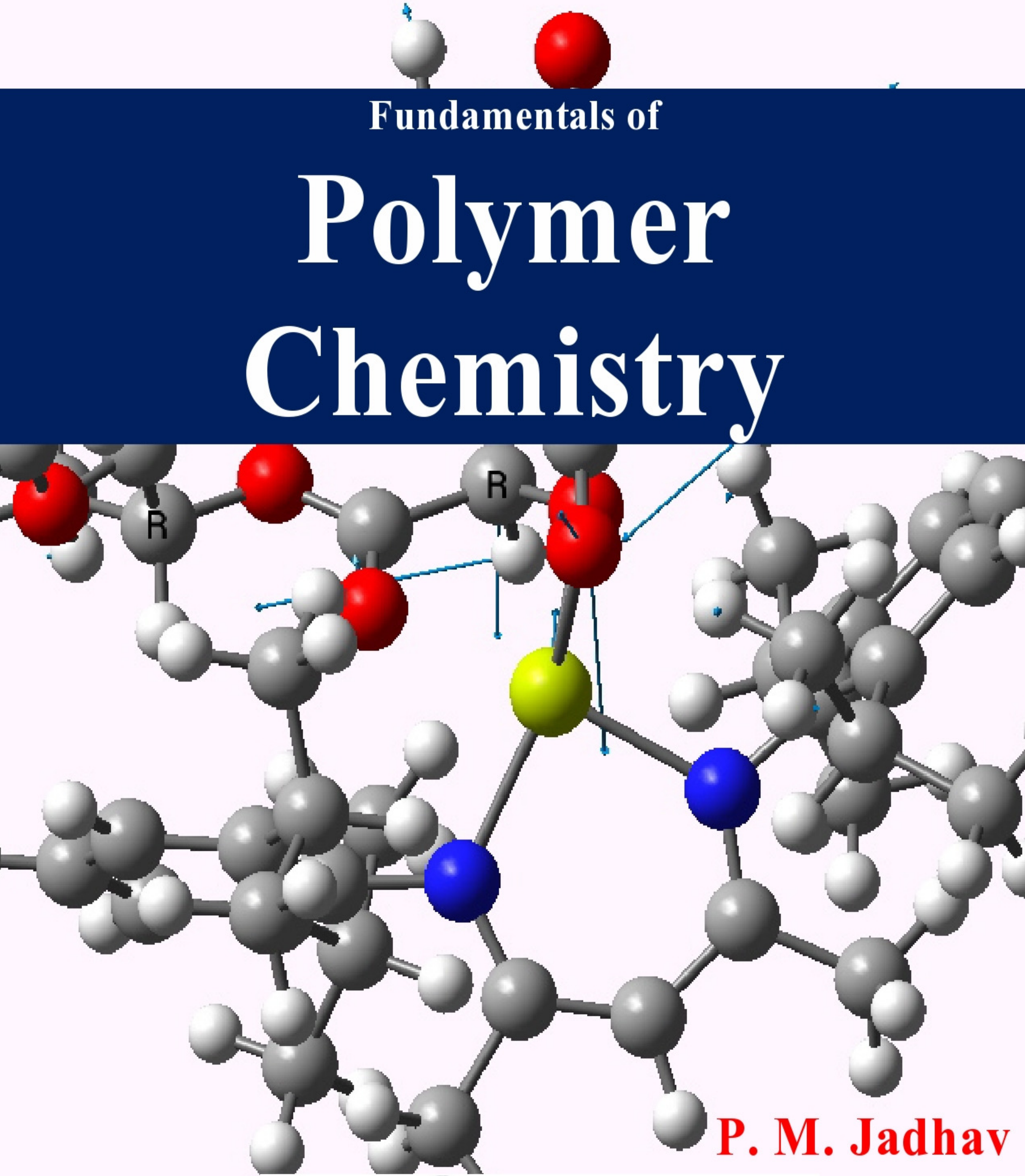
Fundamentals of

Polymer Chemistry



P. M. Jadhav

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Polymer Chemistry

P. M. Jadhav

Assistant Professor
Department of Chemistry
M.S.P Mandals, Shri Muktanand College,
Gangapur Dist.-Aurangabad (MH), India.

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427, Palhar Nagar, RAPTC, VIP-Road, Indore-452005 (MP) INDIA
Phone: +91-731-2616100, Mobile: +91-80570-83382
E-mail: **contact@isca.co.in**, Website:**www.isca.co.in**

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PREFACE

A **"Fundamentals of Polymer Chemistry"**book published by Ideal international e-publication provides information on the polymers, its classification,properties, synthesis and applications of polymers. This book is designed to coversvarious basic concept of polymers chemistry with the help of suitable illustration and reaction mechanism wherever required.

This book contains five chapters in which first chapter is introduction to polymer chemistry and otherchapters give brief information regarding properties and synthesis of polymers.The fouth chapter explains the fundamentals of rubber chemistry and fifth chapter explains the bioderadable polymers chemistry. The long questions are included in the end of every chapter for exercise which helps students to understand concept. I believe that, this book will be very useful for graduate and postgraduate scholar for their study especially in polymer chemistry.

I am thankful to Shri. AppasahebjiPatil, Dr. R. P. Pawar and Dr. ShyamKadam for their valuable guidance and suggestion for this book. I am also grateful to my family and friends who constantly and morally encouraged me.

Likewise I am thankful to Ideal International E-Publication for his cooperation during publishing such nice book.

I am aware that there is more scope for improvement in this book so, useful comments and suggestions for improvement of this book from teachers and students are welcome.

P.M. Jadhav
Jadhavpm767@gmail.com

DEDICATED TO
LATE SHRI. SUKHADEV L. JADHAV
SMT. BHIMBAI S. JADHAV
MY GRANDFATHER AND GRANDMOTHER

Index

01) Introduction to Polymer Chemistry

Contents: Introduction, nomenclature of polymer, structure of polymer, classification of polymer based on the source of polymer, structure of polymer, mode of polymerization, molecular force and growth polymerization, conducting polymers, classification of conducting polymers, liquid crystal polymers and their types, properties and use of liquid crystal polymers.

Polymers play a very important role in human life. Our body is made of lot of polymers, e.g. Proteins, enzymes, etc. Other naturally occurring polymers like wood, rubber, leather and silk are have wide application. Now a day synthetic polymer like useful plastics, rubbers and fiber materials are synthesized. Leo Baekeland patented the first totally synthetic polymer called Bakelite (1910). Bakelite is a versatile, durable material prepared from low-cost materials phenol and formaldehyde and was the most important synthetic polymer material. In the 1920s Hermann Staudinger showed that polymers were high-molecular-weight compounds held together by normal covalent bonds.

The suffix in polymer 'mer' is originated from Greek word meros– which means part. The word polymer is thus coined to mean material consisting of many parts or mers. A macromolecule having high molecular mass (10^3-10^7u) and generally not a well-defined structure or molecular weight. The macromolecules formed by joining of repeating structural units on a large scale. The repeating structural units are simple and reactive molecules linked to each other by covalent bonds. This process of formation of polymers from respective monomers is called polymerization.Most of the polymers are basically organic compounds, however they can be inorganic (e.g. silicones based on Si-O network).

Some important terms in polymer chemistry:

Plastics: Plastics are the substances or compounds of high polymer class which can be molded into articles by heat and pressure. These are mostly synthetic in nature and are called synthetic resins. They possess high elasticity.

Resins: Naturally occurring organic substances which are solid or semi-solid polymeric materials are known as resins. It is of natural or synthetic organic substances of relatively high molecular weight which exhibits no sharp melting point and predominantly amorphous in nature. It is insoluble in water and soluble in some organic solvents. These are organic polymers.

Example: Wood, cotton, silk, leather, amber, rubber, shellac, resin etc.

Fibers: If the inter-chain force of attraction in a polymer is very strong, then it must be hard and durable and is known as fiber. In fiber, the chains are oriented along the direction of the pull and inter-chain forces keep these very strong enough.

Rubber: If the inter- chain forces are very weak, then the polymer is elastic, flexible and soft in nature and is known as rubber. The molecular chains are stretched on pulling but the inter chain forces not being strong enough to keep it in the oriented position, then the chains regain their original position after removal of the deforming forces.

Micelles: They are aggregation of the crystallites of colloidal dimensions that exist in the solid state or in solution as spherical or rod likes shapes. The uniform chemical or mechanical treatment such as soaps or colloidal electrolytes in plastic it has been observed that these long chains wonder successively through disordered, random regions, through bundles of organized regions (micelles) amorphous, again ordered regions and so on.

Polymer:

A large molecule having high molecular mass formed by joining a repeating unit of smaller molecules (monomers) through a covalent bonding is called as polymer. Monomer is small individual repeating unit or molecules are called monomers. Monomer is basic unit of polymer. E.g. In polyethylene is an ethylene is monomer. Polymers usually contain more than five monomers, and some may contain hundreds or thousands of monomers in each chain. The process by which polymers are formed by linking monomers through chemical reaction called **polymerization.**

n.[Monomer] → Polymer

Some examples of polymer listed in the following table

Sr. No.	Monomers	Polymers
1	Ethylene	Polyethylene
2	Vinyl chloride	Polyvinyl chloride (PVC)
3	Styrene	Polystyrene
4	Butadine	Polybutadine
5	Propylene	Polypropylene
6	Acrylonitrile	Polyacrylonitrile
7	Caprolactum	Nylon-6
8	Glycol and Terephthalic acid	Terylene or Decron
9	Hexamethylenediamine and Adipic acid	Nylon-6,6
10	Phenol and Formaldehyde	Novolac

Nomenclature of Polymers:

1. Simple vinyl polymers are designated by attaching the prefix poly to the monomer name. To name a polymer prefix **"poly"** to the monomer from which the polymer derived.

Examples:

Sr. No.	Name of monomer	Name of polymer
1	Styrene	Polystyrene
2	Ethylene	Polyethylene
3	Propylene	Polypropylene

2. When the monomer name consists of more than one word or is preceded by a letter or number, the monomer is enclosed by parentheses preceded by the prefix ***"poly"***.

Example**:** The polymer obtained from the polymerization of 4-chlorostyrene is poly(4-chlorostyrene) and that from vinyl acetate is poly (vinyl acetate).

3. Tacticity may be noted by prefixing the letter *i* (isotactic) or *s* (syndiotactic) before prefix ***"poly"*** as in *i*-polystyrene.

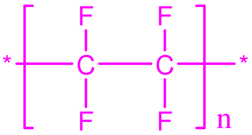
4.Geometric and structural isomers may be indicated by using the appropriate prefixes, cis or trans and 1,2- or 1,4-, before prefix ***"poly"***. Example: trans-1,4-poly(1,3-butadiene).

Nomenclature rules for non-vinyl polymers such as condensation polymers are generally more complicated than for vinyl monomers. The non-vinyl polymers are usually named according to the initial monomer or the functional group of the repeating unit.

Example: The most important commercial nylon, commonly called nylon-6,6 is more descriptively called poly(hexamethyleneadipamide) with adipic acid.

The IUPAC structure-based rules for naming organic, inorganic and coordination polymers have been compiled in several publications.

1. Examples: The IUPAC name for polystyrene is poly(1-phenylethylene) and that for polytetrafluoroethylene is poly(difluoromethylene)—a polymer more typically recognized by its trademark, Teflon.



poly(difluoromethylene)
Teflon

2. The IUPAC name for the polycarbonate of bisphenol-A mentioned earlier is poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene).

Some useful set of two, three, and four-letter abbreviations for the names of many common thermoplastics, thermosets, fibers, elastomers, and additives are developed. These abbreviations are convenient and widely used.

Examples

Sr. No.	Abbreviation	Name of polymer
1	PS	Polystyrene
2	PVC	Poly(vinyl chloride)
3	PMMA	Poly(methyl methacrylate)
4	PTFE	Polytetrafluoroethylene
5	PC	Bis-phenol-A polycarbonate

The copolymers are named by incorporating an italicized connective term between the names of monomers contained within parentheses or brackets or between two or more polymer names. The connective term designates the type of copolymer as indicated for six important classes of copolymers mention in following table.

Scheme for Naming Copolymers

Type	Connective	Example
Unspecified	-co-	Poly[styrene-co-(methyl methacrylate)]
Statistical	-stat-	Poly(styrene-stat-butadiene)
Random	-ran-	Poly[ethylene-ran-(vinyl acetate)]
Alternating	-alt-	Poly[styrene-alt-(maleic anhydride)]
Block	-block-	Polystyrene-block-polybutadiene
Graft	-graft-	Polybutadiene-graft-polystyrene

Polymer Structure:

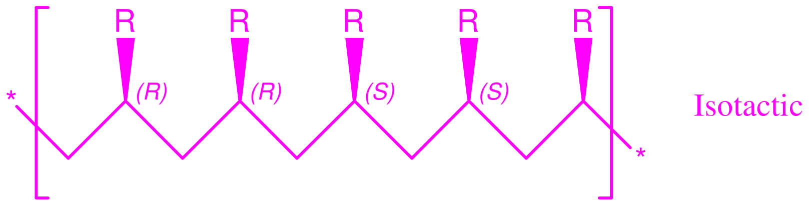
Tacticity:

The difference in configuration due to the orientation of different functional groups with respect to the main chain is called tacticityin addition to the type, number, and sequential arrangement of monomers along the chain, the spatial arrangement of substituent groups is also important in determining properties. The possible steric configurations of an asymmetric vinyl-polymer chain can be best represented by drawing the chain in its extended-chain or planar zigzag conformation.

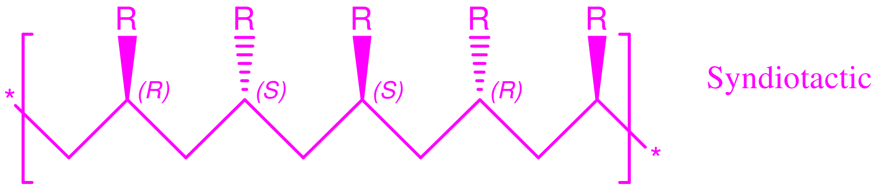
A conformation describes the geometrical arrangement of atoms in the polymer chain while configuration denotes the stereo chemical arrangement of atoms. Unlike the conformation, the configuration of a polymer chain cannot be altered without breaking chemical bonds. For long, flexible polymer chains, the total number of conformations is nearly infinite. The extended-chain conformation for vinyl polymers is often the lowest-energy conformation.

Several different placements of the asymmetric substituent groupsR are possible. As examples, a substituent group may be a methyl group as in polypropylene, a chlorine atom as in poly(vinyl chloride), or a phenyl ring as in polystyrene.

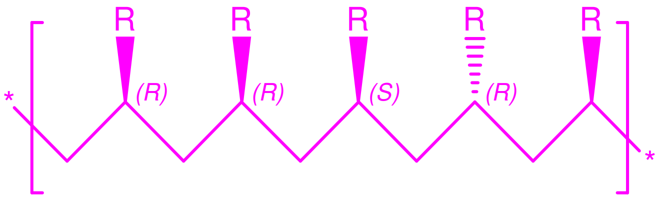
Isotactic – If all the functional groups are arranged on the same side of main chain is called isotactic. In one configuration, all the R groups may lie on the same side of the plane formed by the extended-chain backbone. Such polymers are termed isotactic.



Syndiotactic- If all the functional groups are arranged in the alternative fashion of main chain is called Syndiotactic. If the substituent groups regularly alternate from one side of the plane to the other, the polymer is termed syndiotactic.



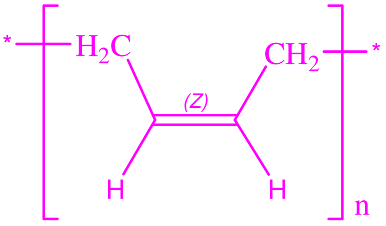
Atactic- If all the functional groups are arranged in random of main chain is called atacticpolymers with no preferred placement are atactic.



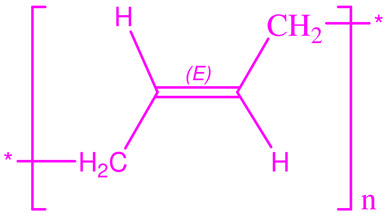
Generally, the isotactic or syndiotactic polymers are partially crystalline, while atactic polymers are amorphous indicating the absence of all crystalline order. In addition to crystallinity, other polymer properties like thermal and mechanical behavior also affected by the tacticity of the polymer. Whether a specific polymer will be atactic, isotactic, or syndiotactic depends upon the specific conditions of the polymerization, such as the temperature and choice of solvent. Commercial polypropylene is an important example of an isotactic polymer. Atactic and syndiotactic forms of this polymer can also be prepared by controlling the polymerization conditions. Atactic polypropylene is an amorphous, tacky polymer with no commercial importance. Commercial poly(vinyl chloride) is an example of a polymer with imperfect tactic structure. Although the overall structure of commercial-grade PVC can be reasonably characterized as atactic, there are populations of repeating units whose sequences are highly syndiotactic and that impart a small degree of crystallinity to the commercial resin

Geometric Isomerism:

Polymers with unsaturated sites double bond in the repeat unit in chain give rise to different geometric isomers. 1,3-butadiene can be polymerized to give poly(1,2-butadiene) or either of two geometric isomers of poly(1,4-butadiene). These two polymers are called cis and trans poly(1,4-butadiene). In the cispolybutadiene, first and four carbons lie on the same side of central double bond while in transpolybutadiene, first and four carbon lie on the opposite side of central double bond.



Cis-1,4-polybutadiene



Trans-1,4-polybutadiene

Classification of polymers:

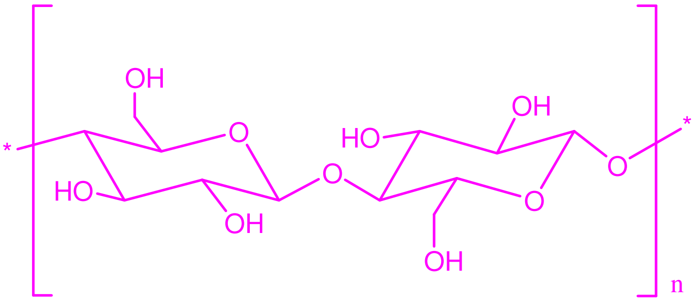
Polymers are numerous in numbers with different behaviors and can be found naturally or prepared synthetically, they can be classified in various ways. Polymers are classified in several ways by how the molecules are synthesized, by their molecular structure, or by their chemical family. There are several ways of classification of polymers based on some special considerations

01. Classification Based on Source

Based on the source of polymer they are classified into three sub categories.

a) Natural polymers

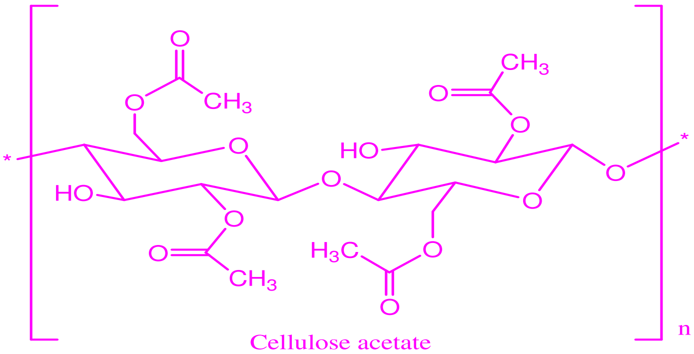
Polymers which are isolated from natural origin are called natural polymers. These polymers are found in plants and animals. E.g. Proteins, cellulose, starch, some resins and rubber.



Cellulose

b) Semi-synthetic polymers

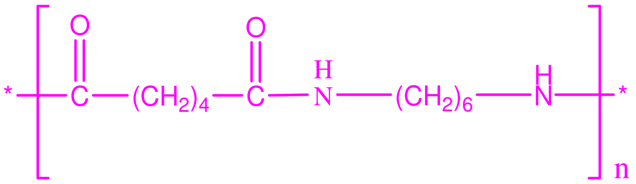
The polymers are obtained by chemical treatment of natural polymer to improve their physical properties are called semisynthetic polymers. Semisynthetic polymers are simply chemically modified natural polymers. E.g. Cellulose acetate (rayon) and cellulose nitrate from cellulose.



Cellulose acetate
Rayon

c) Synthetic polymers

Polymers are synthesized in laboratory from monomers are called synthetic polymers. E.g. Polyethylene, Nylon 6,6, Buna–S, Polystyrene, Terylene, etc.



$$*\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\right]_n*$$

Nylon 6,6

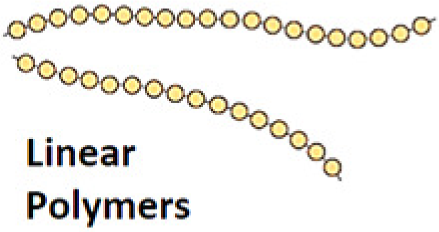
2. Classification Based on Structure of Polymers

On the basis of the polymers structure they are divided into three subgroups.

a) Linear polymers

These polymers consist of long and straight chains well packed structure. The examples are high density polythene, polyvinyl chloride, etc. They have high melting point, high densities and high tensile strength.

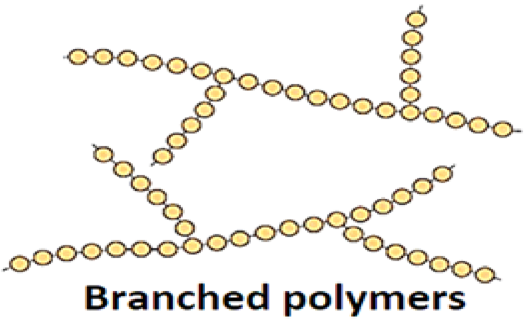
The structural arrangement is represented as:



b) Branched chain polymers

These polymers contain linear chains having some branches and irregular packed structure. e.g., low density polythene and glycogen. They have low tensile strength, low density and lower melting point in comparison with linear polymers.

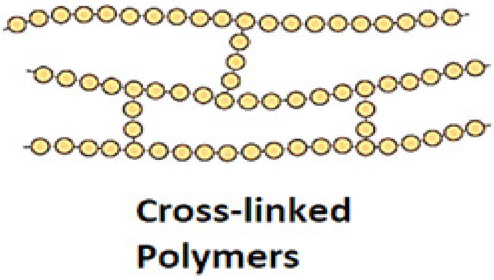
These are depicted as follows:



c) Cross linked or Network polymers

These are usually formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. They are hard and rigid. E.g. Bakelite, melamine, etc.

