# Polymer Chemistry

## Notes by

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**Part-I**

**(History and classification of polymers)**

**Paper-DSE 4T (6th Sem)**

**Lecture Note-1**

## 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.

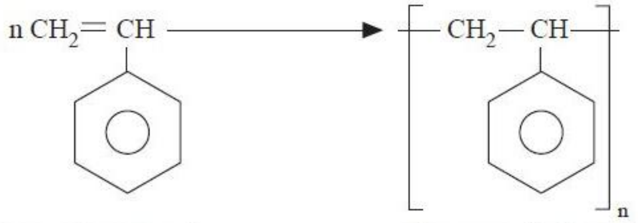
*Introduction of Plastics Materials*

| **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 |
| 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 |

## 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.



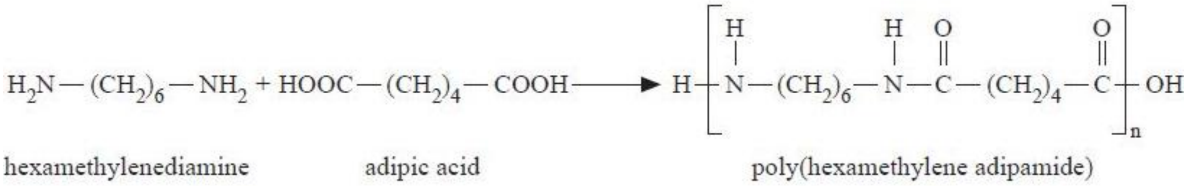
styrene (monomer) polystyrene (polymer)

(1) (2)

*Equation 1*

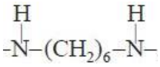
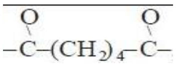
The styrene molecule (1) contains a double bond. The resulting structure, enclosed in square brackets, is the polymer polystyrene (2). Styrene is a ***monomer***, which is defined as **“any molecule that can be converted to a polymer by combining with other molecules of the same or different type**”. 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).



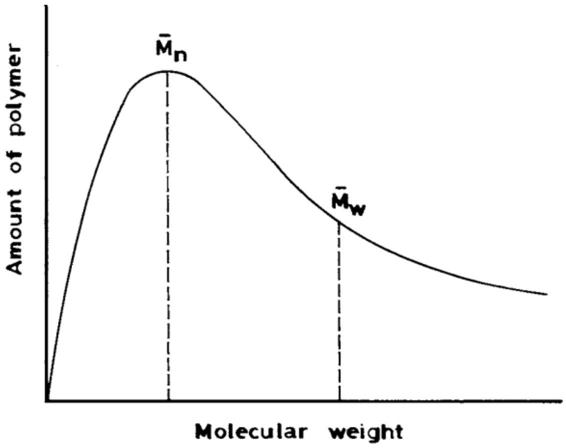
(3) (4) (5)

*Equation 2*

The repeating unit here consists of two structural units:  $-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-$ the residue from hexamethylenediamine; and  $-\overset{O}{C}-(CH_2)_4-\overset{O}{C}-$ , 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.

## DIFFERENT SCHEMES OF CLASSIFICATION OF POLYMERS

Polymers can be classified in many different ways. The classification is based on the origin of the polymer, polymer structure, polymerization mechanism, preparative techniques, or thermal behaviour.

### A. ORIGIN

### Natural vs. Synthetic

Polymers may either be naturally occurring or purely synthetic. Enzymes, nucleic acids, proteins, carbohydrates are polymers of natural origin. Their structures, are normally very complex. Starch, cellulose, and natural rubber, on the other hand, are examples of polymers of plant origin (natural) but have relatively simpler structures than those of enzymes or proteins.

On the other hand there are a large number of synthetic (man-made) polymers consisting of various families: fibres, elastomers, plastics, adhesives, etc.

## B. POLYMER STRUCTURE

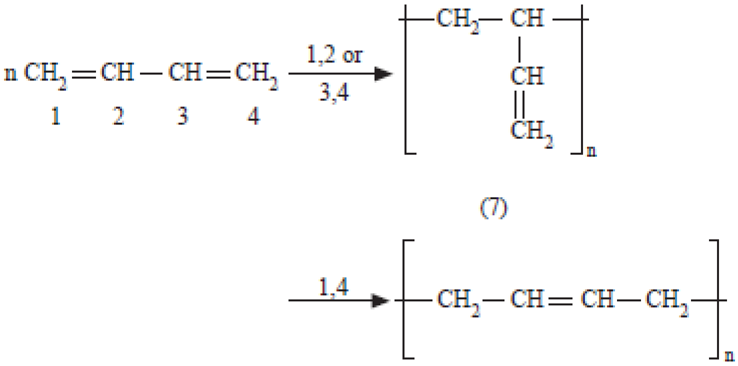
### 1. Linear, Branched or Cross-linked, Ladder vs. Functionality

A polymer is formed when a very large number of structural units (repeating units, monomers) are made to link up by covalent bonds under appropriate conditions. Certainly even if the conditions are "right" not all simple (small) organic molecules possess the ability to form polymers. In order to understand the type of molecules that can form a polymer, two terms are important to know.

