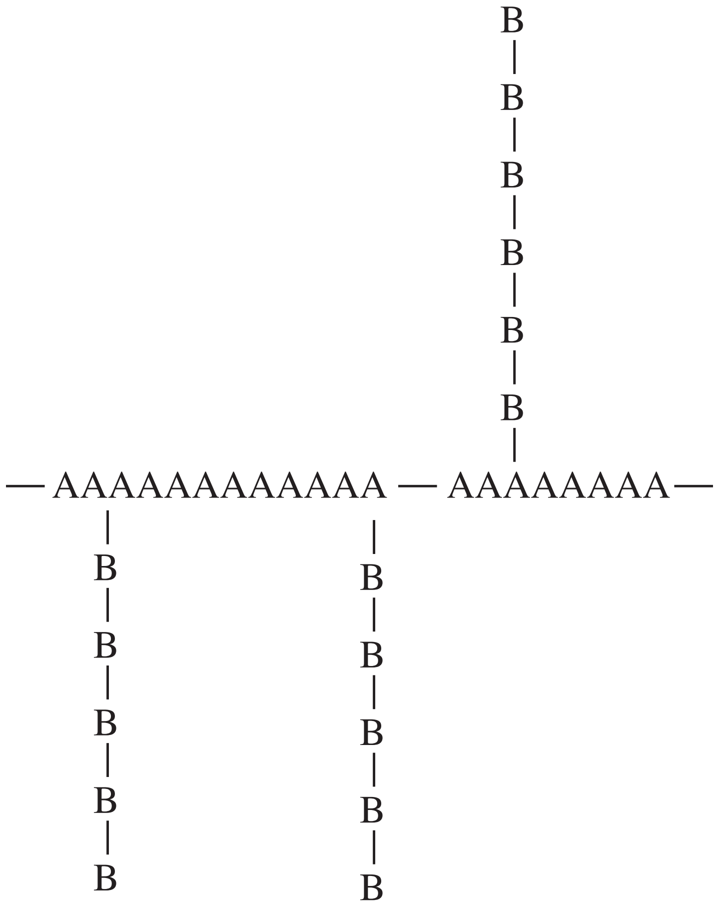
- **Alternating copolymer** — There is an ordered (alternating) arrangement of the two repeating units along the polymer chain:

— ABABABABABAB —

- **Block copolymer** — The chain consists of relatively long sequences (blocks) of each repeating unit chemically bound together:

—AAAAA— BBBBBBBB —AAAAAAAAA — BBBB—

- **Graft copolymer** — Sequences of one monomer (repeating unit) are “grafted” onto a backbone of the another monomer type:



4. Fibers, Plastics, or Elastomers

Fibers are linear polymers with high symmetry and high intermolecular forces that result usually from the presence of polar groups. They are characterized by high modulus, high tensile strength, and moderate extensibilities (usually less than 20%).

Elastomers are molecules with irregular structure, weak intermolecular attractive forces, and very flexible polymer chains. Elastomers exhibit high extensibility (up to 1000%) from which they recover rapidly on the removal of the imposed stress. Elastomers generally have low initial modulus in tension, but when stretched they stiffen.

Chain segments of elastomers can undergo high local mobility, but the gross mobility of chains is restricted by the introduction of a few cross-links into the structure. In the absence of applied (tensile) stress, molecules of elastomers usually assume coiled shapes.

Plastics fall between the structural extremes represented by fibers and elastomers.

Polymers such as polypropylene and polyamides can be used as fibers and as plastics by a proper choice of processing conditions.

C. POLYMERIZATION MECHANISM

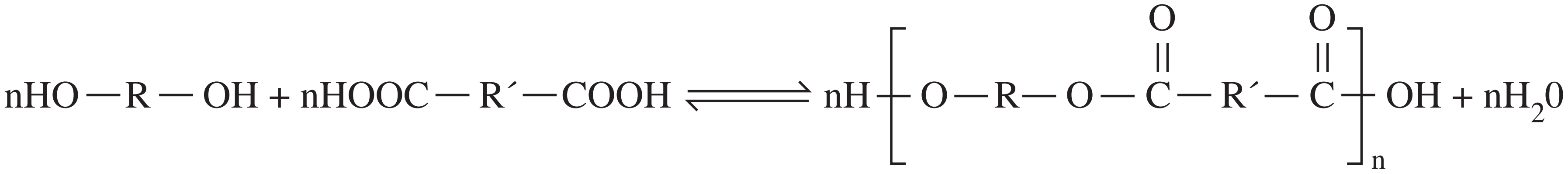
Polymers may be classified broadly as *condensation, addition,* or *ring-opening* polymers, depending on the type of polymerization reaction involved in their formation.

Condensation polymers are formed from a series of reactions, in which any two species (monomers, dimers, trimers, etc.) can react at any time leading to a larger molecule.

In condensation polymerization, the stepwise reaction occurs between the chemically reactive groups or functional groups on the reacting molecules. In the process, a small molecule, usually water or ammonia, is eliminated.