These polymers are depicted as follows:

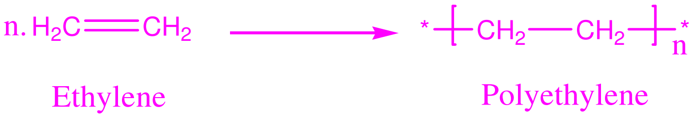


03. Classification Based on Mode of Polymerization

On the basis of mode of polymerization,they are classified into two sub groups.

a) Addition polymers

The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds. E.g. The formation of polythene from ethene and polypropene from propene. However, the addition polymers formed by the polymerization of a single monomeric species are known as homopolymer. E.g. Polythene.

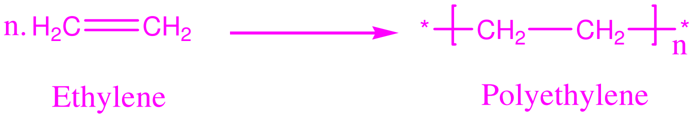

$$n.\,H_2C{=}CH_2 \longrightarrow {*}\!\left[CH_2{-}CH_2\right]_n\!{*}$$

Homopolymer:

When all the monomers are the same, the molecule is called a Homopolymer. A homopolymer consist of identical monomers. When monomer A joined to form polymer, such kind of polymer is known as homopolymers.

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-

Eg. Monomers ethylene's joined together to give polymer polyethylene.


$$n.\,H_2C{=}CH_2 \longrightarrow {*}\!\left[CH_2{-}CH_2\right]_n\!{*}$$

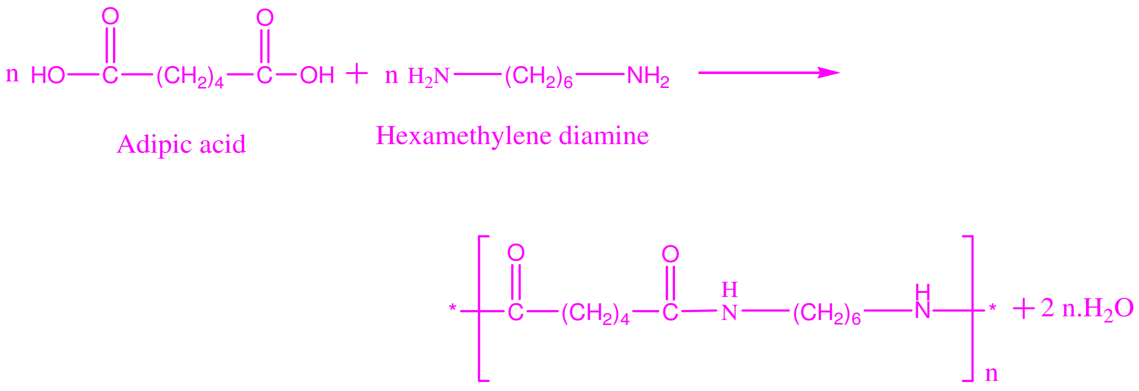
Examples: Polystyrene, Polypropylene, Polybutadine, Polyvinyl chloride, etc.

Copolymer:

When there is more than one type of monomer present, the molecule is called a copolymer. A copolymer consists of monomers of different chemical structure. When two different monomers A and B joined to form polymer is known as copolymers.

- A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-

Eg. Monomers hexamethylenediamine and Adipic acid joined together to give polymer Nylon-6,6.



$$n\ HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\ H_2N-(CH_2)_6-NH_2 \longrightarrow *\!\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}\right]_n\!* + 2\,n.H_2O$$

Nylon 6,6

Examples: Terylene, Novolac, etc.

Copolymers, polymers made from more than one monomer, are as common as homopolymer. The presence of more than one monomer in a chain makes some control of properties possible. Some structural units stiffen the chain, others make it more flexible. Often a second monomer is added to allow cross linking. Copolymers are classified according to the distribution of monomers in the macromolecule. In copolymerization different monomers incorporated during the growth of the polymer chain can lead to:

a) Alternating
b) Random
c) Block
d) Graft

a. **Alternating copolymer:** there is alternate pattern to the distribution of monomer units in a alternating copolymer.

- A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-

b. **Random copolymers:**As the name implies, there is no pattern to the distribution of monomer units in a random copolymer.

-A-A-B-A-B-B-A-A-B-B-A-B-A-B-B-B-A-B-A-B-A-A-A-

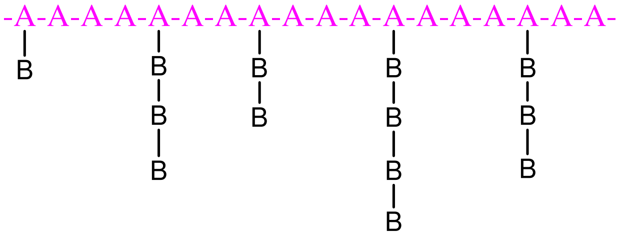
Styrene–butadiene rubber is a random copolymer. It is prepared by two methods, free-radical and anionic polymerization, both of which are carried out on a mixture of styrene and 1,3-butadiene. Free-radical initiation is essentially nonselective and gives the random copolymer. Anionic initiation is carried out under conditions designed to equalize the reactivity of the two monomers so as to ensure randomness.

c. Block copolymers: The main chain contains sections (blocks) of repeating units derived from different monomers. The sequence:

-A-A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B-B-

The copolymer shows only two blocks, one derived from A and the other from B. A macromolecule derived from A and B can contain many blocks. The living polymers generated by anionic polymerization are well suited to the preparation of block polymers. The properties of the block copolymer prepared by anionic living polymerization are different from the random styrene–butadiene copolymer.

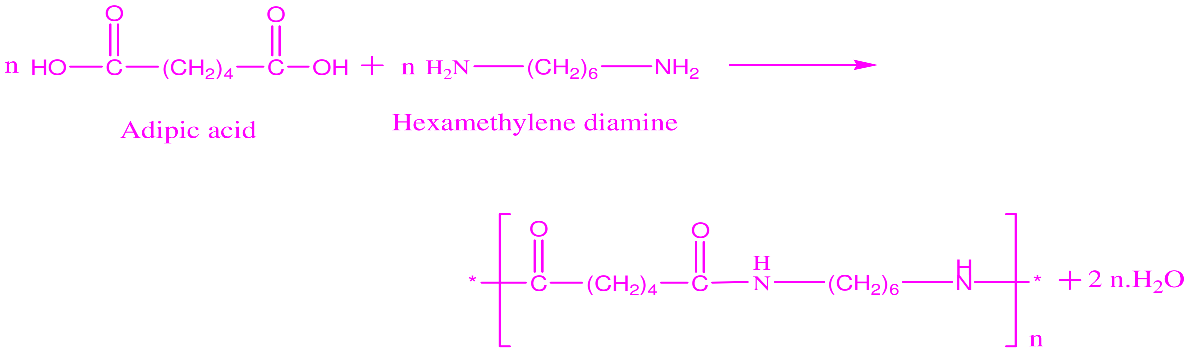
d. Graft copolymer: If main chain consists of one monomer and branched chain consists of other monomers are called Graft copolymers. The main chain bears branches (grafts) that are derived from a different monomer.



The polymers made by addition polymerization from two different monomers are termed as copolymers, e.g., Buna-S, Buna-N, etc.

b) Condensation polymers

The condensation polymers are formed by repeated condensation reaction between two different bi-functional or tri-functional monomeric units. In these polymerization reactions, the elimination of small molecules such as water, alcohol, hydrogen chloride, etc. take place. The examples are terylene (dacron), nylon6,6 nylon6 etc. For example, nylon 66 is formed by the condensation of hexamethylenediamine with adipic acid.



$$n\ HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH + n\ H_2N-(CH_2)_6-NH_2 \longrightarrow$$

Adipic acid

Hexamethylene diamine

$$*\!\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\right]_n\!* + 2\,n.H_2O$$

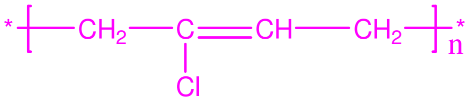
Nylon 6,6

04. Classification Based on Molecular Forces

A large number of polymer applications in different fields depend on their unique mechanical properties like tensile strength, elasticity, toughness, etc. These mechanical properties are governed by intermolecular forcesi.e. van der Waals forces and hydrogen bonds present in the polymer. These forces also bind the polymer chains. Under this category, the polymers are classified into the following four sub groups on the basis of magnitude of intermolecular forces present in them.

a) Elastomers

Elastomers are also known as rubbers. These are solids with elastic properties. In these elastomeric polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces permit the polymer to be stretched. A few crosslinks are introduced in between the chains, which help the polymer to retract to its original position after the force is released as in vulcanized rubber. These are polymers which can undergo large elongations under load, at room temperature, and return to their original shape when the load is released. The examples are buna-S, buna-N, neoprene, etc. There are number of man-made elastomers in addition to natural rubber.



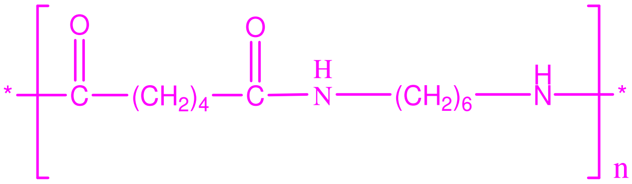
$$*-\left[CH_2-\underset{\underset{Cl}{|}}{C}=CH-CH_2\right]_n-*$$

Neoprene

b) Fibers

Fibers are the thread forming solids which possess high tensile strength and high modulus. These characteristics can be attributed to the strong intermolecular forces like hydrogen bonding. These strong forces also lead to close packing of chains and thus impart crystalline nature.

Example: Nylon 6, 6, Terylene, etc.



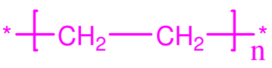
$$*-\left[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-\overset{H}{N}-(CH_2)_6-\overset{H}{N}\right]_n-*$$

Nylon 6,6

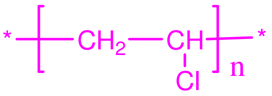
c) Thermoplastic polymers

These plastics soften when heated and harden when cooled. These materials are normally fabricated by the simultaneous application of heat and pressure. They are linear polymers without any cross-linking in structure where long molecular chains are bonded to each other by secondary bonds and/or inter-wined. They have the property of increasing plasticity with increasing temperature which breaks the secondary bonds between individual chains. These are the linear or slightly branched long chain molecules easily moulded in desired shapes and capable of repeatedly softening on heating and hardening on cooling. These polymers possess intermolecular forces of attraction intermediate between elastomers and fibers.

Example: polythene, polystyrene, polyvinyls(PVC), acrylics, nylons, polypropylene, polymethyl methacrylate etc.



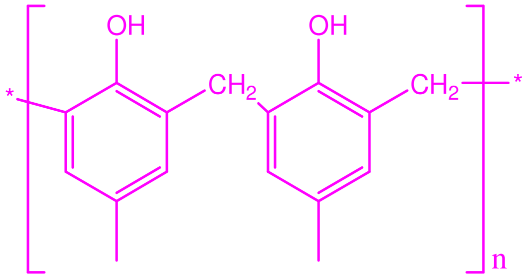
Polyethylene



PVC

d) Thermosetting plastic polymers

These plastics require heat and pressure to mold them into shape. These polymers are cross linked or heavily branched molecules. They are not soft on heating under pressure and not remolded. Thermosetting polymers on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reused. Example: Bakelite, urea-formaldehyde resins, etc.



Bakelite

The Thermoplastics and Thermosetting plastics polymer are differentiated in the following table:

S. No.	Thermoplastics	Thermosetting Plastics
1	Formed either by addition or by condensation polymerization reactions	Formed by condensation polymerization reactions
2	They have either linear or branched structures.	They have three-dimensional cross-linked network structures
3	Adjacent polymer chains are held together by either vanderwaals forces, or by dipole dipole forces or by hydrogen bonds	Adjacent polymer chains are held together by strong covalent bonds called crossed-links
4	They soften on heating and stiffen on cooling	They do not soften on heating.
5	Low molecular weight thermoplastics are soluble in their suitable solvents.	They are insoluble in any solvent.
6	They can be remoulded, re-shaped and re-used.	They can be reclaimed from waste i.e., they can be recycled
7	There is no change in chemical composition and structure during moulding process.	They undergo chemical changes such as further polymerization and cross-linking during moulding process.
8	They are soft and flexible	They are hard, rigid and infusible.

9	They can be reclaimed from waste i.e.; they can be recycled.	They cannot be reclaimed from waste. They cannot be recycled.
10	They undergo reversible changes, on the application of heat.	They undergo irreversible changes on the application of heat.
11	They swell or dissolve in organic solvents.	They neither dissolve nor swell in organic solvents.
12	They are tough materials.	They are brittle materials.
13	The moulded articles are to be cooled to room temperature before taking out from the moulds to avoid deformation.	The moulded articles can be taken out of the moulds even when they are still hot without any deformations
14	Curing can be done by cooling.	Curing can be done by applying heat and pressure.
15	Examples: Polyethylene (PE), Bakelite.	Examples: Phenol- formaldehyde resin (PF), urea- formaldehyde resin

05. Classification Based on Growth polymerization

The addition and condensation polymers are now days also referred as chain growth polymers and step growth polymers depending on the type of polymerization mechanism, they undergo during their formation

Chain Growth Polymers

Addition polymers are also called as chain growth polymers as they are formed by repeated addition of monomers unit.

Step growth polymers

Condensation polymers are also called as step growth polymers as they are formed as a result of stepwise condensation reactions.

Conducting polymers

A polymer that can conduct electricity is known as conducting polymer. Most organic polymers are acts as insulators by nature. However, a few conducting polymers exist that have alternating single and double bonds along the polymer backbone (conjugated bonds) or that are composed of aromatic rings such as phenylene, naphthalene, anthracene, pyrrole, and thiophene which are connected to one another through carbon-carbon single bonds.

The first polymer with significant conductivity synthesized was polyacetylene. Its electrical conductivity was discovered by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid who received the Nobel Prize in Chemistry in 2000 for this discovery.

Classification of conducting polymers:

1. Intrinsic conducting polymers: The polymers are characterized by have intensive conjugation of the double bonds in their structure or backbone which is responsible for conductance. The intrinsic conducting polymers are of two types.

a. Conjugated conducting polymer

b. Doped conducting polymer

2. Extrinsic conducting polymers: The polymers are characterized by have extensive conjugation of the double bonds in their backbone which is responsible for conductance. The intrinsic conducting polymers are of two types.

a. Polymer with conducting element.

b. Polymer with conducting blends.

Conducting polymers having conjugation:

Such polymers contain conjugated electrons in the backbone which possess their conductivity due to π electrons. Overlapping of conjugated electrons over the entire backbone results in the formation of valence bands as well as conduction bands that extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap. Thus, electrical conduction occurs only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band. Conductivity of these polymers having conjugated electrons in the backbone is not sufficient for their use in different applications.

The conductivity of non-doped, conjugated polymers such as polyacetylene is due to the existence of a conducting band similar to a metal. In a conjugated polymer three of the four valence electrons form strong σ bonds through sp^2 hybridization where electrons are strongly localized. The remaining unpaired electron of each carbon atom remains in a p_z orbital. It overlaps with a neighboring p_z orbital to form a π bond. The π electrons of these conjugated p_z orbitals overlap to form an extended p_z orbital system through which electrons can move freely (delocalization of π electrons).

Doped conducting polymers:

The conducting polymers having conjugated double bonds (π electrons) in their backbone can easily be oxidized or reduced because they possess low ionization potential and high electron affinities. Hence their conductance can be increased by introducing a positive charged (electron is removed from the valence band by oxidation) or negative charged is added to the conducting band by reduction does the polymer become highly conductive. This process is similar to semiconductor technology and is known as doping. Doping is again classified into four types are explain below.

a) **P-doping**: P-doping is done by oxidation of a conducting polymer such as polyacetylene in presence of lewis acid or iodine vapour, chlorine, arsenic pentafluoride etc. Some of the π-bonds are oxidized by treating the polymer with an oxidizing agent. During oxidation process the removal of π electron from polymer backbone leads to the formation of delocalized positive ions having hole in between valence band and conducting band. This positive charge delocalized and responsible for conduction when place in electric field.

b) **n-doping**: n- doping is carried out by reducing process by the addition of an electron in polymer backbone by reducing agents like lithium, and sodium naphthaline. Some of the π-bonds are reduced by treating the polymer with a reducing agent.

c) **Electrochemical p- and n-doping**: Electrochemical p and n doping is achieved by cathodic reduction (p) or by anodic oxidation (n).

d) **Photo-Induced Doping**: The polymer is exposed to high energy radiation that allows electrons to jump to the conducting band. In this case, the positive and negative charges are localized over a few bonds.

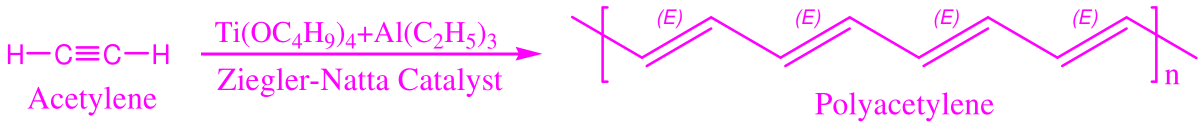
Doping increases the conductivity by many orders of magnitude. Another method to increase conductivity is mechanical alignment of the polymer chains. The table below lists typical conductivities of some common conjugated polymers. The actual conductivity not only depends on the structure and morphology of the polymer but also on the type of doping and its concentration.

Sr. No.	Compound	Conductivity
1	Polyaniline	$2\cdot10^{2}$
2	trans-Polyacetylene	10^{3}-10^{5}
3	Polypyrrole	10^{2}-$7.5\cdot10^{3}$
4	Polythiophene	10^{3}
5	Poly(p-phenylene)	10^{2}-10^{3}

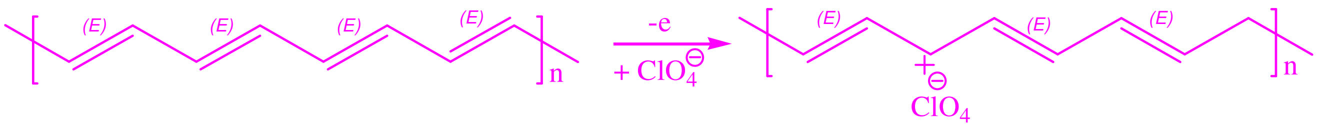
Conducting polymers:

1. Polyacetylene:

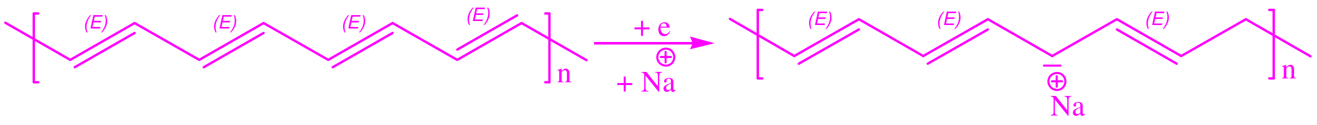
Poly acetylene is conjugated polymers with simple chemical structure. Polymerization of acetylene with Ziegler Natta gives polyacetylene which in its used form with increasing temperature get transformed to more trans form. This polymer is infusible, insoluble and brittle on exposure to air. The conductivity of polyacetylene is magnified by doping. The doping of polyacetylene is done by addition of doping agents (oxidative or reductive) like AgF_5, Br_2, I_2, $HClO_4$ to give higher conductivity.



p-type doping: Oxidation with anions e.g.ClO_4^-



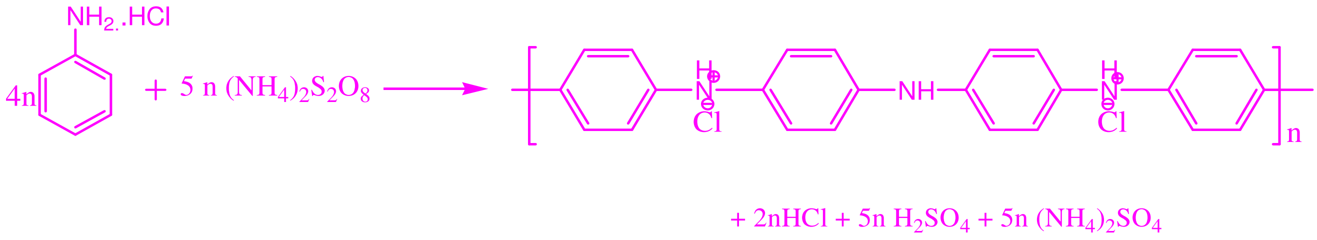
n-type doping: reduction with cations e.g. Na^+



2. Polyaniline:

Poly aniline possesses unique conducting properties. Polyaniline is conjugated polymer and is reactive. Polyaniline is considered as an organic metal. Polyaniline is a stable conducting polymer. It has wide range of conductivity. It shows multi-colourelctrochromism and chemical sensitivity.

Preparation: Polyaniline is prepared by the redox polymerization of aniline in protonic and aqueous solution in presence of ammonium perdisulphate as oxidant. It can be regarded as conducting polymer under certain stimulating condition like UV light, heat or addition of the suitable doping agent to the polymer.



Properties: Due to presence of extended π bond system of conjugated polymers, it is highly susceptible to chemical and electrochemical oxidation or reduction. As a result, the electrical and optical properties of the polymer alter. Electronically conducting polymer is extensively conjugated molecules and possess specially delocalized band line structure.

Uses: Polyaniline is used for corrosion protection, sensor, smart windows, printed circuit boards, conductive fabrics and conductive pipes for explosives.

Applications of Conducting Polymers:

1. In rechargeable Light weight batteries based on perchlorate doped Polyacetylene-lithium Systems: These are about 10 times lighter than conventional lead storage batteries.

2. These can produce current density up to $50mA/cm^2$.

3. Inelectrochromic displays and optical filters: ICP's can absorb visible light to give colored products so can be useful for electrochromic displays and optical filters.