***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 whether it has one, two, or greater than two sites available for linking with other molecules. For example, styrene is bi functional. Because, it has an extra pair of electrons in the double bond by which it can form two bonds. The presence of two condensable groups in both hexamethylene diamine (–$NH_2$) and adipic acid (–COOH) makes them bifunctional. However, functionality as defined in case of polymers differs from the conventional terminology of organic chemistry where, for example, the double bond in styrene represents a single functional group. The interlinking capacity of a monomer is ordinarily apparent from its structure, functionality (as used in polymerization reactions) is specific for a given reaction.

A few examples will illustrate this.

- A diamine like hexamethylenediamine has a functionality of 2 in amide-forming reactions such as that shown in equation 2. However, in esterification reactions a diamine has a functionality of zero.
- Butadiene, due to the presence of two double bonds is expected to be tetrafunctional, but it can also have a functionality of 2 depending on the reaction conditions



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

(7)

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

*Equation 3*

Since 1,2/ 3,4 /1,4 linking makes it bi functional. In all these cases one double bond still remains unreacted. But under appropriate reaction conditions such as high temperature or crosslinking reactions, the molecule can undergo additional reaction at this double bond .Butadiene thus becomes tetra functional even though all the reactive sites may not be activated under the same conditions.

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

Now let us consider the reaction between two monofunctional monomers such as in an esterification reaction (Equation 4). It is observed that the reactive groups on the acid and alcohol are used up completely and that the product ester (11) is incapable of further esterification reaction.

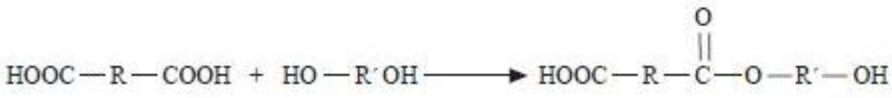
$$R-COOH + R'-OH \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-R'$$

acid (9) alcohol (10) ester (11)

*Equation 4*

But when two bifunctional molecules react in an esterification reaction (Equation 5), the product , ester (14) is itself bifunctional because it is terminated on either side by groups that are capable of further reaction. And this process can be repeated almost indefinitely.

Polyfunctional molecules also behave like this. **So, the generation of a polymer through repetition of one or a few elementary units requires that the molecule(s) must be at least bifunctional.**

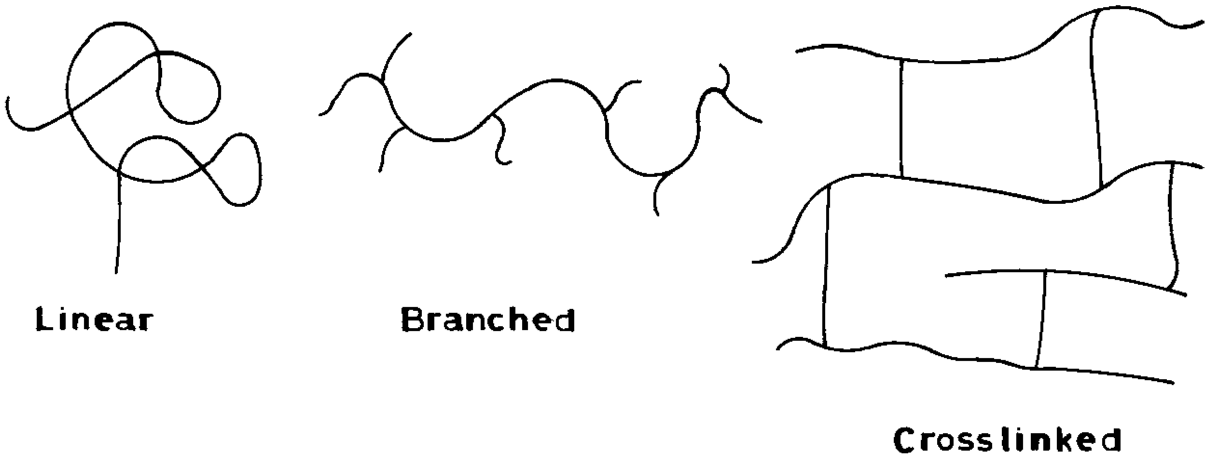


$$HOOC-R-COOH + HO-R'OH \longrightarrow HOOC-R-\overset{\overset{O}{\|}}{C}-O-R'-OH$$