A typical condensation polymerization reaction is the formation of a polyester through the reaction of a diol and a dicarboxylic acid, e.g., poly(ethylene terephthalate).

Other condensation polymers such as polyamides (e.g., nylon 6,6); and urea-formaldehyde and phenol–formaldehyde resins.



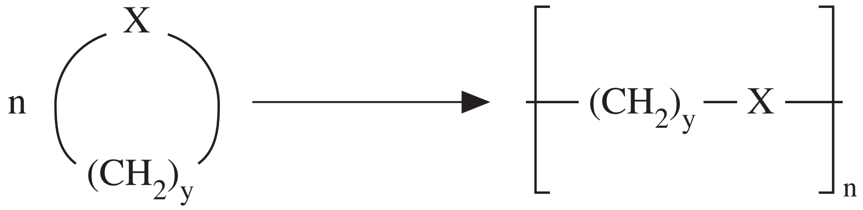
$$nHO-R-OH + nHOOC-R'-COOH \rightleftharpoons nH\left[O-R-O-\overset{O}{\overset{||}{C}}-R'-\overset{O}{\overset{||}{C}}\right]_n OH + nH_2 0$$

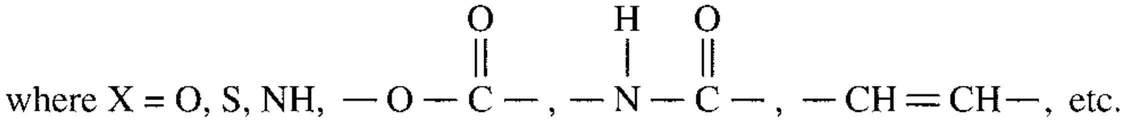
Addition polymers are produced by reactions in which monomers are added one after another to a rapidly growing chain.

The growing polymer in addition polymerization proceeds via a chain mechanism. Like all chain reactions, three fundamental steps are involved: initiation, propagation, and termination.

Monomers generally employed in addition polymerization are unsaturated (usually with carbon-carbon double bonds). Examples of addition polymers are polystyrene, polyethylene, polyacrylonitrile, poly(methyl methacrylate), and poly(vinyl chloride).

Ring-opening polymerization polymers are derived from the cleavage and then polymerization of cyclic compounds.



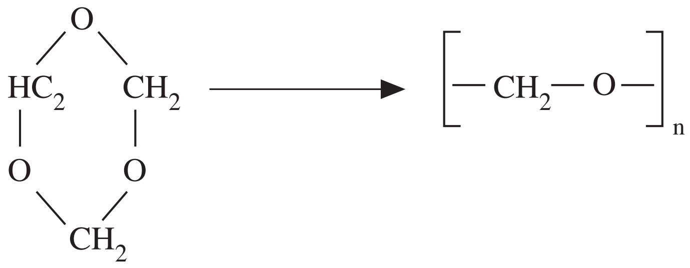


where $X = O, S, NH, \; -O-\overset{\overset{O}{\|}}{C}-, \; -\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-, \; -CH{=}CH-$, etc.

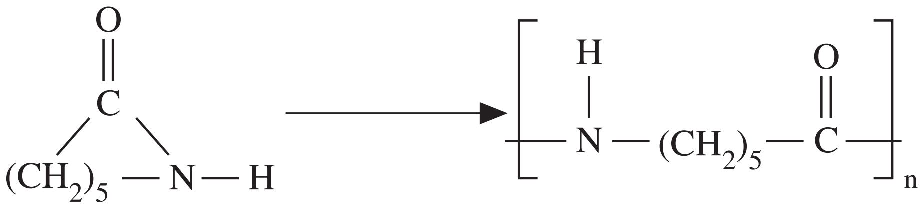
The nature of the cyclic structure is such that in the presence of a catalyst it undergoes equilibrium ring-opening to produce a linear chain.

X is usually a heteroatom such as oxygen or sulfur; it may also be a group such as lactam or lactone.

Trioxane (33) can be polymerized to yield polyoxymethylene (34) and caprolactam (35) undergoes ring-opening to yield nylon 6 (36), an important textile fiber.



(33) (34)



(35) (36)

The original classification of polymers as either condensation or addition polymers as proposed by **Carothers**.

Consequently, this classification has been replaced by the terms ***step-reaction*** (condensation) and ***chain-reaction*** (addition) *polymerization*.

D. THERMAL BEHAVIOR

For engineering purposes, the most useful classification of polymers is based on their thermal (**thermomechanical**) response: ***thermoplastics*** or ***thermosets***.

Thermoplastic polymers soften and flow under the action of heat and pressure. Upon cooling, the polymer hardens and assumes the shape of the mold (container).

Thermoplastics, when compounded with appropriate ingredients, can usually withstand several of these heating and cooling cycles without suffering any structural breakdown. This behavior is similar to that of candle wax.

Examples of thermoplastic polymers: polyethylene, polystyrene, nylon.

Thermoset is a polymer that, when heated, undergoes a chemical change to produce a cross-linked, solid polymer.