4. Thus the conducting polymers can be used as electro chromic materials i.e., the materials that change colour reversibility during the electrochemical processes of charge and discharge.

5. In wiring in aircrafts and aerospace components.

6. In telecommunication systems.

7. In electromagnetic screening materials.

8. In electronic devices such as transistors and diodes.

9. In solar cells, drug delivery system for human body etc., In photovoltaic devices.

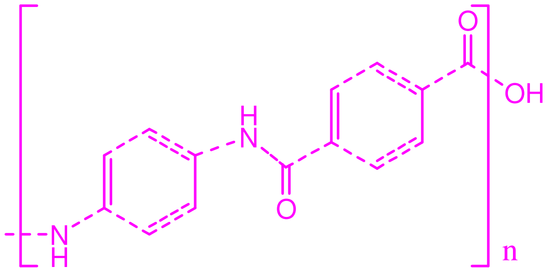
10. In molecular wires and molecular switches.

11. Membranes made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc., Hence they are useful for ion-exchangers and controlled release of drugs.

12. Conducting polymers are also used for making sensors for P^H, O_2, NOx, SO_2, NH_3 and glucose.

Liquid crystal polymers(LCP)

Liquid crystals are material that behaves like solid and liquid. The scientist Stephanie made first liquid crystal polymer solution of polyamide and named Kevlar. The macromolecule with the above structure produces very strong fibers. When this polymer dissolved in tetramethyl urea and calcium chloride, the polymer molecule behaves strongly. The kevlar molecule which were long, straight, and lined up like logs floating down a river, because of the strange opalescent look of the solution.



This is unusual because normally molecule in a solution or pure liquid is not arranged in any orderly manner. Molecule of solid material is arranged in orderly fashion called crystal.

Since kevlar solution is a liquid, but its molecules are orderly arranged, this solution is called a liquid crystal. Liquid crystals are of two types.

1. Liquid crystalline in polymers may occur by dissolving a polymer in a solvent which are called lypotropic liquid crystal polymers. Eg. Kevlar

2. Liquid crystalline in polymers may occur by heating a polymer above its glass transition temperature or melting transition point, which are called thermotropic liquid crystal polymers E.g. Vectra.

Properties of LCP:

1. The liquid crystal polymers have high mechanical strength at high temperature.
2. They possess extreme chemical resistance.
3. The liquid crystal polymers possess inherent flame retardancy and good weather ability.
4. The LCP can be easily fabricated into a variety of forms.
5. The liquid crystal polymers has high Z-axis coefficient of thermal expansion.
6. The liquid crystal polymers can be welded.
7. The LCP are capable of forming regions of highly ordered structure while in liquid phase.
8. LCP resist stress cracking the presence of most chemicals at elevated temperature.

Uses of LCP:

1. The electrical motor components are made from LCP.
2. LCP has application in information storage media.
3. The liquid crystal polymers have extensive application as coating, composites and additives.
4. LCP has space application as well as high performance ropes and tennis rackets.
5. LCP finds application in electronic industry as LEDs and SMT components.

Questions:

1. Define the term polymer with suitable examples.
2. Discuss the term homopolymer and copolymer.
3. Explain the classification of polymer based on the source.
4. Explain the classification of polymer based on the structure of polymer in detailed.
5. Explain the classification of polymer based on molecular force with suitable example in detailed.
6. Write the difference between Thermoplastics and Thermosetting plastics polymer.
7. Write the difference between Homopolymer and Copolymer.
8. Discuss the term liquid crystal polymer.
9. Write the properties and use of liquid crystal polymer.
10. Define conducting polymer. Give its classification in detailed.
11. Explain the application of conducting polymer with suitable examples.
12. Write note on the following term
    i) Monomer
    ii) Polymer

iii) Copolymer
iv) Homopolymer
v) Natural polymer
vi) Synthetic polymer
vii) Thermoplastics
viii) Thermosetting plastics
ix) Elastomer
x) Fiber
xi) Liquid crystal polymer

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02. Properties of Polymers

Contents: Physical properties- Degree of polymerization, number-average molecular weight, weight average molecular weight, polymer crystallinity. Thermal properties- Glass transition temperature, melting point, factors affecting the glass transition temperature. Mechanical properties- Factors affecting the strength of polymers.

1. Physical Properties:

The molecular weight of a polymer molecule is the product of the degree of polymerization and the molecular weight of the repeating unit. The polymer molecules are not identical but are a mixture of many species with different degrees of polymerization, that is, with different molecular weights. Therefore, in the case of polymers we talk about the average values of molecular weights.Polymerization reactions produce a distribution of molecular weights and shapes. Polymer molecular weight could be expressed as number average molecular weight, weight average molecular weight, and polydispersity.

Some of the most common methods for determining these parameters are colligative property measurements, light scattering techniques, viscometry, and size exclusion chromatography. Gel permeation chromatography is used to determine the number average molecular weight, weight average molecular weight, and polydispersity. Physical properties of polymers include molecular weight, molar volume, density, degree of polymerization, crystallinity of material, and so on. Some of these are discussed here with in the following sections.

Molecular Weight: Molecular weight of polymer is defined as sum of the atomic weight of each of the atom in a molecule, which is present in the polymer, is known as molecular weight.

Degree of Polymerization: Degree of polymerization is a number, which indicates the number of repetitive units' monomers present in the polymer. By knowing the value of degree of polymerization, the molecular weight of the polymer can be calculated.

Molecular weight of the polymer =Degree of polymerization(n) x Molecular weight of each monomer.

Degree of polymerization is represented as 'n'.

Example: Polyethylene

Here 'n' is the degree of polymerization.

i) Calculate the molecular weight of the polythene polymer given degree of polymerization is 100.

Molecular weight of the polythene = Degree of polymerization(n) x Molecular weight of Polyethene

$= 100 \times 28$

$=2800$.

Polymer chain distribution in synthetic polymers is always presented as average molecular weight calculated from the molecular weights of all the chains in the polymer sample. The number average molecular weight (Mn), weight average molecular weight (Mw), and higher average molecular weight (Mz) are defined by the general expression:

Number-Average Molecular Weight:

The total weight of all polymer molecule in a sample divided by the total number of polymer molecule in a sample.

$Mn = \Sigma n_iM_i / \Sigma n_i \ = \Sigma w_i / \Sigma w_i/M_i$

Where, n= moles of molecule i.e. number of molecules ($n_1+n_2+n_3+.........+n_i$)

W= Weight of individual molecule ($w_1+w_2+w_3+.........w_i$)

M=molecular weight of each molecule($M_1+M_2+M_3+.........M_{i)}$

The physical properties of polymer such as viscosity, transition temperature and mechanical properties like strength, stiffness, and toughness depend on the molecular weight of polymer. The lower the molecular weight, viscosity, lowers the transition temperature and the mechanical properties. Due to increased molecular weight, viscosity of the polymer increased in molten state.

Weight-Average Molecular Weight.

The weight-average weight is given by:

$$Mw = \Sigma W_iM_i / \Sigma w_i$$

W= Weight of individual molecule ($w_1+w_2+w_3+.........w_i$)

M=molecular weight of each molecule($M_1+M_2+M_3+.........M_{i)}$

The number-average molecular weight is less than the weight-average molecular weight.

Polydispersity Index or Heterogeneity Index: The ratio of the weight-average molecular weights to the number-average molecular weights is called polydispersity index (PDI) or heterogeneity index, which measures the polydispersityof the polymer mixture.

PDI = Weight average molecular weight (Mw) / Number average molecular weight (Mn)

The dispersitymeasures heterogeneity of sizes of molecules or particles in the mixture. The mixture is called monodisperseif the molecules have the same size, shape, or mass. If the molecules in the mixture have adifferent size, shape and mass distribution, the mixture is called polydisperse.The natural polymers are generally monodispersed as all synthetic polymers are polydispersewith some exceptions. The PDI is equal to or greater than 1where as the polymer chains approach uniform chain length, the PDI tends to unity.

Polymer Crystallinity:

The polymer chains being very large hence found in the two polymeric forms. Crystalline Polymers: Lamellar crystalline form in which the chains fold and make lamellar structure arranged in the regular manner. Amorphous Polymers: Amorphous form in which the chains are in the irregular manner.A typical range of crystallinity can be defined as amorphous to highly crystalline. The polymers having simple structural chains as linear chains and slow cooling rate will result in good crystallinity as expected.

In slow cooling, sufficient time is available for crystallization to take place. Polymers having high degree of crystallinity are rigid and have high melting point, but their impact resistance is low. However, amorphous polymers are soft and have lower melting points. For a solvent, it is important to state that it can penetrate the amorphous part more easily than the crystalline part.

Examples: Amorphous polymers: polystyrene and poly(methyl methacrylate). Crystalline polymers: polyethylene, and PET polyester.

When the molten polymer is cooled down, then the crystalline lamellae grow in radial direction from a nucleus along the three dimensions leading to a spherical structure called spherulite. Spherulite formation and its diameter depend on various parameters such as the number of nucleation sites, polymer molecule structure and rate of cooling. Due to highly ordered lamellae in the spherulite, it shows higher density and hardness.

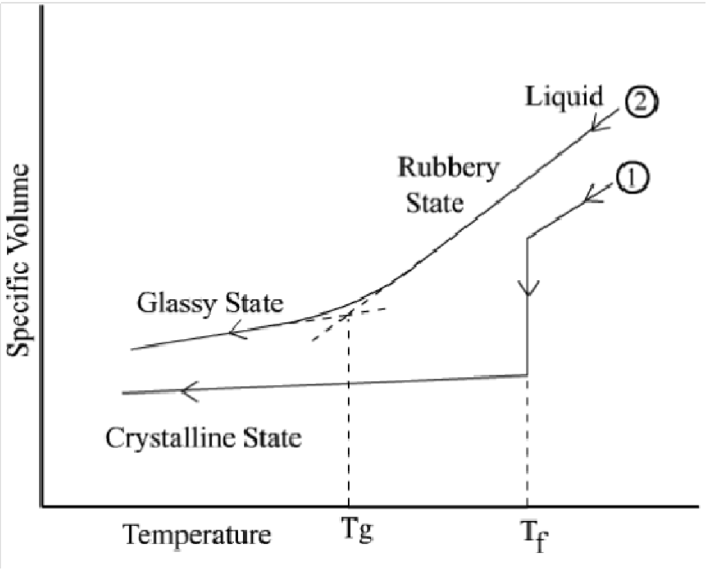
02. Thermal Properties:

a)Polymer Glass Transition temperature:

In the study of polymers and their applications, it is important to understand the concept of the glass transition temperature, Tg. As the temperature of a polymer drops below Tg, it behaves in an increasingly brittle manner. As the temperature rises above the Tg, the polymer becomes more rubber-like. Thus, knowledge of Tg is essential in the selection of materials for various applications. In general, values of Tg well below room temperature define the domain of elastomers and values above room temperature define rigid, structural polymers.

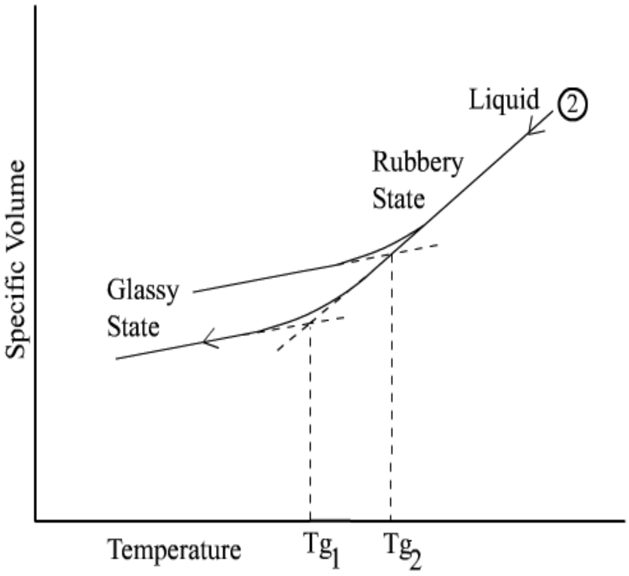
This behavior can be understood in terms of the structure of glassy materials which are formed typically by substances containing long chains, networks of linked atoms or those that possess a complex molecular structure. Normally such materials have a high viscosityin the liquid state. When rapid cooling occurs to a temperature at which the crystalline state is expected to be the more stable, molecular movement is too sluggish or the geometry too awkward to take up a crystallineconformation.

Therefore, the random arrangement characteristic of the liquid persists down to temperatures at which the viscosity is so high that the material is considered to be solid. The term glassy has come to be synonymous with a persistent non-equilibrium state. In fact, a path to the state of lowest energy might not be available. To become more quantitative about the characterization of the liquid-glass transition phenomenon and Tg, we note that in cooling an amorphous material from the liquid state, there is no abrupt change in volume such as occurs in the case of cooling of a crystalline material through its freezing point (Tf). Instead, at the glass transition temperature, Tg, there is a change in slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value in the rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in the figure below. Note that the intersections of the two straight line segments of curve (2) define the quantity Tg.



The specific volume measurements shown here, made on an amorphous polymer (2), are carried out in a dilatometer at a slow heating rate. In this apparatus, a sample is placed in a glass bulb and a confining liquid, usually mercury, is introduced into the bulb so that the liquid surrounds the sample and extends partway up a narrow bore glass capillary tube.

A capillary tube is used so that relatively small changes in polymer volume caused by changing the temperature produce easily measured changes in the height of the mercury in the capillary. The determination of Tg for amorphous materials, including polymers as mentioned above, by dilatometric methods are found to be rate dependent. This is schematically illustrated in the figure below, again representing an amorphous polymer, where the higher value, Tg_2, is obtained with a substantially higher cooling rate than for Tg_1.



In the amorphous region of the polymer, at lower temperature, the molecules of the polymer are in, say, frozen state, where the molecules can vibrate slightly but are not able to move significantly. This state is referred as the glassy state. In this state, the polymer is brittle, hard and rigid analogous to glass. Hence name glassy state. The glassy state is similar to a supercooled liquid where the molecular motion is in the frozen state.

The glassy state shows hard, rigid, and brittle nature analogous to a crystalline solid with molecular disorder as a liquid. Now, when the polymer is heated, the polymer chains are able to wiggle around each other, and the polymer becomes soft and flexible similar to rubber. This state is called the rubbery state. The temperature at which the glassy state makes a transition to rubbery state is called the glass transition temperature Tg. Note that the glass transition occurs only in the amorphous region, and the crystalline region remains unaffected during the glass transition in the semi-crystalline polymer.

b) Melting Point and Glass Transition Temperature:

The glass transition temperature is the property of the amorphous region of the polymer, whereas the crystalline region is characterized by the melting point. In thermodynamics, the transitions are described as first and second order transitions. Glass transition temperature is the second order transition, whereas the melting point is the first order transition. The value of glass transition temperature is not unique because the glassy state is not in equilibrium. The value of glass transition temperature depends on several factors such as molecular weight, measurement method, and the rate of heating or cooling.

The semi-crystalline polymer shows both the transitions corresponding to their crystalline and amorphous regions. Thus, the semi-crystalline polymers have true melting temperatures (Tm) at which the ordered phase turns to disordered phase, whereas the amorphous regions soften over a temperature range known as the glass transition (Tg).

It should be noted that amorphous polymers do not possess the melting point, but all polymers possess the glass transition temperature. The polymer melting point Tm is increased if the double bonds, aromatic groups, bulky or large side groups are present in the polymer chain, because they restrict the flexibility of the chain. The branching of chains causes the reduction of melting point, as defects are produced because of the branching.

Factors Affecting the Glass Transition Temperature:

The glass transition temperature depends on the mobility and flexibility of the polymeric chains. If the polymeric chains can move easily, then the glassy state can be converted to the rubbery state at lower temperature, that is, the glass transition temperature is lower. If somehow the mobility of the chains is restricted, then the glassy state is more stable, and it is difficult to break the restriction causing the immobility of the polymer chains at the lower temperature, because more energy is required to make the chains free. Thus, in this case, the glass transition temperature is raised.

a). Intermolecular Forces: Strong intermolecular forces cause higher Tg. For example, PVC (Tg= 80^0C) has stronger intermolecular forces than polypropylene (Tg= -18^0C) because of the dipole–dipole forces from the C—Cl bond.

b).Chain Stiffness: The presence of the bulky groups (such as amide, sulfone, carbonyl, p-phenylene etc.) in the polymer chain reduces the flexibility of the chain, leading to higher glass transition temperature. For example, polyethyleneterephthalete is stiffer than polyethylene adipate due to the presence of benzene ring. Therefore, Tg value is higher for polyethyleneterephthalate.

c). Cross-Linking: The cross-links between chains restrict rotational motion and raise the glass transition temperature. Hence, higher cross-linked molecule will show higher Tg than that with lower cross-linked molecule.

e).Pendant groups: The presence of pendent group can change the glass transition temperature. The presence of bulky pendant group like benzene ring can restrict rotational freedom, leading to higher glass transition temperature. As in polystyrene, the presence of benzene ring increases the Tgrotational motion, tending to less Tg value. In polybutylmethacrylate, the presence of large aliphatic chain reduces the Tg value when compared with that of polymethylmethacrylate.

f).Plasticizers: Plasticizers are low molecular weight and non-volatile materials added to polymers to increase their chain flexibility. They reduce the intermolecular cohesive forces between the polymer chains, which in turn decrease Tg.

g).MolecularWeight: The glass transition temperature is also affected by the molecular weight of the polymer.Tg is increased with the molecular weight. The molecular weight is related to the glass transition temperature by the Fox–Flory Equation:

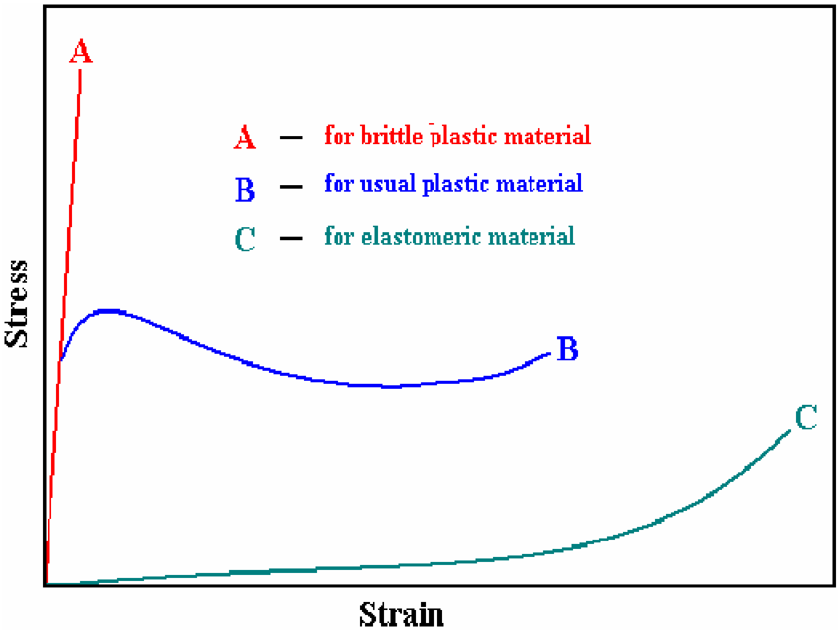
$$Tg = Tg^{\infty} - K/Mn$$

whereTg^{∞} is the glass transition temperature at the molecular weight of infinity. K is the empirical parameter called Fox–Flory parameter related to the free volume inside the polymer. Mn is the number average molecular weight. It is observed that Tg is increased up to the molecular weight of approximately 20 000, and after this limit, the Tg is not affected appreciably.

03. Mechanical Properties:

Mechanical properties are time and temperature dependent. Mechanical properties can be specified with many of the same parameters that are used for metals such as modulus of elasticity, tensile strengths, etc. However, polymers many respects, mechanically dissimilar to metals. To a much greater extent than either metals or ceramics, both thermal and mechanical properties of polymers show a marked dependence on parameters namely temperature, strain rate, and morphology. In addition, molecular weight and temperature relative to the glass transition play an important role that are absent for other type of materials.

A simple stress- strain curve can describe different mechanical behavior of various polymers. As shown in following figure. The stress-strain behavior can be brittle, plastic and highly elastic. Mechanical properties of polymers change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures. Highly crystalline polymers behave in a brittle manner, whereas amorphous polymers can exhibit plastic deformation. These phenomena are highly temperature dependent, even more so with polymers than they are with metals and ceramics. Due to unique structures of cross-linked polymers, recoverable deformations up to very high strains also observed with polymers (elastomers). Tensile modulus and tensile strengths are orders of magnitude smaller than those of metals, but elongation can be up to 100 % in some cases. The tensile strength is defined at the fracture point and can be lower than the yield strength.



Figure

It is of great importance to be familiar with some basic mechanical properties of the material before its application in any field, such as how much it can be stretched, how much it can be bent, how hard or soft it is, how it behaves on the application of repeated load and so on.

a. Strength: The strength is the stress required to break the polymer sample. There are several types of the strength, namely tensile, compressional, flexural, torsional, etc. The polymers follow the following order of increasing strength:

Linear < Branched < Cross-linked < Network.

Factors Affecting the Strength of Polymers:

1. Molecular Weight: The tensile strength of the polymer rises with increase in molecular weight and reaches the saturation level at some value of the molecular weight. The tensile strength is related to molecular weight by the following equation.

$$\sigma = \sigma^{\infty} - A / M$$

Where $\sigma\infty$ is the tensile strength of the polymer with infinity molecular weight. A is some constant and M is the molecular weight.

At lower molecular weight, the polymer chains are loosely bonded by weak van der Waals forces and the chains can move easily, responsible for low strength, although crystallinity is present. In case of large molecular weight polymer, the chains become large and hence are entangled, giving strength to the polymer.

2. Cross-linking: The cross-linking restricts the motion of the chains and increases the strength of the polymer.

3. Crystallinity: The crystallinity of the polymer increases strength, because in the crystalline phase, the intermolecular bonding is more significant. Hence, the polymer deformation can result in the higher strength leading to oriented chains.