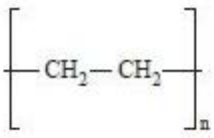
bifunctional (12) bifunctional (13) bifunctional (14)

*Equation 5*

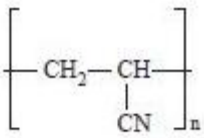
The structural units resulting from the reaction of monomers may be linked together in any possible arrangement. Bifunctional structural units can only link with two other structural units in linear fashion. The resulting polymer is therefore essentially linear. Whereas the reaction between polyfunctional molecules produce structural units that may be linked so as to form nonlinear structures. In some cases the side growth of each polymer chain may be terminated resulting in the formation of branched polymers. In other cases, growing polymer chains become chemically linked to each other, resulting in a cross-linked system.



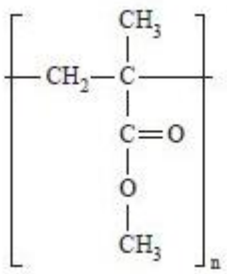
Polystyrene (2), polyethylene (21), polyacrylonitrile (22), poly (methyl methacrylate) (23), and poly(vinyl chloride) (24) are typical examples of linear polymers.

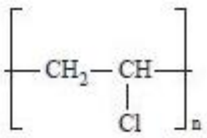

$\left[-CH_2-CH_2-\right]_n$

(21)


$\left[-CH_2-CH(CN)-\right]_n$

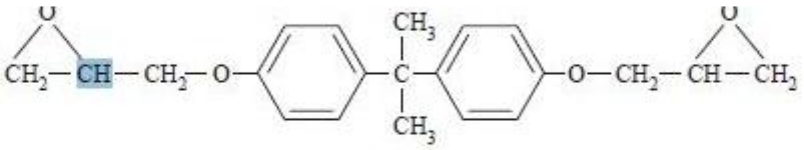
(22)


$\left[-CH_2-C(CH_3)(COOCH_3)-\right]_n$


$\left[-CH_2-CH(Cl)-\right]_n$

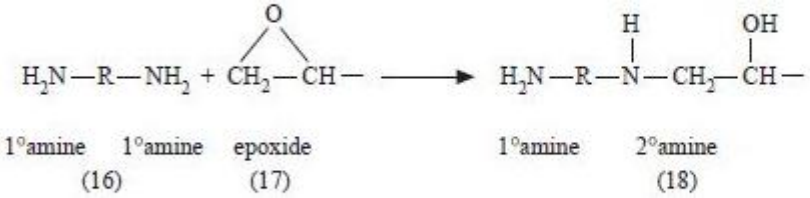
(24)

The formation of a cross-linked polymer is exemplified by the reaction of epoxy polymers, which is used traditionally as adhesives, coatings, as the most common matrix in aerospace composite materials etc. Epoxides at ordinary temperature exists as low molecular-weight viscous liquids or prepolymers. The most widely used prepolymer is diglycidyl ether of bisphenol A (DGEBA),



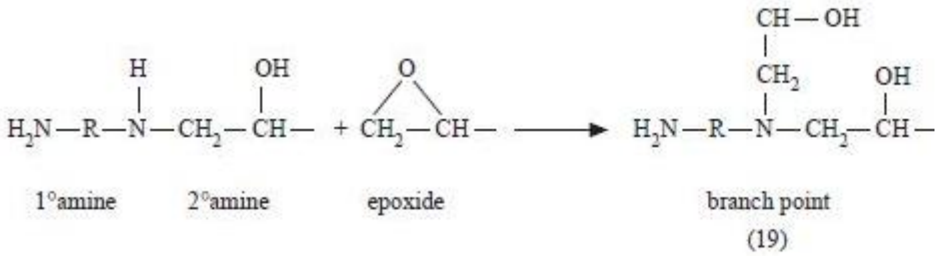
diglycidyl ether of bisphenol A (DGEBA)

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 known as *curing*. Stepwise reactions are shown below
Step-I The attack of an epoxide group by the primary amine



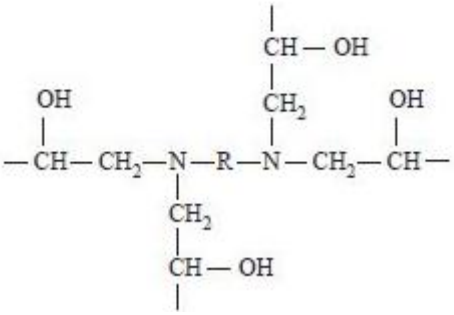
Equation 6

Step-II : The combination of the resulting secondary amine with a second epoxy group to form a branch point (19).