Thermosets usually exist initially as liquids called **prepolymers**; they can be shaped into desired forms by the application of heat and pressure, but are incapable of undergoing repeated cycles of softening and hardening.

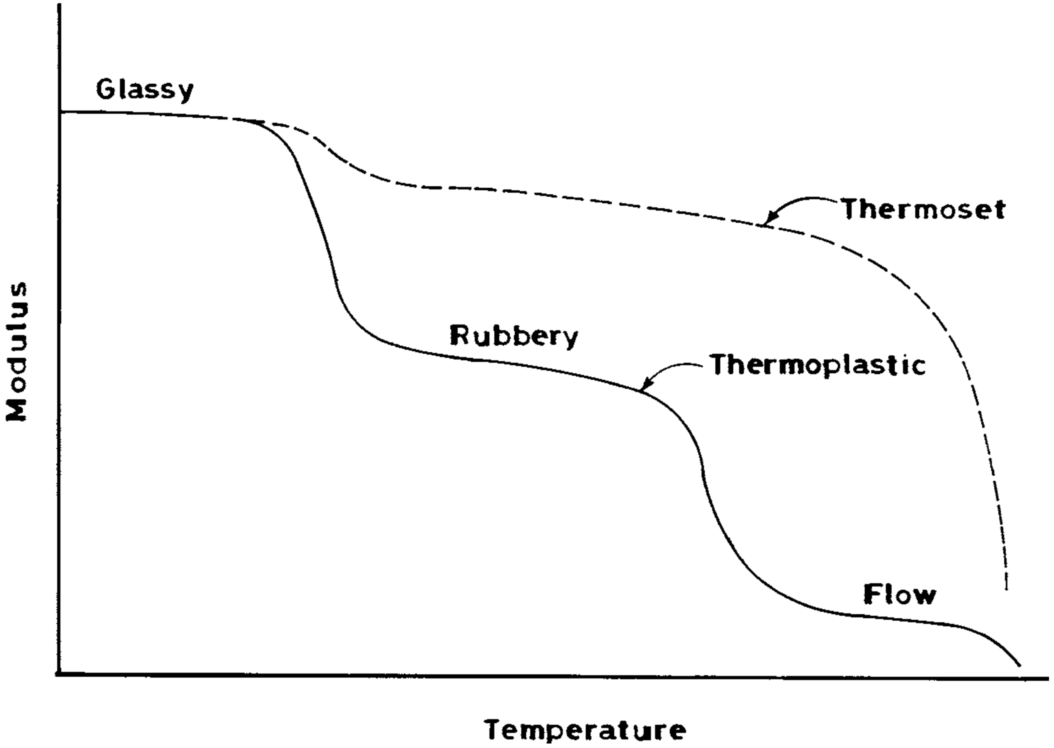
Examples of thermosetting polymers: urea–formaldehyde, phenol–formaldehyde, epoxies.

The basic structural difference between thermoplastics and thermosets: thermoplastics are composed of **linear and branched** molecules, whereas thermosets are made up of **cross-linked** systems.

Linear and branched polymers consist of molecules that are not chemically tied together. It is possible for individual chains to slide past one another.

For cross-linked systems, chains are linked chemically. Chains will not flow freely even under the application of heat and pressure.

The differences in the thermal behavior is considering the change in modulus with temperature for both polymers:



At low temperatures, a thermoplastic polymer (both crystalline and amorphous) exists as a hard and rigid glass. As the temperature is increased, it changes from a glass to a rubbery elastomer to a viscous melt that is capable of flowing — the flow region.

The transitions between the different phases or regions of thermal behavior are characterized by drops in the magnitude of the modulus — usually two to three orders.

For the thermosetting polymer, the modulus remains high in the rubbery region, while the flow region disappears.

E. PREPARATIVE TECHNIQUE

Polymers can be classified according to the techniques used during the polymerization of the monomer.

Bulk polymerization: only the monomer (and possibly catalyst and initiator, but no solvent) is fed into the reactor. The monomer undergoes polymerization, at the end of which a (nearly) solid mass is removed as the polymer product.

Bulk polymerization is employed widely in the manufacture of condensation polymers, where reactions are only mildly exothermic and viscosity is mostly low thus enhancing ready mixing, heat transfer, and bubble elimination.

Solution polymerization: involves polymerization of a monomer in a solvent in which both the monomer (reactant) and polymer (product) are soluble.

Suspension polymerization: refers to polymerization in an aqueous medium with the monomer as the dispersed phase. Consequently, the polymer resulting from such a system forms a solid dispersed phase.

Emulsion polymerization: is similar to suspension polymerization but the initiator is located in the aqueous phase (continuous phase) in contrast to the monomer (dispersed phase) in suspension polymerization.

In emulsion polymerization, the resulting polymer particles are considerably smaller (about ten times smaller) than those in suspension polymerization.

Precipitation polymerization:

Interfacial polymerization:

F. END USE

Polymers may be classified according to the end use of the polymer, associated with a specific industry (end use):

diene polymers (rubber industry); olefin polymer (sheet, film, and fiber industries); and acrylics (coating and decorative materials).