Questions:

1. Discuss the mechanical properties of polymers.
2. Write the different factor that affecting on polymer strength.
3. Explain the physical properties of polymer. How will you calculate molecular weight of polymer with suitable example?
4. Discuss the mechanical properties of polymers.
5. Explain the term glass transition temperature. Write the factor affecting glass transition temperature.
6. Write note on polymer crystallinity.
7. Explain the thermal properties of polymers.
8. Explain the term number average molecular weight and weight average molecular weight.
9. Define the term degree of polymerization with suitable examples.
10. Explain the melting points and glass transition temperature of polymer in detailed.

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03. Polymer Synthesis

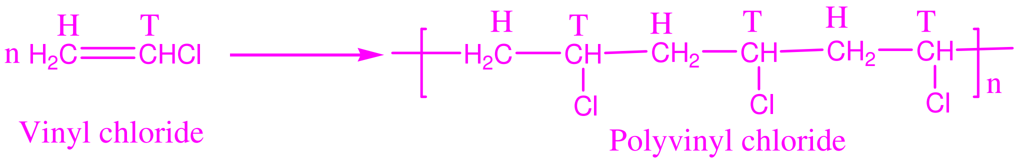
Content: Introduction, Addition polymerization- Free radical cationic and anionic polymerization, condensation polymerization, coordinationpolymerization, ring opening polymerization, Copolymerization,preparation , properties and use of synthetic polymer, Questions.

The objective of polymer synthesis is to efficiently assemble macromolecules with precisely controlled structures, so as to maximize their utility for a given application. Polymerization can occur via a variety of reaction mechanisms that vary in complexity due to the functional groups present in the reactants and their inherent steric effects.There are two major types of' polymerization methods used to convert small molecules (monomers) into polymers. These methods were originally referred to as addition or chain growthpolymerization and condensation or step growth polymerization. The coordination polymerizationis another variant of chain-growth polymerization.Some of the methods of polymers synthesis are discuss in this chapter.

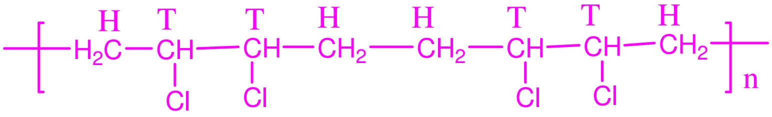
1. Addition Polymerization (Chain growth):

The process of polymerization in which one molecule of the same monomer or different monomers add together and so on to form polymer on large scale. Addition polymerization occur among the molecules containing double bond i.e. unsaturated compounds such as alkenes, dienes and their derivatives. There is no liberation of small molecules in the addition polymerization process. This process of polymerizations leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species. However, the free radical governed addition or chain growth polymerization is the most common mode. There are three possible ways in which addition polymerization can occur are explained below

Head to Tail: - When a molecule has substituent along with double bond, the end at which substituent is present is called as tail and other end as head of the molecule. In this polymerization process one molecule attached to head of the molecule. The tail of the second molecule is attached to head of the third molecule and so on. E.g. Polymerization of vinyl chloride.

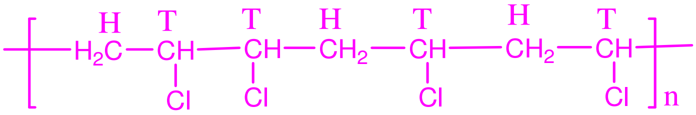


ii) Head to Head and Tail to Tail: - In this process, the head of the first monomer is linked to head of the second monomer. Its tail is attached to the third monomer and so on. E.g. Polymerization of vinyl chloride.



Polyvinyl chloride

ii) Random arrangement: -In this process there is no sequence of attachment of head and tail of the monomers in polymer chain. There is mixed or random arrangement of monomer in the polymer chain. E.g. Polymerization of vinyl chloride.



Polyvinyl chloride

Most of the addition polymerization reaction is carried out in the presence of catalyst. The commonly used catalysts are benzoyl peroxide, hydrogen peroxide or t-butyl peroxide etc. The reaction is accelerated by the formation of reactive intermediate such as free radical, a carbocation or a carbanion. For the addition polymerization monomers used are unsaturated compounds like alkenes; Alkadienes and their derivatives. Depending upon the nature of the reactive species involved, addition polymerization reaction occurs by the following mechanisms:

a. Free radical polymerization

b. Cationic polymerization

c. Anionic polymerization

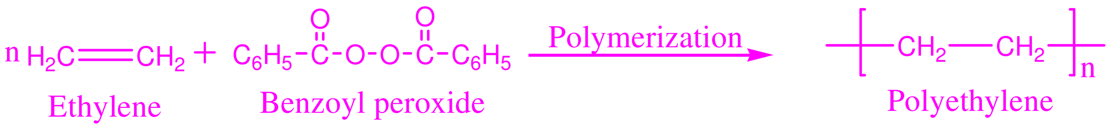
All these addition or chain growth polymerization reaction involves the following steps.

i) Initiation ii) Propagation iii) Termination

a). Free radical polymerization:

The radical polymerization consists of three fundamental steps initiation, propagation, and termination. Initiation steps involves the formation of free radical from catalyst such as benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. followed by the radical reaction with monomer, propagation is the rapid and progressive addition of monomer to the growing polymer chain without change of active center and termination step is the destruction of growth of polymer chain or active center in the growth chain of polymer. A variety of alkenes or dienes and their derivatives are polymerized in the presence of an initiator catalyst like peroxides.

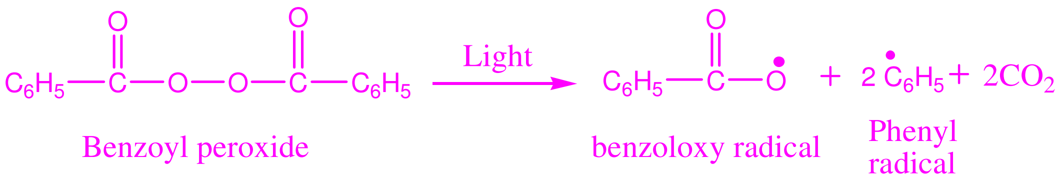
Example: The polymerization of ethylene to polyethylene by heating or exposing to light a mixture of ethylene with a small amount of benzoyl peroxide initiator.



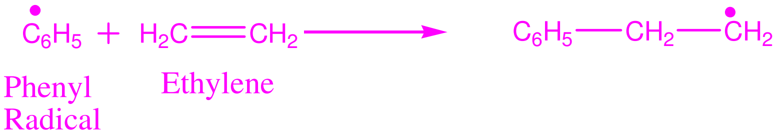
Mechanism: The reaction involves the following steps

i) Initiation: The free radical is needed to initiate the chain reaction. These free radicals are usually produced by decomposing peroxide such as benzoyl peroxide, acetyl peroxide, tert-butyl peroxide etc. In the presence of either heat or light, these peroxides decompose to from pair of free radicals. The process starts with the addition of free radical formed by the peroxide to the ethene double bond thus form a new larger free radical this step is known as chain initiating step.

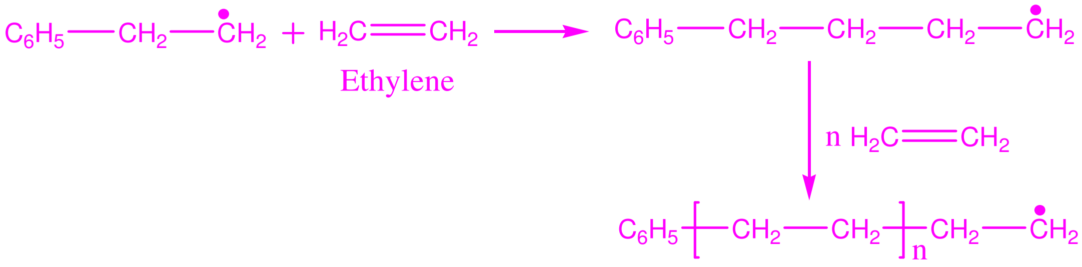
E.g. Benzoyl peroxide on photolysis decomposes to give phenyl free radical.



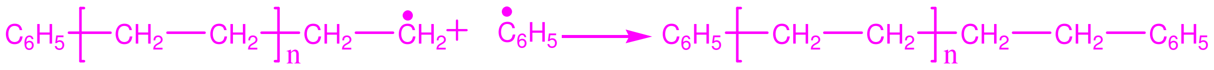
Phenyl radical adds to the monomer like ethylene to form a new free radical.



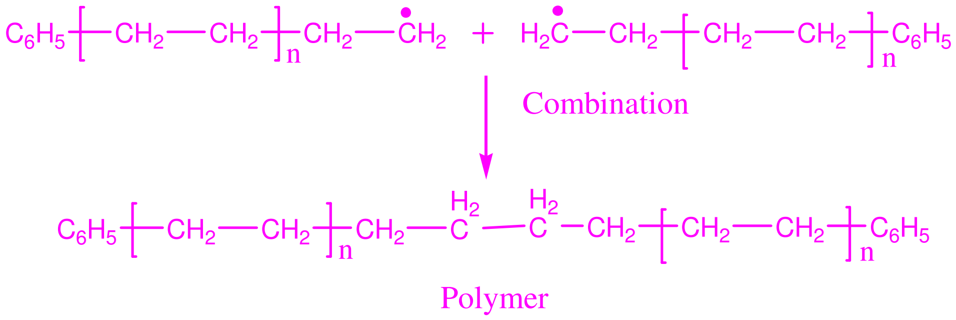
ii) Propagation: This new free radical reacts with another molecule of ethene, another bigger sized radical is formed. The repetition of this sequence with new and bigger radicals carries the reaction forward and the step is termed as chain propagating step.

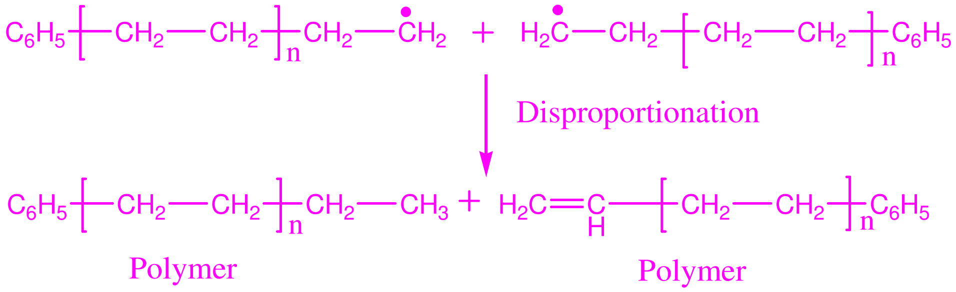


iii) Termination: The product radical thus formed reacts with another radical to form the polymerized product. This step is called the chain terminating step.

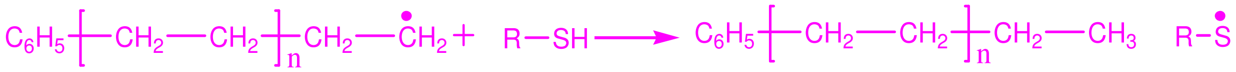


$$C_6H_5\left[CH_2-CH_2\right]_n CH_2-\dot{C}H_2 + \dot{C}_6H_5 \longrightarrow C_6H_5\left[CH_2-CH_2\right]_n CH_2-CH_2-C_6H_5$$





Properties of polymer depend on the length of its chain. The length of polymer molecule may be controlled by using chain transfer agents called telomers. Thiols (R-SH) are often used as telomers which provide hydrogen radical to terminate the polymer chain.

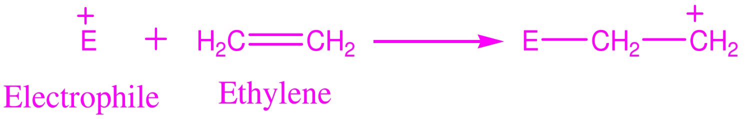


$$C_6H_5\left[CH_2-CH_2\right]_n CH_2-\dot{C}H_2 + R-SH \longrightarrow C_6H_5\left[CH_2-CH_2\right]_n CH_2-CH_3 \quad R-\dot{S}$$

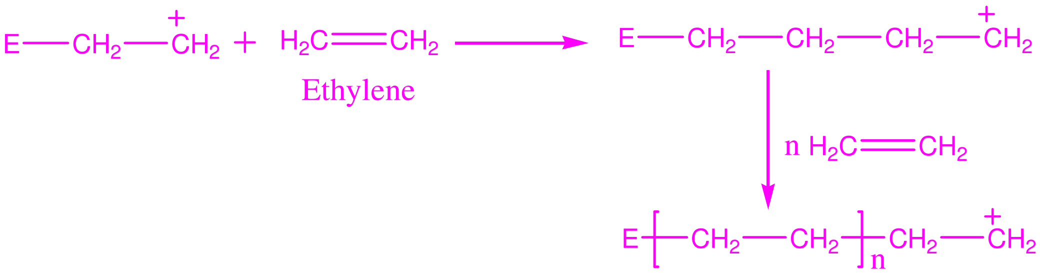
RS radical is not reactive to initiate new monomer chain. Chain reaction can be terminated by using quinones, iodine as inhibitors.

b). Cationic polymerization:

Initiation: In the cationic polymerization reaction initiator is a electrophile which adds to the double bond of ethylene to forms intermediate carbocation. This formed carbocation react with another molecule of ethylene. Thus chain initiated.

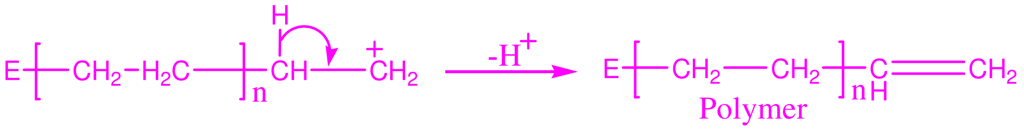


Propagation: In this step continuous addition of ethylene molecule into newly generated carbocation in each addition to give long chain continuous addition polymer chain.



Termination:

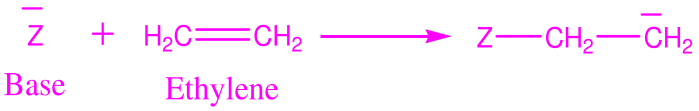
The termination steps involve loss of proton resulting in the formation of double bond at the end of the polymer chain.



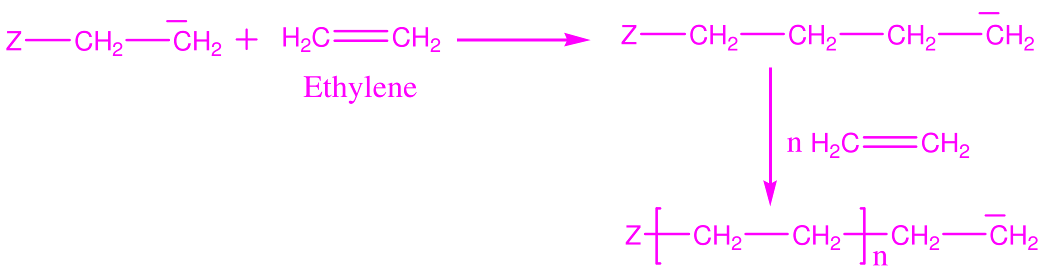
c). Anionic polymerization:

Analogous to the initiation of anionic polymerization by addition of nucleophiles to alkenes, cationic polymerization can be initiated by the addition of electrophiles. The alkenes that respond well to cationic polymerization are those that form relatively stable carbocation when protonated.

Initiation: In the anionic polymerization reaction initiator is a nucleophile or base which adds to the double bond of ethylene to forms intermediatecarbanion. This formed carbanion reacts with another molecule of ethylene. Thus chain initiated.

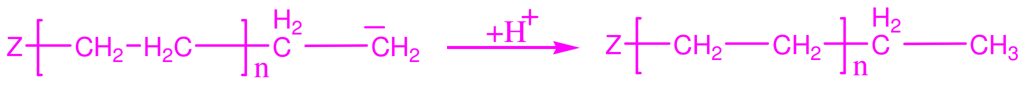


Propagation: In this step continuous addition of ethylene molecule into newly generatedcarbanion in each addition to give long chain continuous addition polymer chain.



Termination:

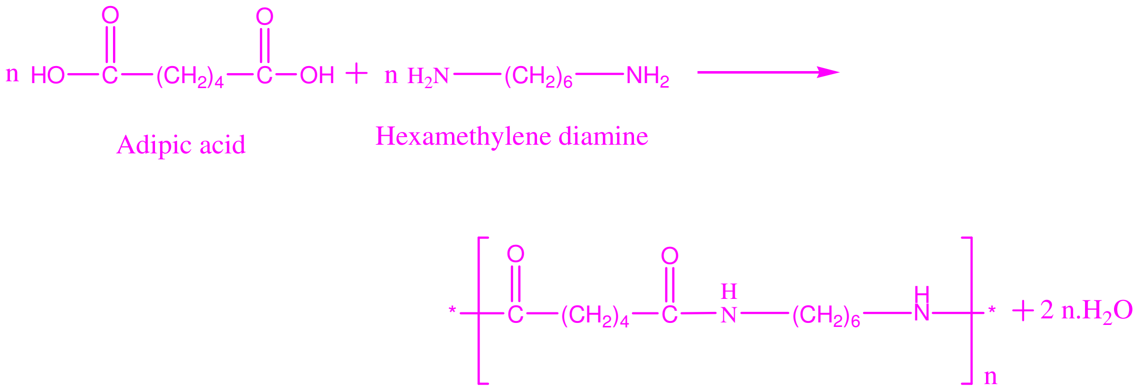
The termination steps involve abstract proton resulting in the formation of polymer chain.



02. Condensation Polymerization (Step growth):

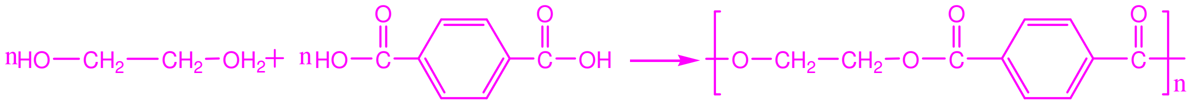
Generally, involves a repetitive condensation reaction between two bi-functional monomers. These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers.

Example: Preparation of Nylon 6,6 by the condensation reaction of adipic acid with hexamethylenediamine with elimination of water molecule.



Nylon 6,6

In condensation reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on. Since, each step produces a distinct functionalized species and is dependent of each other, this process is also called as step growth polymerization.The formation of terylene or dacron by the interaction of ethylene glycol and terephthalic acid is an example of this type of polymerization.



This type of polymerization normally employs two difunctional monomers that are capable of undergoing typical organic reactions. For example, a diacid can be allowed to react with a diol in the presence of an acid catalyst to afford polyester. In his case, chain growth is initiated by the reaction of one of the diacid's carboxyl groups with one of the diol's hydroxyl groups. The free carboxyl or hydroxyl group of the resulting dimer can then react with appropriate functional group in another monomer or dimer. This process is repeated throughout the polymerization mixture until all of the monomers are converted to low molecular weight species, such as dimers, trimers, tetramers, etc. These molecules, which are called oligomers, can then further react with each other through their free functional groups. Polymer chains that have moderate molecular weights can be built in this manner. The high molecular weights common to chain-reaction polymerizations

are usually not reached. This is due to the fact that as the molecular weight increases the concentration of the free functional groups decreases dramatically. In addition, the groups are attached to the ends of chains and, hence, are no longer capable of moving freely through the viscous reaction medium.

The major differences between addition polymerization and condensation polymerization are explain in the following table:

S. No.	Addition polymerization	Condensation polymerization
1	Growth reaction adds repeating units one at a time to the polymeric chain and no byproduct form.	Any two molecular species can react and byproduct form.
2	Number of monomer units increases steadily throughout the reaction.	Monomer disappears early in the reaction.
3	High polymer is formed at once.	Polymer molecular weight (degree of polymerization) rises steadily throughout the reaction.
4	Longer reaction times have very little effect on molecular weight but gives higher yields.	Longer reaction times are essential to obtain higher molecular weights i.e. reaction time influences molecular weight of the polymer.
5	The reaction mixture contains onlymonomers, high polymers and verysmall amount (10^{-8}) of growing chains.	All types of molecular species arepresent at any stage.
6	E.g. Polyethylene, Polystyrene, Polyvinyl chloride, Polypropylene etc.	E.g. Nylon, PET, Polycarbonate, Polyurethane etc.
7	Homo chain polymers are form.	Hetero chain polymers are form.

Characteristics of step-growth polymerization:

1. The group of polymer molecules proceeds by a stepwise intermolecular reaction only and only one reaction type in involved in the polymerization.
2. Monomer units can react with each other or polymers of any size.

3. The functional group at the end of a monomer is usually assumed to have the same reactivity as that on a polymer of any size.
4. A high conversion of functional groups is required in order to produce high-molecular-mass product.
5. Many step-growth polymerization reactions are reversible.
6. Condensation polymerization is usually produced by step-growth polymerization but not all step-growth polymerization are condensation reactions.

03. Coordination polymerization:

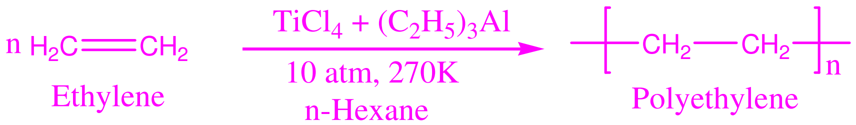
Polymerization reaction especially of olefins and dienes are catalyzed by organometallic compounds which involves addition of monomer to growing macromolecule throughan organometallic active center is known as coordination polymerization. The coordination polymerization involves formation of monomer-catalyst complex between organometallic compound and monomer.

In the formation of monomer-catalyst complex, a coordination bond is involved in between a carbon atom of the monomer and the metal of the catalyst. Hence the polymerization effected by such catalyst system is called coordination polymerization.

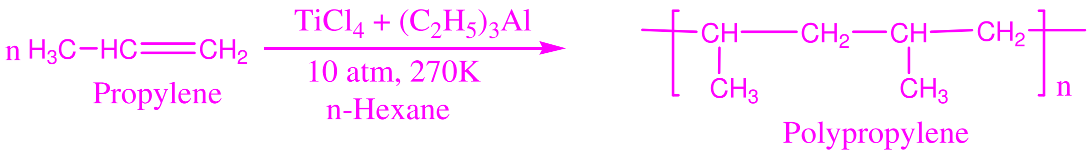
It is also a subclass of addition polymerization. It usually involves transition-metal catalysts. Here, the "active species" is a coordination complex, which initiates the polymerization by adding to the monomer's carbon-carbon double bond.