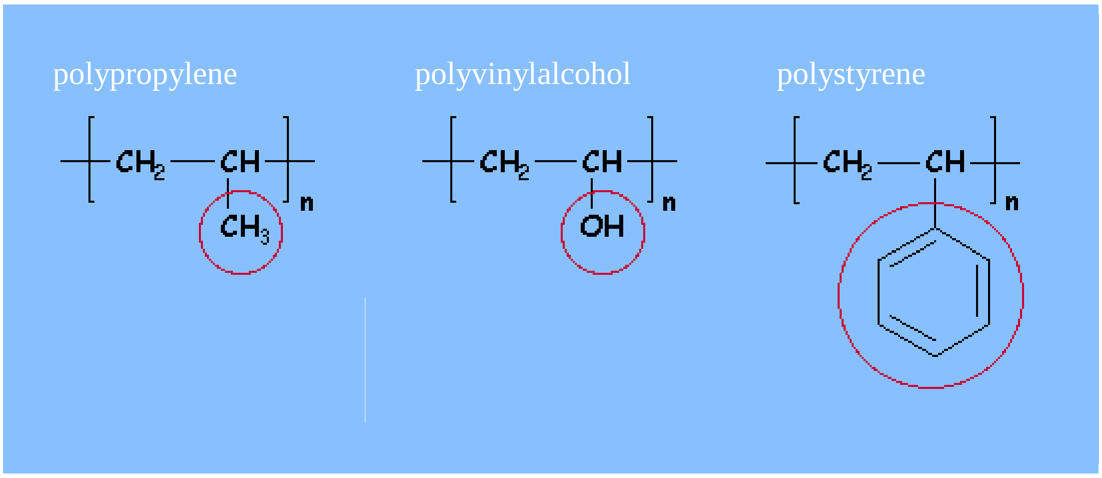
*Equation 7*

The presence of these branch points ultimately leads to a cross-linked infusible and insoluble polymer with structures such as (20).



(20)

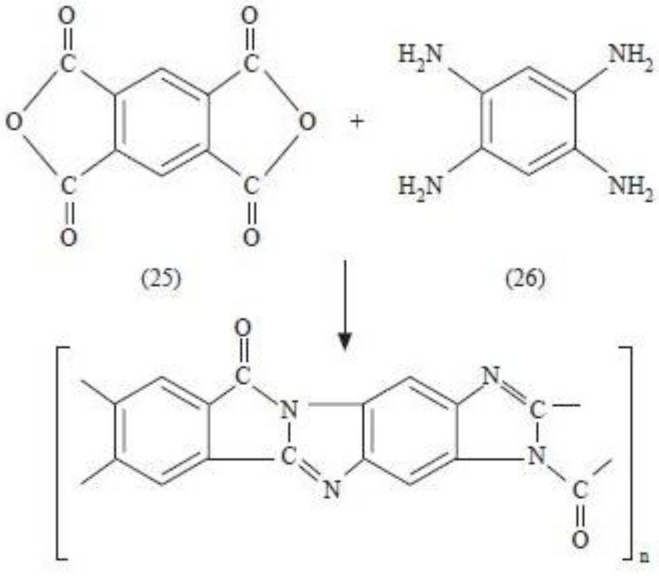
**Pendant group:** It is a small group of atoms (even a small chain sometimes) that hangs off from the main chain (that is, the backbone of the polymer). Pendant groups are usually part of the repeat unit of the polymer



**Properties:** Their structure and chemical nature can confer unique properties on a polymer. For example, linear and branched polymers are usually soluble in some solvent at normal temperatures. But the presence of polar pendant groups can considerably reduce their solubility at room temperature. 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.

**Ladder polymers:** This 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) (27), which is obtained by the polymerization of aromatic dianhydrides such as pyromellitic dianhydride (25) or aromatic tetracarboxylic acids with orthoaromatic tetramines like 1,2,4,5-tetraaminobenzene (26).



(25) (26)

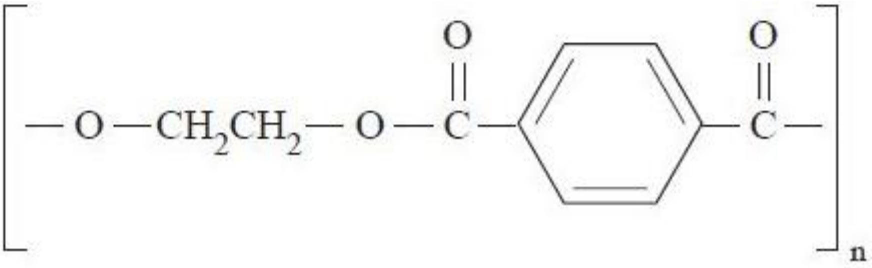
(27)

The molecular structure of ladder polymers is more rigid than that of conventional linear polymers. Many such polymers display exceptional thermal, mechanical, and electrical behaviour. Their thermal stability is due to the molecular structure, which requires that two bonds must be broken at a cleavage site in order to disrupt the overall integrity of the molecule; when only one bond is broken, the second holds the entire molecule together

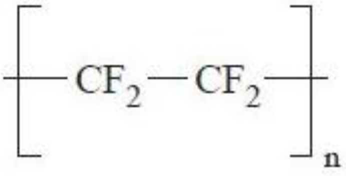
## 2. Amorphous and Crystalline

**Structurally, polymers in the solid state may be classified as *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 leading to ***crystalline polymers*.** For some polymers, individual chains are folded and packed regularly in an orderly fashion resulting in formation of a solid crystalline polymer with a long-range, three-dimensional, ordered arrangement.

However, since the polymer chains are very long, it is impossible for the chains to fit into a perfect arrangement, and 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 (21), polyacrylonitrile (22), poly (ethylene terephthalate) (28), and polytetrafluoroethylene (29).

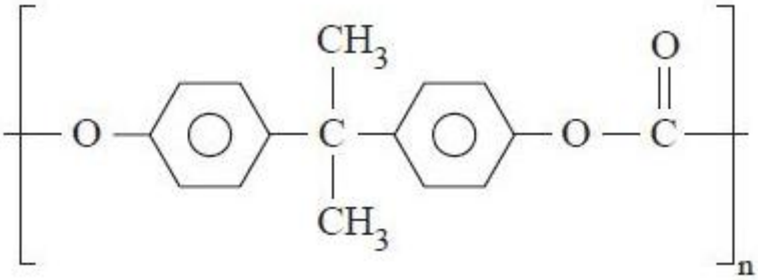


(28)



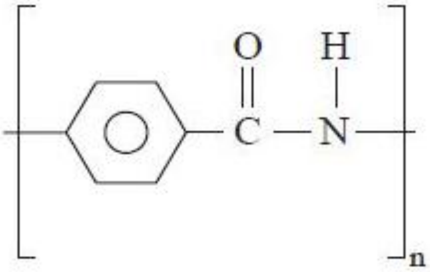
(29)

In contrast to crystallised polymers, **t**he polymers consisting of chains lacking ordered arrangement are known as ***amorphous polymers*.** 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) (23) and polycarbonate (30) are typical examples.



(30)

Melting of either polymers marks the beginning of disorder. There are, however, some polymers which differ 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 (31). 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.



(31)

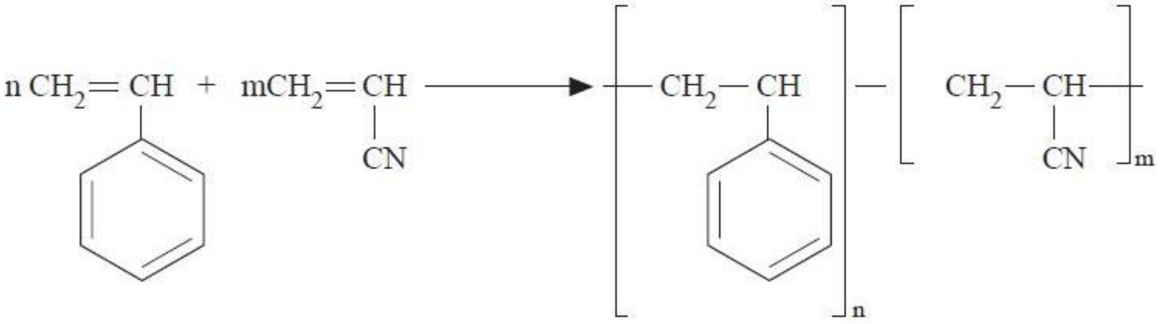
## 3. Homopolymer and Copolymer

Depending on the composition polymers may be further classified into two categories homo polymers or copolymers. 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***.

As indicated earlier, some polymers such as nylon 6,6 (5) and poly(ethylene terephthalate) (28) have repeating units composed of more than one structural unit. Such polymers are still considered homopolymers.