Polymerization of propene produces polypropene with high selectivity. Branching will not occur through this mechanism since no radicals are involved; the active site of the growing chain is the carbon atom directly bonded to the metal.

Zeigler-Nata catalysts: These are a special type of coordination catalysts, comprising two components, which are generally referred to as the catalyst and the cocatalyst. The catalyst component consists of chlorides of titanium ($TiCl_3$ and $TiCl_4$) and the cocatalysts are organometallic compound such as triethylaluminium ($Al(C_2H_5)_3$).



$$\underset{\text{Ethylene}}{n\ H_2C{=}CH_2} \xrightarrow[\text{10 atm, 270K}\ \text{n-Hexane}]{TiCl_4 + (C_2H_5)_3Al} \underset{\text{Polyethylene}}{\left[CH_2{-}CH_2 \right]_n}$$

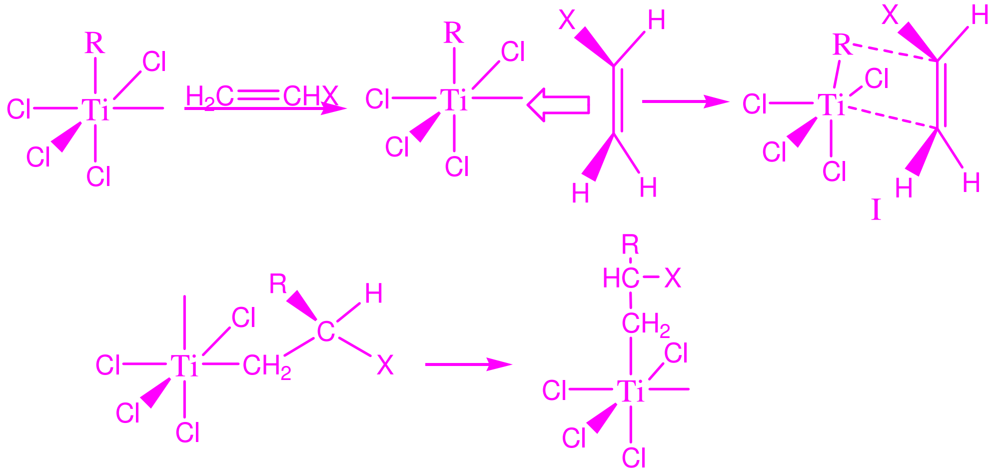


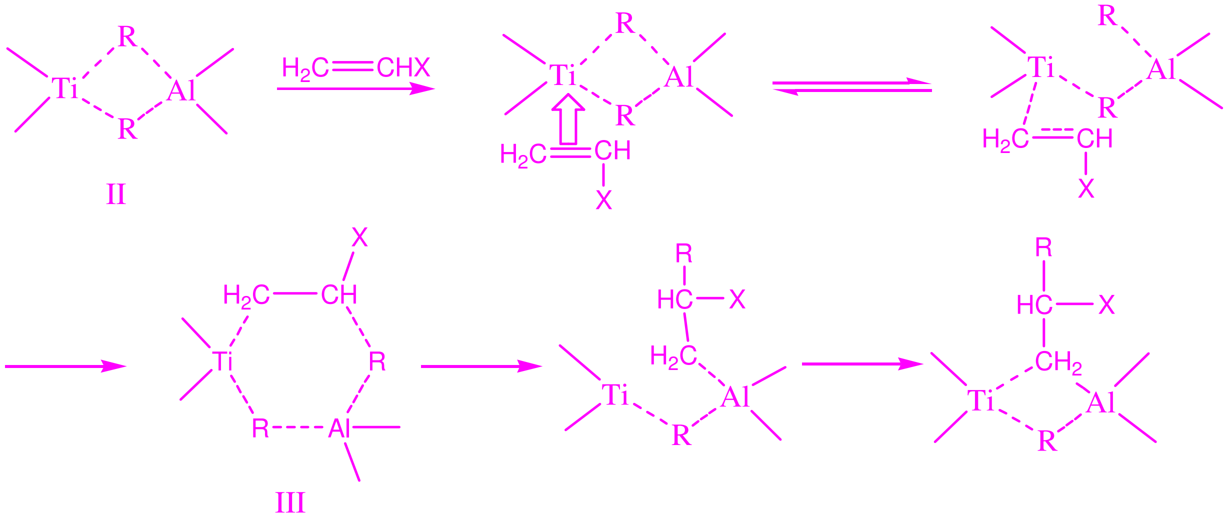
$$\underset{\text{Propylene}}{n\ H_3C{-}HC{=}CH_2} \xrightarrow[\text{10 atm, 270K}\ \text{n-Hexane}]{TiCl_4 + (C_2H_5)_3Al} \underset{\text{Polypropylene}}{\left[\underset{CH_3}{CH}{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2 \right]_n}$$

Triethylaluminium act as the electron acceptor whereas the electron donor is titanium halides and the combination, therefore, readily forms coordination complexes. The complex formed, now acts as the active center. The monomer is complexes with the metal ion of the active center in a way that the monomers attached towards the Ti-C bond (C from the alkyl group R) in the active center, when it forms a π complex with the Ti ion.

Reaction Mechanisms:

The coordination polymerization of alkene can be preceded either by monometallic mechanism or bimetallic mechanism depending on the catalyst.The reaction mechanism of substituted alkene being polymerized by using titanium compound catalyst. The double bond of alkene will undergo cis addition and coordinate with the empty orbital of titanium compound to form four membered ring coordinates intermediate -I. The stereo specificity of substituted alkene is preserved via intermediate-I. Then the bond is formed on the Ti compound catalyst. If the catalyst is made from aluminum compound and titanium compound, the polymerization will proceed through bimetallic mechanism as shown below. The bridge structure II is formed between two metal compounds first. Then the substituted alkene is coordinated with Ti compound to form six-membered ring coordination III. The stereo specificity of substituted alkene is preserved via intermediate III.





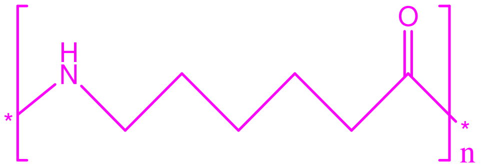
The polymer chain grows from the catalyst surface by successive insertion reactions of complexed monomer and the R group originally present in the organometallic cocatalyst ends up as the terminal group of the chain. Monomer activity decreases with increasing steric hindrance about the double bond as shown below:

$CH_2{=}\ CH_2 > CH_2{=}CH\ CH_3 > CH_2{=}CHCH_2CH_3 > CH_2{=}CH\ CH_2CH(CH_3)_2 > CH_2{=}CHCH(CH_3)_2 > CH_2{=}CHCH\ (CH_2\ CH_3)_2 > CH_2{=}CH{-}C(CH_3)_3$

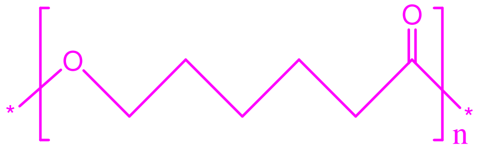
The reaction has the characteristic of living anionic polymerization. The reaction is usually terminated by active hydrogen as shown in the following equations. Hydrogen is the preferred transfer agent for controlling molecular weight due to low cost and clean reaction but the termination reaction is usually carried out by hydrogen containing compounds

04. Ring-opening polymerization (ROP):

A ring opening polymerization is chain growth polymerization in which the terminal end group of polymer chain is acts as a reactive center where next cyclic monomers can be added by ring opening. Generally,difunctional monomer can polymerize via ring opening polymerization. Some cyclic monomers that can polymerize through ring opening polymerization include cyclic ether, lactones, carbonates, lactams, epoxides, etc. E.g. Polycaprolactone(PCL) and Polycaprolactam(Nylon-6) synthesized via ring opening polymerization of caprolactone and caprolactam respectively.



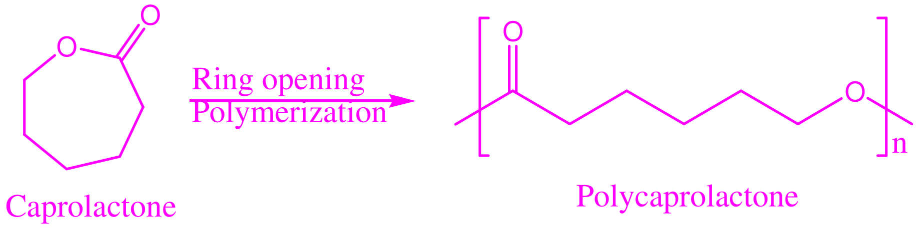
Polycaprolactam

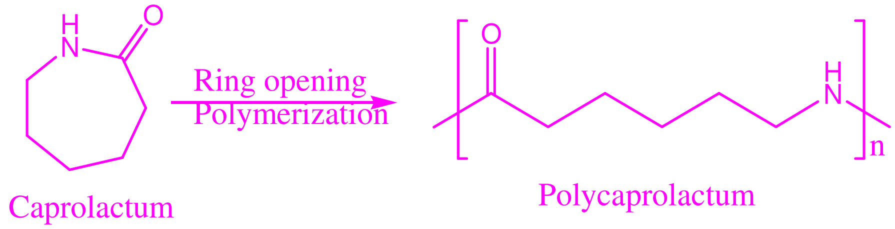


Polycaprolactone

Ring opening polymerization of cyclic monomer depends on the ring size, ring strain and nonbondinginteraction between substituent attached to the ring. Cyclic ring with large ring strain of 3,4,5-membered rings polymerized readily through ring opening polymerization while large ring size of cyclic monomer i.e. 7, 8-membered ring are less reactive.

Ring opening polymerization can proceed via cationic, anionic or free radical polymerization mechanism.





Typical cyclic monomers that can be polymerized via ring opening polymerization are di-functional monomers that carry two different reactive groups like one amine or alcohol and one carboxylic acid that have undergone a cyclization reaction.

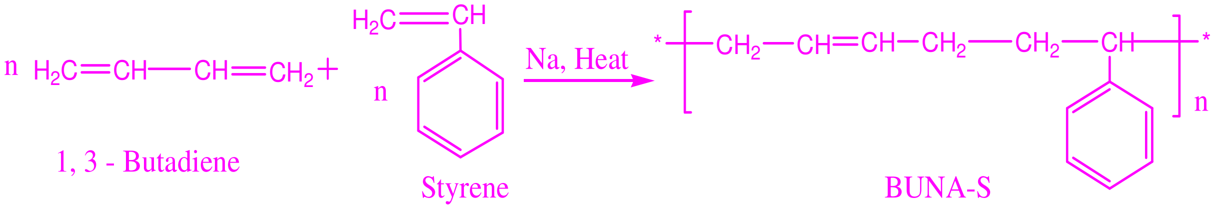
To polymerize these moieties, one of the rings has to open for polymerization reaction. This can be achieved, for example, by adding a small amount of a nucleophilic reagent (Lewis base) as an initiator this reaction is called anionic ring-opening polymerization.If a small amount of an electrophilic reagent (Lewis acid) is added to the monomer as initiator this reaction is known as cationic ring-opening polymerization. Whether and how readily a cyclic monomer undergoes cationic ring-opening polymerization depends on the ring size, to be more specific, on the ring strain.

Ring-opening polymerization can also proceed via free radical polymerization. The introduction of oxygen into the ring will usually promote free radical ring-opening polymerization, because the resulting carbon–oxygen double bond is much more stable than a carbon-carbon double bond. Thus, cyclic hetero monomers that carry a vinyl side group like cyclic ketene acetals, cyclic ketene animals, cyclic vinyl ethers, and unsaturated spiroortho esters will readily undergo free radical ring-opening polymerization. Copolymerization of these monomers with a wide variety of vinyl monomers will introduce ester, amide, keto or carbonate groups into the backbone, which results in functionally terminated oligomers.

Copolymerization:

It is a polymerization reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer. The copolymer can be made not only by chain growth polymerization but by step growth polymerization also. It contains multiple units of each monomer used in the same polymeric chain.

Example: A mixture of styrene and 1, 3 – butadiene can form a copolymer called styrene butadiene rubber (SBR). A reaction in which a mixture of two or more monomers is allowed to undergo polymerization is known as copolymerization. The polymer is known as copolymer.

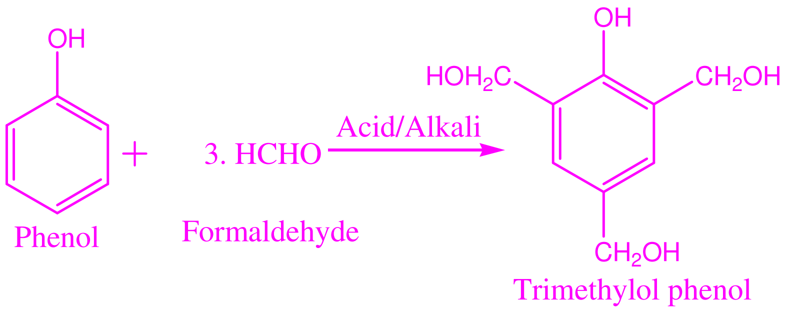


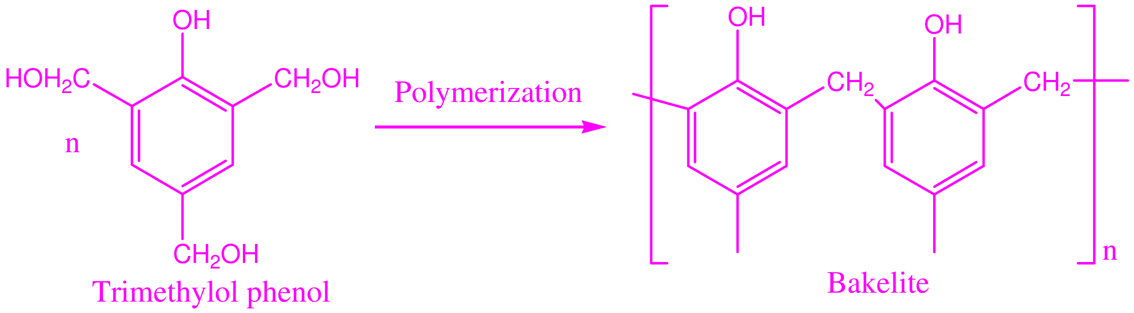
Synthesis of polymers:

Phenol Formaldehyde resins (Bakelite):

Preparation: It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst. The initial reaction results in the formation of O- and P- hydroxyl methyl/phenol which reacts to form linear polymer. During modeling hexamethylenetetraamine is added, which converts to insoluble solid of cross-linked structure Bakalite. Commercially these are available into two forms nova lacks &resols.

Nova lacks are phenol formaldehyde resins obtained by condensation of phenol & formaldehyde in presence of acid as catalyst when phenol to formaldehyde ratio is greater than one.





Properties:

1. Phenolic resins are hard, rigid and strong materials.
2. They have excellent heat and moisture resistance.
3. They have good chemical resistance.

4. They have good abrasion resistance.
5. They have electrical insulation characteristics
6. They are usually dark coloured.
7. Lower molecular weight grades have excellent bonding strength and adhesive properties.

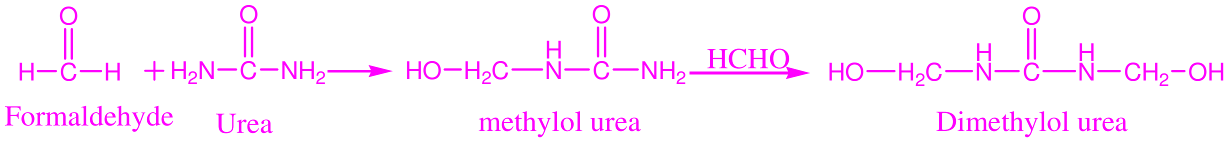
Uses:

1. Phenol formaldehyde resins are used for domestic plugs, switches, handles for cooker and saucepans.
2. Distributor heads for cars.
3. Used as adhesives for grinding wheels and brake linings. Varnishes, electrical insulation and protective coatings.
4. Used for the production of ion exchange resins.

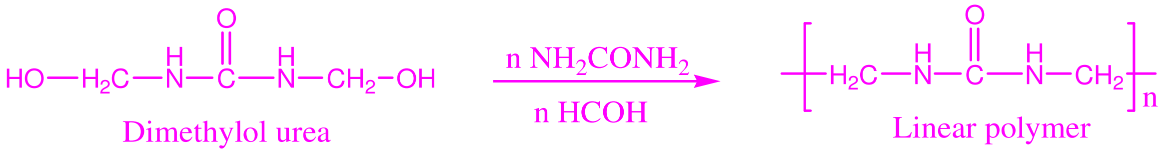
Urea Formaldehyde resins:

Preparation:

Urea formaldehyde resins are prepared by dissolving urea in aqueous formaldehyde and heat to give monomethylurea which further reacts with other urea and formaldehyde to form linear polymer.

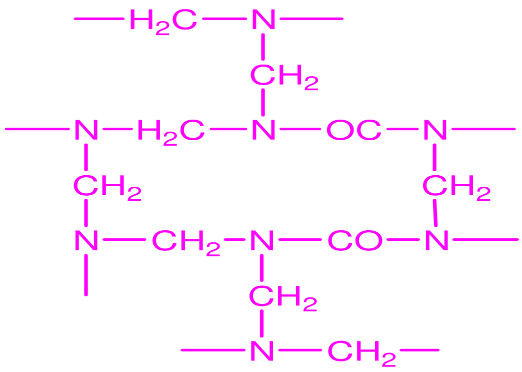


$$H-\overset{O}{\overset{\|}{C}}-H + H_2N-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow HO-H_2C-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{HCHO} HO-H_2C-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2-OH$$



$$HO-H_2C-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2-OH \xrightarrow[n\ HCOH]{n\ NH_2CONH_2} \left[-H_2C-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-CH_2-\right]_n$$

The –NH- group in the linear polymer becomes site of new reaction site with formaldehyde which cross link the linear polymer chain. Thus, on treatment of excess formaldehyde linear polymer gets converted into three-dimensional polymeric network of high molecular mass.



cross linked urea formaldehyde resin

Properties:

1. Urea formaldehyde resin iscolourless.

2. During moulding, these resins can be impregnated by all desired colours by adding proper pigment and dye.

Uses:

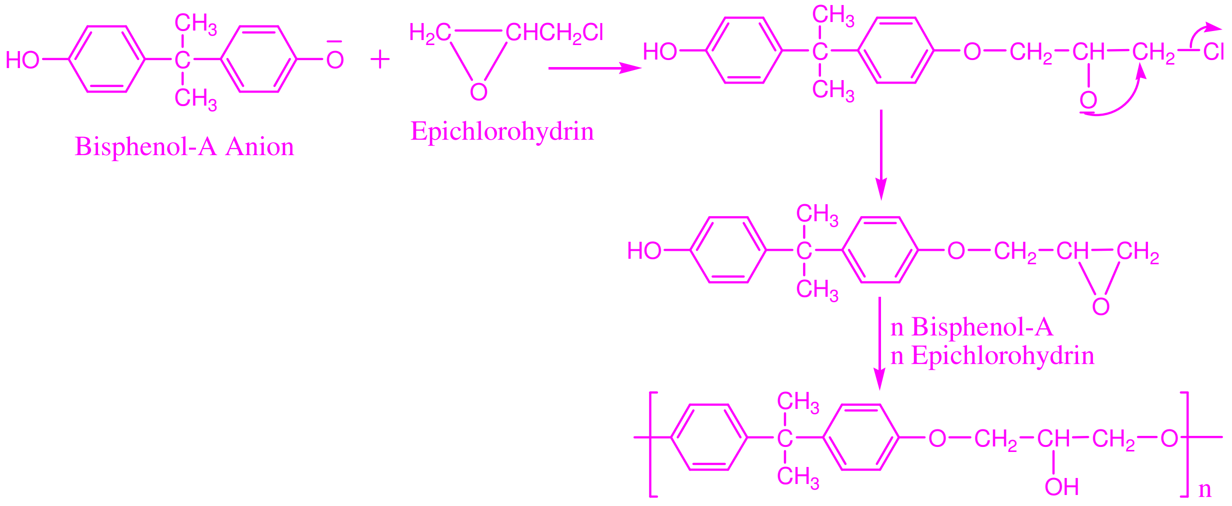
1. Urea formaldehyde resins used in the manufacture of laminates, buttons, surgical items, household applications, etc.

2. They are used as adhesive in plywood industries and as resins for enamels and other surface coatings.

Epoxy Resins:

Preparation:

The epoxy resins are basically polyether’s. They are prepared by reacting bisphenol-A in presence of base with epichlorohydrin to form product containing epoxide ring. Which further react with bisphenol-A and epichlorohydrin to give linear polymer which has epoxide ring at one end andbisphenol ring at the other end.



Epoxy resin

Properties:

1. Epoxy resins are highly viscous liquids or solid with high melting points.

2. They have remarkable chemical resistance and good adhesion.

Uses:

1. Epoxy resin when mixed with polyamidepolysulfides amines yield very tough material which is used in foam, potting materials.

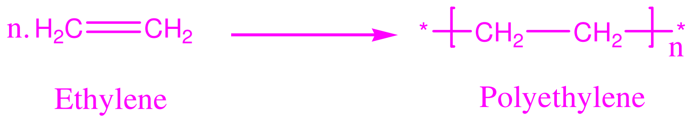
2. Epoxy resins used for electrical insulation and in industrial flooring.

3. Epoxy resins used to bind glass, porcelain, wood and metals.

4. Epoxy resins used in making excellent protective coating because of their inertness, hardness and flexibility.

Polyethylene:

Preparation: Polyethylene can be prepared by the polymerization of ethylene at 1500 atm and a temperature 150–250^{0}C in presence of traces of oxygen.