An example is the copolymer (32) 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.



(32)

*Equation 8*

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. If we represent the repeating units by A and B, then the random copolymer might have the structure shown below:

-AABBABABBAAABAABBA-

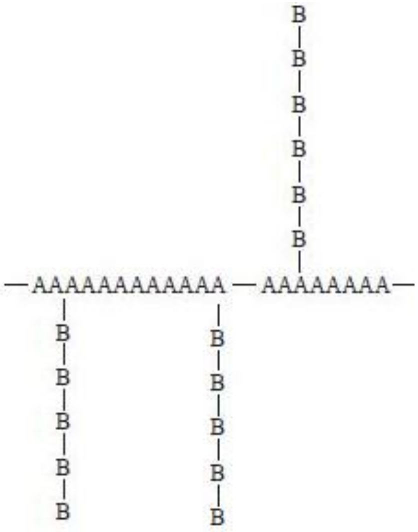
- **Alternating copolymer** -There is an ordered (alternating) arrangement of the two repeating units along the polymer chain:

-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 other monomer type



## 4. Fibers, Plastics, or Elastomers

Polymers may also be classified as fibers, plastics, or elastomers. The reason for this is related to how the atoms in a molecule (large or small) are hooked together. To form bonds, atoms employ valence electrons. Consequently, the type of bond formed depends on the electronic configuration of the atoms.

Depending on the extent of electron involvement, chemical bonds may be classified as either primary or secondary. Primary bonds are of three types: ionic, metallic, and covalent. The atoms in a polymer are mostly, although not exclusively, bonded together by covalent bonds. The forces of attraction responsible for the cohesive aggregation between individual molecules are referred to as secondary valence forces such as van der Waals, hydrogen, and dipole bonds.

Since secondary bonds do not involve valence electrons, they are weak (generally hydrogen and dipole bonds are much stronger than van der Waals bonds.) bonds molecules must come together as closely as possible for secondary bonds to have maximum effect. The ability for close alignment of molecules depends on the structure of the molecules.

Those molecules with regular structure can align themselves very closely for effective utilization of the secondary intermolecular bonding forces. The result is the formation of a *fiber*. ***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. There are, on the other hand, some molecules with irregular structure, weak intermolecular attractive forces, and very flexible polymer chains. These are generally referred to as **elastomers**. Chain segments of elastomers can undergo high local mobility. In absence of applied (tensile) stress, molecules of elastomers usually assume coiled shapes. Consequently, 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.

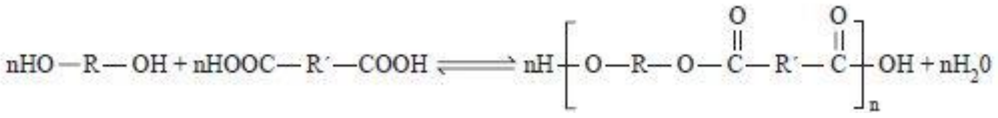
***Plastics*** fall between the structural extremes represented by fibers and elastomers. However, in spite of the possible differences in chemical structure, the demarcation between fibers and plastics may sometimes seem to be unclear. Polymers such as polypropylene and polyamides can be used as fibers and as plastics by a proper choice of processing conditions.

## C. POLYMERIZATION MECHANISM

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

***Condensation*** polymers are formed from a series of condensation reactions type, in which any two species (monomers, dimers, trimers, etc.) can react at any time leading to a larger molecule where 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 glycol and a dicarboxylic acid (Equation 9 )

Examples of condensation polymers include polyamides (e.g., nylon 6,6) (5); polyesters (e.g., poly(ethylene terephthalate) (28); and urea-formaldehyde and phenol–formaldehyde resins.

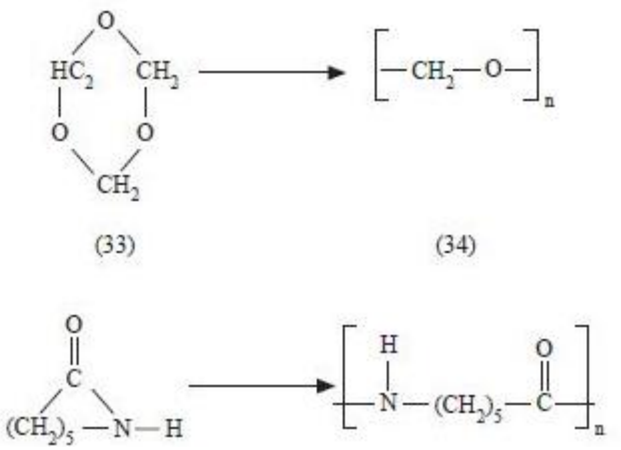


$$nHO-R-OH + nHOOC-R'-COOH \rightleftharpoons nH\left[O-R-O-\overset{\overset{O}{\|}}{C}-R'-\overset{\overset{O}{\|}}{C}\right]_n OH + nH_20$$

*Equation 9*

***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 (2), polyethylene (21),polyacrylonitrile (22), poly(methyl methacrylate) (23),and poly(vinyl chloride) (24).

As the name suggests, ***ring-opening polymerization polymers*** are derived from the cleavage and then polymerization of cyclic compounds. An example of ring-opening polymerization is shown below:

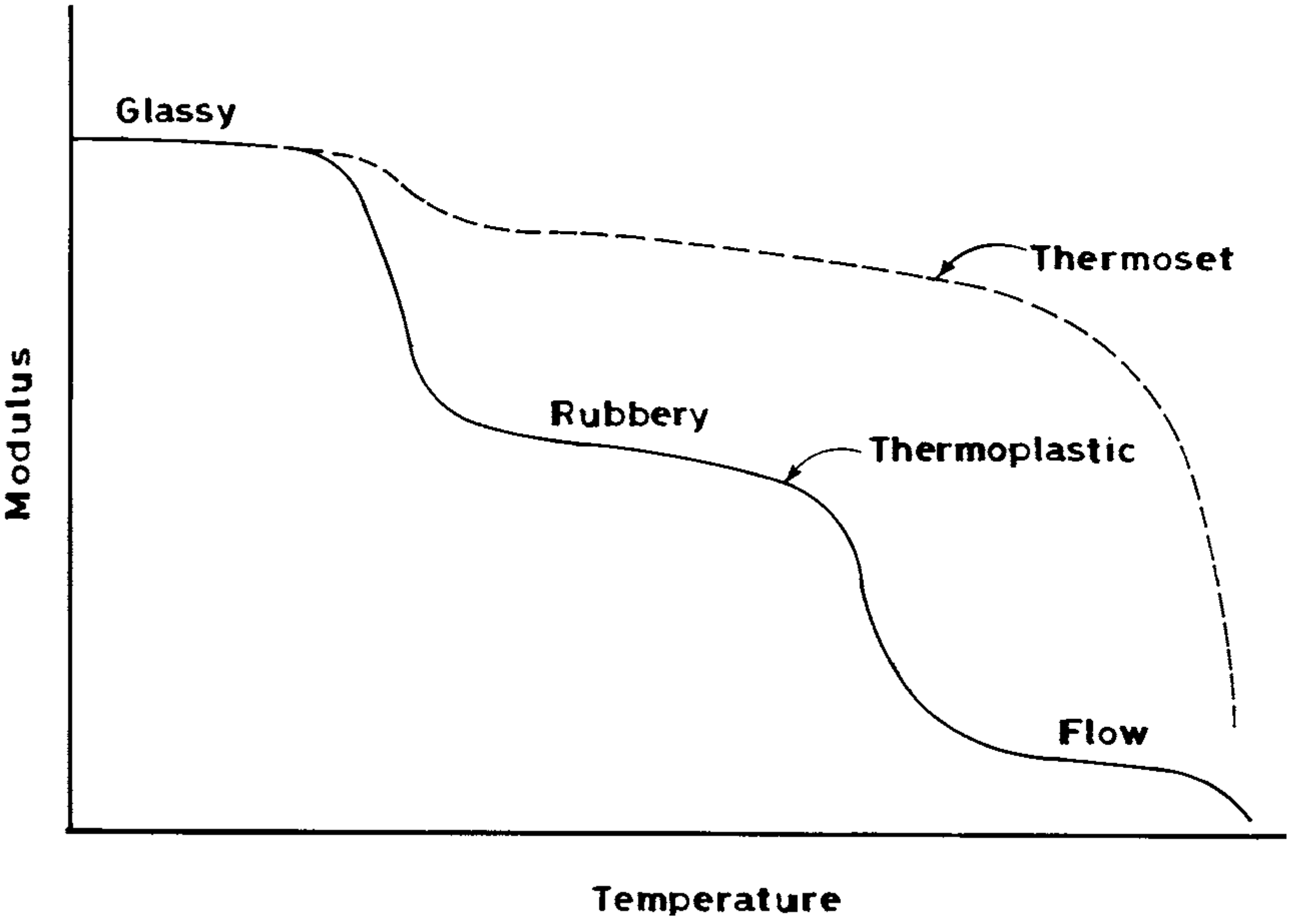


Equation 10

## D. THERMAL BEHAVIOR

On the basis of thermal (thermomechanical) response polymers can be classified as *thermoplastics* and *thermosets*.