Properties:

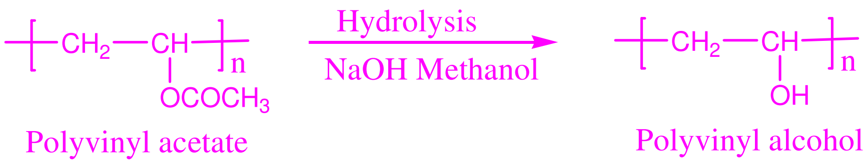
1. Depending upon the density, they may be LDPE and HDPE.
2. If we use free radical initiator, LDPE is the product while use of ionic catalysts results in the formation of HDPE. LDPE has a density 0.91 to 0.925 g/cm^3 HDPE has a density 0.941 to 0.965 g/cm^3
3. HDPE is linear and has better chemical resistance.
4. It is a rigid, waxy white solid and translucent.
5. It is permeable to many organic solvents.
6. It crystallizes easily.

Uses:

1. These are useful in the preparation of insulator parts, bottle caps, flexible bottles, pipes etc.
2. LDPE is used in making film and sheeting.
3. Pipes made of LDPE are used for both agricultural, irrigation and domestic water line connections.
4. HDPE is used in manufacture of toys and other household articles.

Polyvinyl Alcohol (PVA):

Preparation: Poly Vinyl alcohol is manufactured by the polymerization of vinyl acetate followed by partial hydrolysis. The process of hydrolysis is based on the partial replacement of ester group in vinyl acetate with the hydroxy group in presence of aqueous sodium hydroxide followed by gradual addition of saponification agents. Polyvinyl alcohol is precipitated, wash and dried.



$$-\!\!\left[CH_2-\underset{\substack{|\\OCOCH_3}}{CH}\right]\!\!-_n \xrightarrow[\text{NaOH Methanol}]{\text{Hydrolysis}} -\!\!\left[CH_2-\underset{\substack{|\\OH}}{CH}\right]\!\!-_n$$

Properties:

1.It is a soluble in water.

2. It is effective in film forming, emulsifying and has an adhesive quality.

3. It has no odor and is not toxic.

4. It is resistant to grease, oil and solvents.

5. It is strong, flexible and functions as a high oxygen and aroma barrier.

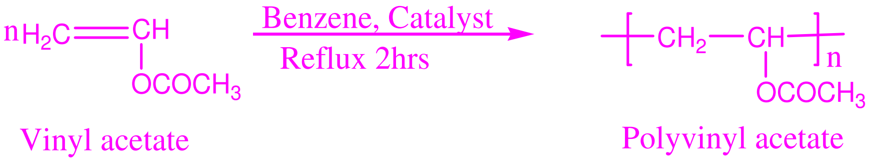
Uses:

1.It is widely used in fresh water sports fishing.

Polyvinyl Acetate:

Preparation:

It is prepared by solution polymerization. In this method a mixture of pure vinyl acetate and dry benzene is refluxed for two hours in the presence of catalyst.



$$n\,H_2C{=}\underset{\substack{|\\OCOCH_3}}{CH} \xrightarrow[\text{Reflux 2hrs}]{\text{Benzene, Catalyst}} -\!\!\left[CH_2-\underset{\substack{|\\OCOCH_3}}{CH}\right]\!\!-_n$$

Properties:

1. Polyvinyl acetate is soft and sticky.

2. It cannot be moulded.

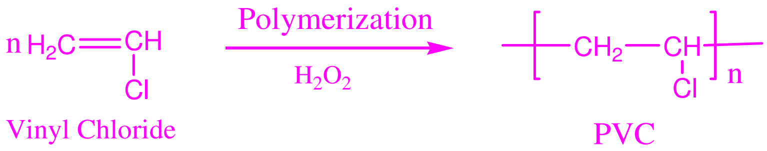
3. It can be easily deformed even at room temperature.

Uses:

1. It is used in the manufacture of paints, lacquer's, emulsion, adhesive and gramophone records.

Polyvinyl Chloride (PVC):

Preparation: Poly vinyl chloride is prepared by heating a water emulsion of vinyl chloride in presence of a small amount of benzoyl peroxide or hydrogen peroxide under pressure. Vinyl chloride monomer is prepared by treating acetylene with hydrogen chloride at 60^0C to 80^0C in the presence of metal chloride as catalyst.



Properties:

1.It is a colourless rigid mater

2. It is having high density and low softening point.

3.It is resistant to light, atmospheric oxygen, inorganic acids and alkalis.

4.It is most widely used synthetic plastic.

Uses:

1.It is mainly used as cable insulation, leather cloth, packing and toy

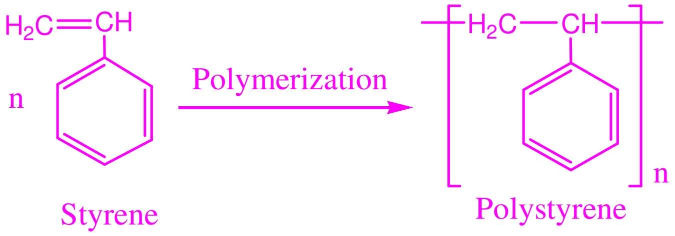
2.It is used for manufacturing of film, sheet and floor covering.

3.PVC pipes are used for carrying corrosive chemicals in petrochemical factories.

Polystyrene (polyvinyl benzene):

Preparation:

Polystyrene is aromatic polymer that is made from the monomer styrene. It is long hydrocarbon chain that has a phenyl group attached to every carbon atom. Styrene is an aromatic monomer commercially manufactured from petroleum. Polystyrene is vinyl monomer prepared from the styrene monomer by free radical vinyl polymerization.



Properties:

1. Polystyrene can be rigid or foamed.

2. Polystyrene is naturally transparent, brittle and hard.

3. It is rigid plastic material with high impact strength.

4. It has thermal insulation and shock absorption characteristic provide performance of the products.

Uses:

1. Polystyrene used for packaging of food and cold drinks or meals.

2. Polystyrene is versatile and cost-effective solution for rigid packaging and food service disposable.

3. Polystyrene is used in electronics make cassette tape housing and clear jewel boxes, to protect CDs and DVDs.

4. Polystyrene resin is most popular materials for building and construction applications.

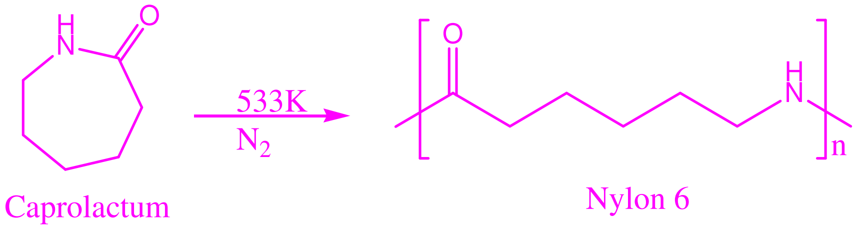
5. It is used for wide range of disposable medical applications.

6. It is used in cosmetics for making container for powder, creams, shaving soap, kajal, etc.

Nylon 6:

Synthetic fiber forming polyamides are termed as 'Nylons'.

Preparation: Nylon – 6 can be prepared by self-condensation or ring opening of caprolactam at about 533K in an inert atmospheric nitrogen for about 4-5hrs. The rings break and undergo polymerization to form nylon 6.



Uses:

1. Nylon6 is primarily used for fibers that find use in making socks, undergarments, carpets etc.,

2. Nylon 6 is also used in mechanical engineering for well-known applications like gears,bearings, bushes, cans etc.,

3. Mouldings have application in medicine and pharmacy because of sterilisability.

4. Durable but costly hair combs.

5. Nylon 6 is also used for racketing electrical ware to provide a tough,abrasion resistant outer cover to protect the primary electrical insulation.

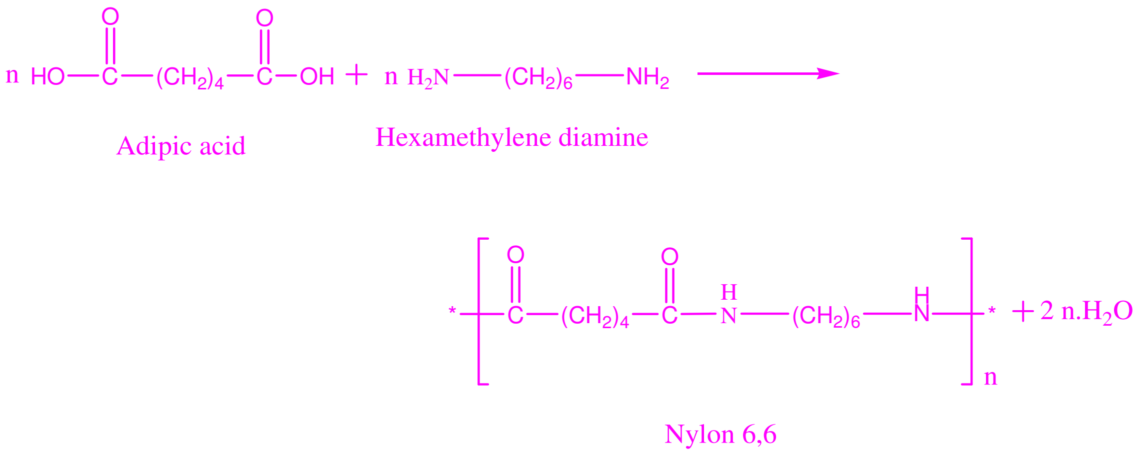
6. Nylon 6 is mainly used for making tire cords.

7. Nylon 6 is suitable for monofilaments that are used for bristles, brushes etc.,

8. Glass reinforced Nylon plastics are used in housings and domestic appliances, radiator parts of car and for relay coil formers.

Nylon-6,6:

Preparation: It is prepared by the condensation reaction of hexamethylenediamine and adipic acid with loss of water molecule.



Properties: This is linear polymer not resistant to alkali and mineral acids. Oxidizing agents like hydrogen peroxide, potassium permanganate etc. is able to degrade the fibers.

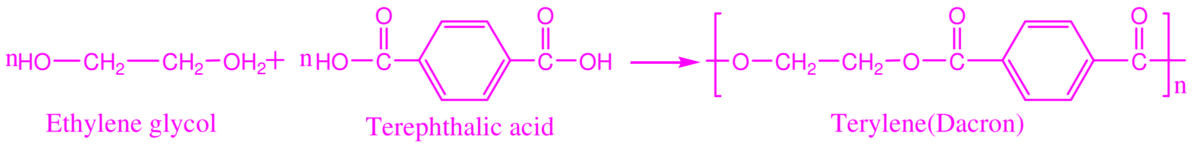
Uses:

1.Nylon-6,6 is mainly used for moulding purposes for gear bearings and making car tires, used for fibers etc.

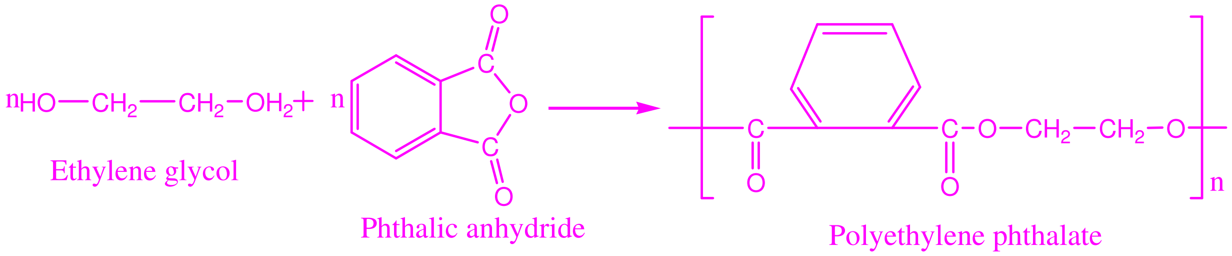
2.This is mainly used in manufacture of tire cord. Other uses include manufacture of carpets, rope, fiber cloth etc.

POLYESTER:

Preparation: Terylene is a polyester fiber made from ethylene glycol and terephthalic acid. Terephtalic acid required for the manufacture of terylene is produced by the catalytic atmospheric oxidation of p-xylene.



Important polyester is polyethylene phthalate which is obtained by the condensation reaction of ethylene glycol and phthalic anhydride.



Properties:

1.This occurs as a colourless rigid substance.

2. This is highly resistant to mineral and organic acids but is less resistant to alkalis.

3. This is hydrophobic in nature. This has high melting point due to presence of aromatic ring.

4. Polyester fiber is very strong and possesses high elasticity.

5. They are insoluble in organic solvents. These fibers are water repellent.

Uses:

1.It is mostly used for making synthetic fibers.

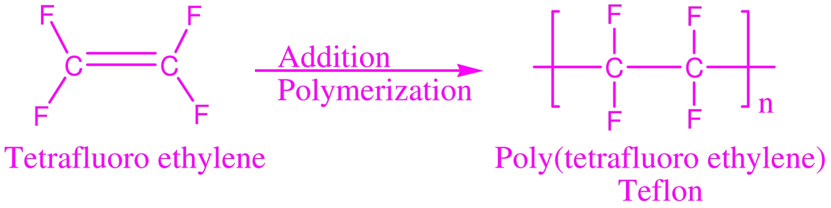
2. It can be blended with wool, cotton for better use and wrinkle resistance.

3. Other application of polyethylene terephthalate film is in electrical insulation.

4. Polyesteris used to prepare garments, fishing nets, conveyor belts etc.

TEFLON (Poly tetra fluoro ethylene):

Preparation: Teflon is obtained by polymerization of water-emulsion tetrafluoroethylene, under pressure in presence of benzoyl peroxide as catalyst.



Properties:

1. Due to the presence of highly electronegative fluorine atoms and the regular configuration of the polytetrafluoroethylene ethylene molecule results in very strong attractive forces between the different chains.

2. These strong attractive forces give the material extreme toughness, high softening point.

3. Exceptionally high chemical-resistance towards all chemicals, high density, waxy touch, andvery low coefficient of friction.

4. Extremely good electrical and mechanical properties: It can be machined, punched and drilled.

5. The material has the disadvantage that it cannot be dissolved and cannot exist in a true molten state.

6. Around 350^0C, it sinters to form very viscous, opaque mass, which can be moulded into certain forms by applying high pressures.

Uses:

1. Teflon is a insulating material for motors, transformers, cables, wires, fittings, etc.

2. It is used for making gaskets, packing, pump parts, tank linings, chemical-carrying pipes, tubing's and tanks, etc.

3. It is used for coating and impregnating glass fibers, asbestos fibers and cloths; in non- lubricating bearings and non-sticking stop-cocks etc.

Questions:

1. Explain the addition polymerization in detailed with suitable example.
2. Discuss the free radical polymerization of vinyl chloride with mechanism.
3. Write the anionic polymerization with suitable example.
4. Write note on coordination polymerization.
5. Explain the ring opening polymerization of caprolactum.
6. Explain the copolymerization with suitable example.
7. Write the preparation properties and use of following polymers

   a. Nylon 66 b. Polystyrene c. PVC
   d. Polyurethane e. Polyester f. PVA

8. Explain the preparation properties and application of polyethylene with addition polymerization mechanism.
9. Write note on Bakelite.
10. Explain the preparation of phenol formaldehyde resins.

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04. Rubber

Content: Introduction, Types of Rubber- Natural rubber and synthetic rubber, rubber latex, preparation properties and use of synthetic rubber, compounding rubber, Vulcanized Rubber, questions.

Introduction:

Rubber is an elastomer type polymer, where the polymer has the ability to return to its original shape after being stretched or deformed. The rubber polymer is coiled when in the resting state. The elastic properties arise from the its ability to stretch the chains apart, but when the tension is released the chains snap back to the original position.

Natural rubber is an addition polymer that is obtained as a milky white fluid known as latex from a tropical rubber tree. Natural rubber is from the monomer isoprene (2-methyl-1,3-butadiene). Since isoprene has two double bonds, it still retains one of them after the polymerization reaction. Natural rubber has the cis configuration for the methyl groups.Rubber is a natural polymer of Isoprene (2-Methyl -1, 3 – Butadiene). It is a linear, 1, 4 – addition polymer of Isoprene. Natural rubber has elastic properties and it undergoes long range reversible extension even if relatively small force is applied to it. Therefore, it is also known as Elastomer. Rubber polymer is coiled when in the resting state. The rubber polymer molecules contain at least some unit derived from conjugated diene monomer.

Charles Goodyear accidentally discovered that by mixing sulfur and rubber, the properties of the rubber improved in being tougher, resistant to heat and cold, and increased in elasticity. This process was later called vulcanization. Vulcanization causes shorter chains to cross link through the sulfur to longer chains.

Types of Rubber:

1. Natural Rubber:

Natural rubber has vegetable origin. Natural rubber is prepared from latex which is a colloidal solution of rubber in water. It is created by enzymatic processes in many plants, belonging mainly to families of Euphorbiacea, Compositea, Moracea and Apocynacea. It is industrially achieved mainly from the tree called HeveaBrasiliensis belonging to Euphorbiacea family. Rubber trees are basically found in tropical & semitropical countries. It is grown in plantation way in warm (average monthly temperature 25–28°C) and humid (humidity around 80%) climate of South-Eastern Asia (Malaysia, India, China, Sri Lanka), in Western Africa and in North part of South America.

Natural Rubber latex:

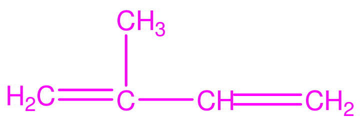
Latexin HeveaBrasiliensis is located in latex vessels to be founded in various parts of the tree. Natural rubber latex is white milky fluid colloid system having the rubber particles dispersed in water. It is obtained from them by tappingbased on cutting of the tree bark by special knife. Latex spontaneously flows out of this slot and It is collected into special bowls. Some rubber products such as foam rubber, gloves, condoms and glues are produced directly from latex. The latex is modified to have higher DRC values (minimum 60–65% of rubber). It is performed by means of its concentrations, the most often by centrifugation and sedimentation, but also water evaporation thickening and electro-decantation is used. During these operations also eventual dirtiness and non-rubbery additives are removed from rubber besides increase of the dry rubber content in latex.

Composition of fresh NR latex

Sr. No.	Constituent	Content
1	Rubber	30 – 40 %
2	Proteins	1.0 – 1.5 %
3	Resins	1.5 – 3.0 %
4	Minerals	0.7 – 0.9 %
5	Carbohydrates	0.8 – 0.1 %
6	Water	55 – 60 %

Structure of Natural Rubber:

Natural rubber is a polymer of Isoprene. To understand the structure of rubber we shall concentrate on structure of Isoprene. Isoprene is a conjugated diene containing double bonds at alternate position.

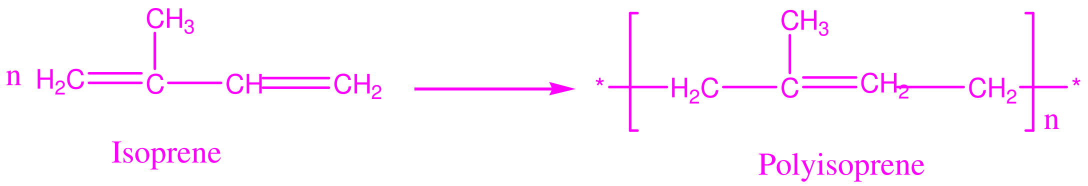


$$H_2C{=}\overset{\displaystyle CH_3 \atop |}{C}{-}CH{=}CH_2$$

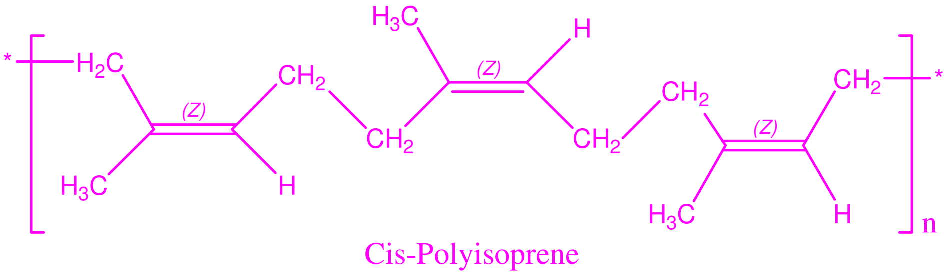
Isoprene
(Monomer of Natural Rubber)

Isoprene undergoes free radical polymerization like substituted ethylene. Isoprene polymerizes to give polyisoprene polymer, a simple alkene having each unit still containing one double bond.

Now, polymerization of Isoprene may follow either of the two pathways; either of cis-polymerization or trans-polymerization. The rubber formed from cis-polymerization is called cis-polyisoprene or natural rubber. Similarly, the rubber formed from trans-polymerization is called synthetic rubber.



Isoprene (2-Methyl -1, 3-butadiene) undergoes cis-polymerization to form natural rubber



Structure of Natural Rubber (Cis–Polyisoprene)

By observing structure of natural rubber, we can infer that there is no polar group in this structure. As a result of this the intermolecular forces of attraction are weak Vander Waal forces of attraction. These forces of attraction are further weakened because of the cis-configuration of all the double bonds that does not permit the close interaction of polymer chains. Thus, natural rubber (CisPolyisoprene) does not have a straight chain but has a coiled structure. Thus, it gets elastic property.

Deficiencies of natural rubber:

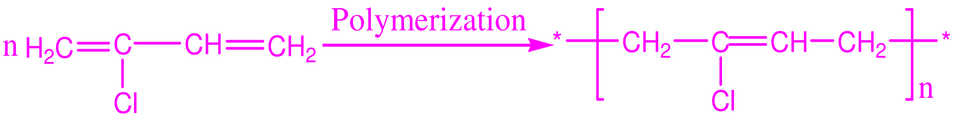
Natural rubber as such has no practical utility value. It is because of many inherent deficiencies.