As the name suggests, ***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 behaviour is similar to that of candle wax. Examples of thermoplastic polymers are polyethylene, polystyrene, and nylon.



A ***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 include urea–formaldehyde, phenol– formaldehyde, and epoxies.

**The basic structural difference between thermoplastics and thermosets is that** thermoplastic polymers are composed mainly of linear and branched molecules, whereas thermosets are made up of cross-linked systems. Recall from our previous discussion that linear and branched polymers consist of molecules that are not chemically tied together. It is therefore possible for individual chains to slide past one another. For cross-linked systems, however, chains are linked chemically; consequently, chains will not flow freely even under the application of heat and pressure.

The differences in the thermal behavior of thermoplastics and thermosets are best illustrated by considering the change in modulus with temperature for both polymers (Figure 1.3). 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 - hence this phase is also known as 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. As we shall see later, differences exist between amorphous and crystalline thermoplastics in the details and nature of these transitions). For the thermosetting polymer, on the other hand, 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 into ***bulk, solution, suspension*** *and* ***emulsion polymerization.***

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

## F. END USE

Finally, polymers may be classified according to the end use of the polymer. In this case, the polymer is associated with a specific industry (end use): ***diene polymers*** (rubber industry); ***olefin polymer*** (sheet, film, and fiber industries); *and* ***acrylics*** (coating and decorative materials).

## A few points to remember

1. Polymers or macromolecules are giant molecules with molecular weights at least 100 times greater than those of smaller molecules such as water or methanol.

2. If we disregard metals and inorganic compounds, we observe that practically everything else in this world is polymeric. This includes the protein and nucleic acid in our bodies, the fibers we use for clothing, the protein and starch we eat, the elastomers in our automobile tires, and the paint, plastic wall and floor coverings, foam insulation, dishes, furniture, pipes, and so forth in our homes.

3. In spite of the many varieties of fibers, elastomers, and plastic, they all have a similar structure and are governed by the same theories. Linear polymers, such as high-density polyethylene (HDPE), consist of long chains made up of thousands of covalently bonded carbon atoms. The repeating unit for HDPE is represented as [CH2CH2]n, where n is the number of repeating units.

4. Most linear polymers such as HDPE are thermoplastic, i.e., they may be softened by heat and hardened by cooling in a reversible physical process. However, linear polymers like cellulose, which have very strong intermolecular forces (hydrogen bonds), cannot be softened by heating below the decomposition temperature.

5. Thermoset polymers are cross linked and cannot be softened by heating. Thermoplastics such as natural rubber and A-stage resole Bakelite resins can be transformed to thermosetting polymers by the introduction of crosslinks between the polymer chains.

6. Early developments in polymer technology were empirical because of a lack of knowledge of polymer science. Advancements in polymer technology were rapid in the 1930s and 1940s because of the theories developed by Staudinger, Carothers, Mark, and other polymer scientists.

7. Thermoplastic resole resins that may be thermoset by heating are obtained by heating phenol and formaldehyde on the alkaline side. Novolacs are obtained when an insufficient amount of formaldehyde is reacted in acid solution. Novolacs are converted to infusible plastics by heating with hexamethylenetetramine.

## Excercise

1. Name six polymers that you encounter daily.
2. Which would be more likely to be softened by heat?
(a) (1) unvulcanized rubber, or (2) ebonite.
(b) (1) A-stage, or (2) C-stage resole
(c) (1) cellulose, or (2) cellulose acetate.
3. Name a polymer having the following repeating units:
(a) ethylene ($MCH_2CH_2M$)
(b) phenol and formaldehyde residual units.

(c) amino acid residual units

4. In which of the following polymers will hydrogen bonding predominate?

(a) natural rubber (NR).

(b) linear polyethylene (HDPE)

(c) cellulose.

(d) cellulose nitrate

5. Which of the following products are polymeric?

(a) water

(b) wood

(c) meat

(d) cotton

(e) rubber tires

(f) paint

6. Which of the following is a thermoset or cross-linked polymer?

(a) cellulose

(b) unvulcanized rubber

(c) A-stage resole

(d) cellulose nitrate

(e) molded Bakelite

(f) ebonite

7. Which of the items in question 6 are thermoplastic?

8. Why are so many outstanding polymer scientists alive today?

9. What is the molecular weight of $H(CH_2CH_2)1000H$?

10. What is the principal difference between rayon and cellophane?

11. Which is the more heat stable, a resole or a novolac phenolic (Bakelite) resin?