They are –

1. It is hard and brittle at low temperature and soft and sticky at high temperature.
2. It is soft and soluble in many hydrocarbon solvents and carbon disulphide (CS_2).
3. It has high water absorption power.
4. It is a sticky substance, rather difficult to handle.
5. It is readily attacked by acids and alkalies.
6. It has low tensile strength.
7. It has poor abrasion resistance.
8. It is sensitive to oxidative degradation

2. Synthetic Rubber:

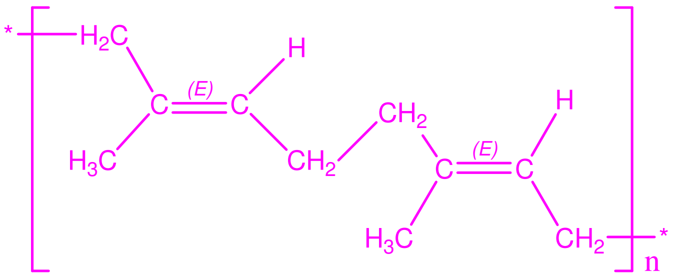
Polymerization of dienes molecules containing double bond (unsaturated) to form substitutes for rubber is the forerunner of the enormous present-day plastic industry. Chloroprene was the first commercially successful rubber substitute produced. Chloroprene undergoing trans-polymerization to produce synthetic rubber (Polychloroprene).



$$n\,H_2C{=}\underset{\substack{|\\ Cl}}{C}{-}CH{=}CH_2 \xrightarrow{\text{Polymerization}} *{-}\left[CH_2{-}\underset{\substack{|\\ Cl}}{C}{=}CH{-}CH_2\right]_n{-}*$$

The properties of rubber so formed are determined by the nature of the substituent groups. For example, Polychloroprene is inferior to natural rubber in some properties but superior in its resistance to oil, organic solvents. These differences are due to difference in nature of their monomers: Isoprene (for natural rubber) and Chloroprene (for synthetic rubber).

Synthetic rubber was obtained by the free radical polymerization of Isoprene. The rubber so formed has all trans-configuration. As a result of this, synthetic rubber has a highly regular zig-zag chain which cannot be stretched. This accounts for non-elasticity of synthetic rubber.



Trans-Polyisoprene

Structure of Synthetic Rubber (trans – Polyisoprene)

Difference between Natural and Synthetic Rubber

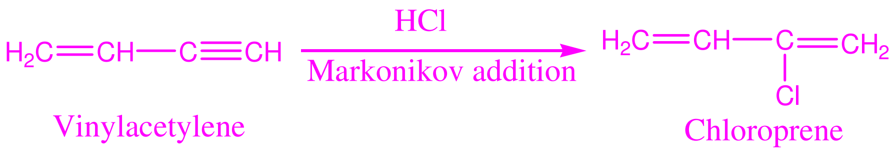
Sr. No.	Natural rubber	Synthetic rubber
1.	The rubber which is made from latex of Hevea plant.	The rubber which is made from unsaturated hydrocarbon.
2.	*Heveabraziliensis* is the equipment for natural rubber.	Polymer or monomer is the equipment for synthetic rubber.
3.	Coagulation is required	No coagulation
4.	Have no definite chemical formula.	Have a definite chemical formula.

5.	There is no classification.	It has many types.
6.	Polymerization is not occurred.	Polymerization recurred during manufacturing.
7.	Tensile strength is high.	Tensile strength is low.
8.	Tear resistance relatively high.	Tear resistance relatively low.
9.	Example: Hevea rubber.	Example: BUNA-S, BUNA-N, Butyl Rubber etc.

Preparationof Synthetic Rubber:

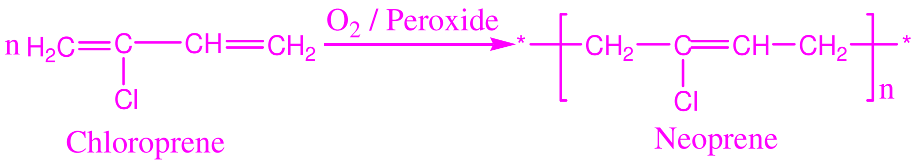
Neoprene:

Neoprene is a polymer of chloroprene. It is also known as polychloroprene. To synthesize Neoprene its monomer chloroprene is required. Chloroprene required for this process is synthesized from Vinylacetylene which performs Markonikov addition under acidic condition to produce chloroprene.



$$H_2C{=}CH{-}C{\equiv}CH \xrightarrow[\text{Markonikov addition}]{HCl} H_2C{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH_2$$

The chloroprene undergoes polymerization to gives neoprene. There are no specific catalysts are needed for this process but the polymerization becomes faster in the presence of oxygen or peroxide.



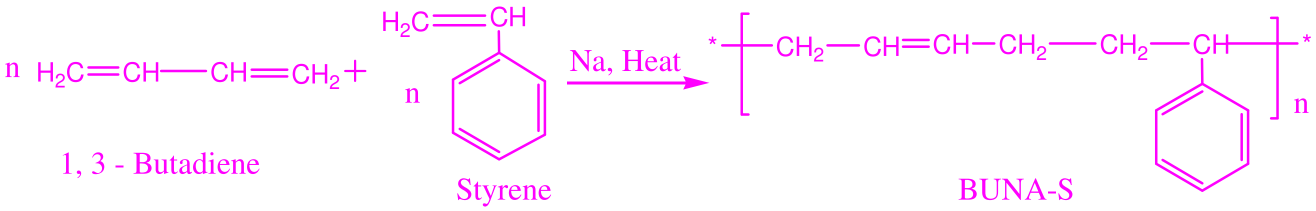
$$n\ H_2C{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \xrightarrow{O_2\ /\ \text{Peroxide}} *{-}\left[CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2\right]_n{-}*$$

Uses:

1. It is used in the manufacture of hoses, gaskets, shoe heels, stoppers, conveyor belts and printing rollers etc.
2. It is also used as an insulator.

BUNA–S:

BUNA–S is a copolymer of a mixture of 1,3- Butadiene and styrene in the ratio of 3:1 in the presence of sodium (which is polymerizing agent) gives styrene – butadiene copolymer (styrene – butadiene rubber) or BUNA –S. The name BUNA–S is made up of Bu which indicates 1, 3 – Butadiene, NA is for Sodium (Na) and S indicates Styrene.



Properties:

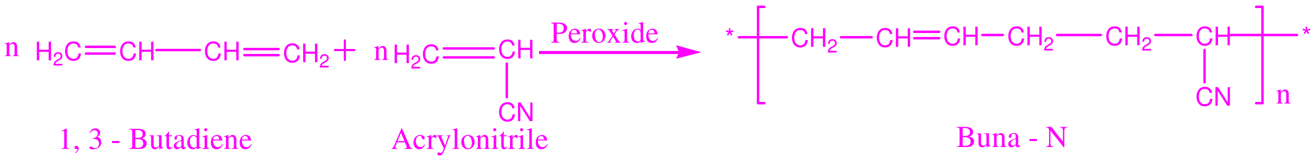
1. It is very tough and a good substitute for natural rubber.
2. It possesses high abrasion resistance.
3. It has high load bearing capacity.
4. It can be vulcanized in the same way as natural rubber.

Uses:

1. It is used for manufacturing automobile tires.
2. It is used for making floor tiles, footwear components, wire and cable insulation etc.

BUNA–N:

BUNA–N is obtained by copolymerization of 1, 3 – Butadiene and acrylonitrile in presence of a peroxide catalyst. The name BUNA–N is made up of Bu which indicates 1, 3 – Butadiene, NA is for sodium (Na) and N indicates acrylonitrile. 1, 3-Butadiene reacts with acrylonitrile to produce Buna-N.



Properties:

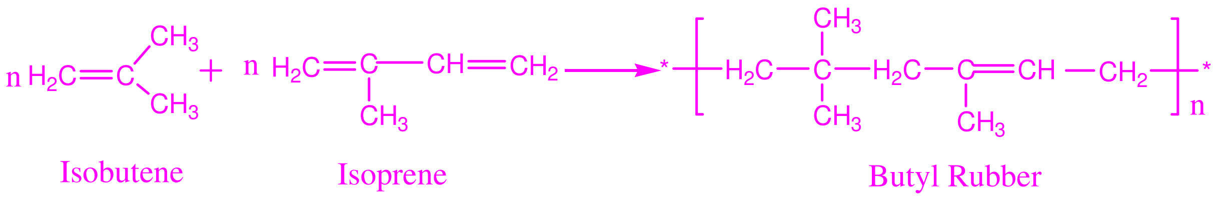
BUNA-N is resistant to the action of petrol, lubricating oils and organic solvents.

Uses:

BUNA-N is used in making oil seals, hoses, tank linings etc.

Butyl Rubber:

Butyl rubber is prepared by aluminium chloride initiated cationic copolymerization of isobutene with small amount of isoprene.



Properties:

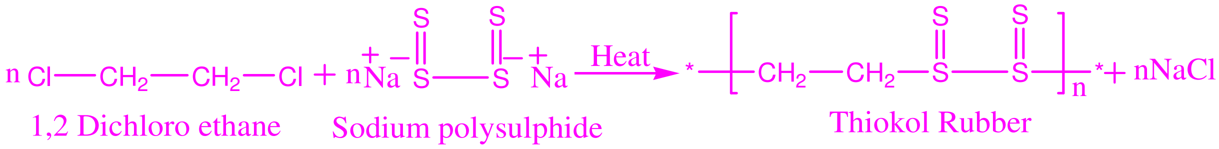
1. Under normal condition it is amorphous but it crystallizes when stretching.
2. It is quite resistant to oxidation due to low degree of unsaturation.
3. It can be degraded by heat or light to sticky low molecular weight product so stabilization is must.
4. Butyl rubber soluble in benzene but has excellent resistance to polar solvents like alcohol and acetone.
5. Compared to natural rubber it possesses outstanding low permeability to air and other gases.

Uses:

1. Insulation of high voltage wires and cables.
2. Inner tubes of automobile tiers.
3. Conveyor belts for food and other materials.
4. Lining of tanks and houses.

Thiokol Rubber:

Thiokol is prepared by copolymerization of 1, 2 – dichloroethane (ethylene dichloride) with sodium tetrasulphide (Na_2S_4) in presence of magnesium hydroxide. Thiokol is also known as polysulphide rubber. Its tensile strength is slightly less than that of natural rubber. It's different from vulcanized rubber.



Properties:

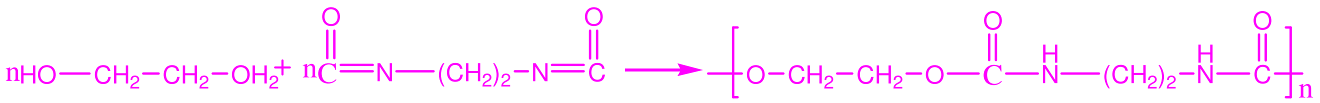
1. Thiokol is resistant to the action of mineral oils, solvents, oxygen & ozone.
2. Thiokol films are impermeable to gases to a large extent.
3. Thiokol is outstanding resistance to swelling by organic solvents.
4. Thiokol is resistant to the action of petrol lubricants and organic solvents.
5. Thiokol has poor heat resistance and low tensile strength.

Uses:

1. Thiokol mixed with oxidizing agents is used as a solid fuel in rocket engine.
2. It is used to engine gaskets and other such product that come into contact with oil.
3. Thiokol’s are used for hoses and tank lining for the handling and storage of oil and solvents.
4. Printing rolls.
5. Containers for transporting solvents.

Polyurethanes Rubbers:

Preparation: Polyurethane or isocyanate rubber is produced by reacting ethylene glycol with ethylene di- isocyanates.



$$nHO{-}CH_2{-}CH_2{-}OH_2 + n\overset{O}{\overset{\|}{C}}{=}N{-}(CH_2)_2{-}N{=}\overset{O}{\overset{\|}{C}} \longrightarrow \left[O{-}CH_2{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}(CH_2)_2{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}\right]_n$$

Ethylene Glycol Ethylene di-isocynate Polyurethane Rubber

Properties:

1. Polyurethanes are highly resistant to oxidation, because of their saturated character.

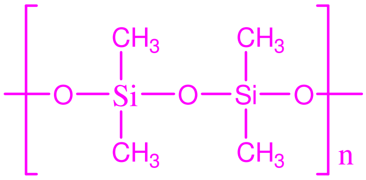
2. They also show good resistance too many organic solvents, but are attacked by acids andalkalis, especially concentrated and hot.

3. The polyurethane foams are light, tough and resistant to heat, abrasion, chemicals andweathering

Uses: It is used for surface coatings and manufacture of foams and spandex fibers.

Silicone rubber:

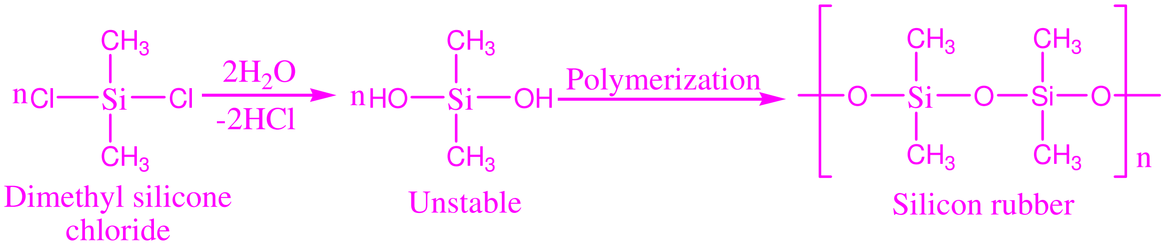
Silicone resins contain alternate silicone-oxygen structure, which has organic radicals attached to silicon atoms.



$$\left[O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O\right]_n$$

Silicon rubber

Preparation: Thedimethyl silicone chloride is polymerized by carefully controlled hydrolysis to give silicon rubber.



1. Dimethyl-silicon dichloride is bifunctional and can yield very long chain polymers.

2. Trimethyl silicon chloride is monofunctional and a chain-stopper. Thus, used in proportions to limit the chain- length.

3. Monomethyl silicon chlorides aretrifunctional and goes cross- linking to the final polymer. Its proportion used in polymerization, determines the amount of cross-linking that can be obtained.

Properties:

1. Depending on the proportion of various alkyl silicon halides used during their preparation, silicones may be liquids, viscous liquids, semi- solid, rubber- like and solids.

2. Because of silicon-oxygen links, they exhibit outstanding-stability at high temperatures, good water resistance, good oxidation-stability, but their chemicalresistance is generally lower than that of other plastics.

3. Their specific gravity ranges from 1.03 to 2.1.

4. Their physical properties are much less affected by variations in temperature.

5. They are non-toxic in nature.

Different types of silicones and their uses: Liquid silicones or silicone oils are relatively low molecular-weight silicones, generally of dimethyl silicones. They possess great wetting-power for metals, Low surface tension and show very small changes in viscosity with temperature.

Uses:

1. They are used as high temperature lubricants, antifoaming agents, water-repellent finishes for leather and textiles, heat transfer media, as damping and hydraulic fluids. They are also used in cosmetics and polishes.

2. Silicone greases are modified silicone oils, obtained by adding fillers like silica, carbon black, lithium soap, etc.

3. They are particularly used as lubricants in situations where very high and very low temperatures and encountered.

4. Silicone rubber is highly inert and does not react with most chemicals.

5. Due to inertness, it is used in many medical applications.

Compounding of rubber:

The process of mechanical mixing of various additives with polymers without chemical reaction to impart some special properties to the end product is known as compounding of plastics".

1. The additives get incorporated into the polymer to give a homogeneous mixture.
2. The functions of additives are to modify the properties of the polymer
3. To introduce new properties into the fabricated articles.
4. To assist polymer processing
5. To make the polymer products more pleasing and colorful. They should be cheap and sufficient in their functions.
6. They should be stable under processing and service conditions.
7. They should not impart taste or odour.
8. They should be non-toxic for food grade application of final compound after processing.
9. They should not adversely affect the properties of polymer.

The principal additives used in compounding process are 1) Softeners and Plasticizers 2) Vulcanizing Agents 3) Antioxidants 4) Accelerators 5) Fillers 6) Dyes

1. **Softeners and Plasticizers**: These are added to give greater plasticity and flexibility to reduce the brittleness of the products e.g.waxes stearic acid and vegetable oils.
2. **Vulcanizing agents:** When rubber is heated with Sulphur, its tensile strength,elasticity and resistance to swelling are increased.The Sulphur atoms chemically bond with double bonded carbons of rubber chains and bring about excellent changes in their properties.The percentage of sulphur added varies from 0.15 to 32%. S_2Cl_2,H_2S, H_2O_2, benzoyl chloride etc., are other vulcanizing agents.
3. **Antioxidants:** Natural rubber has tendency for oxidation. Antioxidants like phenyl naphthyl-amine and phosphites are added for preventing the oxidation of rubber.
4. **Accelerators**: These shorten the time required for vulcanization and give toughness to the rubber. e.g.Palmiticacid, 2-Mercaptol, zinc salt, oleic acid etc.
5. **Filler**: These are added to give rigidity and strength to the rubber. E.g., carbon black, zinc oxide and calcium carbonate
6. **Dyes**: These materials provide pleasing colour to the rubber product. E.g., Titanium oxide, White Ferric oxide, Red Lead chromate, Yellow Antimony oxide, Crimson Chromic oxide, zinc oxide etc.

Vulcanized Rubber:

Vulcanization of rubber is a process of improvement of rubber elasticity and strength by heating it in presence of sulfur, which results in three-dimensional cross linking of the rubber chain molecule bonded to each other by sulfur atoms. Vulcanization process was invented by Charles Goodyear in 1839.

Vulcanization is the chemical process used for converting rubber or related polymers into more durable materials by adding sulfur or equivalent curatives. Vulcanized type of rubber material is less sticky and has superior mechanical properties than natural rubber. The hardness of vulcanized rubber depends upon the amount of Sulphur used during the process and the degree of this hardness determines as to which industry could use the vulcanized rubber for making various products. For example, if 5% of sulphur is used during vulcanization, it will produce tire rubber. Ebonite is made by adding 20 to 25% sulphur and battery case rubber is made by adding 30% of Sulphur during vulcanization. Other products made from hard vulcanized rubber include bowling balls and saxophone mouth pieces etc. Less hard vulcanized rubber is used for making various household and industrial rubber products like shoe soles, hoses etc.

Natural rubber is not an important polymer for commercial purpose because of its softness & sticky properties. Softness of natural rubber increases with the increase in temperature while brittleness increases at low temperature. Therefore, ideal temperature for using rubber is 283 – 335K where its elasticity is maintained.

Other properties which decrease the quality of natural rubber are:

- It has large water absorption capacity.
- It has low tensile strength & low resistance to abrasion.
- It is not – resistant to abrasion.
- It is easily attacked by organic reagents.

The properties of natural rubber can be improved by a process called vulcanization. Vulcanization is the process of introduction of sulphur bridges between different chains by heating raw rubber with sulphur at 373-415K. In the absence of catalyst, the process of vulcanization is slow. Some additive such as zinc oxide is added to accelerate the rate of Vulcanization.

Difference between Vulcanized rubber and Natural rubber:

The synthetic rubber obtained has properties that are just opposite to that of natural rubber. These properties are

- Vulcanized rubber has excellent elasticity.
- Low water absorption tendency
- It is resistant to the action of organic solvents
- It is resistant to attack of oxidizing agents.

Vulcanized rubber is an improved form of natural rubber. In vulcanized rubber, sulphur bridges are introduced either at their reactive allylic sites or at the site of double bond. The presence of double bond in the rubber molecule makes it’s highly reactive as it provides allylic hydrogen that permits formation of cross links between different chains. The presence of these cross links increases the toughness, strength and hardness of rubber. Due to the presence of Sulphur bridges, individual chains can no longer slip over one another but are locked together in a giant size molecule. Cross-links being formed between the rubber polymer chains during vulcanization. Amount of sulphur used for vulcanization process determines the extent of hardness or toughness of the rubber.5% Sulphur is used for making tire rubber, 20 – 25% Sulphur is used for making Ebonite. 30% of Sulphur is used for making battery case rubber.

Questions:

1. What is rubber? Explain different types of rubber with suitable example.
2. Discuss the term natural rubber with suitable example.
3. Discuss the term synthetic rubber with suitable example.
4. Write the difference between natural rubber and synthetic rubber.
5. Write the difference between natural rubber and vulcanized rubber.
6. Discuss the preparation properties and use of following synthetic rubber
    a. Silicone rubber
    b. BUNA-S
    c. BUNA-N
    d. Butyl rubber
    e. Thiokol rubber
    f. Polyurethane rubber.
7. Explain the compounding rubber in detailed.
8. Write the preparation properties and use of BUNA-S and BUNA-N rubber.
9. Write note on silicone rubber.
10. Define term vulcanization of rubber? Give its advantages.
11. Which of the additives used in compounding of natural rubber?
12. Gives the application of synthetic rubber.
13. Write note on rubber latex.

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05. Biodegradable Polymers

Contents: Introduction, Classification of biodegradable polymers, facture affecting biodegradation, mode of biodegradation, chemistry of biodegradation, ways of polymer degradation, application of biodegradable polymers, Non-biodegradable polymers, application of biodegradable polymers.

Introduction:

Naturally occurringpolymeric materials satisfying the conditions of biodegradability, biocompatibility and release of low-toxicity degradation products but the resistance of synthetic polymers to chemical, physical and biological degradation has become a serious concern when used in areas such as surgery, pharmacology, agriculture, packaging, consumer products, building materials, industry, aerospace materials etc. The environmental problems, including the increasing difficulties of waste disposal and of global warming due to carbon dioxide released during incineration caused by the non-biodegradability of polyethylene used in packaging and agriculture field have raised concerns allover the world.

The use of biodegradable polymers as an alternative to non-biodegradable polymers but the degradable polymers available until recently have inferior physical properties in terms of strengthand dimensional stability and most of them are very expensive and are technically difficult to process. Thus, we have been made polymers by including biodegradability into polymers in everyday use through slight modifications of their structure to solve such problems.

The biodegradable polymers from renewable resources have attracted much interest for environmental and medical applications because of their desirable properties of biodegradability, biocompatibility and natural abundance.

The biodegradationof polymer depend on the field of application such as biomedical area or natural environment. The biodegradation can be takes place through the action of enzymes or chemical decomposition associated with living organisms and their secretion products. It is also necessary to consider abiotic reactions like photo degradation, oxidation and hydrolysis, which may alter the polymer before or during biodegradation because of environmental factors. In this chapter, we include brief content regarding classification biodegradable polymer, biodegradation and properties and applications of biodegradable polymers.

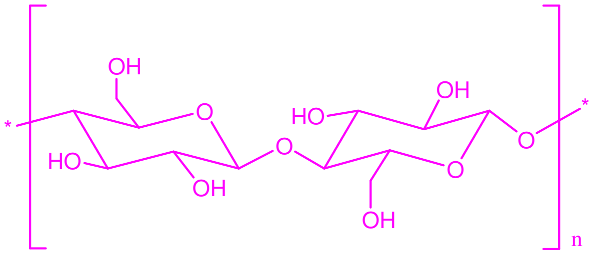
Classification of Biodegradable Polymers

Biodegradable polymers can be divided into three classes based on the origin of the raw materials and the process used in their manufacture of polymers.

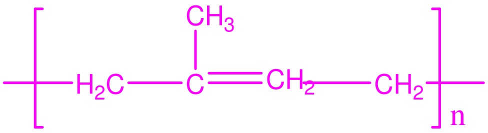
1. Natural Biodegradable Polymers:

The natural polymers or polymers from renewable resources have four broad groups:

1. Polysaccharides (starch, cellulose, lignin, chitin and chitosan)
2. Proteins (wool, silk, collagen, gelatin and casein)
3. Bacterial polyesters (polyhydroxyalkanoates (PHAs))
4. Others (lignin, shellac, natural rubber(polyisoprene) etc.)



Cellulose

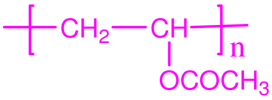


$$\left[-H_2C-\overset{CH_3}{\overset{|}{C}}=CH_2-CH_2- \right]_n$$

Polyisoprene

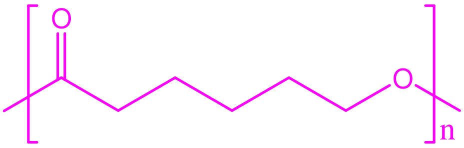
2. Synthetic Biodegradable Polymers:

Polymers produced from feed stocks derived from petrochemical or biological resources such as polyesters, polycaprolactone (PCL), polyamides, polyurethanes, polyureas, polyanhydrides, poly(vinyl alcohol) (PVA), poly(vinyl esters) etc. are the synthetic biodegradable polymers.

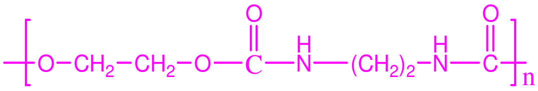


$$\left[-CH_2-\underset{OCOCH_3}{\underset{|}{CH}}- \right]_n$$

Polyvinyl acetate



Polycaprolactone



$$\left[O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-(CH_2)_2-\overset{H}{N}-\overset{O}{\overset{\|}{C}} \right]_n$$

Polyurethane Rubber

3. Biodegradable Polymer Blends:

The blending of biodegradable polymers from renewable and nonrenewable resources is a method of reducing the overall cost of the material and offers a method of modifying both properties and degradation rate.

Example: Melt processability, humidity resistance and mechanical properties of starch can be improved by blending starch with synthetic polymers such as PLAN, PCL, PHAs etc.

Factors Affecting Biodegradation

Factors on which the biodegradation of a polymer depends are explained below;

1. Polymer characteristics

a. Chemical structure:

Polymers containing hydrolysable linkages along the chain or easily oxidizable functional groups on the chain are susceptible to biodegradation by microorganisms and hydrolytic enzymes. Most of the biodegradable polymers, therefore, have easily hydrolysable linkages. Furthermore, the polymer chainsmust be flexible enough to fit into the active sites of the enzyme structure.

b. Degree ofhydrophilicity:

Polymers containing hydrophilic segments such as PVA, poly(acrylic acid), polyether are seemed to be more biodegradable than hydrophobic polymers of comparable molecular weight. The biodegradability of a polymer could be promoted by increasing the hydrophilicity of the polymer by chemical modifications. Hydrophilicity in a polymer not only helps in better penetration of microorganism in the polymer but also induces the production of necessary enzymes within the microorganism relatively more easily compared to hydrophobic polymer.

c. Stereochemistry:

Stereochemistry has a role in biodegradation of polymers. Huang et al. reported that when the poly(ester-urea) s synthesized from D-, L-, and D, L6 phenylalanines subjected to enzyme catalyzed degradation, the pure L-isomer was degraded much faster than the D, L-isomers“.

i. **Degree and type of branching:** The main factors affecting the enzymatic degradation of synthetic polymers are the steric configuration of the polymer itself and the nature of the substituents adjacent to the susceptible bond. Branching of the molecular chain inhibits biodegradation.

ii. **Crystallinity:** Crystalline regions of a polymer are difficult to penetrate and are inaccessible to microbes as well as to abiotic agents. Amorphous regions are selectively degraded prior to the degradation of the crystalline regions in synthetic polymers as well as in biopolymers. The size, shape and number of crystallites have a pronounced effect on the chain mobility of the amorphous regions and thus affect the rate of degradation.

iii. **Molecular size:** Initiation process of biodegradation takes place due to the presence of end groups in the form of unsaturation, hydroperoxide or any other functional groups in the polymer structure. High molecular weight polymer has lesser concentration of these chain end functionality and thus is more resistant to biodegradation. However, biopolymers (such as cellulose or starch) as well as some synthetic polymers (e.g. polycaprolactone) are readily biodegradable despite the long chain structure. Degradation of these polymers depends on the presence of hydrolysable linkages and hydrophilic functional groups present in their chemical structure.

2. Environmental Factors:

In biological environment, certain factors such as temperature, moisture.salts, pH and oxygen are essential for the biodegradation process. The most significant element is the moisture factors.

Mode of Biodegradation

1. Microorganisms:

The term microorganism covers a heterogeneous group of living beings (e.g. bacteria and fungi), which have a microscopic size and are, for the most part, unicellular. The degradative action of microorganisms is chiefly a result of the production of enzymes, which breakdown nonliving substrates in order to obtain nutrient materials present in polymer compositions. Certain environmental conditions such as optimal ambient temperature.The presence of nutrient materials and high humidity are essential for optimum growth and degradative activity of microorganisms3’5.

2. Enzymes:

Enzymes are essentially biological catalysts, with the same action as chemical catalysts. The activity of enzymes is closely related to the conformational structure, which creates certain regions at the surface forming an active site. At the active site the interaction between the enzyme and substrate takes place leading to chemical reaction, giving a particular product. The active sites are specific for a given substrate or a series of substrates. For optimal activity certain enzymes must associate with cofactors that can be metal ions (Na, K, Mg, Ca and Zn) or organic cofactors called coenzymes.

Different enzymes have different actions; some enzymes change the substrate through a free radical mechanism while others follow alternative chemical routes typically of biological oxidation and biological

Biological oxidation

Certain enzymes react directly with oxygen (e.g. cytochromoxidase). In many cases oxygen is directly incorporated into the substrate (e.g. hydroxylases or oxygenases). In another type of biological oxidation, the oxygen molecule function as a hydrogen acceptor (i.e. electron acceptor) e.g. oxidases.

Biological hydrolysis

Several different hydrolysis reactions occur in biological organisms. Proteolytic enzymes (proteases) catalyze the hydrolysis of peptide bonds and also the related hydrolysis of an ester bond.

Chemistry of Biodegradation

Biodegradation is the only degradation path way that is able to completely remove a polymer or its degradation products from the environments. Biodegradation takes place in two stages. The first stage is the depolymerization of the macromolecules into shorter chains. This step normally occurs outside the organism due to the size of the polymer chain and the insoluble nature of many polymers. Extra-cellular enzymes and abiotic reactions are responsible for the polymeric chain cleavage. During this phase the contact area between the polymer and the microorganisms increases. The second step corresponds to the mineralization.

Once sufficient small size oligomeric fragments are formed, they are transported into cells where they are bio assimilated by the microorganisms and then mineralized. Biodegradation takes place in two different conditions depending upon the presence of oxygen; aerobic biodegradation in the presence of oxygen and anaerobic biodegradation in the absence of oxygen. Complete biodegradation or mineralization occurs when no residue remains, i.e., when the original product is completely converted into gaseous products and salts.

Way of Polymer Degradation

Polymer degradation in natural environment occurs in two stages. The first stage is mainly abiotic and the second stage is purely biotic.

1. Abiotic Degradation

As microbes cannot act upon high molecular weight polymers, they have to be fragmented into smaller chains before microbial degradation. The environmental factors, causing chemical degradation of polymers under natural conditions are given below.

a) Thermal degradation

All polymers can be degraded by the influence of heat, whether present at the service temperature or applied during polymer processing. When heated to the extent of bond rupture, polymer degradation results from the production of free radicals, which causes either random scission to smaller molecules of varying chain length (e.g. polyethylene) or depolymerization of the polymer to monomer or monomers (e.g. polymethylmethacrylate). Thermal degradation of polymers like poly(vinyl chloride) is caused by elimination of side groups, resulting in the formation of polyethylene followed by chain scission, aromatization and char formation.

b) Photo-oxidative degradation

Chemical bonds in polymers can be broken by the highest energy UV waves of the solar spectrum, leading to their photo-oxidative degradation. Photooxidative degradation is a radical-based auto-oxidative process. Chromophoric species such as carbonyl groups, hydroperoxides, unsaturation, metallic impurities such as iron and titanium, polynuclear aromatic compounds (PNA) such as anthracene, phenanthrene and naphthalene are responsible for the UV absorption. They are incorporated into polymers during processing or introduced intentionally into the polymer structures either by copolymerization or by mixing with polymers.

c) Hydrolytic degradation

Hydrolysis is the most important mode of degradation of biodegradable polymers especially synthetic polymers. Depending on the erosion mechanism degradable polymers are classified into surface and bulk erosion materials.

There are several factors that influence the hydrolytic degradation are chemical bond, pH, copolymer composition, chain stiffness, formation of crystalline nature and water uptake are the most important. Hydrolysis can be catalyzed by acid or basic compounds and by enzymes.

d) Degradation due to environmental stress cracking:

Environmental stress cracking is defined as the catastrophic failure of a material at a stress much lower than its ultimate strength, due to combined effects of stress and environment. The stress-cracking agents that occurred in the environment are detergents, alcohols, oils, solvents, chemicals and vapors of polar liquids.

e) Chemical degradation:

Chemical degradation of corrosive gases and liquids can affect most polymers, except polytetrafluoroethylene and polyether ether ketone. Ozone, atmospheric pollutants such as nitric and sulfuric oxides and acids like sulfuric, nitric and hydrochloric will attack and degrade most polymers.

f) Mechano-chemical degradation:

Depending on their length, polymers have the ability to convert mechanical energy applied in shear into main-chain bond energy resulting in bond scission. When polymers are subjected to shear, during processing in a screw extruder, macro alkyl radicals are formed that lead to accelerated oxidation.

g) Radiation-induced degradation:

Transfer of energy by gamma ray or electron beam irradiation onto polymer backbone results in severe degradation of the polymer. Irradiation produces free radicals, which, depending on the chemistry of the polymer, initiates degradation’s. g. polyethylene, polypropylene.

h) Degradation due to weathering:

All plastics subjected to long-term exposure to weather degrade to different extent, depending on their composition. “Weathering” implies the action of individual; or a combination of various environmental factors on polymers: heat, light, ionizing radiation, oxygen, ozone, humidity, rain, wind, dust, bacteria, and chemical pollutants (SO_2 and nitric oxides etc.).

2. Biotic Degradation:

In this stage the low molecular weight products formed by the abiotic degradation are consumed by microorganisms, leaving CO_3, water, and other harmless substances at the end of the metabolic process.

Applications of Biodegradable Polymers

For economic reasons, even for health and safety reasons, biodegradable plastic products are establishing themselves as viable alternative in a number of important niche markets. Some of these used in the fields of medicine, textiles, hygiene and agriculture, as well as some specific packaging application.

The commercially available biodegradable polymers are listed in Table

Sr. No.	Trade Name	Composition	Use
1	Dexon&Medifit	Polyglycolic acid	Absorbable sutures
2	Lupron Depot	PLA/PLGA	Drug delivery products
3	Tone &Enviroplastic-C	Poly(e-caprolactone)	Agricultural planting Container
4	Bionolle	Poly(butylene succinate)	Agriculture & Packaging
5	Mater-Bi	Starch & Vegetable oil	Disposable items, packaging, personal care & hygiene
6	Cereplast	Corn & potato starch	Biodegradable utensils

Non-Biodegradable Polymers:

The non-biodegradable does not degrade in water or biological environment. These polymers have long chain contains carbon and hydrogen atoms. The interatomic bonding of these polymers is very strong, hence making them resistant to microbe which tries to break their bonds and digest them and long period is required to decompose them.

E.g. Polyethylene have high strength and lubricity. Teflon is chemically and biologically inert and has high lubricity thus they are non-biodegradable polymers.

Examples: Polypropylene, Polyamides, Polycarbonate, Polyesters, etc.

Sr. No.	Biodegradable polymer	Non-biodegradable polymer
1	Biodegradable polymers easily and quickly undergo biodegradation.	Non-biodegradable polymers does not undergo biodegradation.
2	Rate of biodegradation is very high.	Rate of biodegradation is very low.
3	Biodegradable polymers are non-pollutants.	Non-biodegradable polymers are pollutants.
4	Most of the biodegradable polymers are natural.	All the non-biodegradable polymers are synthetic.
5	Examples: Starch, cellulose, wool, silk etc.	Examples: Polyethylene, PVC, Polyester etc.

Applications of Non-Biodegradable Polymers:

Non-biodegradable polymers have been widely used in making various medical devices, such as disposable supplies, implants, drug delivery systems and tissue engineering scaffolds. The advantages of using polymers, as biomaterials, are their manufacturability. Polymers are easy to fabricate into various sizes and shapes compared to metals and ceramics. They are also light in weight and with a wide range of mechanical properties for different applications.

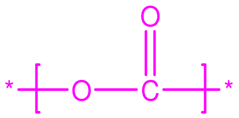
Polyethylene:

There are three type of polyethylene: linear high-densitypolyethylene (HDPE), branched low density polyethylene (LDPE) and ultrahigh molecular weight polyethylene. The HDPE and ultrahigh molecular weight polyethylene are frequently used as biomaterials.

Porous HDPE has been successfully used for craniofacial applications, such as chin, malar area, nasal reconstruction, ear reconstruction, orbital reconstruction, and the correction of craniofacial contour deformities. The ultrahigh molecular weight polyethylene has exceptional mechanical properties, chemical inertness, impact resistance, and low coefficient of friction.

Polyester:

Polyester is a family of polymers which have ester linkage connecting the polymers. Polyester is the leading synthetic fibers and films. The typical synthetic reaction of PET uses dimethyl terephathalate and ethylene glycol.

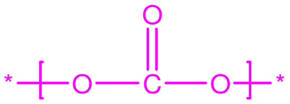


$$*-\!\left[O-\overset{\overset{\displaystyle O}{\|}}{C}\right]\!-*$$

Polyester is considered to be biocompatible. It has very good mechanical properties. Therefore, PET fibers and the structures made from fibers, such as woven, knitted, felted and braided structures, are used as sutures, internal patches, pledgets, ligamentous prosthesis, artificial blood vessels, heart valve sewing cuffs, etc.

Polycarbonate:

Polycarbonate family polymers have carbonate linkages in their polymer chains. Polycarbonate can be synthesized by the reaction of phosgene with bisphenol A.

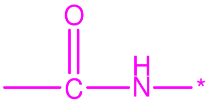


$$*-\!\left[O-\overset{\overset{\displaystyle O}{\|}}{C}-O\right]\!-*$$

Polycarbonate is tough and transparent plastic commercially available and these polymers used to make components for oxygenator for open heart surgery, venous reservoir, and arterial filter due to its sterilizability, ease of processing, biocompatibility, and clarity.

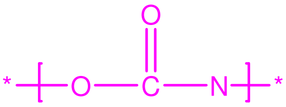
Polyamides:

Polyamide polymers (nylon) have amide linkages in their polymer chains.The first polyamide synthesized was Nylon-66. It was synthesized through the polycondensation of hexamethylenediamine and adipicacid. Nylon has been used as surgical sutures.



Polyurethane:

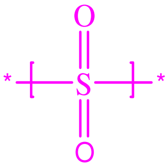
Polyurethanes are a class of polymer with urethane linkage. Polyurethane elastomers are frequently used as biomaterials due to their excellent fatigue resistant properties and biocompatibility.



Polyurethanes have been used as catheters and gastric balloons which only need to be used for a short period of time. Polyurethane polymers have excellent mechanical properties and biocompatibility, segmented polyurethanes have been frequently used in the medical devices as blood contacting materials, such as totally implantable artificial hearts and left ventricular assist devices. Polyurethanes were introduced as pacemaker lead insulators due to their hydrolytic stability.

Polysulfones:

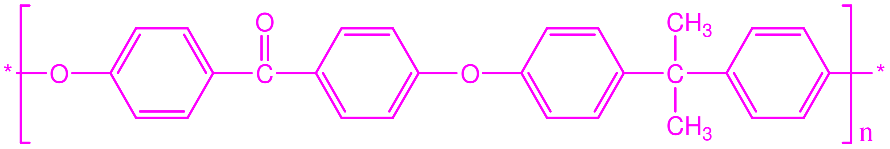
Polysulfons are a family of polymers which have linkages in their backbones. Polysulfones have excellent mechanical properties and chemical resistance. One of the important polysulfones is poly (arylsulfones). Some of the characteristics of polysulfones are: Heat resistant, excellent hydrolytic stability to hot water and steam sterilization, excellent chemical resistance to inorganic acids & bases, Food, water and medical contact compliance.



They are used as membranes for hemodialysis. Polysulfones have been used as orthopeadic biomaterials due to their excellent mechanical properties.

Poly(ether ether ketone):

Poly(ether ether ketone) is a crystalline polymer with highly crystalline, thermally stable, resistant to many chemicals, and very tough.



Poly(ether ether ketone)

It is useful for special applications like pipes in oil refineries and chemical plants, and parts for scientific instruments, aerospace and biomedical devices where high price is not a limitation.

Questions:

1. Define biodegradable polymer? Give the classification of biodegradable polymer in detailed.
2. Discuss the different types of biodegradable polymers.
3. Define non-biodegradable polymer? Write the application of non-biodegradable polymer.
4. Explain the facture affecting polymer degradation.
5. Write note on mode of polymer degradation.
6. Write the application of biodegradable polymers.
7. Write note on the following
    a) Biodegradable polymer
    b) Non-biodegradable polymer

c) Way of degradation.

    d) Biotic degradation.

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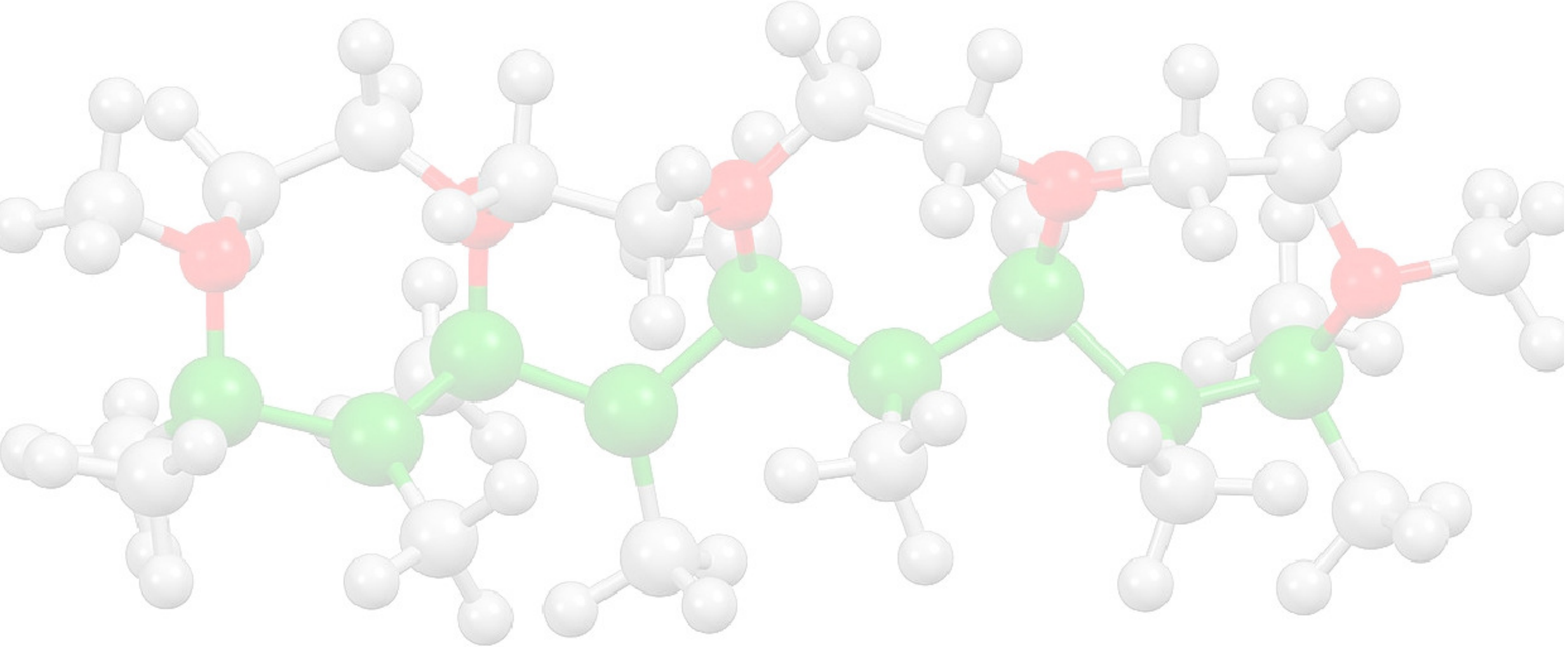
About Author

P.M. Jadhav is working as assistant professor in M.S.P. Mandals, Shri Muktanand College, Gangapur Dist-Aurangabad. He completed his B.Sc in chemistry from Pune University in 2011 and M.Sc degree in organic chemistry from the department of chemistry, university of Pune(2013). He has six year of teaching experience in organic and analytical chemistry. He has published several research papers in the international reputed journals. He has published two books from reputed publications. He is actively working in the research area of Schiff bases and their metal complexes in biological activates, green chemistry and organic synthesis.



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